Transport and Deposition of Metals in Sodium-Stainless Steel Systems, (III)

Deposition of Cesium in Stainless Steel Capsules under a Large Temperature Gradient

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With the object of gaining an insight into cesium behavior in its relation to oxygen concentration in sodium-stainless steel systems, a deposition experiment was carried out with use made of stainless steel capsules containing 20 g of sodium and a trace amount of radioactive cesium.

The capsule was vertically set to establish a steep axial temperature gradient, descending forward the bottom, and maintained during a period considered ample for the sodium oxide contained in excess of saturation to settle on the capsule bottom. The oxygen concentration in the sodium was varied by adjusting the temperature of the capsule bottom. The radial distribution of cesium across samples sectioned from different parts along the length of the capsule tube were determined on annular samples extruded from sections of the capsule after chilling for rapid solidification of the sodium.

The activation energy for cesium deposition was obtained from partition coefficients—defined as the ratio of cesium concentration on the stainless steel surface and that in the bulk sodium. The resulting data on activation energy indicate that cesium radioisotope deposits in the temperature region below 440°C presumably by physical adsorption on the stainless steel surface when it has previously been exposed to high temperature sodium, and that this surface adsorption appears to be insensitive to differences in oxygen concentration in the sodium.

KEYWORDS: fission products, cesium isotopes, stainless steel, sodium capsule, mass transfer, oxygen concentration, deposition, adsorption, activation energy, temperature gradient

I. INTRODUCTION

Transport and deposition of radioisotopes possessing long half-lives introduced in the primary coolant of Fast Breeder Reactors will create maintenance problems and bring about performance degradation. Cold traps are commonly utilized to collect metallic impurities as well as sodium oxide\(^{(1)\sim(3)}\), but the mechanisms involved are yet scarcely understood.

The radioisotopes of cesium have long half-lives and large fission yields, and for this reason much experimental effort has been directed toward obtaining a better understanding of cesium behavior in sodium systems\(^{(4)\sim(6)}\). Recent studies by Guon\(^{(5)}\) and by Cooper & Taylor\(^{(6)}\) have established that (a) cesium deposits on a stainless steel surface from sodium by reversible and irreversible adsorption, which is affected by the prior temperature history of the surface exposed to the sodium, (b) the rates of adsorption

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and dissolution of cesium are so rapid that they are scarcely affected by the rate of sodium flow, and (c) oxygen present on the stainless steel surface appears to reduce its ability to adsorb cesium.

Whether or not oxygen contained in the sodium affects the adsorption of cesium on the stainless steel surface is of interest in connection with the removal of cesium from sodium by cold trapping methods. In the present study, an attempt was made to determine the partition coefficient for surface adsorption of cesium in sodium, with use made of a capsule containing stagnant sodium. The effect on adsorption brought by the presence of oxygen in the sodium is discussed on the basis of the activation energy of adsorption derived from the partition coefficients determined as above. This paper describes a practical experiment in partition coefficient determination, together with results obtained therein and discussion of the results.

II. EXPERIMENTAL

1. Experimental Apparatus

The capsule used for the adsorption experiment consists of a tube 10 mm in inner diameter and 180 mm long, sealed at the bottom and with the top end connected to a vessel provided with plugged nozzles for introducing the sodium and cesium radioisotope, as shown in Fig. 1. The capsule is made entirely of AISI type 304 stainless steel. It is filled with about 20 g of sodium, which reaches the level of the vessel, and the free surface of the liquid sodium is protected by argon cover gas. The radioisotope dissolved in the sodium deposits on the inner surface of the tube.

The capsule is installed vertically as shown in Fig. 2, with the vessel part at the upper end inserted into a resistance furnace and with the bottom standing in a brass cooling stand. The heat flux flowing from the vessel toward the tube bottom establishes a steep temperature gradient along the tube axis. Glass wool insulation surrounding the tube levels the temperature across the tube, to establish a one-dimensional distribution. Thermocouples are attached on the surface of the tube at 10 mm intervals to measure the temperature along the tube.

