

# Solubility of Nickel in Liquid Sodium of High Oxide Content

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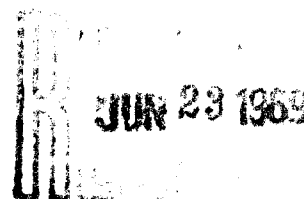
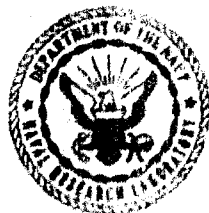
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#### ABSTRACT

The influence of oxide content on the solubility of Ni in liquid Na at 400°C was investigated. The solubility of Ni increased with increasing oxide content of the Na up to the saturation level of Na<sub>2</sub>O in Na. The temperature-dependent-equilibrium solubility of Ni in liquid Na saturated with Na<sub>2</sub>O (oxygen added as NiO) was found to vary between 4 ppm at 300°C and 21 ppm at 500°C. The soluble species is postulated to be a compound of the type (NiO)<sub>x</sub>(Na<sub>2</sub>O)<sub>y</sub>.

#### PROBLEM STATUS

This is the final report on NRL Problem C 06-01. Unless otherwise notified, this problem will be considered closed 30 days after the issuance of this report.

#### AUTHORIZATION

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## SOLUBILITY OF NICKEL IN LIQUID SODIUM OF HIGH OXIDE CONTENT

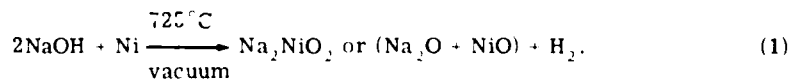
### INTRODUCTION

The increased rate of corrosion associated with the degree of oxygen contamination in various solid metal-liquid Na systems at elevated temperatures has been reported in recent years by a number of investigators in the field of liquid metal technology. However, very little attention has been given to the reaction mechanisms involved. Two of the earliest and perhaps most exhaustive studies on the effects of dissolved oxide in liquid Na on the solubility and corrosion of Fe are those of Bogard (1) and Batutis, et al. (2), respectively. It was concluded from these studies that the solubility and corrosion rate of Fe in liquid Na saturated with oxide were greater by two to three orders of magnitude over values found in pure Na. However, no general reaction mechanisms were advanced by the authors.

Discrepancies in solubility data of metals and alloys in liquid alkali metal solvents frequently appear in the literature. One of the most prominent examples is the solubility of Fe in liquid Na (1,3,4). Over a comparable temperature range the results disagree by roughly three orders of magnitude. Considerable emphasis is placed on the sensitivity of the analytical methods employed as the principal cause of the discrepancy. While this is admittedly a valid argument, especially in situations where trace quantities of solutes in solvents, such as liquid metals, are to be determined, it is equally important to consider the effects of impurity reactions on such solubility data.

On the basis of the studies of the liquid Na-Fe system, the distinction between the terms solubility and corrosion appears to be purely academic. Fundamentally, the corrosion process appears to proceed by the interaction of dissolved impurities with the Fe surface and subsequent dissolution in liquid Na of the reaction products formed. Horsley has suggested the formation of the compound  $\text{FeO}(\text{Na}_2\text{O})_2$  to explain the increased rate of corrosion in the presence of oxygen (5).

With this concept in mind, the Ni-liquid Na system was chosen for investigation. Aside from the importance of Ni as a component of containment vessels in high-temperature liquid-metal technology, the reasons for selection of this system were practical ones. First, as the solubilities of metals and their compounds in liquid Na are reputedly low (in the parts per million range), an analytical method of high sensitivity was required. The favorable nuclear characteristics of Ni made it amenable to analysis by the thermal neutron activation method. Second, some information was available on reactions of Ni with molten NaOH. Previous work by Williams, et al. (6), on the NaOH-Ni system described reactions that involved chemical species considered to be the principal impurities of the Ni-liquid Na system. A chemical analysis of the reaction residue indicated the primary product to be composed of  $\text{Na}_2\text{O}$  and NiO in equimolecular ratios. The primary reaction reported is:



This study did not establish whether the oxides were chemically combined or were just an admixture; however, Smith (7) has reported the isolation of single crystals of the

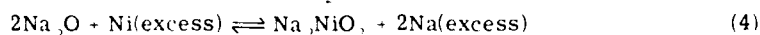
reaction product and their identification as a sodium nickelate (II) compound ( $\text{Na}_2\text{NiO}_2$ ) by x-ray methods. It is interesting to note that  $\text{Na}_2\text{O}$  and  $\text{NiO}$  are the principal impurities expected to be found in the Ni-Na system under investigation.

