SODIUM CHEMISTRY LOOP
FACILITY DESCRIPTION

By

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ABSTRACT

An experimental facility, the Sodium Chemistry Loop (SCL), was constructed at Atomics International to study the equilibrium between sodium oxide and metal oxides in sodium systems. Operational data indicate the SCL meets or exceeds specifications.

Although new data on the oxygen probe has been developed, the probe's performance is not yet understood well enough to evaluate its effectiveness in developing kinetic data for the sodium-oxygen-metal systems to be studied.

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Figure 1. Free Energy of Formation of Single and Double Oxides

I. INTRODUCTION

It has long been recognized that in sodium systems, oxygen plays an important role in such problems as corrosion and mass transfer, and fission-product deposition. The details of the oxygen dependence are not known because little knowledge exists on the oxygen-sodium-metal systems of interest. Observations by various workers have suggested the presence of double oxides appreciably more stable than single metal oxides. Figure 1, based on what limited data are available, bears this out. Therefore, if the role of oxygen is to be understood, data relating the interaction of oxygen in sodium to various metals of interest must be developed. To this end a program has been formulated and an experimental facility constructed. The description of this facility, the Sodium Chemistry Loop (SCL), is the subject of this report.

II. EXPERIMENTAL APPROACH

Considering the present state of knowledge, the experiment that would best define the role of oxygen in sodium-metal systems is the one that measures the oxygen equilibrium between sodium and various metals. Assuming chemical reactions can be written to describe the system, one possible set of reaction equations is as follows:

Equation 1 represents the dissolution equilibrium of the metal and Equation 2 the equilibrium between sodium oxide and the single metal oxide. The third equation represents that between the single metal oxide in solution and on the surface. The fourth and fifth equations represent the double oxide equilibrium in solution and its equilibrium with the surface. Equations 1 through 3 can be combined to represent the case where the single oxide is the predominant specie, or:

Equations 1, 2, 4, and 5 can be combined to represent the case where the double oxide is the predominant specie, or:

*(s) and (l) refer to the species on the surface and in solution, respectively.

Defining unit activity ($a = 1$) for sodium oxide as the situation when the sodium is saturated with sodium oxide, then in both Equations 6 and 7, $M(s)$ and $Na(l)$ will have unit activity as long as free metal exists.

The equilibrium constant K for Equation 6 is $K = a_{MO}/a_O$, where a_{MO} is the activity of the single oxide on the surface, and a_O is the activity of sodium oxide in solution.

The equilibrium constant for Equation 7 is $K = a_{NaMO}/(a_O)^{y+1}$, where a_{NaMO} is the activity of the double oxide on the surface.

A discussion of the thermodynamic considerations of the above expressions is beyond the scope of this report, although measurement of the equilibrium between the liquid and surface at different oxygen concentrations should yield such valuable information as the free energy of formation of the metal oxides and the identity of the predominant oxide.

Several experimental difficulties immediately arise in the design of the proposed experiment. One difficulty is, of course, in assuring that equilibrium has been established. Continuously monitoring the oxygen activity in the sodium using the liquid metal oxygen meter* and providing good stirring should give reasonable assurance that equilibrium has been achieved. (If the oxygen probe has a sufficiently rapid response and flowrates across the test specimen are sufficiently high, valuable kinetic data can be obtained.)

A second difficulty is the measurement of liquid and surface activity. For the work here, activity of oxygen in sodium is defined as:

$$a_O = \frac{\gamma C}{C_O} \quad , \quad \dots (10)$$

where

γ = the activity coefficient,

C = the concentration of sodium oxide, and

C_O = the saturated concentration of sodium oxide.

For a sufficiently dilute solution, γ is unity.

*United Nuclear Corporation

An expression analogous to Equation 10 can be written for oxygen on the surface, or:

$$a_{MO} = \frac{\gamma S}{S_O} , \quad \dots (11)$$

where

S = the surface concentration of metal oxide, and

S_O = the saturated surface concentration of metal oxide.

If the oxygen probe operates as it should, measurement of the sodium oxide activity in the liquid will be no problem, the probe response being directly related to liquid activity. Measurement of the surface oxygen concentration should represent no major experimental problem, in that this value can be arrived at both by a material balance in the loop and by measurement of metal tab weight changes (assuming an adequate method is available to remove residual sodium). Measurement (and even definition) of the saturated surface concentration and γ may represent a serious limitation in the ability to translate experimental results into thermodynamic data. Not enough is known at this time to estimate the degree of uncertainty that will exist because of this difficulty. However, relative K 's and ΔF 's will be developed which will allow comparisons of metals and permit the unscrambling of some of the data that exist in the areas of corrosion and fission-product deposition.