2. Sodium Filling

The inner surface of the capsule was washed clean with oil-removing solvent and dilute nitric acid, and then rinsed with pure water. Possible contamination of sodium was further prevented by flushing the capsule with argon gas, evacuating and baking. The capsule was then filled through one of noz-
zles with reactor grade sodium at 150°C, after filtering through a porous stainless steel screen. Sodium adhering to the nozzles was wiped off, after which both nozzles were sealed with stainless steel plugs welded on in an argon gas chamber. Prior to sealing, drops of hydrochloric acid containing 200 mCi of radioactive cesium were evaporated onto the tip of one of the plugs.

3. Surface Cleaning and Radioisotope Dissolution

The experiment was preceded by cleaning of the stainless steel surface to receive radioisotope deposition. This was done by exposing the surface to hot sodium for 100 hr prior to radioisotope dissolution. During this cleaning operation, the plug carrying the radioisotope was isolated from the liquid sodium by the argon cover gas, as shown in Fig. 3(a). The cleaning exposure was performed at 400°C, which was the average sodium temperature of the capsule tube during the adsorption experiment. The duration of the exposure was determined from preliminary tests.

After capsule cleaning, the radioisotope fixed on the holder was dissolved into the sodium by inverting the capsule as illustrated in Fig. 3(b) and heating in a resistance furnace. The temperature of the sodium was controlled at 150°C, which assured that the surface exposed to the sodium retained its activity for surface adsorption. Since cesium is easily soluble in sodium, 100 hr was considered adequate for complete dissolution, which was accelerated by frequent shaking of the capsule. The progress of cesium dissolution was monitored by observing the radioactivity of the capsule near the bottom. From the free energy of formation of metal chlorides, it is indicated that cesium chloride is more stable than sodium chloride yet when a trace amount of cesium chloride is added to sodium, the cesium is known to transform into metal.

After cesium dissolution, the capsule was again inverted and cooled to solidify the sodium. The radioisotope holder was replaced by a new stainless steel plug, which was
seal-welded to the nozzle in an argon gas chamber. Prior to this seal-welding, sodium peroxide powder was added to the capsule. The amount of oxide was regulated to ensure that the oxygen concentration in the sodium averaged about 500 ppm in the capsule.

4. Control of Oxygen Level

The capsule bottom, resting in the brass cooling stand, was maintained at the lowest temperature of the whole capsule, where such impurities as sodium oxides would deposit, while their concentration throughout the stagnant sodium would equalize by diffusion. After lapse of a sufficient period, an equilibrium would be established between the impurities in the sodium and the deposits. The period required for this stabilization was estimated not to exceed 700 hr, from calculations on ordinary and thermal diffusion of impurities through sodium in a tube under initial and boundary conditions similar to those of the present system.

Details of the analysis will be described further on in the chapter containing the discussion. From the foregoing observations, it may be assumed that the sodium after attaining equilibrium contains oxygen in concentration corresponding to the solubility in liquid sodium at the temperature of the capsule bottom.

5. Sampling after Deposition Process

Upon terminating the deposition process, the capsule was immersed slowly into quenching oil cooled directly with dry-ice, in order to fix the radioisotope in solid sodium. The capsule tube containing the sodium thus solidified was sectioned with a saw into samples 10 mm long. The contaminated surfaces of the sodium were scraped off with a knife. The sodium was then extruded from selected tube sections of representative portions along the capsule axis, and further successively cut to form two concentric annular pieces and a core, as illustrated in Fig. 4. The resulting pieces of sodium were separately dissolved in 20 ml of methyl alcohol. The sodium adhering to the tubes was also removed by dissolution in methyl alcohol. The radioactivity in the solutions was counted in a shielded well with a NaI crystal detector, and the counts were analyzed by a multichannel analyzer. The amount of sodium in the solution was determined by titration.

