AD 486 073

ADSORPTION OF LANTHANUM BY NAVY GRAY PAINTED SURFACES

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ABSTRACT

Lanthanum adsorption by Navy gray paint surfaces and by powdered TiO_2 (a pigment in paint) was studied as a function of lanthanum concentration, pH, and inert electrolyte concentration and for the paint only as a function of contact time. Lanthanum adsorption was measured by use of the radiotracer La^{140}.

The paint was found to readily adsorb lanthanum up to approximately 3×10^{-6} g/cm^2, while adsorption by the TiO_2 was very small and could not account for the adsorptivity of the paint.

SUMMARY

Problem

Many of the gamma-emitting fission product elements in seawater fallout are strongly adsorbed by ship painted surfaces. In situations where the ship's washdown system was not activated, later application of shipboard decontamination methods would be required to reduce radiation levels. Developing techniques and/or materials capable of facilitating removal would require knowledge of the adsorption processes involved.

Findings

Adsorption of lanthanum (a significant contributor to the gamma radiation of fallout) by Navy paints and by TiO_2, a paint component, was studied. Lanthanum adsorption by the paint was found to be essentially complete for surface concentrations of adsorbed lanthanum less than about 3×10^{-6} g/cm^2, while adsorption by the TiO_2 was very small.

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CHAPTER 1

INTRODUCTION

In nuclear warfare at sea, and especially in situations where the ship's washdown system was not activated, ship surfaces would be contaminated by seawater fallout* from water surface nuclear explosions. Subsequent application of shipboard decontamination methods would be required to reduce radiation levels. Since many of the gamma-emitting fission product elements in fallout are strongly adsorbed by ship painted surfaces, non-destructive decontamination techniques would have to reverse the adsorption processes. Development of such techniques therefore requires knowledge of such processes. An initial study has been made and is described in this report.**

1.1 BACKGROUND

The seawater fallout from a nuclear detonation near the surface of the ocean consists of concentrated seawater containing fission and bomb (and possible target) products. This seawater fallout is difficult to decontaminate because a large fraction of the radioactive material in the fallout is in ionic or colloidal form, reacting readily with most solid surfaces as long as the fallout remains wet. Decontamination of smooth, impervious surfaces, such as Navy paint, contaminated with seawater fallout usually does not require physical removal of the outer surface material. However, following adsorption reactions, decontamination of painted surfaces may be difficult and require a large effort.

The removal of fission product elements from the seawater fallout contamination of many surfaces, including Navy paint, has been studied at NRDL. These studies were concerned with developing and evaluating decontamination methods for use in the field. They have shown that

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*Ship-hull contamination encountered during passage through a fallout contaminated ocean surface is not considered an operational hazard.

**Since the experimental work reported here was completed, unpublished USNRDL operations research studies indicated that shipboard decontamination was not likely to be a critical operational requirement, and research in this area was phased out.

fission product elements differ greatly in their ease of removal, that many of the ionic and colloidal fission product elements are strongly adsorbed by Navy painted surfaces,* and that significant radiation levels remain after decontamination by standard washing methods.[1] At present, the only method of complete decontamination is removal of the contaminated paint, which requires sandblasting at a shore installation. This method is inconvenient under any circumstances and cannot be used in a tactical situation.

There are at least five methods that can be used to reduce the contaminability of surfaces: (1) Improve the effectiveness of the ship washdown system by increasing water flow and by designing exterior ship surfaces to facilitate complete coverage by the water film (as is being done to some extent by the Canadian Navy). (2) Develop a Navy paint formulation with minimum adsorptive properties. (3) Discover an agent that could saturate the adsorption capacity of the paint, preventing subsequent adsorption of radioactive material. (4) Discover a decontaminating agent that would effectively desorb all the radioactive material. (Certain complexing agents have been found to effectively remove adsorbed ionic material; however, they are generally incompatible with seawater, restricting their use at sea.) (5) Develop a paint that is easily removable at sea without sacrificing the durability of present Navy paints. (Strippable paints**have been developed at the Mare Island Paint Laboratory, Mare Island Division, San Francisco Bay Naval Shipyard, and tested[2] in contamination-decontamination studies at NRDL. However, they were not accepted for use by the Navy primarily because of unsatisfactory durability.)

The work reported here is an outgrowth of the most recent[1] of the contamination-decontamination studies conducted at NRDL. It represents the first attempt to investigate the surface reactions responsible for decontamination difficulty, independent of the other phenomena that occur while the contaminant is on the surface. These other phenomena, such as evaporation, sea salt crystallization, and entrapment of the radioactive material by the salt crystals, severely handicap the study of surface reactions in contamination by seawater fallout.

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* Although ship washdown systems wash a large fraction of the arriving fallout off the ship, the system is ineffective in removing contaminant which has already been adsorbed, and may even increase adsorption if it is used only after contamination.[1]

**The thickness of paint removed is proportional to the alkalinity and the contact time of the decontaminating solution. U. S. Patent No. 3,063,873 issued to J. Saroyan, Nov. 1962.

1.2 PURPOSE

The development of non-adsorptive paints or methods of promoting desorption requires knowledge of the adsorption process. The adsorption of one of several important fission-product elements, lanthanum, was studied on typical Navy paints and on one paint component, titanium dioxide (pigment). Similar studies with other important fission product elements and other paint components could indicate which elements are preferentially adsorbed by different paint components. Eventually, the paint components primarily responsible for the adsorption could be replaced by less adsorptive species.

1.3 APPROACH

The adsorption of lanthanum from aqueous solution by Navy paint was measured as a function of lanthanum concentration in solution, duration of exposure, solution pH and inert electrolyte* concentration. Lanthanum 140 was selected because it is an important gamma-emitter in fallout, and the recent ship radiological countermeasure study[1] showed that lanthanum is strongly adsorbed by Navy paint.

The adsorption of lanthanum on powdered TiO_2 was measured as a function of the solution concentrations of lanthanum and inert electrolyte. A metal oxide was chosen as the component because the surface reactions of metal oxides in aqueous solution are fairly well understood.

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*Inert electrolytes are surface-inactive solutes (i.e., they affect surfact reactions only via their ionic strength).

CHAPTER 2

THEORY

Radiological contamination of ship surfaces by seawater fallout is the result of surface reactions between a solid (Navy paint - a mixture of metal oxides, organic resins and other materials listed in Table 1) and a liquid solution (seawater fallout - an aqueous solution-suspension of sea salts, fission products, and bomb and target materials).

This chapter discusses the surface chemistry (see the Appendix for further discussion) necessary for an understanding of the reactions occurring between these two complex systems. The adsorption reaction processes are discussed in terms of (1) general aspects of adsorption by solid surfaces in contact with aqueous solution, (2) the effects of parameters such as solution properties on this adsorption, and (3) the adsorption behavior of Navy paint.

2.1 ADSORPTION BY SOLID SURFACES IN CONTACT WITH AQUEOUS SOLUTION

A solid surface in contact with a solution may react with the solvent and any solutes or suspended colloids. The solvent reactions are important because they influence the solute reactions. For instance, all of the components of the Navy paints (Table 1), with the exception of lampblack, will hydrolyze (chemically react with water) to some extent. As discussed below, the degree of surface hydrolysis can have a large effect on the adsorption of ionic and colloidal materials from solution.

Three types of surface reactions that might occur between the solid and the solution are physical adsorption, chemical adsorption and ion exchange. The process operating in a particular situation may be identified through the reaction characteristics[3] (Table 2). Dissolution of the solid is a fourth process which is of limited importance.

TABLE 1

Composition of Navy Paints Used in Adsorption Tests

Paint Formulation: Ship Exterior, Gray Military Specification No.:	No. 20 MIL-P-699B	No. 5H MIL-E-15130C
Ingredients	Pounds per 100 gallons	
Titanium Dioxide	36	55
Zinc Oxide	125	200
Lampblack	13	1.1
Magnesium Silicate	135	140
Pulverized Silica	100	
Alkyd Resin Solution	221	460
Phenolic Varnish	240	
Petroleum Spirits	159	205
Lead Naphthenate	15	4.2
Cobalt Naphthenate	2	1.6
Manganese Naphthenate	1	1.6
Total Weight	1047	1068.5

TABLE 2

Some Characteristics[3] of Three Types of Adsorption Reactions
(solid adsorbent in contact with aqueous solution)

	Chemical Adsorption	Physical Adsorption	Ion Exchange
Nature of bonding forces.	Strong-hydrogen and covalent.	Weak-non-polar, Van der Waals attraction.	Strong-electrostatic.
Bond energy (heat of adsorption related to bond strength).	Large - heat of adsorption similar to chemical reaction energies ($\Delta H \sim 10^4$ cal/gm-mole, exothermic).	Small - since Van der Waals forces are thought to be responsible for liquifaction, ΔH similar to heats of vaporization ($\sim 10^2$ cal/gm-mole, exothermic).	Large.
Temperature effect (related to ΔH).	Large - (exothermic adsorption decreases as temperature increases).	Small (exothermic).	Negligible (slightly exothermic).
Rate.	Slow relative to physical adsorption - rate decreases with increasing activation energy of adsorption.	Rapid.	Rapid.
Reversibility (desorption).	Difficult - slow if adsorption required activation energy.	Easy - desorbs by rapidly re-equilibrating in fresh solvent.	Easy - requires solution of different ion having same polarity as that to be exchanged - exchange increases with concentration of replacing ion.
Extent of reaction.	Limited to a single (surface) monolayer - usually only a small fraction thereof.	Not limited to a single layer although adsorption in layers removed from surface is generally weaker and requires larger solution concentrations.	Limited to a small fraction of the surface monolayer.
Examples or applications.	Oxide films on metals, catalysis.	Chromatography, gas purification.	Water softening, separation/purification of chemicals.

The ion exchange process is considered in connection with paint adsorption because of polymeric binders in paint which chemically resemble ion exchange media. However, the ship radiological countermeasures studies[1] indicated that ion exchange is not an important process in the contamination of Navy paint. If it were important, seawater should decontaminate much better than fresh water due to the high ionic strength of seawater, but no such large difference was detected.

Physically adsorbed contaminant should be readily removed by prolonged washing because of the easy reversibility of physical adsorption compared to chemical adsorption. Although the countermeasure studies[1] showed that certain fission product elements (Ba and Zr) did not appreciably contaminate Navy paint, residual contamination levels did not decrease appreciably with prolonged washing for any of the elements tested. This, together with the observation that La and Nb were strongly adsorbed by the paint, indicates that chemical adsorption is primarily responsible for the contamination-decontamination problem.

A solid which reacts with ions or colloidal particles in a solution will generally alter its surface charge.[4] Such a change in surface charge may cause the solid to react with additional charged species in the solution. For many solids, including the metal oxides (which are used as pigments in Navy paint), the pH of an aqueous solution is primarily responsible for determining the surface charge by controlling the extent of surface hydrolysis.[5-7] The pH resulting in an electrically neutral surface is called the zero point of charge (ZPC). This condition permits adsorption to be studied independently of the effects of the charged surface. Adsorption of dissolved La, or other positively charged species, from solution should increase as the surface becomes more negatively charged. If pH is the primary charge determining parameter, then adsorption of La should increase with pH. Figure 1 shows the distribution of electric potential and of charged solution species near a charged solid surface.

The conditions corresponding to the ZPC of a solid can be evaluated by using inert (indifferent) electrolytes.[6] These are dissolved substances which are inactive with respect to the solid surface (e.g., uni-univalent salts which are not preferentially adsorbed), but can affect the adsorption of other species by changing the dielectric properties of the solution (as a result of ionic strength) and, consequently, the charge distribution. Since they affect adsorption only through the surface charge, they will not affect adsorption at the ZPC of the solid.

For paint in contact with aqueous solution, the potential determining ions are probably H^+ and OH^-. At sufficiently high pH, the paint should acquire a negative charge due to the hydrolysis reaction, resulting in increased adsorption of the positively charged lanthanum ions (the pH must not be so high as to precipitate $La(OH)_3$).