A requirement for this experiment is that the SCL be constructed of a material that will be inert to oxygen in sodium. Observations^{(1)*} of the sodium/stainless-steel system can be explained if the steel acts as a "buffer" for oxygen, absorbing oxygen from the sodium when the oxide content of the sodium is increased and releasing oxygen into the sodium when the oxide content of the sodium is decreased. Were this to happen to an appreciable extent in the SCL, stoichiometric calculations to determine the change in surface activity could not be made. Based on available thermodynamic data of all materials with suitable physical properties, nickel should be the most inert to oxygen in sodium. This metal was therefore selected as the material of construction for the SCL.

*Superscript numbers in parentheses are for References at the end of this report.

Figure 2. Sodium Chemistry Loop Schematic Diagram

Figure 2 shows the loop schematically. The loop consists of a surge (free-surface) tank containing the oxygen probe, a pump, a flowmeter, two specimen stations, a cold-trap and reheater, and a sodium ballast tank. A typical experiment would be run as follows:

Weighed tabs of known surface oxygen content would be placed in each specimen station. Sodium would be flowed through the cold-trap circuit, after the cold-trap temperature is adjusted for a predetermined oxygen concentration in the sodium. The cold-trap circuit would be valved from

the system and flow started through one specimen station. Sodium from the ballast tank would be used to adjust the level in the surge tank. After equilibrium, as indicated on the oxygen probe, the first specimen station would be valved from the system and the procedure repeated with a second station for another run. The tabs would then be removed from the specimen stations and a chemical sample of the sodium taken. The tabs would be cleaned and weighed, and preparations made for another run.

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III. LOOP DESCRIPTION

Nickel 270^{*} was chosen as the material of construction of the loop for all surfaces in contact with sodium. This is the highest purity nickel commercially available in shapes suitable for loop fabrication. Tables 1 and 2 report the chemical analysis and mechanical properties of the nickel used to fabricate the SCL. After machining and before welding, parts (except for valves) were degreased in acetone, etched in a nitric-hydrofluoric acid mixture,[†] thoroughly rinsed in distilled water, and dried for at least 16 hr at 110°C. All welding (except for valves) was done in a high-purity argon atmosphere. The design and fabrication of the valves are discussed in Section III-C. Weld joints were designed to minimize the use of filler rod. When required, Nickel 270 filler metal was used. All welds were inspected using dye penetrant and radiographic procedures. The assembled loop and all interconnecting lines were helium-leaktight (sensitivity 5×10^{-10} std cc/sec).

The assembled loop is pictured in Figure 3. Figure 4 is the piping and instrumentation diagram, and 5 is an isometric drawing of the loop. Table 3 lists the volume of sodium in various loop components.

A description of the various components of the SCL follows.

A. SURGE TANK

The surge tank is fabricated from 2-in.-diam bar. The tank's ID and height are 1.75 and 4-3/4 in., respectively. The bottom is tapered to improve the flow pattern. The sodium level is fixed by the overflow line to the sodium waste tank. For normal operation the waste tank also acts as a gas plenum. The oxygen probe is immersed in the sodium to a depth of 1 in. Conoseal fittings, near both the top and bottom of the probe housing, provide a leaktight connection to the loop. A side-arm and integral pump on the surge tank provide stirring action.

^{*}Registered trademark International Nickel Company, Inc.

[†]Mixture of 30 cc conc HNO₃, 6 drops conc HF, water to 100 cc.

TABLE 1
CHEMICAL ANALYSIS OF NICKEL 270 USED FOR THE
SODIUM CHEMISTRY LOOP, WPPM*

Element	Tubing			Round Bar		
	3/8-in. OD 0.035-in. Wall	1/2-in. OD 0.035-in. Wall	1-in. OD 0.035-in. Wall	2-in. OD	1-in. OD	1/2-in. OD
Ag	<1 ND [†]					
Al	<10 D					
B	<1 ND					
Ba	<10 ND					
Be	<1 ND					
Bi	<5 ND					
Ca	<10 ND					
Cd	<5 ND					
Co	<5 ND					
Cr	<5 D					
Cu	3	3	3	3	3	2
Fe	10	10	10	10	10	<10 D
Mg	<10 D	<10 D	<10 D	<10 D	<10 ND	<10 ND
Mn	<1 ND					
Mo	<5 ND					
Na	<500 ND					
Pb	<5 ND					
Si	<10 D					
Sn	<5 ND					
Ti	<5 ND					
V	<10 ND					
Zn	<100 ND					
Zr	<50 ND					
C	210	260	160	120	<100	<100

By Spectrographic analysis, except carbon by conductometric analysis
[†]D - detected ND = not detected.