Williams, et al. (6), further observed that on heating this reaction product in the presence of excess Ni, a secondary reaction occurred, involving only the  $\text{Na}_2\text{O}$  portion of the residue to produce  $\text{NiO}$  according to



This reaction, however, goes to completion only on removal of the residual Na.

On the basis of reactions 1 and 2, a general mechanism for corrosion in the Ni-Na system has been proposed, and its feasibility investigated. The overall process is described by



At high temperatures Na will reduce  $\text{NiO}$  to the metallic state, and in the presence of excess Na reaction 3 will proceed to completion. The next step (reaction 4) involves an equilibrium which is shifted partially to the right; the extent of formation of the indicated  $\text{Na}_2\text{O}$ - $\text{NiO}$  complex should be temperature dependent. In any event, both  $\text{Na}_2\text{O}$  and  $\text{NiO}$  impurities would be present (reaction 3); they have the potential for interaction in liquid Na by reactions 4 and 5 to produce the compound  $\text{Na}_2\text{NiO}_2$ .

The solubility of Ni and its reaction products in liquid Na can be sensitively monitored by the determination of Ni in equilibrated, filtered Na samples by thermal neutron activation analysis. The addition of variable amounts of  $\text{NiO}$  to a standard volume of liquid Na at a particular temperature should produce changes in the concentration of soluble Ni compounds in samples removed after similar reaction periods, consistent with the law of mass action, if a chemical reaction is actually occurring, and provided the equilibrium solubility of the product is not exceeded. It was also planned to determine the temperature-dependent solubility of the suggested  $\text{Na}_2\text{NiO}_2$  compound (as equivalent Ni concentration) in liquid Na over a convenient temperature range to further support the impurity interaction and corrosion mechanism proposed.

## EXPERIMENTAL DATA

### Apparatus

The susceptibility of liquid Na to reaction with various solid, liquid, and gaseous substances requires that any reactions of this material be studied in a well-defined environment. As a precaution against gaseous contaminants, liquid Na reactions are generally carried out in controlled, inert atmospheres, such as Ar or  $\text{N}_2$ , free of  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . The solid and liquid contaminants of the liquid metal are usually eliminated by distillation procedures. Solid contaminants originating from the reaction vessel itself can be controlled by the selection of fabrication materials of specified composition. The apparatus used in this study, shown in Fig. 1, was designed to minimize the above impurity problems during the course of the reaction and also to expedite the various manipulations required for the safe sampling of the liquid metal at high temperature.

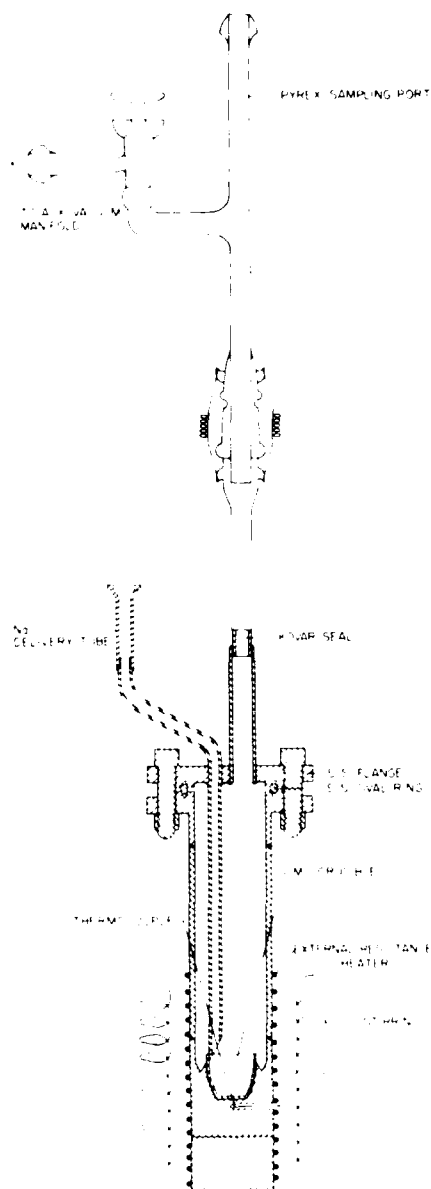


Fig. 1 - Reaction vessel

With the exception of the glass sampling port and adjacent Kovar metal-to-glass seal, the entire auxiliary apparatus was fabricated of type 304 stainless steel. The reaction crucible was made of Mo because of its excellent resistance to corrosion by Na in the 300 to 500 C temperature range (8). From a consideration of its free energy of formation,

$\text{Na}_2\text{O}$  is thermodynamically more stable than  $\text{MoO}$ ,  $\text{MoO}_2$ , and  $\text{MoO}_3$ , the principal oxides of Mo. Hence, any oxygen or oxide in the system would react with Na to produce  $\text{Na}_2\text{O}$ .

