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THE PENETRATION OF IODINE INTO PROTECTIVE COATINGS

R. R. Hammer, B. J. Newby, and K. L. Rohde

IDAHO NUCLEAR CORPORATION

NATIONAL REACTOR TESTING STATION

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A B S T R A C T

The penetration of iodine (released as I_2) into protective coatings, which are used for the interior of reactor buildings, is described by a simple model derived from Fick's basic diffusion concepts. Diffusion coefficients for four commercial coatings are given for the temperature range 20-140°C.

SUMMARY

Of the radioactive isotopes which could be released to a reactor containment building as a result of certain nuclear reactor accidents, radioactive iodine is considered to be one of the greatest health hazards. It is, therefore, of prime interest to understand the release, transport, and deposition characteristics of iodine. The penetration of iodine into protective coatings characteristic of those used in reactor containment buildings has been studied, and the following generalized findings resulted: 1) penetration of iodine into the coating occurs with the four types of paint coatings tested, epoxy, vinyl, chlorinated rubber, and phenolic; 2) the penetration is at least in part reversible; and 3) the degree of penetration is associated with the temperature of the coating and its physical state. A model for unidirectional diffusion in a semi-infinite solid, derived from Fick's basic diffusion concepts, adequately describes the penetration of iodine into these coatings to thicknesses as great as 0.25 mm. Diffusivities for iodine (generated as I_2) in the protective coatings tested ranged from 10^{-8} to $10^{-10} \text{ cm}^2\text{-sec}^{-1}$. Effects of coating type, additives, and exposure time are also reported.

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I. INTRODUCTION

Under loss-of-coolant accident conditions in a pressurized or boiling water reactor, short-lived fission products may be released to the atmosphere of the reactor containment building. The behavior of iodine under these conditions is of prime importance since it is a major health hazard and will represent more than 90 percent of the non-rare gas fission products released from the reactor vessel. In the course of the evaluation program^[1] for the protective coatings for LOFT (Loss of Fluid Test) it was discovered that iodine, released as I_2 in experimental studies, penetrated deeply into all of the protective coatings studied. In order to determine the impact of this penetration on the feasibility of decontamination of the protective coatings after a loss-of-coolant accident, quantitative data for the amount of penetration as a function of depth were obtained^[a]. From other decontamination studies it was learned that the penetration of iodine was, at least in part, reversible^[b]. Because of the importance of the phenomenon of penetration to both the contamination and decontamination aspects of the loss-of-coolant accident, it appeared desirable to fit the experimental data for the penetration to a mathematical model so that extrapolation of the data would be possible. This was done earlier with reasonable success using a few sets of experimental data on two different coatings and a simple analytical approach. Using the solution of Fick's second law for unidirectional diffusion in a semi-infinite solid, diffusivities of the order of $1 \times 10^{-9} \text{ cm}^2\text{-sec}^{-1}$ were calculated^[c].

Recently additional experimental data have been obtained for several coatings of significance to the LOFT program and to the reactor safety program in general. These data are reported here. The potential of this sorption of iodine on protective coatings as an engineered safeguard is being evaluated elsewhere^[2].

II. EXPERIMENTAL

For penetration measurements, coated steel coupons were exposed to iodine-containing vapors (I_2) under controlled conditions^[3]. After contamination the contaminated coating on the coupon was removed from all except one surface of the coupon, and a small area of the remaining coating was counted in standard geometry to obtain the initial activity. Then this small area was sanded away incrementally so the activity could be determined as a function of depth. The amount of coating removed was determined by measuring the total thickness of the coating and coupon before and after sanding.

[a] See page 76 of Reference 1

[b] See page 77 of Reference 1

[c] See page 80 of Reference 1

III. RESULTS AND DISCUSSION

Four generic types of protective coatings, epoxy, vinyl, chlorinated rubber, and phenolic have been tested and all show penetration of iodine. Figure 1 shows a typical set of original experimental data plotted as the log of the ratio of the activity observed at a given depth to the activity observed at the surface. The dashed lines on Figure 1 represent the maximum and minimum penetration observed over the whole range of coatings and conditions studied.