6. Sampling for Oxygen Analysis

In order to verify that the oxygen level had been well maintained during the deposition process, the oxygen distribution along the axis was determined in capsules identical to those used in the experiment but without radioisotope charge. After solidification of the sodium in the capsule, the surface of the capsule was cleaned with polishing paper to prevent contamination of the sodium during sampling. In a chamber containing extra high-purity argon gas, sections 20 mm long were sawn off from various parts of the capsule; core samples were extruded from the sections, and placed in a pyrex cylinder for vacuum distillation. After distilling the sodium, the oxygen contained in the residuals was determined by titration.
III. RESULTS

1. Distribution of Oxygen in Sodium along Capsule Tube Axis

The oxygen concentrations along the capsule tube axis after stabilization with bottom temperatures of 190°, 250° and 320°C, are plotted in Fig. 5, in Arrhenius presentation on semi-log scale, against the reciprocal of the average absolute temperature of the sodium samples during the deposition process. The experimental results represented by the solid lines in Fig. 5 indicate that in the higher temperature parts of the sodium core, the oxygen concentration maintains a fairly constant level, but abruptly increases in the vicinity of the lower temperature extremity of the specimen. This abrupt increase indicates that during the process, the excess amounts of sodium oxide contained in the sodium have deposited on the capsule bottom.

In the higher temperature region of the capsule, oxygen concentration in the sodium increases with the bottom temperature, (cf. plots for 190° and 250°C bottom temperature). This indicates that the oxygen concentration in the sodium is determined by the bottom temperature. The plots for 320°C bottom temperature represents a run made without the addition of sodium oxide, and it is seen that the oxygen concentration remains on a fixed level along the capsule tube, (cf. dotted line), except at the bottom. This slight increase near the bottom, however, is hardly indicative of sodium oxide deposition on the capsule bottom.

The foregoing observations indicate that an equilibrium should be established between the sodium oxide dissolved in the sodium and that deposited on the capsule bottom when sodium oxide is contained in quantities exceeding saturation. The relationship between the oxygen concentration read from the neighborhood of 400°C in Fig. 5 and the corresponding bottom temperature is in a reasonable agreement with reported data on oxygen solubility in sodium\(^{(11)-(13)}\).

2. Distribution of \(^{137}\text{Cs}\) in Sodium Sample

(1) Distribution of \(^{137}\text{Cs}\) in Radial Direction

Figure 6 shows the radial distribution of \(^{137}\text{Cs}\) on three different cross sections of a capsule. The specific radioactivity of \(^{137}\text{Cs}\) on all three cross sections shows a relatively flat distribution in the central portion, adjoining by a slight fall nearer the tube wall, and then a sharp rise upon approaching the tube wall. The above data indicate that \(^{137}\text{Cs}\) tends to segregate and collect on the tube wall. The concentration of \(^{137}\text{Cs}\) collected on the tube wall differs little between 669° and 479°C, while a notably higher level is resisted at 267°C.

The foregoing observation would justify considering, for practical purpose, only two—instead of the initially envisaged four—regions, to represent the radial distribution of \(^{137}\text{Cs}\)—a core region of 8 mm diameter with the uniform distribution and a peripheral layer of much higher radioactivity\(^{(10)}\).
Distribution of $^{137}\text{Cs}$ in Axial Direction

With the view to obtaining the distribution of $^{137}\text{Cs}$ in reference to the sodium temperature, the logarithm of the specific radioactivity of $^{137}\text{Cs}$ in both the core and the peripheral layer were plotted against the reciprocal of the absolute temperature of the samples resistered during the runs. Figures 7(a), (b) and (c) represent the Arrhenius plots of experimental results obtained with different bottom temperatures. These data indicate the establishment of more or less uniform $^{137}\text{Cs}$ distribution along the core over the temperature range covered, and confirm the generally higher level of radioactivity in the peripheral layer expected from the data given in the preceding Sec. (1). In the peripheral layer also, the axial distribution is uniform in the region where the temperature exceeds $417^\circ\text{C} (1,000/T=1.45)$, but in the cooler parts, the specific radioactivity increases roughly linearly with decreasing sodium temperature. Further, around $227^\circ\text{C} (1,000/T=2.0)$, the Arrhenius plots show a second steepening of the slope. And below about $203^\circ\text{C} (1,000/T=2.1)$, the corresponding plots for the core also abruptly acquire a gradient. Another trend worth noting is that with rising bottom temperature ($155^\circ, 230^\circ$ to $330^\circ\text{C}$), the difference in specific radioactivity between the core and the peripheral layer appears to diminish.