#### Preparation of NiO Source

Reagent-grade NiO was used as the source of the oxygen impurity initially added to the pure Na. To prevent the displacement of finely divided NiO powder from the Mo crucible by the evacuation and gas-purging procedures used prior to the introduction of Na, the NiO powder was pressed into pellets at a pressure of approximately 15,000 lb/in.<sup>2</sup> and fired in air in a muffle furnace at 1400°C for 15 hr. This procedure resulted in sintered, high-density NiO pellets, which facilitated the weighing and quantitative handling of the source.

#### Procedure

A known weight of sintered NiO was introduced into the Mo crucible, which was subsequently positioned in the apparatus. The apparatus was hermetically sealed and connected to a Na still fitted with a Pyrex glass receiver; the entire system was evacuated and purged with purified Ar. The still was charged with 35 ml of liquid Na and, following evacuation of the entire system, the Na was distilled into the receiver. The solidified Na was reheated to a temperature just above its melting point and filtered by differential Ar pressures through an in-line sintered glass frit into the reaction crucible. The apparatus was disconnected from the filter-still assembly by flame sealing the glass connecting line; the internal Ar pressure was adjusted to allow for expansion to near atmospheric pressure at the specified reaction temperature. After transfer to a furnace, the apparatus was heated to the desired temperature, controlled to  $\pm 2^\circ\text{C}$ , and the melt stirred electromagnetically throughout the reaction period. Preparatory to sampling, purified Ar gas was admitted to the apparatus from an auxiliary gas train, following which the seal at the end of the sampling port was opened and Ar allowed to flow into the room atmosphere. Sampling of the liquid metal at temperature was accomplished against this back flow of Ar by siphoning a liquid Na sample into a previously evacuated and Ar-purged pipette made of Pyrex glass having a fine-porosity sintered frit sealed at the tip.

#### Preirradiation Sample Preparation

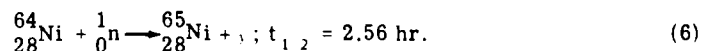
The Ni content of the Na samples was determined by thermal neutron activation analysis. Due to the high cross section of Na for thermal neutrons, a separation of the Ni-containing solute from the bulk Na was necessary. An analytical scheme for the quantitative recovery of Na-soluble Ni compounds was devised which included the following steps:

1. Reaction of the sample (conversion of Na to NaOH) with absolute EtOH and distilled  $\text{H}_2\text{O}$ .
2. Evaporation of EtOH and dilution to 1-l volume with distilled  $\text{H}_2\text{O}$ .
3. Acid titration of 10.0-ml aliquot for determination of the size of the Na sample.
4. Acidification of the entire reaction mixture with concentrated  $\text{H}_2\text{SO}_4$ .
5. Addition of 10 mg  $\text{Fe}^{3+}$  carrier (as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in dil. HCl).
6. Quantitative coprecipitation of  $\text{Ni}(\text{OH})_2$  with the  $\text{Fe}(\text{OH})_3$  carrier by addition of NaOH solution.

7. Filtration of the  $\text{Fe}(\text{OH})_3$  carrier and ignition to  $\text{Fe}_2\text{O}_3$ . The  $\text{Fe}(\text{OH})_3$  served as a quantitative scavenger for the minute amount of  $\text{Ni}(\text{OH})_2$ ; any Ni compound removed with the Na sample was contained in the final  $\text{Fe}_2\text{O}_3$  sample.

#### Irradiation of $\text{Fe}_2\text{O}_3$

The Ni in the irradiated  $\text{Fe}_2\text{O}_3$  samples represented the Ni content of essentially the total Na sampled. A correction was applied to compensate for the small portion used to determine the sample size. The nuclear reaction of interest is described as



Iron and oxygen, which comprise the bulk matrix of the sample bombarded, did not interfere with the radiometric analysis of Ni under the irradiation conditions used.

A preliminary investigation was made of the Ni scavenging efficiency of  $\text{Fe}(\text{OH})_3$  and of the apparent Ni content (blank determination) in the carrier and the various solvents and chemicals used in the preirradiation sample processing. This was accomplished by subjecting 30-g samples of pure Na to the analytical scheme prescribed for the unknown samples of equal size, with the addition of measured quantities of  $\text{Ni}^{2+}$  just prior to the Fe floc precipitation in step 6. The  $\text{Fe}_2\text{O}_3$  samples from step 7 were encapsulated in gelatin and irradiated for 30 min in the NRL reactor. The Ni activity was separated from the dissolved  $\text{Fe}_2\text{O}_3$  samples and purified by standard carrier radiochemical techniques, as described in the Appendix. The Ni-65 ( $\beta$  energies of 2.1 (57%), 1.01 (14%), and 0.60 MeV (29%)) was finally recovered and counted as nickel dimethylglyoxime (Ni-DMG) using a thin-window gas-flow proportional counter. A fixed quantity (50.0 mg) of the Ni-DMG was counted, and the appropriate chemical yield correction applied based on the quantity of added Ni carrier. The purity of the separated Ni activity was established by radioactive decay measurements.