TABLE 2
ROOM TEMPERATURE MECHANICAL PROPERTIES OF NICKEL 270
USED FOR THE SODIUM CHEMISTRY LOOP*

Property	Tubing			Round Bar		
	3/8-in. OD 0.035-in. Wall	1/2-in. OD 0.035-in. Wall	1-in. OD 0.035-in. Wall	2-in. OD	1-in. OD	1/2-in. OD
Yield strength, 0.2% offset, psi	21,000	18,000	17,000	25,000	20,000	20,000
Ultimate psi	54,000	56,000	55,000	50,000	50,000	50,000
Elongation 2 in., %	28	48	51	56	58	58
Reduction of area, %	NR [†]	NR	NR	81	NR	NR
Hardness, Rockwell B	NR	NR	NR	43	35	35

As reported in suppliers' material certifications
[†]Not reported

A

B

C

Figure 3. Sodium Chemistry Loop

TABLE 3
VOLUME OF SODIUM IN COMPONENTS OF THE
SODIUM CHEMISTRY LOOP

	Volume (cc)
Surge tank	183.6
Stirrer arm	11.6
Pump	16.6
Flowmeter, valves, and interconnecting lines	<u>24.4</u>
Total surge-tank circuit	236.2
One specimen station	22.3
One set valves* and interconnecting line	<u>16.3</u>
Total for each specimen station	38.6
Cold trap	31.3
Reheater	33.4
Ballast tank	0 to 198.3
Valves* and interconnecting lines	<u>42.9</u>
Total cold-trap circuit	107.6 to 305.9

*Excluding bellows region

B. PUMP AND FLOWMETER

The main and surge-tank pump and the flowmeter are dc Faraday devices. The main pump is prepared from 1/2-in.-OD by 0.035-in.-wall tubing. All other lines are fabricated from 3/8-in.-OD by 0.035-in.-wall tubing. Pump leads are 304 stainless steel, welded directly to the pump throat. The field strength of the surge-tank magnet is 500 gauss and the field strengths of the main pump and flowmeter magnets are 1700 gauss. Pumps are powered by 0-to-3-volt 0-to-50-amp unfiltered dc supplies. The output voltage from the flowmeter is amplified using a dc differential amplifier and read on a 0-to-50-mv meter.

C. VALVES

Valves were fabricated by a vendor^{*} to Hoke[†] configuration 4235Q6Y. These are all welded bellows-sealed valves. Standard 316 stainless-steel bellows and head assemblies were used. The body, plug, and tube studs are Nickel 270. Parts were inspected before assembly and appeared to be free of dirt, oil, and water. Welds were made using the TIG process. Nickel-61 filler rod was used as required. As a condition for acceptance the valves were helium-leaktight (sensitivity 5×10^{-10} std cc/sec). Subsequent radiographic inspection indicated some porosity on the weld root passes, with no evidence of porosity or inclusions on the final weld passes.

D. COLD TRAP AND REHEATER

The cold trap and reheater are fabricated from 1-in.-diam by 0.035-in.-wall tubing 3 in. long. The cold trap is packed with Nickel 270 turnings. A 1/4-in.-diam by 0.035-in.-wall stainless-steel tube is tightly wrapped on the cold trap. Water circulating through this tube and an auxiliary fan provide cooling. An Inconel[§]-sheathed nichrome heating element is tightly wrapped around the reheater to heat the sodium from the cold-trap to loop temperature.

E. BALLAST TANK

The ballast tank is fabricated from 2-in.-diam bar. The tank's ID and height are 1.75 and 4.75 in., respectively. The bottom is tapered to improve the flow pattern. The purpose of the ballast tank is to provide a reservoir of conditioned sodium for the loop.

F. SPECIMEN STATION

The specimen stations are fabricated from 1-in.-diam by 0.035-in.-wall tubing 4-1/2 in. long. A Conoseal fitting at the top of the station is used to insert and remove metal tabs under test. A Nickel 270 plug, welded into the upper part of the fitting, is used to prevent contact between the loop sodium and

*Castle Controls, Pasadena, California

†Hoke Incorporated, Creskill, New Jersey

§Registered trademark International Nickel Company, Inc.

the 347 stainless-steel Conoseal. The sodium level in the station is established by the elevation of the outlet line.

G. CHEMICAL SAMPLING

A bypass line is provided for sampling of the loop sodium. The configuration shown in Figures 4 and 5 is for flowthrough sampling. By replacing the sample tube with a vacuum bulb, dead-end samples can be collected.

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Figure 4. Piping and Instrumentation Diagram, Sodium Chemistry Loop

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Figure 5. Isometric Drawing, Sodium Chemistry Loop

IV. INSTRUMENTS AND CONTROLS

A. HEATERS AND THERMOCOUPLES

Loop heaters are Inconel-sheathed MgO-insulated nichrome elements. The lengths and diameters of the heaters were selected for their particular service in the loop. For low-temperature application asbestos-insulated nichrome heater cable is used. The thermocouples (1/16-in.-diam stainless-steel-sheathed MgO-insulated chromel-alumel) have calibrations traceable to NBS standards. Where practical a minimum "immersion" depth of 6 in. is accomplished by wrapping the element around what is believed to be an isothermal portion of the loop. A tab is used to secure the junction end to the loop, and wire wrap or additional tabs are used to support the element. The heater and thermocouple wiring schedule is included in Appendix A.