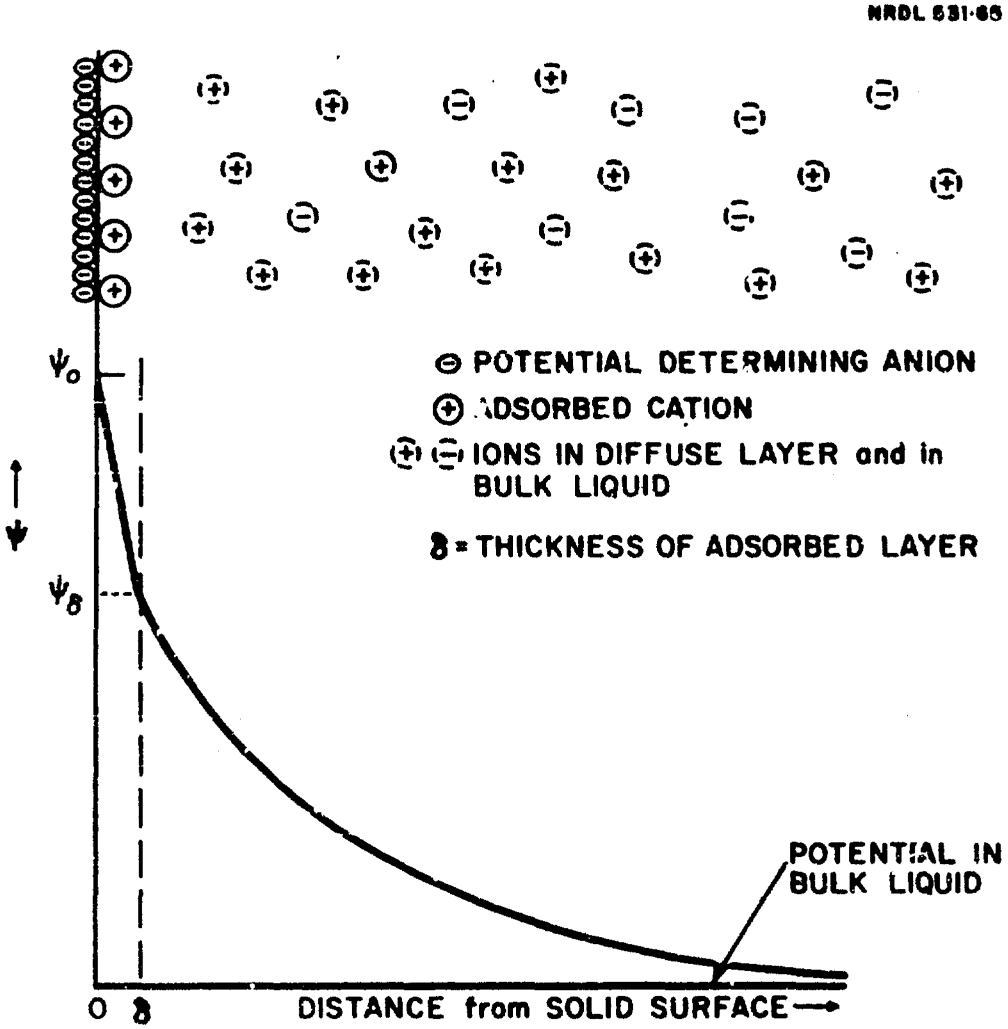

Fig. 1 Electric Potential (ψ) Across the Double Layer (adsorbed and diffuse layers) at a Solid-Liquid Interface.

Additional discussion of surface chemistry is given in the Appendix.

2.2 EFFECTS OF VARIOUS PARAMETERS ON ADSORPTION

Adsorption is studied experimentally by measuring (1) the kinetics of adsorption and desorption under various conditions, and (2) the amount adsorbed at equilibrium as a function of temperature, and solution composition (including adsorbate concentration). The importance of pH and surface-inert electrolytes in the study of adsorption was discussed in the previous section. The effects of additional parameters on adsorption are now considered.

2.2.1 Adsorbate Concentration

The effect of adsorbate concentration on the amount adsorbed at equilibrium for a given set of conditions (i.e., temperature, adsorbent properties, and solution composition exclusive of the adsorbate concentration) is described by adsorption isotherms. Adsorption by solids from dilute solution usually follows the Freundlich isotherm: $\Gamma = kC^n$, where Γ is the amount adsorbed per unit area, C is the equilibrium adsorbate concentration, and k and n are experimentally determined constants. The Freundlich isotherm can apply to both chemical and physical adsorption. In those cases where both mechanisms operate, each predominating over a different concentration range, the constants should be different for each mechanism. Similarly, if physical adsorption occurs both in the surface layer and in succeeding layers, different Freundlich constants should reflect the different adsorbing surfaces: the solid itself for the surface layer, and the adsorbate for succeeding layers. Adsorption of H^+ and OH^- on metal oxides has been observed[5] to follow the Langmuir isotherm: $S = k_1C/(1 + k_2C)$, where S is the fraction of surface monolayer filled, C is adsorbate concentration, and k_1 and k_2 are experimentally determined constants.

Using the Freundlich isotherm, Miller[8] derived an equation to predict the decontamination behavior of individual fission product elements in seawater fallout. He showed that the equation fits some experimental decontamination data, and obtained values for the Freundlich constants for several elements. It should be noted, however, that the constants determined in this manner probably do not give a true indication of the adsorption behavior for several reasons: (1) Adsorption is stopped after a short time by crystallization (drying) of the contaminant seasalts. (2) Not all of the unadsorbed material is in equilibrium with that adsorbed because much of the unadsorbed contaminant is held away from the adsorbing paint surface by the seasalt crystals. (3) Decontamination may remove some adsorbed material in addition to the unadsorbed material. (4) This particular decontamination data was obtained using an immersion-stirring apparatus, which may have smeared contaminant over initially uncontaminated surface and thereby increasing adsorption.

The concentrations of most fission product elements in seawater fallout are extremely small. There are fourteen elements which each contribute over 1 % of the total gamma energy of unfractionated U^{235} fission products and which together account for 97-98 % between 1 and 10 hr after fission.[9] The total concentrations of eight of these (Rb, Sr, Y, I, Cs, Ba, La and Ce) in seawater fallout are determined largely by their occurrence in natural seawater. Four of the others (Zr, Nb, Sb and Te) do not occur appreciably in seawater, so their concentrations are due largely to fission products. The remaining two, the rare gases Kr and Xe, fractionate during fallout formation and are not present in seawater fallout at early times. Elements whose gamma contributions become important only at later times are not of interest because fallout arrival, fallout crystallization (drying) and fallout reactions with ship surfaces will have ceased. Table 3 lists the important elements, their concentrations in natural seawater,[10] their fission product concentrations in seawater fallout,[8] and the percent of their total fallout concentration that is due to fission products. The fission product concentrations are with respect to the quantity of natural seawater containing the same amount of seasalts as the fallout, since the water content of the arriving fallout is far below that of the natural seawater.

The seasalt concentration of the fallout simulant used in the ship radiological countermeasure study[1] was about ten times that of natural seawater, this value being based on observations at Operation Redwing. Therefore, the maximum concentrations in seawater fallout are between 10^{-10} and 10^{-9} g/cc. The maximum concentrations for the trace elements of natural seawater (including lanthanum) would be between 3×10^{-9} and 5×10^{-7} g/cc. Concentrations of rubidium and strontium could be as high as 10^{-6} and 10^{-4} g/cc, respectively.

Ions which are neither potential-determining nor surface-inert can affect the adsorption of other ions by competing for adsorption sites (i.e., by being preferentially adsorbed). Saturating an adsorbed surface monolayer would remove about 5×10^{-6} g/cc of ionic material from solution in the 200 μ diameter fallout droplets used in the ship radiological countermeasure study[1] (this drop size is based on observations at Operation Redwing). Since this is more than the sum of all fission-product element concentrations, excluding strontium, nearly all fission products could conceivably adsorb in the surface layer unless one or more of the abundant ions in natural seawater (this could include strontium) were preferentially adsorbed.

TABLE 3

Concentrations of Fission Product Elements in Seawater and Seawater Fallout. Each element contributes over 1 % of the total gamma energy (air-ionization rate three feet above a uniformly contaminated, infinite plane) of unfractionated U^{235} fission products. Together they account for 97-98 % of this total, between 1 and 10 hr after fission. They are listed in decreasing order of their gamma contribution.[9]

Fission Product Element	Concentration of Element in Natural Seawater ($g/cc \times 10^6$)	Total Concentration of Element in Fallout Having Same Water Content as Natural Seawater ($g/cc \times 10^{10}$)	Percent of Total Fallout Concentration of Element Due to Fission Products
I	0.05	0.3	0.6
Y	0.0003	0.1	3
Te		0.4	~100
Cs	0.002	0.7	3
Kr*			
Nb		0.05	~100
Sr	13	0.4	0.0003
La	0.0003	0.3	10
Rb	0.2		< 0.01
Pr		0.3	~100
Ce	0.0004	0.9	20
Ba	0.05		< 0.001
Sb			~100
Xe*			

*The rare gases Kr and Xe are severely fractionated in seawater fallout so as to have negligible radiation contributions.

The high concentration of alkali metal ions (sodium and potassium) in seawater indicates that the alkali metal fission products (rubidium and cesium) should not be adsorbed appreciably. The fraction of total alkali metals present as fission products is only $\sim 10^{-9}$. Also, these monovalent ions should behave as inert (surface inactive) species with respect to the paint. A similar situation exists regarding the concentrations of the alkaline earths. Although the concentrations of these elements (magnesium, calcium, and strontium) in natural seawater are not as high as those of the alkali metals, the fission products account for only $\sim 10^{-8}$ of the total in seawater fallout. Some of this will be precipitated since the alkaline-earth-sulfates exceeding their solubilities. The alkaline earths, being divalent, are surface active and should be adsorbed to some extent.

The concentrations of all higher-valence metals in seawater fallout are extremely small. There is uncertainty as to whether these materials will be ionic or colloidal (as oxides or hydroxides) in seawater fallout. Since colloids adsorb to about the same extent as triply charged ions[11] (in the absence of specific chemical reactions), the exact states of these particular elements may make little difference. Any ionic species charged more than + 2 should be adsorbed strongly, especially if the paint acquires a negative charge due to the slightly basic seawater (pH $\sim$ 8). Colloidal basic oxides may acquire a positive charge (as described in section 2.1) and then be adsorbed like metal ions by the paint. They also may adsorb other fission products before being adsorbed.

The only important anionic fission-product species should be the halides and possibly $HTeO_3^-$.[12] Colloidal acidic oxides may acquire a negative charge and thus behave as anions. Iodide may be adsorbed appreciably in spite of the high chloride concentration, because the halogens differ more in chemical reactivity than do the alkali metals or alkaline-earth groups. Even if a significant fraction of fission products were anionic, anion adsorption would be less important than cation adsorption due to the slightly basic seawater fallout.

2.2.2 Kinetics

The adsorption rate is one indication of the adsorption mechanism. For instance, rapid adsorption indicates physical rather than chemical adsorption, as shown in Table 2. If adsorption occurs very rapidly, the only constraint on adsorption will be diffusion of the element to the adsorbing surface. Adsorption as a function of time for the experimental set-up used in the subject tests can then be calculated by solving the diffusion equation:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (1)$$

where C is the adsorbate concentration in solution, t is time, D is the diffusion coefficient, and x is a spatial dimension. Boundary conditions for the adsorption cells (which constitute a one-dimensional diffusion-adsorption system, and are described in Chapter 3) are:

$$C(x,0) = C_o \qquad 0 \le x < L$$

$$C(L,0) = 0$$

$$\frac{\partial C}{\partial x}(0,t) = 0$$

$$C(x,\infty) = \frac{LC_o}{K+L}^{*}\text{, if the Freundlich constant } n = 1.0;$$

where k is the other Freundlich constant and L is an adsorption cell dimension as shown in Fig. 2.