Since the standard comparator method of activation analysis was used in the Ni determinations, an unknown and two Ni standards were identically processed and bombarded in a typical irradiation experiment. The standards were prepared by the coprecipitation of  $\text{Fe}(\text{OH})_3$  and  $\text{Ni}(\text{OH})_2$  from solutions composed of equivalent concentrations and volumes of the various chemicals and solvents used in the preirradiation processing of a 30-g Na sample previously described, to which were added 10 mg of  $\text{Fe}^{3+}$  carrier and microgram quantities of  $\text{Ni}^{2+}$ . The hydroxides were ignited to the oxide, packaged in gelatin capsules, taped in a bundle, placed in a nylon container, and irradiated.

#### Radiochemical Method - Calibration

Known quantities of Ni (0, 51, 155, and 310  $\mu\text{g}$ ) were added as  $\text{Ni}(\text{NO}_3)_2$  to 30-g samples of pure Na treated as described in steps 1 through 4, prior to precipitation of the Fe floc and irradiation in order to prepare a calibration curve (Fig. 2). The results of the activation analysis of these solutions are included in Table 1. The consistency of the specific activities of the Ni standards attests to both the scavenging efficiency of the Fe floc and the analytical reproducibility achieved. A comparison of the associated Ni-65 activity of the blank sample with the standard specific activities indicated a total blank of approximately 3  $\mu\text{g}$  Ni inherent in the analytical scheme. In consideration of the 3-g gross Ni blank correction and the average Na sample size analyzed (21 g), the lower limit of sensitivity of the analytical method used was approximately 0.1 ppm Ni.



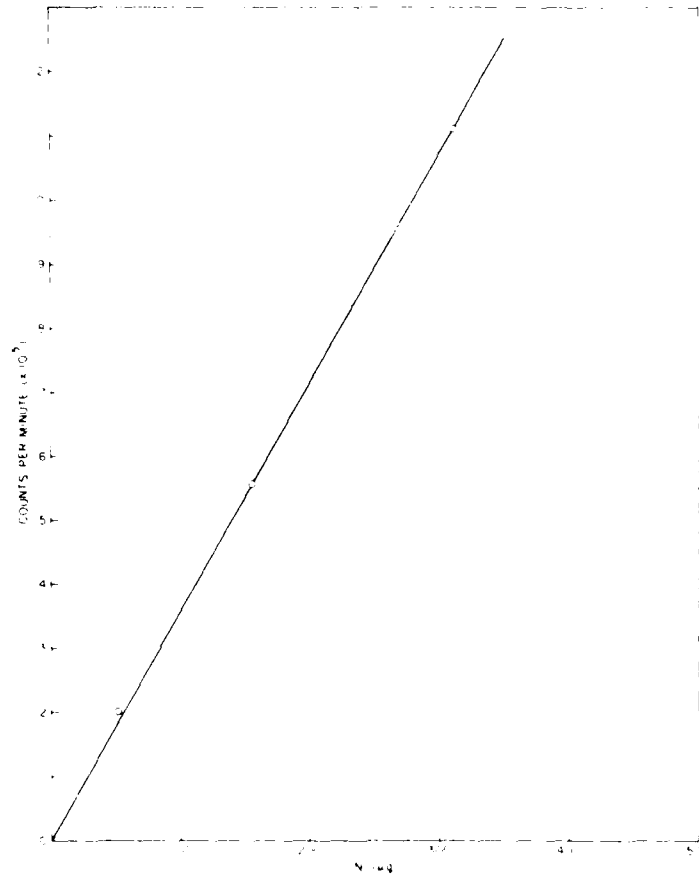


Fig. 2 - Ni calibration curve

Table 1  
Activation Analysis of Fe Scavenger Samples  
of Synthetic Solutions

Sample	Ni added (g)	Ni-65 Activity* (counts min)	Specific Activity (counts min-g Ni)
1	blank	11,920	-
2	51.8	202,580†	3915
3	155.3	558,900†	3600
4	310.5	1,112,500†	3583

\* Corrected to out-of-pile time. Samples were counted approximately 3 hr after irradiation.

† Corrected for reagent blank.