1. REVERSIBILITY OF IODINE PENETRATION

The reversibility of the penetration of iodine into protective coatings is demonstrated in Table I by the difference in decontamination obtained between spraying the surface and autoclaving the coating. Generally, a removal of 50 percent or less of the total iodine was obtained by spraying for 10 minutes each with nitric acid and an alkaline reagent at 80°C, but removal of 80 to 99.9 percent was obtained by autoclaving the coating for three days at 138°C and 3.6 atm. Similar data were obtained for several coatings contaminated by iodine released from molten irradiated uranium dioxide in the Contamination-Decontamination Experiment [d]. These data are interpreted as indicating that autoclaving at the elevated temperature permits the diffusion of iodine to the surface where it is washed off by the condensate. Supporting this interpretation are the facts that coatings contaminated at higher temperature (138°C) and pressure do not decontaminate by autoclaving with uncontaminated steam as readily as

coupons contaminated at 35°C; and for a constant time period, autoclaving at 138°C is more effective than 110°C for iodine decontamination. It should be noted that significant differences in decontamination by spraying have not been noticed between the coatings of different generic types; the variation within the group of coatings nominally called epoxies is as great as the variation between generic types.

Figure 1 Penetration of Iodine into Protective Coatings.

2. MATHEMATICAL MODEL FOR DIFFUSION

A model for unidirectional diffusion in a semi-infinite solid derived from Fick's basic diffusion concepts [4] seems to adequately represent the characteristics

[d] The Contamination-Decontamination Experiment (CDE) is a pilot plant scale facility for melting small, highly irradiated fuel pins in a flowing gas stream and conveying the resultant contaminated vapors and particulates to a simulated containment vessel where plate-out and decontamination studies can be made.

Table I
DECONTAMINATION OF PROTECTIVE COATINGS
PERCENT REMOVAL OF IODINE

<u>Coating</u>	<u>Generic Type</u>	<u>By Spraying</u>	<u>By Autoclaving</u>
Amercoat 66	Epoxy	23	99.6
Devran 500	Epoxy	33	99.9
Devran 600	Epoxy	50	93.1
Phenoline 300	Phenolic	23	98.2
Carboline 1323	Urethane	50	80.0
Carboline B-15	Urethane	38	99.8

of the interaction between iodine and the various types of coatings that have been tested. This model was chosen partially for simplicity and partially because of uncertainty concerning the interaction of the undercoats and carbon steel substrate with iodine. Equation 1 is the solution of Fick's second law for unidirectional diffusion in a semi-infinite solid,

$$\frac{C}{C_s} = 1 - \phi\left(\frac{x}{2\sqrt{Dt}}\right) \quad (1)$$

ϕ defined in equation 2 is the probability integral.

$$\phi = \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\lambda^2} d\lambda \quad (2)$$

Where

C_s is the concentration of iodine in the surface;

C is the iodine concentration at depth x ;

D is the diffusivity and

t is time

Tabulations of this function are available for various values of λ , the integration variable. The derivation is available in a number of texts [4]. The boundary conditions assumed for such a derivation are an initial concentration of 0 in the coating at all depths. The concentration of diffusing material at the surface is assumed to be constant during the diffusion period, and it is also assumed in the derivation that the diffusivity is constant for any one temperature and material.

The derivative of the activity with respect to depth at any point in the coating is the concentration of iodine activity at that point. The concentration of iodine as a function of depth in the coatings was obtained from the slopes of plots of $\ln A$ versus x where A is the activity and x is the thickness of the coating removed. The slope at a

depth x times the activity at that depth gives the concentration of activity of iodine at x . The required concentration ratio was obtained from a ratio of concentration at a depth x to the concentration of iodine at the surface of the coating. The concentration of iodine at the surface of the four coatings tested as a function of temperature for a concentration of iodine in the vessel of 360 micrograms/liter is given in Figure 2. Unfortunately, experimental conditions are such that the concentration of iodine at the surface of the coating probably changes during the experiments due to a reduction in iodine vapor as a result of deposition on the carbon steel surfaces and paint coupons. For some experiments the iodine penetration was observed to approach the carbon steel substrate. Under these conditions, the applicability of the model must be explored carefully to determine if it can be used to represent the system.

A model for diffusion into an infinite slab of finite thickness⁽⁵⁾ was used to represent the penetration data for one of the coatings. There did not appear to be a significant difference in the fit of the two models to the data. Since the calculations using the finite thickness model were much more involved, the model for diffusion into a semi-infinite solid was used for the data presented here.

Figures 3 and 4, respectively, show the fit of the model to diffusion of iodine into Amercoat 66 and Devoe SX 1661 coatings. The Amercoat 66 coating has a relatively high surface concentration of iodine and a relatively small diffusivity. The Devoe SX 1661 coating has a relatively low surface concentration of iodine and a relatively high diffusivity.