Solving Eq. 1 for the boundary conditions, Eq. 2, using standard techniques gives:

$$C(x,t) = C_o\left[\frac{L}{k+L} + \frac{4}{\pi}\sum_{1}^{\infty}\frac{1}{n}\left(\sin\frac{n\pi}{2} - \frac{2L}{K+L}\sin\frac{3n\pi}{4}\right)\exp\left(-D\left(\frac{n\pi}{2L}\right)^2 t\right)\cos\frac{n\pi x}{2L}\right] \qquad (3)$$

The amount adsorbed (Γ) is obtained from a mass balance on the adsorbate:

$$\Gamma(t) + \int_0^L C(x,t)\,dx = LC_o \qquad (4)$$

Substituting 3 into 4 gives:

$$\Gamma(t) = LC_o\left[\frac{k}{k+L} - \frac{8}{\pi^2}\sum_{1}^{\infty}\frac{1}{n^2}\sin\frac{n\pi}{2L}\left(\sin\frac{n\pi}{2L} - \frac{2L}{k+L}\sin\frac{3n\pi}{4}\right)\exp\left(-L\left(\frac{n\pi}{2L}\right)^2 t\right)\right] \qquad (5)$$

Values of D_{La} are calculated from published values of the cation transference number of lanthanum chloride[13] (t_{La}) and the drift velocity of chloride ion[14] (U_{Cl}). The equations relating these values to D are:

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*Derivation as follows:

$$\frac{L^3(C_o - C)}{L^2} = k\,C^h$$

if $h = 1$, $L(C_o - C) = kh$

$$C(k+L) = L\,C_o$$

$$C = \frac{L\,C_o}{k+L}$$

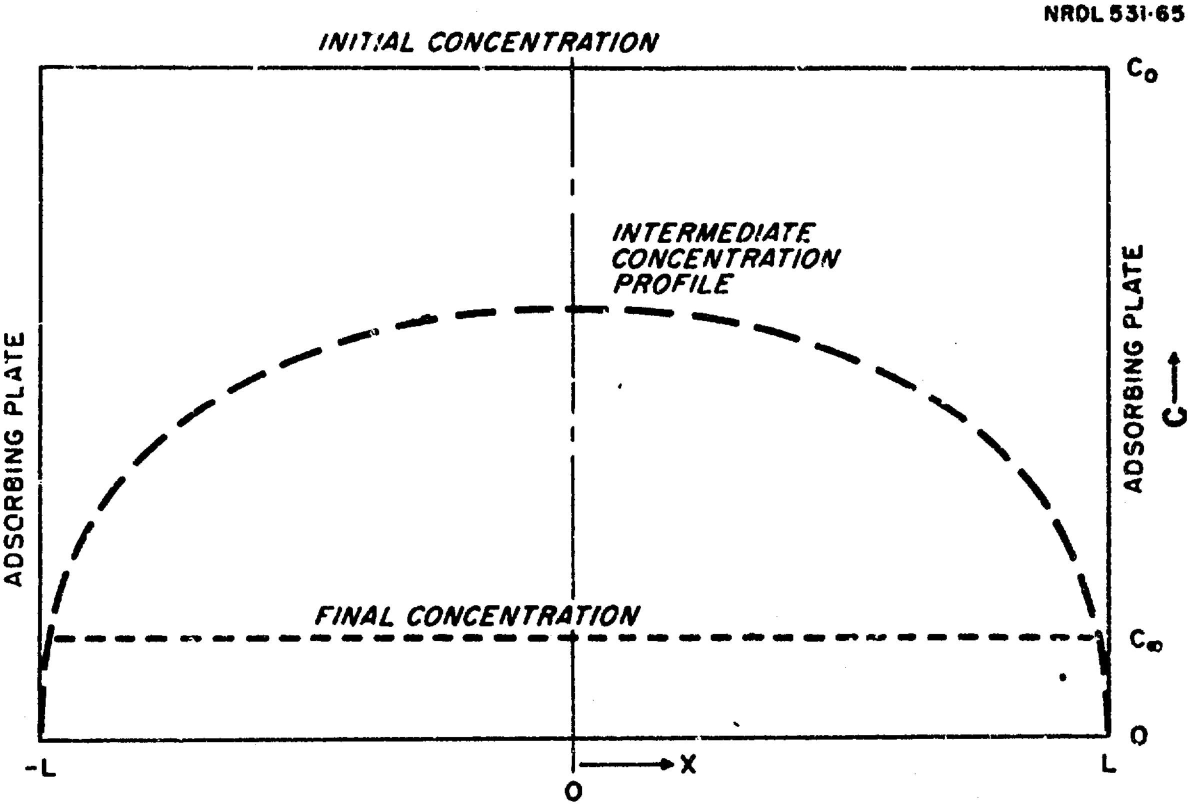

Fig. 2 Boundary Conditions for Solving the Diffusion Equation. Dashed lines indicate intermediate and infinite time solution concentration profiles.

$D = KTU/F$, where K is the Boltzmann constant, T is the absolute temperature, and F is the Faraday constant.

$$t_{La} = U_{La}/(U_{LA} + U_{Cl}) = 0.474.$$

$U_{Cl} = 0.00067$ cm/sec. Therefore, $U_{La} = 0.00060$ cm/sec.

$$D = 1.38 \times 10^{-16} \, (\text{erg}/^{\circ}\text{K}) \times 293^{\circ}\text{K} \times 0.00060 \text{ cm/sec}$$

$$\times \text{ cm-coul}/10^{7} \text{ erg}^{*}/3(1.59 \times 10^{-19} \text{ coul})$$

$$\doteq 5.08 \times 10^{-6} \text{ cm}^{2}/\text{sec} = 0.000305 \text{ cm}^{2}/\text{min}.$$

The solution of the diffusion equation for infinite time corresponds to the equilibrium conditions of adsorption. Adsorption during fallout contamination occurs over a short time, and is dependent on other phenomena such as crystallization, evaporation and diffusion. This was the case in Miller's work. Ideally, experiments designed to elucidate the adsorption behavior should omit the fallout complexities as much as possible. This study represents an attempt to investigate adsorption independent of many of these other phenomena.

Numerical values obtained by programming Eqs. 3 and 5 on the laboratory's IBM 704, using variables corresponding to the experimental parameters, were compared with experimental determinations of Γ and C.

2.2.3 Temperature

The effect of temperature on the amount adsorbed at equilibrium is another indication of the adsorption mechanism. The heat of adsorption is directly related to the adsorption bond energy. The higher heat of chemical adsorption (see Table 2) results in greater irreversibility rendering subsequent decontamination difficult.

The heat of adsorption is normally determined experimentally from the slope of log (Γ') versus reciprocal absolute temperature (Clausius-Clapeyron equation). The heat of adsorption must be evaluated at equilibrium between the adsorbate in solution and on the solid surface. Any nonequilibrium condition may reflect the effect of temperature on the diffusion coefficient rather than on adsorption. In the absence of specific data on the temperature variation of the diffusivity, a useful empirical relation is $D \mu/T$ = constant, where μ is the viscosity. The

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*Drift velocities are given for a gradient of 1 volt/cm.

viscosity of pure water was used for computing D_{La} for the dilute aqueous solutions used in the temperature tests.

2.2.4 Desorption

If a surface containing adsorbed material is brought in contact with uncontaminated water, adsorption equilibrium will be established through desorption. Although desorption of chemically adsorbed species may be extremely slow, the amount desorbed at equilibrium can be predicted from the applicable adsorption isotherm. An equation for the amount desorbed was obtained from the reversible Freundlich isotherm ($\Gamma = kC^n$) and a mass balance on the material initially adsorbed: $\Gamma_0 = \Gamma + LC$, where Γ_0 is the amount initially adsorbed, and Γ and C are the amounts adsorbed and in solution after desorption, and L is the ratio of solution volume to surface area - see Fig. 2. Assuming the Freundlich constant n = 1.0, as was done in solving the diffusion equation, gives: $C = C_0k/(k + L)$, where k is the other Freundlich constant.

For practical decontamination, desorption must be increased, both in extent and rate, by the use of chemical agents. This may result from a shift in equilibrium (decrease in the Freundlich constant k), due to (1) a chemical reaction between the adsorbed material and the chemical agent or (2) modification of the surface by the chemical agent.

2.3 ADSORPTION BY NAVY PAINT

A theoretical analysis of the adsorption behavior of a paint is complicated by the large number of diverse components in the paint. Table 1 listed the composition by weight of the two Navy paints used in this investigation. The composition of the exposed paint surface would be identical to that of the bulk material. The paint surface would be a heterogeneous mixture of the soluble (in the paint solvent) phase and the insoluble particulate material, which constitutes an appreciable percentage of the paint.

The supposition that non-adsorptive (or, at least, less adsorptive) Navy paints can be developed is based on several assumptions: (1) Any strong (i.e., chemical) adsorption by the paint, while homogeneous on a macro scale, is heterogeneous with respect to the various components exposed to the solution at the adsorbing surface. (2) The exposed surfaces of particulate materials in the paint retain the chemisorption properties they exhibit as individual particles. That is, these properties are essentially unaffected by the surrounding soluble phase. This implies that the adsorption behavior of the particulate materials can be adequately studied on an individual basis. (3) Contributions to the overall adsorption behavior of the paint made by any of the components in the soluble phase can be determined. This could possibly be accomplished by comparing the behavior of paint containing the particulat component with paint having that component either omitted or replaced. (4) Those components that are responsible for chemisorption by paint can be satisfactorily replaced by components that do not contribute greatly towards chemisorption. This assumption is based on the fact that each of the functions served by the various paint components (e.g., pigment, binder) can be adequately performed by a wide variety of compounds differing greatly in chemical structure.

Specifying the composition of something as complex as paint does not determine all of the properties of the finished product. The properties of a paint surface depend also on application and drying conditions. Although the composition of Navy paints is set forth in military specifications (as in Table 1), the ultimate criteria for acceptance are performance tests which are outlined in these same specifications. Therefore, some of the component concentrations may be adjusted if the paint does not meet all of the performance requirements.* For instance, pigment may be added if the color is incorrect. In spite of these considerations, the ship radiological countermeasures study[1] results did not vary appreciably with sample weathering, paint batch, or extent of usage of samples in previous contamination-decontamination tests, as long as the samples were rinsed before being used.

Any such non-adsorptive paint formulations as might be developed must meet the Navy's performance specifications. Perhaps the present performance requirements may be relaxed somewhat if a substantial decrease in the chemisorption properties is accomplished.

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*Private communication from J. Saroyan, Mare Island Paint Laboratory.

CHAPTER 3

PROCEDURE

The experimental procedure for measuring lanthanum adsorption from aqueous solution consisted of (1) preparing the adsorbent samples and the radiotraced adsorbate solutions, (2) bringing known amounts of each in contact in the appropriate apparatus, (3) separating the adsorbent from the solution, and (4) gamma-counting each phase to determine the resulting lanthanum distribution. Some of the procedural details, differed in the two experimental phases: adsorption by painted samples and adsorption by pigment powder.

3.1 ADSORPTION BY PAINT

3.1.1 Paint Samples

The painted samples were the same as those used in the ship radiological countermeasure study:[1] 8-1/2-in.-square steel plates painted on both sides with Navy #116 primer and on one side with either #20 Deck Grey (20D) or #5 Haze Grey (5H). They were weathered 90 days in a marine-industrial atmosphere at the Naval Fueling Depot, Point Molate (on San Francisco Bay). Before being used, they were rinsed in fresh water and dried.

3.1.2 Adsorption Solutions

Stock solutions of La^{+3} (usually 10^{-3} g/cc) were prepared by dissolving weighed amounts of $La(NO_3)_3 \cdot 6H_2O$ in known volumes of distilled water. Being hygroscopic, $La(NO_3)_3$ is not a primary standard, so the La^{+3} concentration of these solutions was verified by conductometric titration with $Na_2C_2O_4$. The titration was not sufficiently sensitive to be used to determine residual lanthanum in the adsorbate solutions.

The adsorption solutions, ranging in lanthanum concentration from 10^{-9} to 10^{-3} g/cc, were made by adding predetermined amounts of stock solution to distilled water or to natural seawater and adding the radiotracer, La^{140}, also as $La(NO_3)_3$ solution. The pH was brought to the desired level, by adding NaOH or HCl solution. Surface-inert electrolyte (KNO_3) was added to some of the solutions.

The radiotracer was isotopically purified (i.e., radio-inert lanthanum was removed to insure that its contribution to the total lanthanum concentration was negligible). This was accomplished by chemically separating the La^{140} from a Ba^{140}-La^{140} parent-daughter mixture by acid precipitation of $Ba(NO_3)_2$ that had previously been chemically purified barium (i.e., it may have contained inert barium, but it did not contain any appreciable amount of lanthanum immediately after separation). The amount of La^{140} used to expose individual samples was less than 0.01 curie, which weighs less than 2×10^{-8} g. This represents a maximum lanthanum-140 concentration of $\sim 2 \times 10^{-11}$ g/cc when added to a liter of seawater. The concentration of lanthanum in natural seawater is about 3×10^{-10} g/cc.

3.1.3 Adsorption Cells

In order to use the same painted plates that had been used in the contamination-decontamination studies,[1] an adsorption apparatus was specially designed. It was desired to expose only the central area of one side of the samples painted with the 20D or 5H paint to the absorbate solution in order to (1) eliminate effects due to the edges of the painted samples, and (2) prevent adsorption by the primer on the back side of the sample. This was accomplished by using the apparatus shown in Fig. 3. It consists of five individual adsorption cells held by a frame of aluminum end-plates connected by bolts. Each individual adsorption cell consists of two parallel sample plates with the adsorbing surfaces facing each other and separated by a 1-in.-wide spacer. The spacer is a section of 8 in. O.D. (7-1/2 in. I.D.) lucite pipe, which confines the adsorbate solution between the painted samples. The cells expose 285 cm^2 of each of two sample plates to 765 cc of solution. Rubber O-rings set into grooves along the edges of the spacer provide a water-tight seal against the paint surfaces when the frame is compressed by the bolts. Neither the spacers nor O-rings adsorbed lanthanum appreciably. The spacers are fitted with a flange around a 1/2-in.-diameter filling hole. Corking these holes isolates the interior of the cells. Figure 4 shows details of the spacers.