IV. DISCUSSION

1. Diffusing Time of Impurities along Capsule Tube

The foregoing observations indicate that impurities such as sodium oxide tend to accumulate at the bottom kept at the lowest temperature in the capsule. In order to examine whether or not the deposition of impurities would reach steady state within
the 700 hr allowed for stabilization, two models are considered for the diffusion of the impurities through the sodium toward the capsule bottom: (1) by ordinary diffusion and (2) in combination with thermal diffusion.

Since the temperature in the capsule tube had a downward gradient from top toward bottom, this would have tended to suppress thermal convection in the sodium. Yet in the radial direction, the inner diameter of 10 mm may have sufficed to produce a small temperature difference on the cross section to cause minute thermal convection in the sodium. This thermal convection could be expected to contribute in some degree to impurity transport in the sodium, and tend to shorten the actual time registered for diffusion, as compared with the value calculated from the models described above.

(1) Calculation with Ordinary Diffusion Model

Let the distance from the neck of the vessel to the capsule bottom be \( L \) and the initial impurity concentration be uniform throughout the capsule \( (c=1) \). If the current of mass is considered negligible at the capsule neck (\( x=0 \)) and the concentration at the capsule bottom (\( x=L \)) is constantly maintained at \( c_B \), the diffusion in such a system would be governed by the equation

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2},
\]

which can be solved in the form

\[
\frac{c}{c_B} = 1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{(2n+1)} \cos \left( \frac{(2n+1)\pi x}{2} \right) \exp \left[ -\frac{(2n+1)^2\pi^2 t}{4} \right],
\]

where \( \tau = \frac{D t}{L^2} \), \( \xi = x/L \).

Since the second and succeeding terms of the infinite series in Eq. (2) are much smaller than the first term, Eq. (2) can be validly approximated by

\[
\frac{c}{c_B} = 1 - \frac{4}{\pi} \cos \left( \frac{\pi x}{2} \right) \exp \left[ -\frac{\pi^2 t}{4} \right].
\]

Then, the lapse of time to the instant at which value in brackets of the exponential function becomes negative unity—termed the "relaxation time"—is

\[
\theta = 4L^2/\pi^2D.
\]

(6)

The diffusion coefficient \( D \) of the impurity in the sodium is not known, but can be estimated to be order similar to that of the coefficient for self-diffusion of sodium \( (14) \):

\[
D \approx 2 \times 10^{-4} \text{ (cm}^2/\text{sec}).
\]

Since the length of the capsule is

\[
L = 1.8 \times 10 \text{ (cm)},
\]

the relaxation time becomes

\[
\theta = 183 \text{ (hr)}.
\]

Thus, if the lapse of time required for reaching steady state is assumed to be three times the relaxation time, the diffusing time will be 549 hr.

(2) Calculation with Thermal Diffusion Model

Thermal diffusion of a solute in a dilute solution can be expressed by

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - H \frac{\partial c}{\partial x},
\]

where \( H = (D/L)(\alpha \cdot DT/T_m) \)

and \( \alpha \) is the thermal diffusion constant. When the co-ordinates, as well as the initial and the boundary conditions, are the same as in the preceding case of Sec. (1), Eq. (7) for thermal diffusion has the solution

\[
\frac{c}{c_B} = \exp[2\lambda(\xi - 1)] - 2 \exp[\lambda(\xi - 1)] \cdot \sum_{n=1}^{\infty} \frac{\sin(\gamma_n)}{\lambda^2 + \lambda + \gamma_n^2} \cdot \exp \left[ -\left(1 + \frac{\gamma_n^2}{\lambda^2}\right) \tau \right],
\]

where \( \tau = (H^2/4D)t \), \( \lambda = HL/2D \).

and \( \gamma_n \) are the positive roots of

\[
\lambda + \gamma \cot(\gamma) = 0.
\]