RESULTS

NiO-Liquid Na Reaction

The results of the isothermal reaction of the liquid Na-NiO system are included in Table 2. The general consistency of the data tends to indicate that the system attained equilibrium within 24 hr. The indicated quantities of NiO permitted the dissolved oxide content of the standard 30-g pool of liquid Na at 400 C to be varied from a low value to an excess of that required for saturation (230  $\mu$ g O/g Na). Approximately 32 mg of NiO are required to saturate the liquid Na with oxygen by reaction 3. It is clearly evident that the Ni content of the liquid Na increases as its oxygen content is increased. In Fig. 3 the specific Ni concentrations of the samples are plotted against the corresponding oxygen values on a logarithmic scale. No particular significance is attached to the logarithmic coordinates of Fig. 3, aside from the convenience afforded in noting the above effect. It is apparent that the liquid Na becomes saturated with respect to both oxygen and Ni simultaneously. These results suggest the occurrence of a reaction between Na<sub>2</sub>O and Ni, producing a compound with a finite solubility in liquid Na.

Table 2  
The Liquid Na-NiO System at 400 C

Run	NiO (mg) added to 30 g Na	Oxygen added ( $\mu$ g/g Na)	Equilibration Time (hr)	Sample Size (g)	Ni Found* ( $\mu$ g)	Ni Conc. ( $\mu$ g Ni/g Na)
1	0.29	2.06	163	19.87	5.7	0.29
2	0.43	3.06	24	19.84	12.5	0.63
3	1.16	7.86	72	9.75	10.2	1.05
4	8.70	62.1	94	26.20	294.0	11.2
5	17.90	127.8	141	24.80	288.0	11.6
6	39.20	279.9†	359	25.30	168.2	6.6‡
7	71.10	507.7†	120	20.70	285.5	13.8

\*Corrected for Ni blank (3  $\mu$ g).

†Saturation value (230  $\mu$ g O/g Na).

‡There is no explanation for this low value.

This hypothesis was pursued further in the form of a temperature-dependent solubility study to determine if the resultant data were amenable to a reasonable fit of the Arrhenius equation. Liquid Na was saturated with oxide in the temperature range of 300 to 500 C, as previously described, by the addition of the requisite amount of NiO, and Ni determinations were made of equilibrated, filtered samples. The results are included in Table 3. The solubility data plotted as Ni concentrations on a logarithmic scale against the reciprocal absolute temperature are shown in Fig. 4 and represent a fair straight-line fit of the Arrhenius equation.

Reaction Residue Analysis

In the search for evidence of the formation of Na<sub>2</sub>NiO<sub>2</sub>, an exploratory experiment was run in which large quantities of oxide impurities were present in liquid Na so as to produce a sample of reaction product large enough for as complete and reliable a chemical assay as possible. This was attempted by heating 35 ml of liquid Na at 400 C for several days in the presence of a quantity of oxygen (as NiO) far in excess of the amount

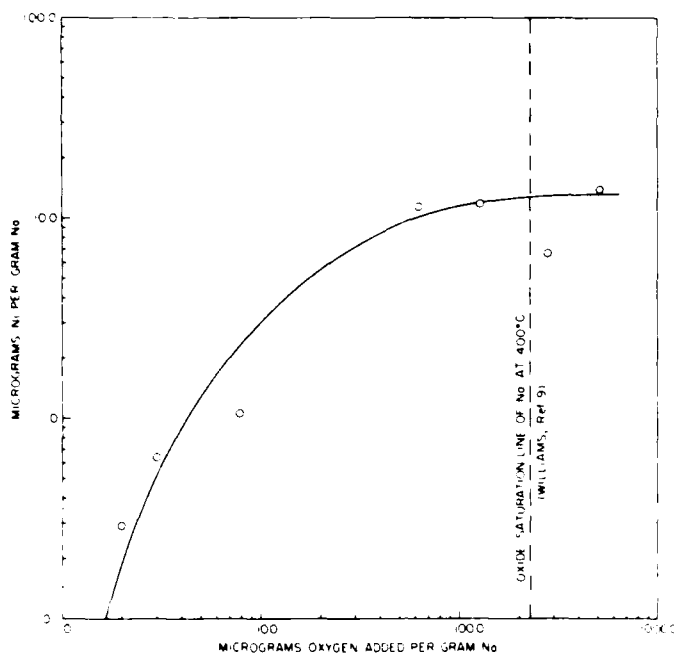


Fig. 3 - Reaction of liquid Na-NiO system at 400°C

Table 3  
Temperature-Solubility Data of Ni-Na<sub>2</sub>O  
Complex in Na

Temp. (°C)	NiO (mg) added to 30 g Na*	Sample Size (g)	Ni Found (μg)	Na <sub>2</sub> NiO <sub>2</sub> Equivalent (μg)	Conc. Na <sub>2</sub> NiO <sub>2</sub> (μg g Na)
300	20	27.75	102	237	8.5
400	40	20.70	283	657	31.7
500	74	16.95	361	839	49.5

\*Sufficient to produce a saturated solution of Na<sub>2</sub>O in liquid Na.

required for saturation of the Na (230 μg g) (9). At the end of the experiment, the apparatus was allowed to cool, dismantled, and the reaction vessel removed. The Na was reacted with EtOH and H<sub>2</sub>O, and the reaction residue (a black, finely divided, highly magnetic powder) was separated from the solution by filtration.