For the first twelve paint adsorption tests, the spacers were square rather than circular, with flat gasket material instead of the imbedded O-rings. Cells thus constructed leaked considerably unless they were submerged in a water bath, partly because the compression tore the glue joints required at the corners of the square cells. The improved, circular, design eliminated leakage completely. The square cells exposed 387 cm^2 of each plate to 1165 cc of solution.

Fig. 3 Frame Containing Five Individual Adsorption Cells. One of the bolts has been removed to show the filling holes. There are two sample plates back-to-back between each lucite spacer.

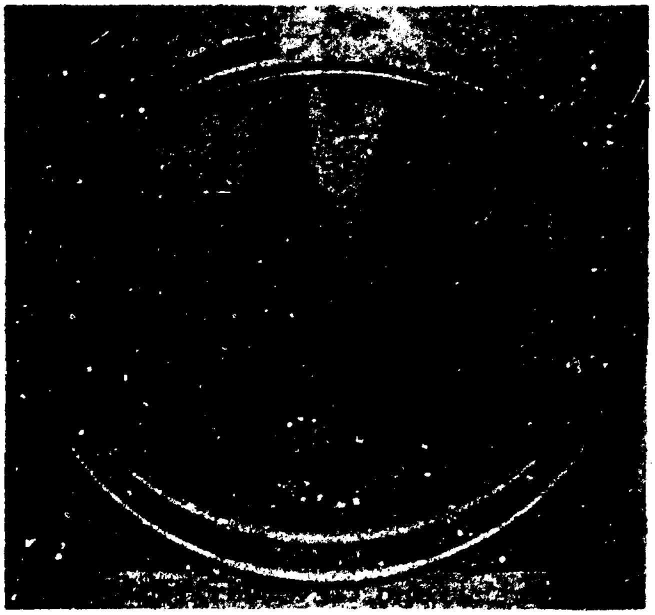

Fig. 4 Lucite Spacer, with Both O-ring, Placed Against a Sample Plate. The filling hole passes through the flange at the top of the spacer. Note the surface irregularities of the paint.

3.1.4 Paint Adsorption Tests

Each paint adsorption test consisted of filling assembled adsorption cells (usually five) with the solutions described in section 3.1.2, placing them in a water bath for temperature control, draining the solutions after some recorded time interval, disassembling the cells and gamma-counting the plates and solution aliquots. The paint type, contact times, and initial solution properties for twenty of the paint adsorption tests are listed in Tables 4 and 5. In addition, two cells (5H paint) containing 10^{-7} g La/cm^3 were exposed at 0°C and 70°C for two hours to investigate the effect of temperature on the adsorption of lanthanum. All solutions were made using distilled water, except those used in Tests 4 and 5, which were made from natural seawater. This was included to determine the applicability of results to seawater fallout.

In order to study desorption, contaminated samples from Test 9 were reassembled in the cells, which were then filled with distilled water. After three days, the cells were again disassembled, and the plates and solution gamma-counted to measure the amount of lanthanum desorbed.

The data for Tests 17, 20 and 21 represents pH and conductivity measurements. No radiotracer was used in the hope that La concentration could be determined by conductometric titration. Although final lanthanum concentrations could not be determined by this method, the conductivity measurements did give significant results. Initial composition, pH and conductivity for the solutions in Test 20 are given in Table 5.

Data for Tests 18 through 21 were obtained for two contact times in each test. Unlike Test 9 (desorption), however, the same solutions were put back in the adsorption cells after dismantling, gamma counting, and reassembling.

Some of the plates containing adsorbed La^{140} were radioautographed to study any possible surface irregularities affecting the distribution of the adsorbed Lanthanum.

3.2 ADSORPTION BY TiO_2

Each of the TiO_2 adsorption tests consisted of bringing powdered TiO_2 in contact with radiotraced lanthanum solution, separating the liquid and solid, and gamma-counting each phase. About two grams of

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TABLE 4A

Paint Type, Contact Time, and Initial Solution Properties for the Paint Adsorption Tests Investigating the Effect of (Solution) Concentration of Lanthanum on the Adsorption of Lanthanum

Test No.	Paint Type	Contact Time (hr)	pH	Lanthanum Concentration (g/cm^3) Cell Number 1	2	3	4	5
1	20D	-	-	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
2	5H	65	5	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
3	20D	68	7	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
4[a]	5H	65	7.8	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
5[a]	20D	66	7.9	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
6	5H	65	6.9	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
7	20D	67	-	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
8	20D	67	-	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}
9[b]	5H	68	-	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
13	5H	96	6.8	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
14	5H	96	10.7	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
15	5H	96	2.9	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
21[c]	5H	96 108	5.6	2×10^{-5}	5×10^{-6}	10^{-6}	2×10^{-7}	-

a. Natural seawater.
b. Desorption test.
c. No radiotracer.

TABLE 4B

Contact Time and Initial Solution Properties for the Paint Adsorption Tests Investigating the Effect of Contact Time on the Adsorption of Lanthanum. All tests used 5H paint. Room temperature.

Test No.	Lanthanum (conc (g/cm3)	Contact Time (min) Cell Number 1	2	3	4	5	6	7	8
11	10^{-5}	20	40	60	90	140	1080	2410	3900
12	10^{-7}	20	40	60	90	140	200	1020	-
16	10^{-6}	4110	9850	14100	18500	21300	-	-	-

TABLE 4C

Contact Time and Initial Solution Properties for the Paint Adsorption Tests Investigating the Effect of pH and Inert Electrolyte on the Adsorption of Lanthanum. All tests used 5H paint. Room temperature.

Test No.	Contact time (hr)	pH Cell Number 1	2	3	4	5	Remarks	Lanthanum conc (g/cm3)
17	1390	10.8	9.8	10.0	3.3	3.0	No radiotracer	0
18	72 168	3.2	3.7	6.2	8	11		2×10^{-5}
19	72 168	3.1	3.7	6.2	8	11	10^{-3} N KNO_3	2×10^{-5}
20	72 168	See Table 5 for solution properties					No radiotracer	

TABLE 5

Initial Solution Composition, pH and Conductivity for Paint Adsorption Test 20. Lanthanum present at 2×10^{-5} g/m^3 (5.6×10^{-5} cm-ohm), KNO_3 at 10^{-3} M (14×10^{-5}/cm-ohm)
Presence of $La(NO_3)_3$ or KNO_3 is denoted by X.

Cell No.	$La(NO_3)_3$	KNO_3	Acid/Base	pH	$(\text{cm-ohm})^{-1}$ $\times 10^{-5}$
1	X		H_2SO_4	2.6	110
2	X	X	H_2SO_4	2.6	128
3			HNO_3	2.7	100
4	X		HNO_3	2.7	106
5			H_2SO_4	2.7	91
6			HCl	2.6	130
7	X		HCl	2.6	136
8	X		NaOH	11.0	23
9	X	X	NaOH	11.0	37
10			NaOH	11.0	17

weighed (milligram accuracy) powdered TiO_2 were placed in a tared glass centrifuge tube. Forty milliliters of La solution were added, and the tube was sealed with parafilm and shaken vigorously for 10 min. Preliminary tests had shown that lanthanum adsorption did not change with longer periods of shaking. The tubes were centrifuged and the clear supernate was poured into a graduated cylinder to measure its volume, and then into a beaker. The centrifuge tube containing wet TiO_2 and the beaker were each gamma-counted. The volume of solution retained by the TiO_2 was determined from the difference between 40 ml and the volume decanted after centrifuging, and verified by weighing the tube immediately after gamma-counting and again after drying in an oven at 110°C overnight. The contribution of this solution to the total gamma count of the TiO_2 was subtracted to obtain the count due to adsorbed lanthanum. Test blanks were run without the TiO_2 to determine the adsorption of the glassware and it was found to be negligible.

The TiO_2 was Baker reagent grade. The average particle diameter was estimated at 1 μ using a microscope with a calibrated eyepiece. The specific area, Σ, of the TiO_2 based on cubic particles, is thus estimated at 6000 cm^2/g.

A stock solution of $La(NO_3)_3$ in distilled water (1.713×10^{-3} g La/cc) was diluted, to make the adsorbate solutions varying in lanthanum concentration from 1.713×10^{-11} to 1.713×10^{-3} g/cc. The amount of radiotracer, La^{140}, per sample was about 10 μc, which weighs $< 2 \times 10^{-11}$ g. This represents a lanthanum concentration of $< 5 \times 10^{-14}$ g/cc.

The pH of the adsorption solutions was not purposely altered but was measured at the conclusion of each test. It turned out to be low (average pH 2.7) due to residual HNO_3 in the tracer from the Ba^{140}-La^{140} separation mentioned in section 3.1.

The inert electrolyte concentration was varied by adding weighed amounts of NaCl. A NaCl concentration of at least ~ 0.1 N was necessary to flocculate the TiO_2 during centrifuging. Smaller electrolyte concentrations were not sufficient to affect the charge distribution in the solution surrounding the TiO_2 particles to decrease the electrostatic repulsion between the particles.

Table 6 lists initial pH and lanthanum and NaCl concentrations for the 21 TiO_2 adsorption tests. Tests 1, 2, 10, 11 and 12 are duplicates to indicate experimental precision.

pH changes of HCl and NaOH solutions in contact with powdered TiO_2 were also measured.

TABLE 6

Initial pH, and La and NaCl Concentrations for the TiO_2 Adsorption Tests

Test No.	pH	La Concentration ((g/cc)/1.713)	NaCl (Normality)
1	2.6	10^{-7}	1.0
2	2.7	10^{-7}	1.0
3	2.9	10^{-6}	1.0
4	2.8	10^{-5}	1.0
5	2.8	10^{-4}	1.0
6	2.8	10^{-3}	1.0
7	2.9	10^{-8}	1.0
8	2.8	10^{-11}	1.0
9	2.8	10^{-9}	1.0
10	2.6	10^{-7}	1.0
11	2.6	10^{-7}	1.0
12	2.7	10^{-7}	1.0
13	2.6	10^{-7}	0.1
14	2.6	10^{-6}	0.1
15	2.6	10^{-5}	0.1
16	2.6	10^{-4}	0.1
17	2.6	0^{-3}	0.1
18	2.6	10^{-3}	0.5
19	2.6	10^{-7}	0.5
20	3.3	10^{-3}	2.0
21	1.9	10^{-3}	4.0

CHAPTER 4

RESULTS

4.1 ADSORPTION BY PAINT

The experimental results obtained using the Navy painted samples mounted in the adsorption cells are arranged with respect to the parameter being studied. Wherever values computed using Eq. (3) or (5) were compared with experimental data, the best comparison was obtained using $k = \infty$ (i.e., adsorption complete at equilibrium - $C \rightarrow 0$ at $t \rightarrow \infty$), and increasing D to 0.0004 cm^2/min (see Section 5.1.2).

4.1.1 Lanthanum Concentration

Lanthanum adsorption by the painted plates as a function of the solution concentration of lanthanum at the conclusion of adsorption is shown in Figs. 5 and 6. The two figures represent different contact times: 67 hours (Tests 2 through 8) for Fig. 5, and 96 hours (Tests 13 through 15) for Fig. 6. Two of the three curves in Fig. 5 represent 10^{-9} to 10^{-5} g/cm^3 initial lanthanum solution concentration for distilled water and natural seawater respectively. The third curve represents a higher concentration range (10^{-7} to 10^{-3} g La/cm^3) distilled water test. The curves in Fig. 6 represent pH's of 6.8 and 9.3 at the concentration range (10^{-7} to 10^{-3} g La/cm^3) distilled water test; the pH's remained at 6.8 and 9.3 at the conclusion of adsorption. Final pH measurements were not obtained for the tests whose data are plotted in Fig. 5.

Any lanthanum that might have desorbed from the Test 9 plates into distilled water was too small to be detected by gamma-counting.