Since the second and succeeding terms of the infinite series in Eq. (9) are again much smaller than the first term, Eq. (9) can be simplified into

\[
\frac{c}{c_B} = \exp[2\lambda(\xi - 1)] - 2 \exp[\lambda(\xi - 1)] \cdot \frac{\sin(\gamma_1)}{\lambda^2 + \lambda + \gamma_1^2} \cdot [\lambda \sin(\gamma_1) + \gamma_1 \cos(\gamma_1)] \exp \left[ -\left(1 + \frac{\gamma_1^2}{\lambda^2}\right) \tau \right].
\]

This equation yields a relaxation time of

\[
\theta = (L^2/D)(1/(\lambda^2 + \gamma_1^2)).
\]
From an experiment on thermal diffusion conducted separately, the measured thermal diffusion constant becomes

\[ \alpha = 1.6. \]

If values of 400 and 673 K, respectively, are adopted for the temperature difference \( \Delta T \) and the average temperature \( T_m \), combination of Eqs. (8) and (11) yields

\[ \lambda = 0.475. \]

Substituting \( \lambda \) into Eq. (12),

\[ \gamma_1 = 1.825 \]

with use made of the values determined as above for \( D \), \( L \) and \( \lambda \), the relaxation time becomes, in the present instance,

\[ \theta = 126 \text{ (hr)}. \]

Three times this relaxation time makes 378 hr, which—as expected—is shorter than the relaxation time obtained in the preceding Sec. (1) by the ordinary diffusion model. In consideration of the uncertainty in the diffusion coefficient of the impurity in sodium, the running period of 700 hr should be considered reasonable period for allowing complete stabilization.

2. Definition of Partition Coefficient

For analyzing the tendency observed of the radioisotope to collect on the tube wall in the lower temperature region of the capsule, a reversible process can be assumed between the radioisotope \( M^* \) in the sodium and that on the surface of the tube, presented by

\[ M^* \text{ in sodium } \rightleftharpoons M^* \text{ on surface} \]

for which the partition coefficient, as defined by Guon and Davies, would become

\[ K_p = \frac{\text{Concentration of } M^* \text{ on surface (cps/cm}^2\text{)}}{\text{Concentration of } M^* \text{ in sodium (cps/cm}^2\text{)}}. \]

(16)

If the amount of the radioisotope deposited on the vessel surface is proportional to the radioisotope concentration in the sodium, the partition coefficient defined by Eq. (16) would have a meaning similar to the chemical equilibrium constant. Provided that \( K_p \) can be determined from experiment, and a linear relationship can be discerned in the Arrhenius plots of \( K_p \) (log \( K_p \) vs. \( 1/T \)), then one could obtain the activation energy of deposition from the inclination of the straight line drawn through the plots. Once the activation energy of deposition is obtained, the mechanism of radioisotope deposition could be discussed more quantitatively. With the measured quantities expressed by

\[ m_A: \text{Amount of sodium adhering to tube surface (g)} \]
\[ a_A: \text{Radioactivity in sodium adhering to tube surface (cps)} \]
\[ m_B: \text{Amount of sodium in core (g)} \]
\[ a_B: \text{Radioactivity in sodium in core (cps)} \]

the radioactivity corresponding to the amount of deposition on the surface becomes

\[ a_A = (a_B/m_B)m_A, \]

(17)

and the radioactivity proportional to the concentration in the sodium

\[ (a_B/m_B)(m_A + m_B), \]

(18)

as illustrated in Fig. 8. Consequently, Eq. (16) can be rewritten in the form

\[ K_p = \frac{(a_B/m_B)m_A/S}{(a_B/m_B)\rho_{20}}, \]

(19)

where \( S \): Surface area of a piece of tube (cm\(^2\))
\( \rho_{20} \): Density of sodium at room temperature (20°C) (g/cm\(^3\)).