B. TEMPERATURE DATA

Potentiometric recording and indicating instruments are used for temperature data acquisition. Compensated lead wire is used to interconnect the thermocouples and instruments. Care was taken during installation to prevent ground loops in cable shields. Instruments are periodically calibrated to assure traceability to NBS standards. Figure 6 is the instrumentation compartment layout diagram. The instrument list is included as Appendix B.

C. HEATER CONTROL

Variations in room temperature and line voltage were too great to permit exclusive use of passive control. Therefore, on selected circuits active control was added. Figure 7 pictures the control configuration. Diagnostic voltage and current meters are periodically calibrated to assure traceability to NBS standards.

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Figure 6. Instrument Component Layout Diagram

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Figure 7. Heater Circuit Schematic Diagram

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V. LOOP TESTING, OPERATION, AND PERFORMANCE

Pre-operational testing of the SCL was divided into three phases — room temperature, hot-dry (no sodium), and sodium-filled tests. The purposes of the room temperature tests were to verify that wiring was correct, measure room temperature heater and thermocouple parameters (resistance between leads and resistance to ground), and demonstrate that no electrical interactions exist between the loop pumps and flowmeter. Hot-dry tests were to further verify that wiring was correct by matching heater to thermocouple response, obtain high temperature parametric data on the heaters and thermocouples, and establish reference heater power for various operating temperatures. Sodium-filled tests were performed to demonstrate the various capabilities of the loop such as filling and draining, cold trapping, and chemical sampling; verify design calculations; determine the precision of control circuitry; and train operating personnel. The oxygen probe was not installed until after pre-operational tests and control modifications were completed. Oxygen probe tests are described in Section VI.

The following filling procedures have been adopted to assure that the sodium ballast tank is filled and the surge tank is not overfilled:

The loop and sodium-supply and waste tanks are preheated to 300°F. The loop and waste tank are evacuated and the pressure in the supply tank adjusted to 10 psig. (Table 4 lists the valve positions for various loop operations.) The pump is turned on and sodium is fed into the loop until there is an overflow indication on TC 10. Valve 3 (cold-trap circuit) is closed and the loop is pressurized to 3 psig through the waste tank. Valve 3 is then opened and the ballast tank is filled with sodium from the surge tank. The surge tank is refilled with sodium from the supply tank until there is an overflow indication on TC 10. Valve 4 is opened and if filling has been proper there should be an immediate and steady (no gas) flow indication on the flowmeter.

For cold trapping, the following procedure has been adopted:

The sodium flowrate through the cold-trapping circuit is reduced to its nominal value for cold-trapping and cooling water is turned on to the cold-trap. Automatic temperature control on the reheater assures adequate

TABLE 4
VALVE POSITION FOR VARIOUS LOOP OPERATIONS

Operation	Valve No.																			
	1	2	3	4	5	7	8	9	10	12	13	14	15	16	17	18	19	20		
Loop Drain	O	O	O	O	O	O	O	O	O	X	X	X	O	O	O	X	O	O		
Flowthrough Chemical Sample	-	-	-	-	X	-	-	O	O	X	X	X	O	X	O	X	X	X		
Specimen Station No. 2	X	O	X	X	X	X	O	X	O	X	X	X	X	O	O	X	X	X		
Specimen Station No. 1	O	X	X	X	X	O	X	X	O	X	X	X	X	O	O	X	X	X		
Cold Trapping	X	X	O	O	X	X	X	X	O	X	X	X	X	O	O	X	X	X		
Loop Fill, Phase 3	X	X	O	X	X	X	X	X	O	O	X	X	T	O	O	X	X	X		
Loop Fill, Phase 2	X	X	T	X	X	X	X	X	O	O	X	X	X	O	O	X	X	X		
Loop Fill, Phase 1	X	X	O	X	X	X	X	X	O	O	X	X	T	O	O	X	X	X		

Legend X = Closed
 O = Opened
 T = Throttle
 - = Depends on other operations in progress

recovery of the sodium temperature before its return to the upper manifold and surge tank. Coarse control of the cold-trap temperature is achieved by varying the flowrate; fine control is achieved using the fan, operating from a control point on TR4-a (Thermocouple 6).