4.1.2 Contact Time (Adsorption Kinetics)

Figure 7 shows lanthanum adsorption as a function of duration of exposure (contact time) of the plates to the lanthanum solution for test 12 (initial lanthanum concentration = 10^{-7} g/cm^3). The same data is plotted semilogarithmically in Fig. 8 for comparison with values computed using Eq. (5). Lanthanum concentration profiles in the adsorption cells,

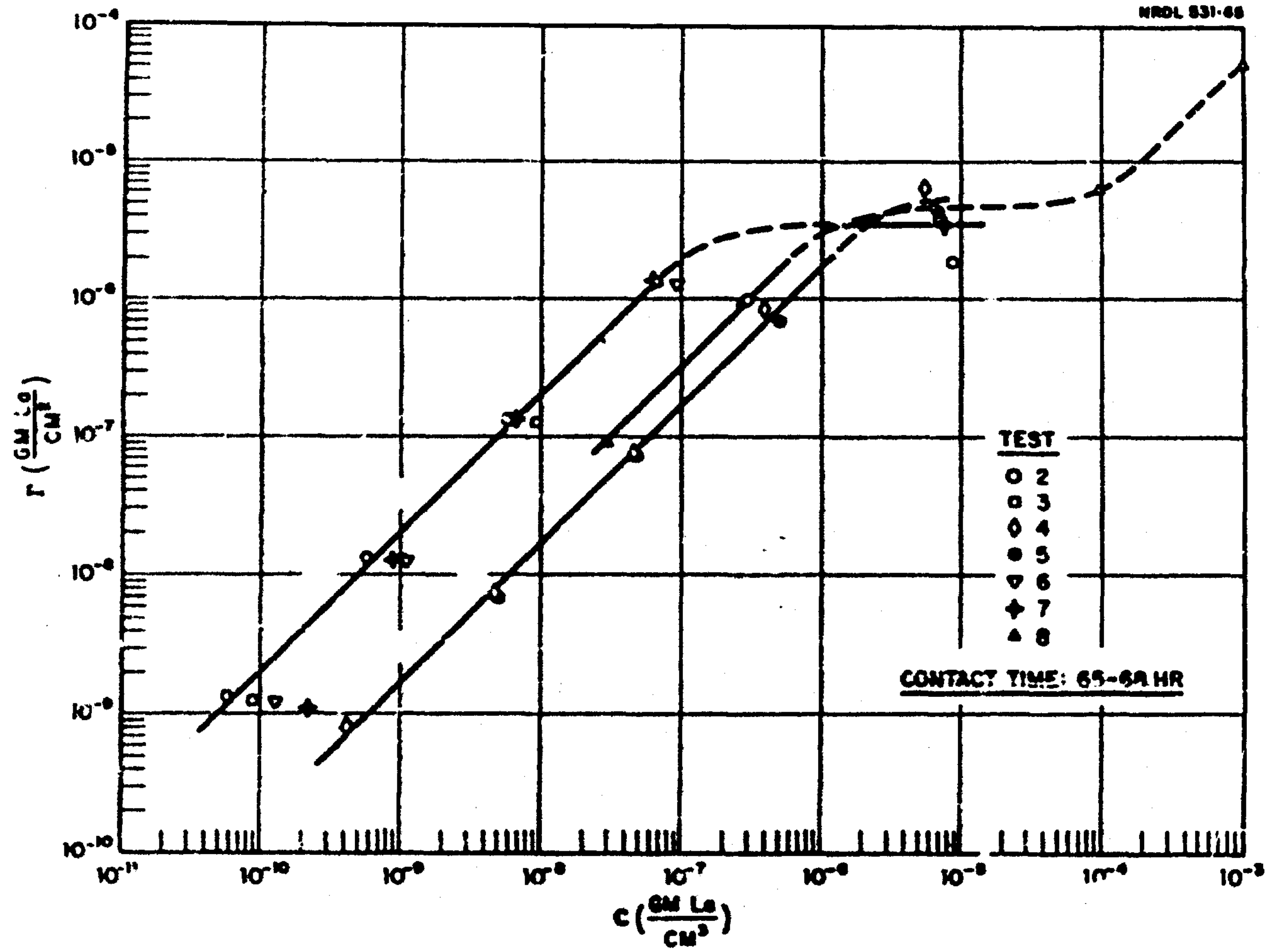

Fig. 5 La Adsorption on Painted Plates as a Function of Final Solution Concentration of La.

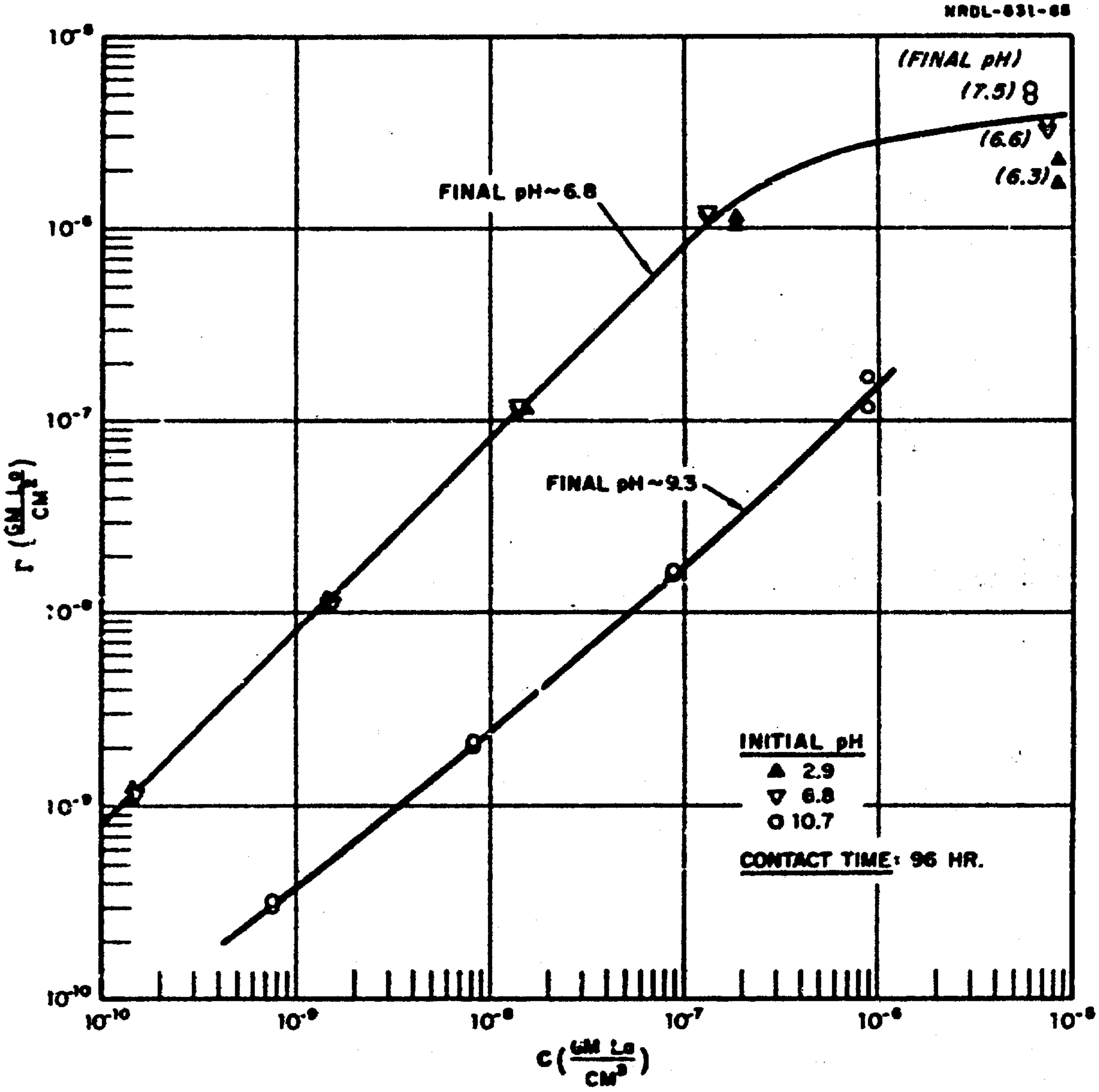

Fig. 6 La Adsorption on Painted Plates as a Function of Final Solution Concentration of La.

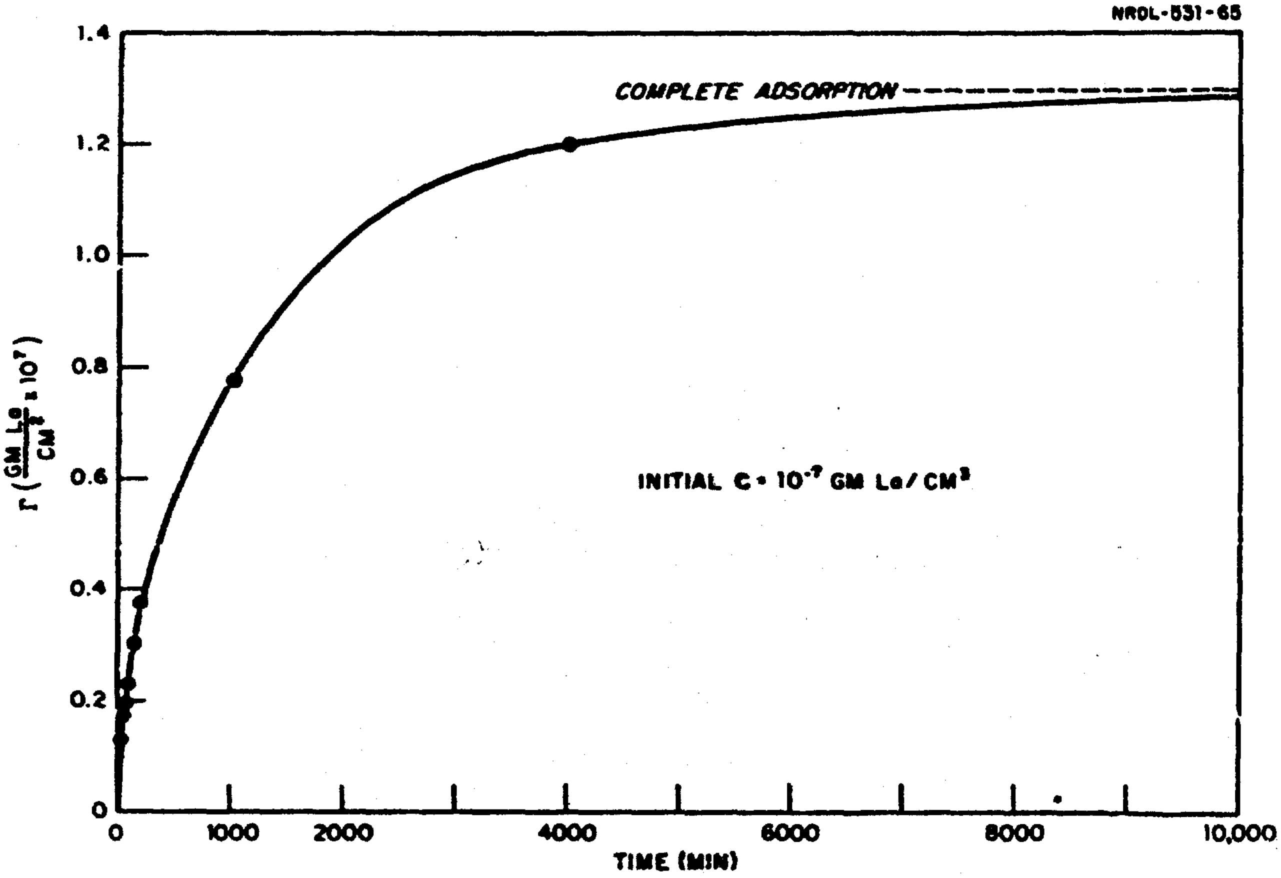

Fig. 7 La Adsorption as a Function of Time.