3. Deposition Mechanism of \( ^{137}\)Cs

Figure 9 represents the Arrhenius plot for the partition coefficients obtained from the results given in Figs. 7(a)~(c). For the sake of comparison, the partition coefficients
obtained from the results of another loop experiment are also shown in the same diagram. The present data show a linear temperature dependence in the region below 440°C (1,000/T=1.40), but above this temperature, the plots appear to lose their consistency in relation to temperature. This implies that the deposition of $^{137}$Cs on stainless steel surfaces can be quantitatively considered only in the region below 440°C. Above this temperature, the mechanism of deposition would appear to be disordered, possibly by segregation of the $^{137}$Cs during the rapid solidification of the sodium. Such segregation of $^{137}$Cs during sodium solidification may also be the cause of the depression observed in the radial distribution of $^{137}$Cs (Fig. 6).

The linear portions of the plots in Fig. 9 show almost identical gradients for the three capsule runs and the loop run, indicating that the deposition of $^{137}$Cs is not affected by oxygen concentration in the sodium and inferring that the deposition in the loop should take place by a mechanism similar to the case in the capsules. The activation energy calculated from the partition coefficients, which were determined by least-square method for the region below 440°C, falls in the range of $-4\sim-5$ kcal/g-atom, as noted in Fig. 9. This would indicate that $^{137}$Cs deposits on stainless steel surfaces by adsorption, especially physical adsorption.

The broken lines in Fig. 9 represent the experimental results reported by Guon. He determined the cesium concentration in the sodium and the amount of deposited cesium in the cold trap by means of in situ counting of the radioactivities respectively in the surge tank and in the cold trap. The two values of radioactivity thus counted served to derive the values of partition coefficient presented in Fig. 9. The two lines marked "activated" and "deactivated" respectively represent the partition coefficients obtained before and after the stainless steel surface had been kept in contact with 500°C sodium for 30 min. According to Guon, the stainless steel surface markedly reduces its activity for the adsorption of cesium, once the surface has been exposed to high temperature sodium. The activation energy of adsorption measured in the experiment on deactivated surface was $-3$ kcal/g-atom, which is unexpectedly close to that of adsorption obtained in our present capsule experiments. The fact that the inner surface of the capsule was preconditioned by contact with 400°C sodium for 100 hr prior to the deposition run may of course have had some relation to this coincidence with Guon’s deactivated surface data. The method of obtaining partition coefficients by rapid solidification of sodium in a non-isothermal capsule and determining the cesium distribution by the dissection of the sodium samples is a simple and practical means of measuring the activation energy of surface adsorption, while admittedly the procedure may not be applicable when accuracy is of essence. Nevertheless, the remarkable closeness of values of activation energy for surface adsorption between those of the present experiment and Guon’s—obtained by entirely different methods—indicates that the

![Fig. 9 Measured partition coefficient for $^{137}$Cs between stainless steel surface and bulk sodium](image)
V. CONCLUSION

(1) Metal sodium, added with sodium oxide in excess of its solubility, was sealed in a stainless steel capsule, which was placed vertically under a steep temperature gradient descending toward the bottom. Upon lapse of sufficient time to stabilize, the excess sodium oxide was seen to deposit at the bottom, which had been kept at the lowest temperature in the whole capsule.

(2) The lapse of time allowed for stabilization was three times the relaxation time derived from analyses of ordinary and thermal diffusion of sodium oxide through liquid sodium in the capsule, which is considered ample for all excess sodium oxide to settle on the bottom.

(3) The sodium oxide concentration in the sodium was varied by adjusting the temperature of the capsule bottom. The measured oxygen concentration in the sodium in its relation to the bottom temperature roughly agreed with reported oxygen solubility data.

(4) Cesium radioisotope added to the sodium was observed to collect on the capsule wall, where the specific radioactivity was found prominently higher than in the bulk sodium, a tendency of that was accentuated at temperature below 440°C.

(5) The partition coefficient—defined as the ratio of cesium concentrations between that on the stainless steel surface previously exposed to high temperature sodium and that in the bulk sodium—was obtained for different temperatures in the range covered. The activation energy obtained from plots of the partition coefficients against temperature ranges from $-4$ to $-5$ kcal/g-atom, indicating that—within the temperature range of interest—cesium radioisotope deposits on the surface presumably by physical adsorption.

(6) The oxygen concentration in the sodium was not observed to affect the surface adsorption of cesium in the range of oxygen concentrations below 100 ppm.

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