The highly ferromagnetic nature of the residue indicated the reaction residue to be composed mainly of reduced Ni. This was experimentally established by heating a sample of the residue in air until the weight increase of the sample became constant, indicating the complete oxidation of Ni to NiO. The observed increase of sample weight was consistent with that expected for the total conversion of the sample to NiO, establishing that the original reaction residue was composed essentially of Ni with, at most, trace quantities of Na<sub>2</sub>NiO<sub>2</sub>.

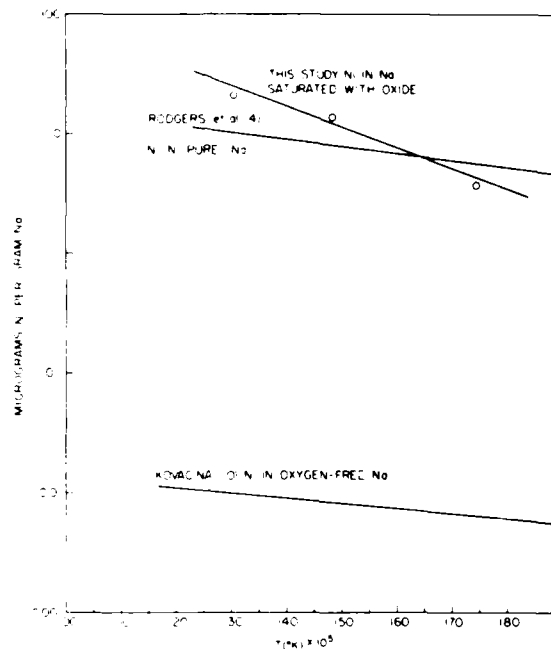


Fig. 4 - Solubility of Ni in liquid Na

## DISCUSSION AND CONCLUSIONS

Figure 3 shows that at 400°C the soluble Ni concentration increased with increasing  $\text{Na}_2\text{O}$  (added as NiO) content of the liquid Na. Likewise, Fig. 4 shows that the soluble Ni content of liquid Na saturated with  $\text{Na}_2\text{O}$  is clearly temperature dependent. Both these phenomena together suggest the occurrence of a reaction between  $\text{Na}_2\text{O}$  and Ni, producing a compound with a finite solubility in liquid Na. It is interesting to note that within the experimental error of the current measurements the slope of the solubility curve (9) of  $\text{Na}_2\text{O}$  in liquid Na is identical with that of the Ni solubility curve of this study (Fig. 4). This in turn indicates that the respective heats of solution of  $\text{Na}_2\text{O}$  (9) and Ni (this study) in liquid Na are the same. It is possible that two mutually exclusive solutes fortuitously have the same temperature coefficient of solubility. However, the possibility of a soluble complex of Ni (or NiO) with  $\text{Na}_2\text{O}$  in liquid Na also exists and would appear to be more plausible, in which case the identical heats of solution noted might also be expected.

Due to the extreme reactivity of liquid Na at high temperature, rigorous impurity controls are essential. Unless experimental conditions are extremely well defined, the interpretation of specific reactions can conceivably be confused by competitive impurity reactions. As a consequence of the solubility determination made of the proposed NiO-liquid Na reaction product discussed in this investigation, it is interesting to speculate further on the reasons for the reported discrepancy of the solubility of Ni (4,10) in liquid Na. As in the case of Fe, Ni solubility data also differ by three orders of magnitude. However, if the equivalent Ni concentration of the proposed soluble reaction product of this study (Fig. 4) is compared with the reported solubility of pure Ni in liquid Na (4,10), fair agreement is observed with the higher literature values. The Ni solubilities reported by Rodgers, et al. (4), were determined in liquid Na of relatively high oxygen content

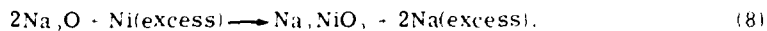
0.005 to 0.010 wt-% in the temperature range of 204 to 537 C. The Ni vessels were initially charged with liquid Na, which had been filtered at 180 C, and thus contained approximately 0.005 wt-% oxygen; however, the oxygen content at the end of an experiment was in the range 0.005 to 0.010 wt-%. If at 400 C it is assumed that one-half of the total oxygen (i.e., 0.005 wt-%) in the liquid Na in these experiments was introduced as NiO from the oxidized Ni surface and the reaction compared to the results of the current study (Fig. 3), the Ni concentration of the liquid Na should be approximately 9 ppm. This is in fair agreement with Rodgers' reported value of 6 ppm, which suggests the possibility that the soluble Ni was of the double-oxide complex form proposed by the current study.