Figure 2 Concentration of Iodine at the Surface for Protective Coatings as a Function of Temperature.

Figure 3 Fit of Data for Epoxy Coating to Diffusion Model.

Figure 4 Fit of Data for Chlorinated Rubber Coating to Diffusion Model.

3. EFFECT OF EXPOSURE AND STORAGE TIME ON THE DIFFUSIVITY

Since the coupons could not be examined immediately after exposure to iodine vapors, the effects of exposure time and storage time before examination on calculated diffusivities were studied. Table II shows the results for the epoxy coating, Amercoat 66. The diffusivities were calculated based on the exposure times. Since for most experiments under similar conditions the diffusivities varied by at least a factor of 2, there did not appear to be a significant effect of exposure on the calculated diffusivity. This indicated that the surface concentration of iodine on the coatings and the iodine partial pressure in the contamination vessel remained reasonably constant for the period of the runs. Also, there was no significant effect of storage time on the diffusivity. This indicates either that diffusion is dependent upon a supply of steam, or that chemical reaction of the iodine with the coating occurred. Since the iodine may be removed from the coatings by autoclaving, the first explanation seems more reasonable at least for the major iodine species.

Table II
EFFECTS OF EXPOSURE AND STORAGE TIMES ON
MEASURED DIFFUSIVITY FOR EPOXY COATING, AMERCOAT 66

<u>Exposure Time</u> (min.)	<u>Storage Time</u> (hours)	<u>Diffusivity</u> (cm ² /sec)
6	18	10 x 10 ⁻¹⁰
60	1	3 x 10 ⁻¹⁰
60	312	3.5 x 10 ⁻¹⁰
150	1	10 x 10 ⁻¹⁰

4. EFFECT OF TEMPERATURE ON DIFFUSIVITY

Figure 5 shows the effect of temperature on diffusivity for an epoxy, Amercoat 66, where D is the diffusivity in cm²/sec. The diffusivity appears to remain reasonably constant for temperatures up to about 90°C. Above this temperature there is a marked increase in the diffusivity with temperature. This effect is probably a result of a softening^[e] of the coating rather than an activation energy associated with the process since the heat distortion point for this coating is 80-90°C.

Figure 6 shows the effect of temperature on diffusivity for a vinyl, Amercoat 33HB. The diffusivity for this coating appears to be constant to about 110°C. Above this temperature there is an increase in the diffusivity with temperature. Again, this is probably a reflection of a softening of the coating.

Figure 7 shows the effect of temperature on diffusivity for a chlorinated rubber coating. Chlorinated rubber coatings such as Devoe SX 1661 are known to have low glass transition points, below room temperature. Softening of the coating is, therefore, a likely explanation for the increase in diffusivity with temperature.

Figure 8 shows the effect of temperature on diffusivity for a phenolic, Phenoline 302. There was much more uncertainty in the calculated diffusivities partially as a result of a surface roughness on the coating. Other effects which could lead to greater scatter in the diffusivity are interaction of iodine with the additive in the coating, and further curing of the coating during the high temperatures of the experiment. The apparent temperature effect on diffusivity is probably not real and an average diffusivity of 10⁻⁹ cm²/sec is recommended.

^[e] Associated with the glass transition point or the heat distortion point of the coating.

Figure 5 Effect of Temperature on Diffusivity for Iodine Penetration into Epoxy Coating, Amercoat 66.

Figure 6 Effect of Temperature on Diffusivity for Iodine Penetration into Vinyl Coating, Amercoat 33.

Figure 7 Effect of Temperature on Diffusivity for Iodine Penetration into Chlorinated Rubber Coating, Devco SX 1661.

Figure 8 Effect of Temperature on Diffusivity for Iodine Penetration into Phenolic Coating, Phenoline 302.

IV. CONCLUSIONS

A model for unidirectional diffusion in a semi-infinite solid seems to adequately describe the penetration of iodine into protective paint coatings. There appeared to be similarities between the Amercoat 66 and Phenoline 302 coatings and between the Amercoat 33HB and Devoe SX 1661 coatings in surface concentration of iodine on the coatings. The temperature effects on the diffusivities were somewhat different for each coating tested; however, the sudden increase in the diffusivity of two of the coatings with rising temperature, is probably associated with passage through the transition temperature for the coatings.

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