To prevent contamination of the specimen station with atmospheric oxygen or water vapor, it was decided to use a small portable glove box for inserting and removing metal tabs from the specimen station. This box bolts directly to a plate welded to the specimen station. Before opening the top of the station the box is helium-leaktested to assure the integrity of the O-ring seals. After the transfer operation the specimen station is pressurized through Valve 19 or 20 (depending on the station) and bubble-checked. The station is then evacuated and helium-leaktested. For sodium filling of the specimen station the upper and lower manifold valves (No. 1 and 7 or 2 and 8) are opened with the pump on. After all gas indications on the flowmeter have ceased, the surge tank is filled from the ballast tank. Care in the operation of Valve 4 is necessary to prevent the transfer of an excessive amount of sodium.

If a flowthrough chemical sample is to be collected, the valve to the waste tank (No. 16) is closed, and the one to the top of the surge tank (9) and the drain valve (15) are opened. The pump generates sufficient head to circulate the

sodium through the overflow line into the surge tank. After a suitable sampling time, water is used to provide a freeze seal to the sample tube. The tube can be crimped and removed from the loop. For dead-end samples a bulb of suitable volume is installed on the sample port near TC11. The bulb is evacuated and helium-leaktested through a separate valve, and after preheating is filled by opening Valve 15. A freeze seal is used to isolate the sample bulb from the loop.

While immersed thermocouples are not used to monitor sodium temperature, the cold-trap TC (No. 6) indicates that the temperatures being read closely correspond to sodium temperatures. During several runs in which a minimum stable cold-trapping temperature was sought, flow in the cold-trap circuit abruptly stopped at an indicated temperature of from 208 to 209°F (melting point of sodium = 208.1°F). Even at the highest planned operating temperature, 1200°F, not more than several degrees difference between the sodium and TC hot-junction temperature is anticipated.

Operations have indicated that the surge tank and specimen stations can be run for long periods of time (weeks) with no detectable drift in temperature (uncertainty in precision is 1°F) and no temperature spikes (instrument response time is approximately 1 sec). The cold-trap can be operated unattended at 225°F or higher. Because of the cyclic nature of the fan operation, TC6 will vary a maximum of 8°F during cold-trapping.

The sodium flowrate in the loop for isothermal operations can be arbitrarily set by varying the pump power. A flowrate of approximately 4 cc/sec has been used. The inventory turnover time for the surge tank and one specimen station is approximately 70 sec. The sodium flowrate during cold-trapping is determined by the difference in temperature between the surge tank and cold-trap. For example, with the surge tank at 500°F and the cold-trap at 225°, the sodium flowrate is 1/2 cc/sec, or an inventory changeover time of 1100 sec. Assuming the cold-trap is 100% efficient and the initial oxygen concentration is 10 times its solubility at cold-trap temperature, after 2 hr the oxygen concentration in the loop should be within 2% of its solubility at cold-trap temperature. The measured cold-trapping rate is slower than this, corresponding to a trap efficiency of 5% over the first 10 hr; this is discussed in more detail in Section VI.

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VI. RESULTS OF OXYGEN PROBE CHARACTERIZATION TESTS

When the oxygen probe was examined before its installation in the SCL, it was found that the probe matrix was contaminated with what appeared to be the thread lubricant used to seal the shipping container. Similar contamination was found on the spare probe. The vendor indicated that the contamination could not have occurred at the assembly site, and that the lubricant could be removed with a chloroform wash followed by an ethyl alcohol rinse. Accordingly, both probes were cleaned in chloroform and alcohol and dried in vacuum at room temperature for 17 hr. Some lubricant still imbedded in the matrix could not be removed by wiping the matrix. The cleaner of the two probes was examined microscopically; no cracks were evident.

The probe was installed on 26 November 1968 after the loop had been drained and cooled to room temperature. After installing, connecting, and testing the required heaters and TC's, the loop was filled with sodium (2 December 1968). Sodium was circulated through the cold-trap circuit with the entire loop as isothermal as practical. The probe voltage drifted rapidly downward. On 9 December, with a surge-tank temperature of 500°F and a probe-head temperature of 130°F the probe voltage was 1.1551 volts. The head temperature was varied in 10°F steps to 170°F in an attempt to establish a suitable head temperature. The reproducibility of the probe's response was very poor; when the 130°F point was repeated on 20 December the probe voltage had decreased to 1.1380 volts. It is not known whether this decrease in voltage was due to probe drift or an increase in oxygen concentration due to removal of oxygen from the loop walls. No basis was found for establishing an "optimum" head temperature, so a reference head temperature of 150°F was arbitrarily selected.