As shown by the current study and the known susceptibility of both Ni and Na to oxygen contamination, it is apparent that reliable solubility determinations of such materials must be made under totally controlled experimental conditions. It is reasonable to assume that the cited discrepancies for both Fe and Ni solubility in liquid Na can be due in large part to the solubility of various oxygen-containing reaction products. As the isolation and identification of such minute quantities of solute compounds are impractical, they can mistakenly be reported as elemental solubilities. This is especially true if the chemical properties of the unsuspected compounds formed are compatible with the analytical procedures devised for the elemental species.

Previous work by the authors (10) on the effect of oxygen concentration in liquid Na on the solubility of Ni at 600 C showed that the solubility increased from 0.012 ppm Ni in pure Na to 0.23 ppm Ni in Na saturated with oxide (0.113 wt-% oxygen). If the temperature-solubility curve (Fig. 4) of the current study is extrapolated to 600 C, the equivalent Ni concentration of the proposed  $\text{Na}_2\text{NiO}_2$  compound would be approximately 50 ppm, a factor of 200 higher than previously found (10). The apparent discrepancy is believed to be inherent in the different mechanisms of formation of the double-oxide compound. In the former study, the liquid Na was oxidized by dry oxygen gas, and the overall mechanism can be described by



and



In reaction 7 there is no readily available NiO to react with the  $\text{Na}_2\text{O}$  initially formed. The formation of NiO through the reaction of  $\text{Na}_2\text{O}$  with Ni (reaction 2) is rapid only at extremely high temperatures (> 800 C), and, moreover, its formation is suppressed by the presence of excess Na (11). Furthermore, differences in the Ni surface area available for reaction could also explain the indicated discrepancy. In the current study, the excess Ni was in the form of a finely divided powder with a relatively large total surface compared to the surface area of a 30-ml Ni crucible used in the former study. In view of these considerations and the similar reaction periods of both studies, it is reasonable to assume that equilibrium conditions were not attained in the previous study under conditions of high oxide concentration.

From the data in Table 2 it can be estimated that the soluble Ni concentration in oxygen-free Na is less than 0.1 g Ni/g Na (0.1 ppm). This value was previously measured as 0.007 ppm Ni (10). Thus, the true solubility of elemental Ni in pure Na appears to favor the lower literature values.

The corrosion of heat-transfer systems fabricated of Ni and employing liquid Na as the coolant proceeds by the principle of temperature-gradient mass transfer. The introduction of oxygen into a hot system from whatever source results initially in the formation of  $\text{Na}_2\text{O}$ , as indicated in reaction 3. The solubility of the Ni-O-Na compound produced

in reaction 4 has been shown by this study to be temperature dependent. Consequently, as the liquid Na coolant cycles through a temperature gradient in a practical heat-transfer system, the solubility of the NiO-Na<sub>2</sub>O complex will vary accordingly, depositing excess solute (and or reduced Ni and Na<sub>2</sub>O) in the cooler regions of the circuit.

The same general corrosion mechanism can be reasonably extended to the Fe-Na system also. Horsley (5) has suggested the formation of a soluble iron oxide-sodium oxide complex (FeO(Na<sub>2</sub>O)<sub>2</sub>) by the reaction between oxygen in the Na and Fe, to explain the increased corrosion rate as a function of oxygen concentration in such systems.

#### SUMMARY

A mechanism for corrosion in the Ni-liquid Na system has been proposed which involves the reaction of Na<sub>2</sub>O with Ni to form a soluble NiO-Na<sub>2</sub>O complex. The overall reaction between the principal oxide impurities (Na<sub>2</sub>O and NiO) of the system is described, and the compound Na<sub>2</sub>NiO<sub>2</sub> (sodium nickelate (II)) is suggested as the primary corrosion product. Indirect evidence for this is the solubility behavior of Ni in liquid Na at 400°C as a function of the oxygen content of the system. The formation and solubility of the Ni compound increases as the oxygen level of the system is raised and reaches saturation at an oxygen level corresponding to the saturation values for Na at the temperature of the reaction. A temperature-dependent solubility determination of the compound was made, and a plot of the logarithm of the solubility (as Ni concentration) against the reciprocal absolute temperature gave a fair straight-line representation of the data collected in the temperature range of 300 to 500°C. While the absolute identity of the corrosion product is structurally indeterminate, it is indicative, however, that the corrosion process in the Ni-liquid Na system proceeds by the genesis of a soluble NiO-Na<sub>2</sub>O compound.