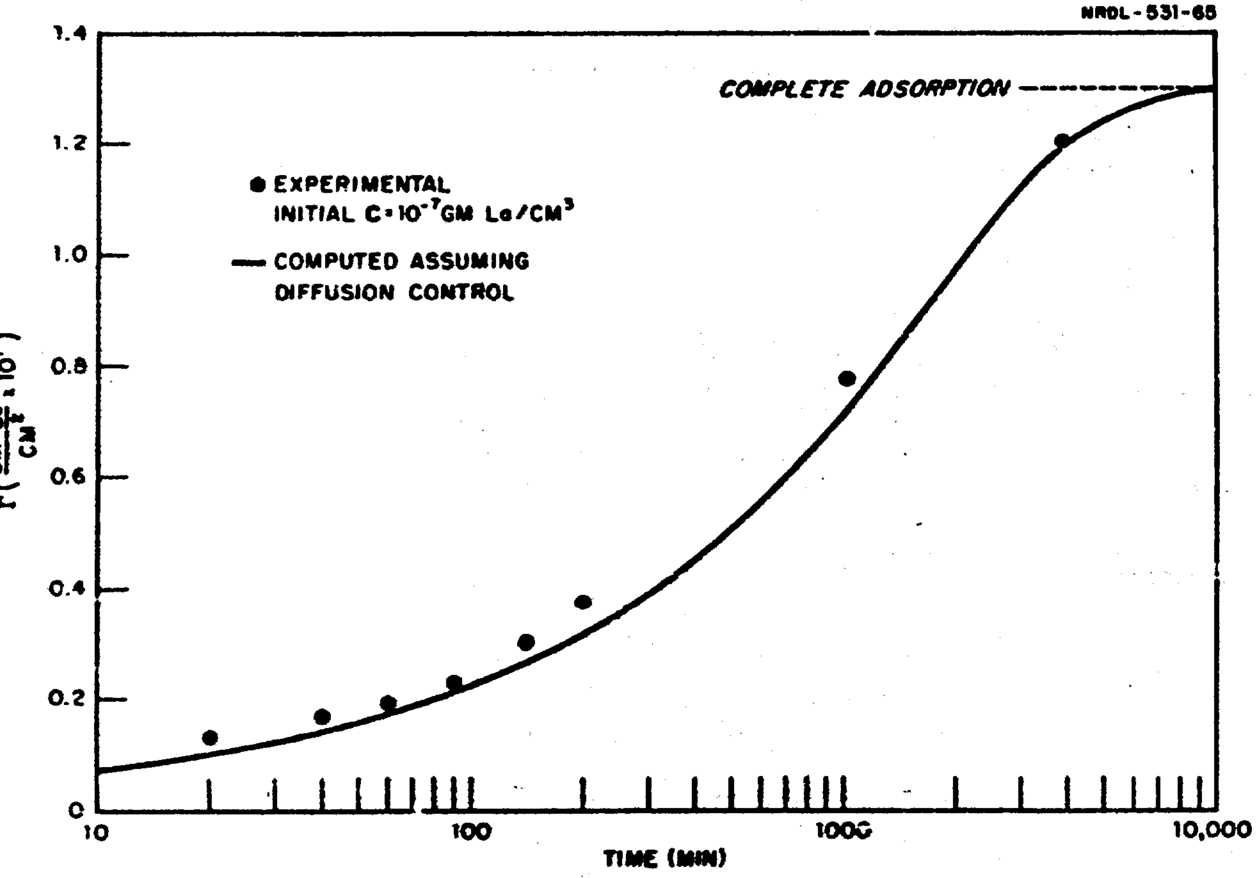

Fig. 8 La Adsorption as a Function of Time Showing Comparison With Computed Values.

computed for several contact times using Eq. 3, are plotted in Fig. 9. In Fig. 9 the average constant gradient profile at t = 4000 min (the average contact time for the tests plotted in Fig. 5) is shown by dashed line. The average solution concentration is thus obtained for comparison with the measured solution concentrations plotted in Fig. 5.

Data from Test 11 was not used because the lanthanum concentrations were above the saturation values (plateau on Fig. 5 discussed in section 5.1.1) which complicated computations of Γ (t).

Data from Test 16 were not meaningful because the radioisotope separation (section 3.1) did not effectively remove the Ba^{140}.

4.1.3 Temperature

The amounts of lanthanum adsorbed by the plates at three different temperatures are given in Table 7. Values for the extreme temperatures are from Test 10, while the room temperature value was interpolated from the kinetics (Test 12) data. Values computed using Eq. 5 for the same 2-hr contact time, and using diffusivities calculated as shown in section 2.2.3, are included for comparison.

TABLE 7

Experimental and Computed Values of Adsorption
for 2-hr Exposure at Three Temperatures

Temperatures	(x 10^7) Experimental	Computed
0	0.34	0.175
20	0.27*	0.24
70	0.60	0.58

*Interpolated from kinetics data.

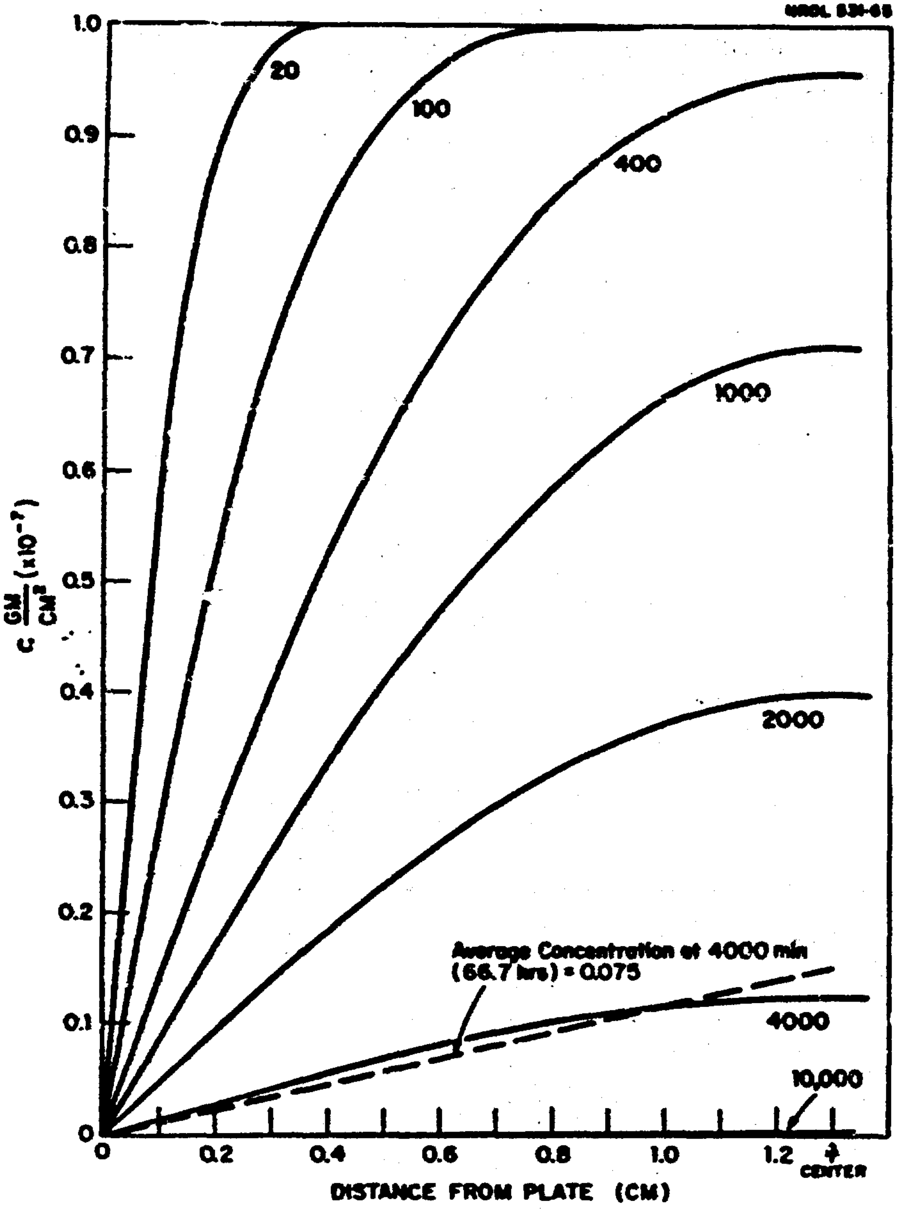

Fig. 9 Computed Concentration Profiles in Adsorption Cells After Various Contact Times.

TABLE 8

pH of Adsorption Solutions for Test 17.
The solution in Cell No. 3 initially contained 2×10^{-5} g La/cc.

Contact Time (hr)	pH in Cell No.				
	1	2	3	4	5
0	10.8	9.8	10.0	3.3	3.0
8	10.0	7.0	8.0	4.4	5.1
22	10.0	6.8	7.4	4.9	5.7
192	9.7	6.9	6.7	6.0	6.3
354	7.7	6.8	6.6	6.3	6.6
647	7.2	6.8	6.7	6.4	6.8
1390	7.2	7.0	6.9	6.6	6.8

TABLE 9

pH and Conductivity of Adsorption Solutions for Test 20. Initial pH given in Table 5.

Cell No.	Contact Time:	3 days		7 days	
		pH	$k \times 10^5$	pH	$k \times 10^5$
1		3.3	46.5	4.1	36.4
2		3.4	57.2	4.3	50.0
3*		5.5	18.0	6.3	19.2
4		3.7	26.7	5.5	23.3
5		4.1	28.2	6.1	28.4
6*		4.9	18.5	6.3	19.8
7		3.8	25.0	5.7	22.8
8*		11.2	46.5	11.0	41.7
9*		11.2	57.2	10.9	52.7
10		11.1	37.8	10.9	32.3

*Solutions cloudy at conclusion of test.

TABLE 10

pH and Conductivity of Adsorption Solutions for Test 21

Cell No.	Contact Time:	0 days	4 days		7 days	
		k x 10^3	pH	k x 10^5	pH	k x 10^5
1		5.9	6.1	6.90	6.7	7.25
2		1.63	6.3	3.64	6.6	4.37
3		0.48	6.5	2.99	6.9	4.02
4		0.27	6.6	2.90	6.9	3.85
5		0.20	6.5	2.65	6.7	3.53

4.1.4 pH and Inert Electrolyte

Specific lanthanum adsorption as a function of pH is shown in Fig. 10 for Tests 18 (distilled water) and 19 (10^{-3} N KNO_3) for each of two contact times: 72 and 168 hours. The pH of each solution approached (but did not necessarily reach) 6.2 to 6.5 with the change during each interval being roughly proportional to the difference between this value range and the solution pH at the beginning of the interval.

pH and conductivity changes of the adsorption solutions in the tests which did not use radiotracer are given in Tables 8, 9, and 10 (Tests 17, 20, and 21, respectively).

4.1.5 Paint Surface Behavior

Radioautographs are required to determine the manner in which the lanthanum is distributed on the paint surface.

Figure 11 is a radioautograph of a plate contaminated in a previous test with La^{140}.

Figure 12 is a photograph of a polyethylene film pressed between a painted plate and a sheet of glass. Striation patterns similar to those in Fig. 12 were present in all radioautographs, apparently on account of a similar polyethylene film used to prevent spread of contamination from the paint to the x-ray film.

Figure 13 is a photograph of a plate which has major surface irregularities as a result of exposure to a basic solution (pH 11) in an adsorption cell.

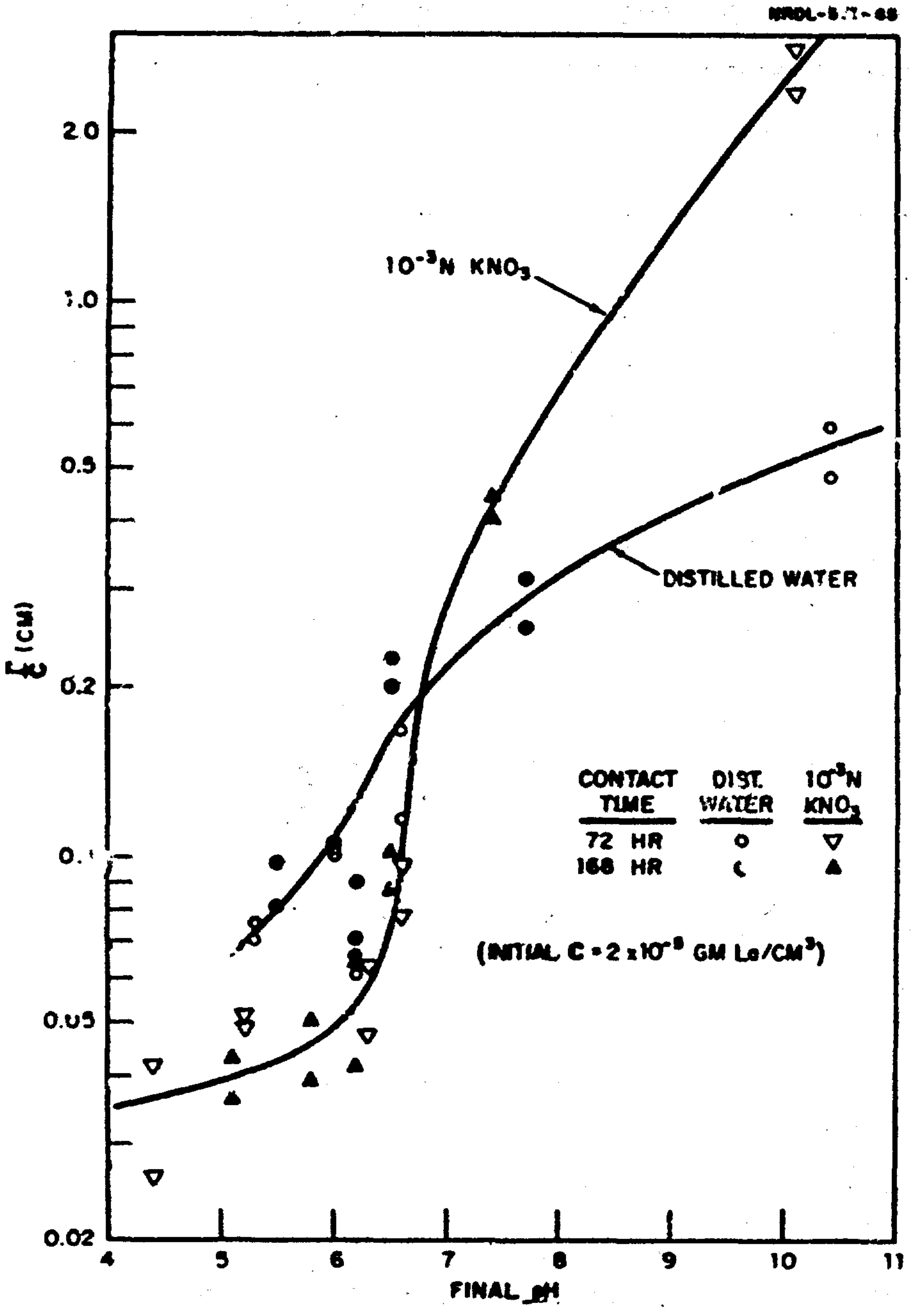

Fig. 10 Specific Adsorption of La on Painted Plates as a Function of Final Solution pH.