On 2 January 1969 the head temperature was increased to 150°F and the probe voltage continued to show a downward drift until 9 January (decreasing from 1.1268 to 1.1202 volts). On that date the loop temperature was increased to 600°F, maintained at this temperature for 3 hr, then cooled to 500°F. The heating and cooling rates were 100°F per hour. The probe voltage responded rapidly to the temperature change, increasing to 1.1486 volts after 3 hr at 600°F (still increasing at this time). It showed a similar response when cooled,

TABLE 5
OXYGEN PROBE COLD-TRAPPING AND HEAD-TEMPERATURE
TEST RESULTS

Temperature (°F)			Oxygen Probe Voltage			
Surge-Tank	Cold Trap	Probe-Head	After 6 hr	After 20 hr	After 48 hr	After 96 hr
500*	500	150	← 1.1146 after 5 days →			
500	300	150	1.1260	1.1375	-	-
500	275	150	1.1450	1.1472	-	-
500	225	150	1.1560	1.1628	1.1637	-
Loop froze, then was remelted.						
500*	500	150	← 1.1086 after 5 days →			
500	300	-	1.1250	1.1336	-	-
500	275	-	1.1420	1.1429	-	-
500	225	150	1.5010	1.1580	1.1604	1.1604
500	225	160	1.1552	-	-	-
500	225	170	1.1498	-	-	-
500	225	160	1.1547	-	-	-
500	225	150	1.1597	-	-	-
500	225	140	1.1634	-	-	-
500	225	130	1.1676	-	-	-
500	225	150	1.1601	-	-	-
500	250	150	1.1534	1.1490	1.1470	1.1470
500	300	150	1.1310	1.1282	-	-
500*	500	150	1.1000	1.1000	-	-
600*	600	150	1.1308	1.1336	-	-
600	300	150	1.1464	1.1622	-	-
600	275	150	1.1676	1.1712	-	-
600	250	150	1.1772	1.1818	1.1833	-
600	250	160	1.1822	-	-	-
600	250	170	1.1799	-	-	-
600	250	160	1.1812	-	-	-
600	250	150	1.1829	-	-	-
600	250	140	1.1838	-	-	-
600	250	130	1.1852	-	-	-
600	250	150	1.1829	-	-	-
600	300	150	1.1660	1.1625	-	-
600*	600	150	1.1264	1.1266	-	-
500	500	150	1.0962	1.0922	1.0896	-

*High flowrate through cold-trap

decreasing to 1.1146 volts after 14 hr at 500°F (or a decrease of 5.6 millivolts from similar conditions 18 hr earlier).

The probe voltage was constant to 14 January; therefore, the first series of cold-trapping experiments was started. The cold-trap temperature was reduced to 300°F on 14 January, 275° on the 15th, and 225° on the 16th. On 20 January a general loss of electrical power was experienced and the sodium in the loop froze before it could be drained. It was remelted and temperature conditions re-established on 22 January. By the 27th the probe voltage appeared sufficiently stable to permit starting of the second series of cold-trapping experiments.

For these tests, the surge-tank and head temperatures were maintained at 500° and 150°F, respectively, and the cold-trap temperature was reduced stepwise to 300°, 275°, and 225°F. With the cold trap at 225°, the head temperature was varied stepwise from 130° to 170°F. With the head at 150° the cold-trap was then heated stepwise to 250°, 300°, and 500°F. A similar set of tests were performed with a surge-tank temperature of 600°F; because it was impractical to operate with the cold-trap at 225°F, the head-temperature tests were conducted at 250°F. In all tests in which head temperature was varied the probe response appeared to stabilize within the first 4 hr. The results of these tests are reported in Table 5. The tests lasted through 3 March 1969.

After completion of the oxygen probe characterization tests, runs were made testing the ability to open and close the specimen stations without contaminating the loop with oxygen. As of the writing of this report these tests are in progress.

Data from Table 5 are graphically displayed in Figures 8 and 9. The oxygen content of the sodium is assumed to be equal to the solubility limit of sodium oxide at cold-trapping temperatures. Oxygen solubility data are taken from Reference 2. The slopes of the curves in Figure 8, relating the effect of head temperature on probe response, cannot be explained based on Seebeck potentials (the temperature coefficient of the copper/stainless-steel system being too small). Neither can they be explained assuming the matrix acts as a thermal barrier causing the temperature of the Cu-CuO junction to be less than the sodium temperature. (The theoretical temperature coefficient of the oxygen

Figure 8. Probe Head Temperature vs Probe Response at Surge Tank Temperature 500°F, Cold Trap 225°F; and at Surge Tank Temperature 600°F, Cold Trap 250°F

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Figure 9. Probe Response vs Oxygen Content of the Sodium

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Figure 10. Historical Record of Probe Response at Reference Conditions

probe is negative;⁽¹⁾ therefore, the slopes observed in Figure 8 are inconsistent with this explanation.) The head-temperature sensitivity of the probe response therefore remains an anomaly at this time.