#### REFERENCES

1. Bogard, A.D., "The Solubility of Iron in Sodium Metal, Sodium-Sodium Oxide, and Sodium-Sodium Oxide-Sodium Hydroxide," NRL Report 4131, Mar. 1953
2. Batutis, E.F., Rodgers, S.J., and Mausteller, J.W., Mine Safety Appliances Co., TR-33, Nov. 1954
3. Epstein, L.F., and Weber, C.E., Knolls Atomic Power Laboratory, KAPL-362, Aug. 1950
4. Rodgers, S.J., Mausteller, J.W., and Batutis, E.F., Mine Safety Appliances Co., TR-27, June 1954
5. Horsley, G.W., J. Nucl. Energy, Part B: Reactor Technology 1:84 (1959)
6. Williams, D.D., Grand, J.A., and Miller, R.R., J. Am. Chem. Soc. 78:5150 (1956)
7. Smith, G.P., "Corrosion of Materials in Fused Hydroxides," ORNL-2048, Mar. 1956
8. Lyon, R.N., et al., "Liquid-Metals Handbook," NavExos P-733 (Rev.):144 (1952)
9. Williams, D.D., Grand, J.A., and Miller, R.R., J. Phys. Chem. 63:68 (1959)
10. Kovacina, T.A., and Miller, R.R., Nucl. Sci. Eng. 10:163 (1961)
11. Williams, D.D., and Miller, R.R., WADC Technical Report 54-185, Part II, Feb. 1955

Appendix

RADIOCHEMICAL ANALYSIS OF IRRADIATED  $\text{Fe}_2\text{O}_3$   
SAMPLES FOR Ni-65

The procedure employed for the separation and purification of the induced Ni-65 activity in the irradiated scavenger samples was as follows:

1. To the irradiated sample in a 30-ml Pt crucible, add 0.5 ml conc.  $\text{H}_2\text{SO}_4$  and 10 ml of conc. HF and evaporate to dryness to eliminate Si-31 contaminant activity ( $t_{1/2} = 2.62$  hr).
2. Fuse the ignited residue with 5 g  $\text{NaHSO}_4$  and dissolve the salt cake in 100 ml  $\text{H}_2\text{O}$  containing 5 drops of conc.  $\text{H}_2\text{SO}_4$ .
3. Add 20 mg each of Ni, Pb, Ag, and Cu standard carriers and saturate with  $\text{H}_2\text{S}$  while heating in a  $\text{H}_2\text{O}$  bath.
4. Filter off and discard the acid sulfide group contaminants.
5. Add 20 mg Fe holdback carrier and 10 ml of 10% Na-citrate solution to the filtrate after boiling to remove  $\text{H}_2\text{S}$ . Precipitate Ni with 15 ml of dimethylglyoxime (DMG) reagent (1% DMG in EtOH) from ammoniacal solution.
6. Dissolve the filtered Ni-DMG in 2 ml conc. HCl, dilute to 15 ml with water, and repeat step 5.
7. Extract Ni-DMG twice with 15-ml portions of  $\text{CHCl}_3$  in a 100-ml separatory funnel. Discard the aqueous layer.
8. Back extract Ni-DMG into 20 ml of 6M HCl and discard the organic layer.
9. Add 10 ml of 10% Na-citrate solution, 15 ml DMG reagent, and make the solution basic with  $\text{NH}_4\text{OH}$  to reprecipitate Ni-DMG.
10. Dry Ni-DMG at  $105^\circ\text{C}$ , weigh 50 mg, and mount on Lucite planchet. Count the Ni-65 activity (2.10, 0.6, 1.0 MeV  $\beta$ 's; 2.56-hr half-life) with a thin-window preflush gas proportional counter.

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13. ABSTRACT <p>The influence of oxide content on the solubility of Ni in liquid Na at 400°C was investigated. The solubility of Ni increased with increasing oxide content of the Na up to the saturation level of Na<sub>2</sub>O in Na. The temperature-dependent-equilibrium solubility of Ni in liquid Na saturated with Na<sub>2</sub>O (oxygen added as NiO) was found to vary between 4 ppm at 300°C and 21 ppm at 500°C. The soluble species is postulated to be a compound of the type (NiO)<sub>x</sub>(Na<sub>2</sub>O)<sub>y</sub>.</p>			



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