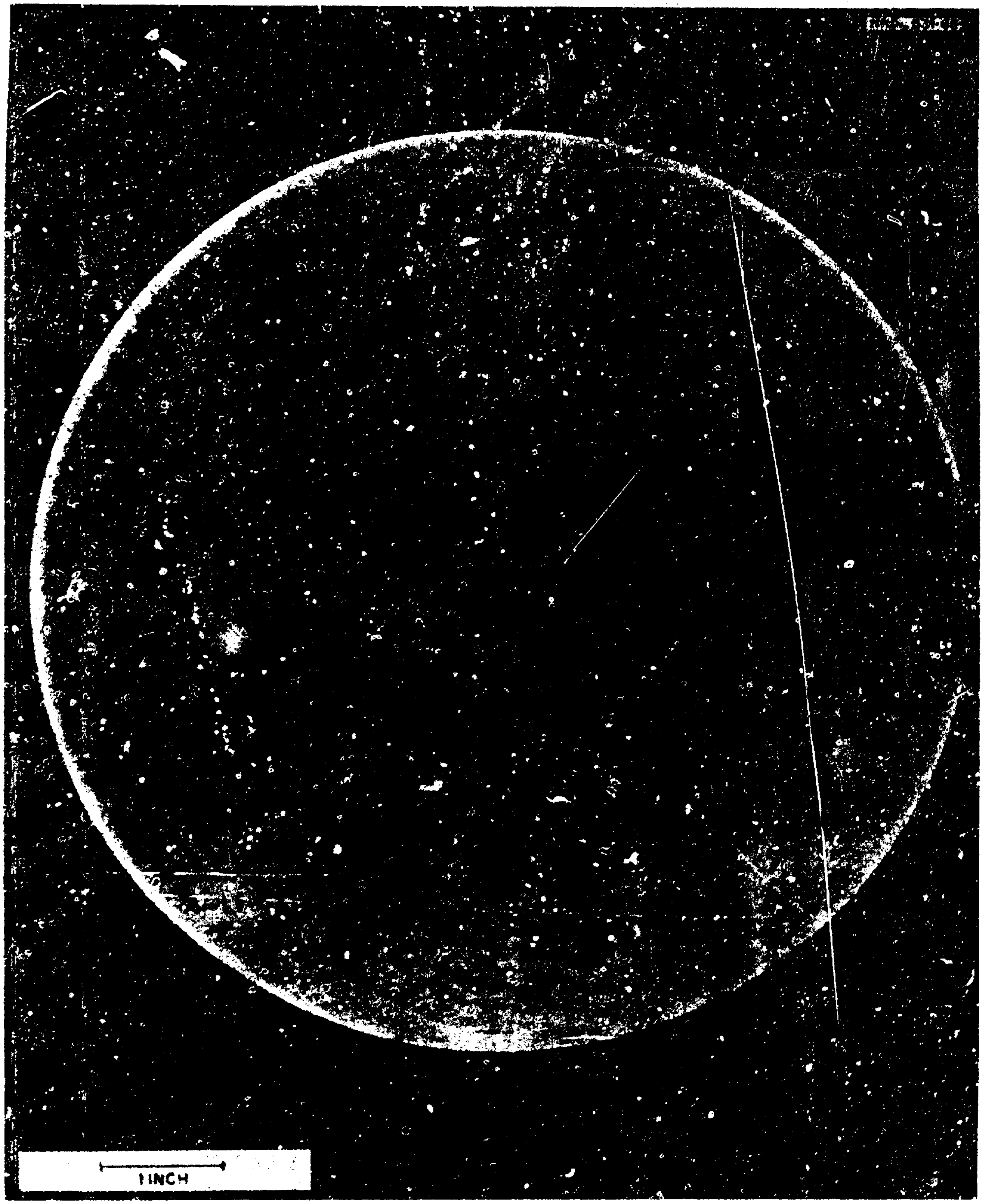

Fig. 11 Radioautograph of Plate Containing Adsorbed La^{140}.

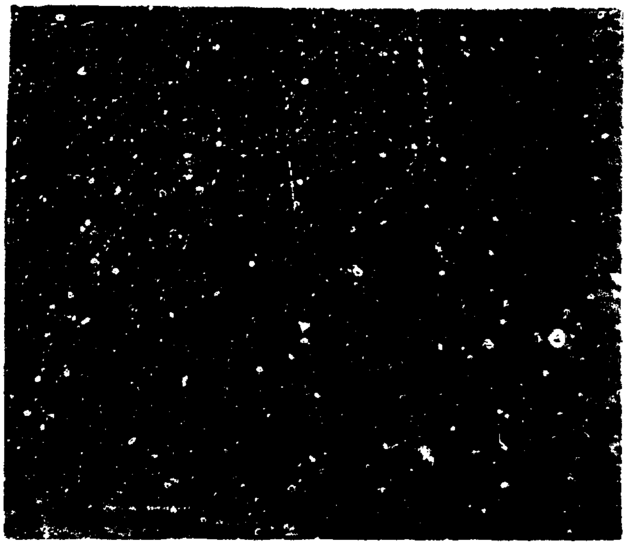

Fig. 12 Striation Patterns in a Polyethylene Film Pressed Between a Painted Plate and a Sheet of Glass. Similar patterns were observed in radioautographs.

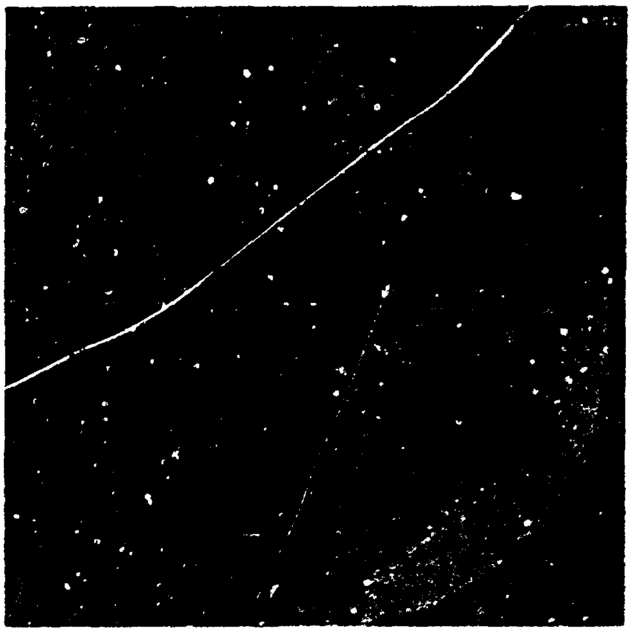

Fig. 13 Painted Plate Which was Exposed to a Basic Solution (pH 11) in an Adsorption Cell. Note the surface irregularities in the circular, exposed region.

TABLE 11

Solution pH at Different Contact Times with TiO_2. Initially, the 40-ml samples were of pH 2.2 HCl and pH 11.8 NaOH, each with 2 g TiO_2.

Time	Acid Sample (pH)	Basic Sample (pH)
5 min	2.2	11.7
15 min*	2.5	11.7
20 hr	2.7	11.3
72 hr	2.9	10.4
168 hr	2.9	9.7
528 hr	3.0	9.2

*KNO_3 added to coagulate the TiO_2.

4.2 ADSORPTION BY TiO_2

Lanthanum adsorption data for all of the TiO_2 tests are plotted in Fig. 14. Curves are drawn for inert electrolyte (NaCl) concentrations of 0.1 and 1.0 N. The arrow indicates the approximate concentration at which the curves change slope.

Specific adsorption as a function of inert electrolyte concentration for the high concentration (initial C = 1.71×10^{-3} g La/cc) data is plotted in Fig. 15.

Changes of pH with time of initially acidic (pH 2.2) and basic (pH 11.8) solutions in contact with powdered TiO_2 are given in Table 11.

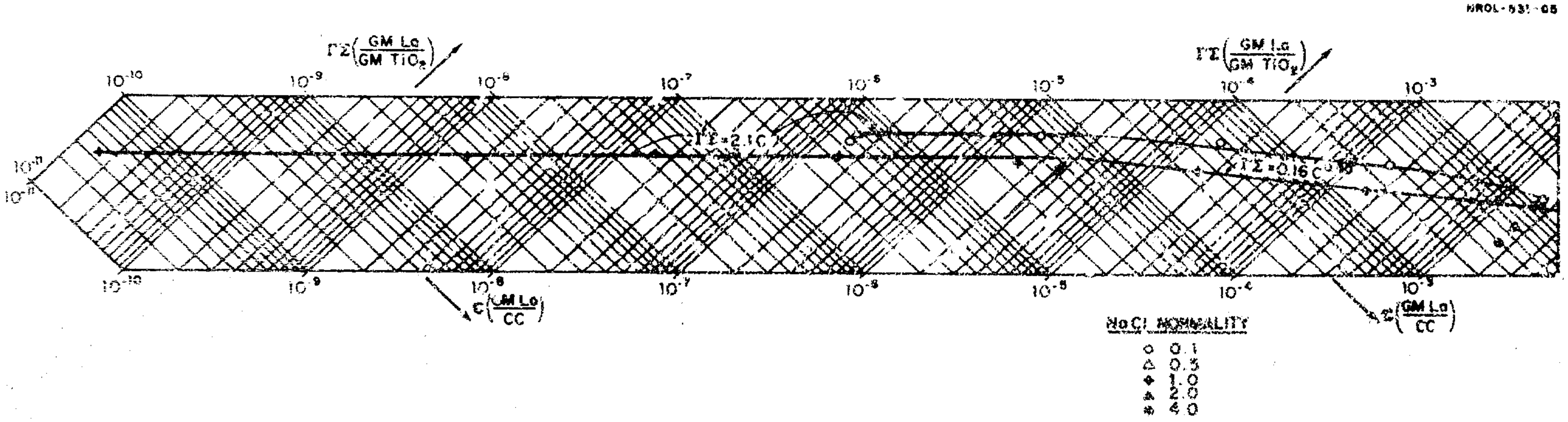

Fig. 14 La Adsorption on TiO_2 as a Function of Solution Concentration of La.

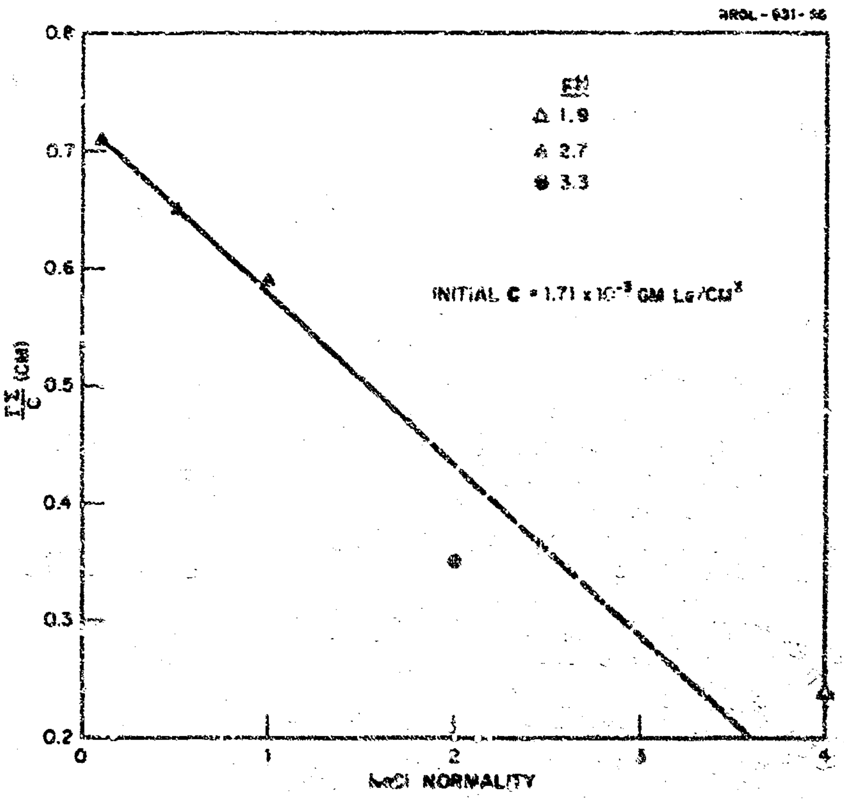

Fig. 15 Specific Adsorption of La on TiO_2 as a Function of Inert Electrolyte Concentration.