Figure 10 is a historical record of the loop and oxygen probe response for reference conditions. It is not clear from this figure whether the long-term drift in probe response is due to a change in the probe's performance or to an oxygen source within the loop (i. e. a leak or desorption of oxygen from the walls). It is also not clear whether operations at 600°F changed the probe's performance.

Of interest in the operation of the SCL is the determination of the rate of response of the probe to changes in the oxygen content of the sodium. The response to increasing oxygen content appears rapid, based on several tests reported in Table 5, where at high sodium flowrates the cold-trap was warmed to loop temperature. The response to decreasing oxygen content is at this time poorly defined, the sluggishness perhaps being due to poor cold-trapping efficiency. An analysis has been made of data from the cold-trapping run of 11 to 15 April 1969. For this run temperatures were: surge-tank, 500°F; probe-head, 150°F; and cold-trap, 225°F. The flowrate was 0.5 cc/sec. Figures 11 and 12 are kinetic plots assuming two forms for trapping efficiency (see Appendix C). The first ten hours are well represented assuming a simple first-order relationship (viz. the trapping efficiency is independent of concentration and time). This could reflect trap efficiency (calculated from the slope to be 5%) or the response time of the probe (0.115 hr^{-1}). The time period from 6 to at least 24 hr is well represented assuming the trapping efficiency is proportional to the difference in inlet and outlet oxygen concentration. The value of the proportionality constant calculated from Figure 12 is 0.14 ppm^{-1} . Results from tests with metal tabs may help determine the probe's kinetic response.

Figure 11. Cold-Trapping Kinetics, Assuming ϵ is Constant

Figure 12. Cold-Trapping Kinetics, Assuming $\epsilon = \eta(C - C_0)$

VII. SUMMARY

An experimental facility, the Sodium Chemistry Loop, has been constructed and is under test to study the equilibrium between sodium oxide and metal oxides in sodium systems. Operational data indicate the loop has met or exceeded design expectations for temperature, flow control, and cold-trapping capability. The performance of the oxygen probe is still not sufficiently well understood to permit an evaluation of its effectiveness in developing kinetic data for the sodium-oxygen-metal systems to be studied. Valuable data have however been developed on the probe's sensitivity to variations in loop oxygen content, and to sodium and head temperatures.

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APPENDIX A
THERMOCOUPLE AND HEATER WIRING SCHEDULE
Sodium Chemistry Loop Thermocouple Locations

Location	Thermo- couple No.	TR2	TI2	Other Recorder	Room Temperature Resistance (ohm)
Top surge tank	1	1	21		63.0
Middle surge tank	2	2	22	TR4-a	63.5
Main pump	3	3	23		63.5
Surge tank side-arm pump	4	4	24		61.5
Lower manifold	5	5	25		59.2
Outlet cold-trap	6	6	26	TR4-b	53.0
Outlet reheater	7	7	27		48.0
Specimen station No. 1	8	8	28	TR5*	58.0
No. 2	9	9	29	TR5*	61.0
Surge tank overflow line	10	10	30		62.0
Sample line	11	11	31		65.5
Sodium fill line	12	12	32		68.0
Glovebox plate, SS No. 1	13	13	33		62.0
SS No. 2	14	14	34		61.5
Sodium supply tank, middle	15	15	35		16.0
top	17		1		14.8
bottom	18		2		15.5
Sodium waste tank, middle	16	16	36		12.5
top	19		3		16.0
bottom	20		4		40.5
Sampler tube	21		5		40.5
Argon ballast tank	22		6		-
Sodium ballast tank	23		7		-
Upper manifold	24		8		-
Top oxygen probe	25			TR3-a	-
Heater plate, oxygen probe	26			TR3-b	-
Center oxygen probe housing	27				-

*Connected as required.

Sodium Chemistry Loop Heater Locations

Location	Heater No.	Control Thermo-couple No.	Option No. 1 Control	Option No. 2 Control	Room Temperature Resistance (ohm)
Pump, surge tank, flowmeter	1	2	TC2-4	TC3-1	5.5
Lower manifold	2	5	TC2-5		37.0
Cold-trap, reheater, Na ballast	3				20.0
Reheater	4	7	TC2-3	TC3-4	5.2
Surge tank side-arm pump	5				-
Argon ballast tank	6				-
Upper manifold	7	24	TC2-6		38.5
Specimen station No. 1	8	8	TC1-1		37.2
No. 2	9	9	TC1-3		37.0
Surge tank overflow line	10				37.0
Sampler line	11				38.0
Sampler tube	12				5.3
Sodium fill line	13				19.2
Sodium supply tank, top	14				30.5
bottom	15				29.5
Sodium waste tank, top	16				25.5
bottom	17				29.0
Glovebox plate, SS No. 1	18	13	TC1-2		7.1
No. 2	19	14	TC1-5		7.1
Spare	20				
Heater plate, oxygen probe	21	26	TC2-2		-
Oxygen probe housing	22	27	TC2-1		-

APPENDIX B
INSTRUMENT LIST

No.	Description	Manufacturer	Model
-	Clock	Sperti-Faraday	-
FA2	Differential amplifier	Video Instruments	R30 C
FM2	Flowmeter	Atomics International	-
-	Lapse timers, 99999.9 hr	General Electric	6651K17P1
PS-2 to -6	Pump dc power supply	Atomics International	-
-	Oxygen probe elec- trometer	United Nuclear Corp.	TP1-1
-	Oxygen probe recorder	Minneapolis Honeywell	Y 153
-	Reference junction	Pace Engineering	-
TC-1 to -3	Temperature controller	Esterline Argus	E6134
TI2	Temperature indicator	Minneapolis Honeywell	156
TR2	Temperature recorder	Minneapolis Honeywell	SY 153
TR3	Temperature recorder	Minneapolis Honeywell	SC 153
TR4	Temperature recorder	Minneapolis Honeywell	KSY 153
TR5	Temperature recorder	Minneapolis Honeywell	RY 153
VC and VO	Power supply, 0-to-130 volts ac	Atomics International	-
-	Voltage stabilizer (-4)	Superior Electric	EMT4106 BR
-	Voltage stabilizer (-5)	Sorensen	500-S
-	Voltage stabilizer (-6)	Sorensen	ACR 3000

APPENDIX C

CALCULATION OF COLD-TRAPPING EFFICIENCY

Assuming the SCL acts as a well-stirred vessel, the cold-trap removes an amount of oxygen proportional to the difference between the inlet and outlet concentrations. Then:

$$\frac{dw}{dt} = -\epsilon f \rho (c - c_o) \quad \dots (A1)$$

where

w = weight of oxygen removed, gm O

ϵ = trap efficiency

f = flowrate through the trap, cc Na/hr

ρ = sodium density, gm Na/cc Na

c = oxygen concentration in the loop, gm O/gm Na

c_o = solubility of oxygen at cold-trap temperature, gm O/gm Na

Since:

$$w = cv\rho \quad \dots (A2)$$

where v is the sodium volume of the loop, cc Na.

Defining the inventory changeover time (t_i hr) as:

$$t_i = \frac{v}{f} \quad \dots (A3)$$

Then:

$$\frac{dc}{dt} = \frac{\epsilon}{t_i} (c - c_o) \quad \dots (A4)$$

Case 1:

Assume ϵ is independent of concentration and time.

Integration Equation A4 yields:

$$\ln \left[\frac{c(o) - c_o}{c - c_o} \right] = \epsilon \frac{t}{t_i} \quad \dots (A5)$$

where

$c(o)$ = the initial oxygen concentration, gm O/gm Na

c = oxygen concentration at time t , gm O/gm Na

t = lapse time, hr .

The expression used to relate probe voltage to oxygen concentration is:

$$\ln \frac{c}{c_o} = k(E_o - E) \quad \dots (A6)$$

where

k = constant, volts⁻¹

E = voltage, volts.

Equation A6 can be rearranged to:

$$c - c_o = c_o \exp[k(E_o - E)] - 1 \quad \dots (A7)$$

Substituting Equation A7 into A5:

$$U = \ln \left\{ \frac{\exp[k(E_o - E(o))] - 1}{\exp[k(E_o - E)] - 1} \right\} = \epsilon \frac{t}{t_i} \quad \dots (A8)$$

If this kinetic form accurately describes the data, a plot of U vs t should be a straight line, with the slope being equal to ϵ/t_i .

Case 2:

Assuming ϵ is proportional to the difference in inlet and outlet concentration,

$$\epsilon = \eta(c - c_o) \quad \dots (A9)$$

where η is the proportionality constant.

Then substituting A9 into A4 we get:

$$\frac{dc}{dt} = - \frac{\eta}{t_i} (c - c_o)^2 \quad \dots (A10)$$

Integrating Equation A10:

$$\frac{1}{c - c_o} - \frac{1}{c(o) - c_o} = \eta \frac{t}{t_i} \quad \dots (A11)$$

Substituting A7 into A11,

$$V = \frac{1}{\exp[k(E_o - E)] - 1} - \frac{1}{\exp\{k[E_o - E(o)]\} - 1} = c_o \eta \frac{t}{t_i} \quad \dots (A12)$$

If this kinetic form accurately describes the data, a plot of V vs t should be a straight line, with the slope being equal to $c_o \eta / t_i$.

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1. Murbach, E. W., Heath, N. W., "Evaluation of an Electrochemical Oxygen Meter," AI-AEC-12700, June 30, 1968
2. Eichelberger, R. L., "The Solubility of Oxygen in Liquid Sodium: A Recommended Expression," AI-AEC-12685, November 1, 1968