CHAPTER 5

DISCUSSION

5.1 ADSORPTION BY PAINT

5.1.1 Lanthanum Concentration

Figures 5 and 6 indicate that lanthanum adsorption by the paint follows the Freundlich isotherm with linear relation for concentrations of adsorbed lanthanum less than ~ 10^{-6} g/cm^2. Most of the data in this concentration range indicate a value of 1.0 for the Freundlich constant n. The curve for the data at solution concentration greater than 10^{-4} g La/cm^3 has been drawn with unity slope, although there is little reason to justify it; certainly, the data are spread sufficiently to permit an additional plateau or at least a point of inflection between the last two data points. Another reason for large uncertainty regarding the high concentration region is the scarcity of data; the spread of some of the "duplicate" tests gives an indication of the uncertainty of any single point. Some further doubt is cast on the validity of conclusions based on this particular data by the requirement of equilibrium for adsorption isotherms. The question of equilibrium in the paint adsorption data is discussed in the following section.

The most obvious feature of these data is the plateau or break in the curves occurring in the neighborhood of $\Gamma = 3 \times 10^{-6}$ g La/cm^2. This value is a factor of 4 larger than that calculated for completion of a surface monolayer by close packing of spheres having the ionic radius of La^{+++} (1.15 Å).[15] Surface roughness and microporosity of the paint could possibly increase the adsorbing area sufficiently to equate these values. If adsorption is indeed uniform up to concentrations representing completion of a surface monolayer, then it is unlikely that lanthanum adsorption by the paint involves a chemical reaction with specific paint components, but rather reaction with a highly hydrolyzed surface. This is because the paint surface on a micro scale should be a heterogeneous mixture of many components differing widely in chemical structure. This is also indicated by the fact that no significant differences were found between the adsorption behavior of the two paints tested, although some of their components differ (as shown in Table 1).

Determination of the values of the Freundlich constant, k is impossible from these data because of the equilibrium requirement. Apparent values can be obtained for the lower concentration range, and comparison of them is of interest. The low concentration data for distilled water in Fig. 5 give an apparent k of 20 cm, while those for distilled water (pH 6.8) in Fig. 6 give an apparent of 8 cm. As will be seen in the next section, the apparent k for Fig. 7 should be slightly larger than that for Fig. 5, because of the longer contact time of the data in Fig. 6. This discrepancy could be due to slightly lower solution pH or increased agitation of the adsorption cells in the tests plotted in Fig. 5.

Although the data for the higher final pH (Fig. 7) may not even follow the Freundlich relation, the average k corresponding to $n = 1.0$ would be about 0.2 cm. Although the pH for these data varied from 9.0 to 9.5, this variation was random with respect to concentration, so that the curve may represent the true shape of the isotherm although undoubtedly shifted due to the difficulty in attaining equilibrium.

The apparent k for the low lanthanum concentration natural seawater data is 1.6 cm. It cannot be determined from these data whether reduced adsorption in seawater is due entirely to the higher pH (~ 7.9 - seawater is sufficiently buffered to prevent pH change during the adsorption tests, which occurred in distilled water tests having initially non-neutral pH) or is partly due to reduction of activity of the La in solution by the high ionic concentration of seawater.

The data for Test 8 give apparent values of k both below and above the plateau: 3 cm and 0.05 cm, respectively - again making the unjustified assumption of $n = 1.0$ above the plateau. Comparing the way the three curves cross and their relative positions in Fig. 5 with the final pH data in Fig. 6, indicates that the solutions in Test 8 may have been slightly basic. For distilled H_2O, the conclusion can be reached that adsorption of lanthanum by Navy paint decreases with increasing pH when concentration is less than approximately 3×10^{-6} g La/cm^2 while the converse is true for the higher concentrations.

5.1.1.1 Desorption

The fact that no desorption of La^{+++} was detected could indicate either or both of two things: the kinetics of desorption is extremely slow compared to adsorption; the Freundlich constant k is indeed very large. Desorption should also have been attempted using samples containing more than one surface layer of adsorbed lanthanum (e.g., samples from test 8) because desorption should occur faster and to a greater extent for the physically adsorbed layers not directly adjacent to the paint surface.

5.1.2 Contact Time

The curve drawn through the Test 12 data (Fig. 7) is characteristic of a one-dimensional, diffusion-controlled reaction. The relatively rapid rate of adsorption for short contact times indicates that the high lanthanum concentration in the bulk of the solution drives the lanthanum to the paint surface where it is adsorbed (see solution lanthanum concentration profiles shown in Fig. 9).

Computed adsorption curves (see Fig. 8) initially used values of k obtained from the low concentration regions of Figs. 5 and 6, and the value of D calculated in section 2.2.2. Even using the largest apparent value of k gave a curve far below the experimental data, so k was made infinite, corresponding to complete adsorption at equilibrium. The resulting curve was still low, so D was increased slightly to 0.0004 cm^2/min. The resulting curve, although still somewhat below the experimental value, is in excellent qualitative agreement with the data. This indicates that adsorption in this experimental set up is diffusion-controlled - i.e., removal of lanthanum from the solution at the paint surface by adsorption occurs rapidly compared to diffusion of the lanthanum to the paint-solution interface. High experimental values could result from agitation of the adsorption solutions during filling and emptying of the cells. The computed curve shows that total equilibrium could not have been attained in the 3-or 4-day contact times used in these tests without continuous stirring of the solutions within the adsorption cells. However, the adsorption reaction may be so rapid compared to diffusion that a "local" equilibrium may have been maintained between the paint and the solution immediately adjacent to it.

While k is certainly not infinite, it is evidently very much larger than the apparent values taken from Figs. 5 and 6. Unfortunately there is no way of accurately determining k from the present data. Because of the large amount of radioactivity which would probably be required to provide accurate measurement of the residual lanthanum in solution at equilibrium, k could probably not be determined using this experimental set-up, even with stirring of the solutions to eliminate diffusion control.

Determination of the rate of adsorption, independent of any diffusion, which could shed light on the mechanisms of the adsorption reaction, would require a much more sophisticated apparatus and procedure than that used in these experiments.

5.1.3 Temperature

The experimental values of Γ measured at 20 and 70°C agree reasonably well with the computed values (Table 7), reflecting the effect of temperature on D. Unfortunately, the experimental value for 0°C is extremely high, probably due to some procedural error such as agitation during the adsorption test.

Since the diffusion equations did not account for temperature effects other than through the diffusivity, one might expect the experimental values at higher temperatures to be significantly less than the corresponding computed values since adsorption reactions are exothermic. If this had occurred, k as a function of temperature could be determined by substituting values of k into Eq. 5 and observing which reduced the computed values of Γ to the experimental values at that temperature. The slope of the Γ (or k, for $n = 1.0$) vs. $1/T_{abs}$ graph would be proportional to the heat of adsorption which would, in turn, indicate whether adsorption were chemical or physical. The data do not permit such an analysis.

5.1.4 pH and Inert Electrolyte

The effect of pH on lanthanum adsorption by the paint was partially illustrated by the data plotted in Fig. 6 - i.e., adsorption increased with increasing pH above the solution concentration corresponding to monolayer completion while it decreased below. The curves in Fig. 10 give a more complete picture of the pH effect in the region above the monolayer completion. Regardless of the presence of inert electrolyte, adsorption does increase with pH in a nonuniform manner, as was indicated by the high concentration data of Fig. 6.

As was discussed in Chapter 2, inert electrolytes influence adsorption of ions by altering the charge distribution in the double layer. At the zero point of charge (ZPC) where there is no net charge distribution, the inert electrolyte has no effect on adsorption. The data in Fig. 10 indicate that the ZPC of the Navy paint occurs at about pH 6.8. Curves representing other concentrations of various inert electrolytes should also pass through the intersection of these lines.

Since the effect of pH on adsorption was unexpected (i.e., adsorption increased with decreasing pH below monolayer saturation), the effect of inert electrolyte should also be reversed at low lanthanum concentration - i.e., inert electrolyte should aid adsorption at low pH and retard it at high pH. This would mean that, for the low lanthanum concentration occurring in seawater fallout, adsorption from seawater should be less than that from distilled water having the same pH.

All paint adsorption data for which pH was measured before and after exposure show that pH tends toward an average value of 6.8. This is another indication of the ZPC since spontaneous processes go in the direction of reducing any driving force, in this case the charge difference across the double layer. The rate of pH change depends on the composition of the solution, as shown by the data in Fig. 10 and Tables 8, 9, and 10. The data for Test 20 (Table 9) show that, for an initially acid solution, this pH change is accomplished most rapidly in the presence of La (or probably any other highly adsorbed ionic species), unless the acid is H_2SO_4 when the converse is true. When the acid is HCl or HNO_3, the adsorbing lanthanum is an efficient charge carrier. However, in the presence of SO_4^{--}, lanthanum forms[16] the complex $LaSO_4^+$ which may not be adsorbed and which is much less efficient as a charge carrier due to decreased diffusivity and ionic charge. The cloudy solutions in Cells 8 and 9 of Test 20 indicate that the high pH precipitated some of the lanthanum. The cloudy solutions in Cells 3 and 6 were apparently due to dissolution of some paint.

Inspection of the values of specific adsorption for the highest pH cells in Tests 18 and 19 shows that desorption of lanthanum occurred between the 72-and 168- hr measurements as the pH was decreasing from ~ 10 to ~ 7.5. This indicates that the adsorption reaction proceeds much more rapidly than the acid-base (hydrolysis) reactions of the paint with the solution.

The conductivities of all of the acid cells in Test 20 dropped drastically during the first exposure period. This indicates a large net adsorption, mostly due to hydrolysis since the conductivity due to the lanthanum was less than 2×10^{-5} $(\text{cm-ohm})^{-1}$ and not all of the cells contained lanthanum. The conductivities of all cells in Test 21 increased steadily, although most of the lanthanum was undoubtedly adsorbed from the four cells containing it. The only explanation for this is dissolution of the paint, a phenomenon which excluded conductivity (and conductometric titrations) as a method of measuring residual lanthanum in solution.

5.1.5 Paint Surface Behavior

The radioautograph shown in Fig. 12 is typical of several made from plates contaminated under various adsorption conditions. The lanthanum deposition appears generally uniform except for three features: (1) a striation pattern, (2) some "hot spots" of more concentrated lanthanum, appearing as white spots, and (3) a ring of increased deposition (white) at the very edge of the circular cell.

When first observed, the striation pattern was thought to be due to actual variation in the adsorption behavior of the paint surface, possibly reflecting non-uniform drying of the paint, although no such irregularities in the paint were visible. Subsequent investigation showed that similar patterns are produced in a polyethylene film when it is compressed between plane surfaces (Fig. 12). The X-ray film packets used in making our radioautographs consisted of the film sandwiched between a thin, opaque, polymeric film and a fiberboard backing, with the edges sealed to exclude light. The adsorption plates are placed with the contaminated side against the opaque film which is in turn adjacent to the emulsion side of the X-ray film. Lead weights are used to press the two together for maximum resolution of the surface contamination on the radioautograph. An additional polyethylene film was used in making this radioautograph to prevent contamination of the X-ray film packet. This should not have been necessary as the adsorbed contaminant was apparently difficult to remove from the paint.

An end-on view of a striated section of a compressed bag showed a sinusoidal pattern with maximum inclination of the plastic to the compressing planes of about 45°. The resulting variation in film thickness apparently attenuates considerably the beta radiations from La^{140} which are primarily responsible for darkening the X-ray film.

The paint surface irregularities causing the "hot spots" representing increased lanthanum adsorption on the radioautograph are usually minute and frequently invisible. Sometimes they are produced by a particle of foreign matter getting in the paint before it is applied, or landing on it during drying; sometimes they result from scratches. The area outside the adsorption ring on the plate in Fig. 13 is typical of the surfaces used in these tests; it is relatively free of visible irregularities. The area inside the ring has been exposed to a basic solution (pH 11) for several days (Test 20), and the hydroxide has obviously damaged the paint, causing it to blister in spots where adsorption may increase. Corresponding concentrations of acid did not produce this effect. The basic solutions also caused a greater color change of the paint; this sample has a relatively high contrast between the exposed and unexposed portions indicating greater change in paint surface properties than occurs by water exposure. Finally of note is the outline caused by the meniscus of the not quite full liquid level at the top of the picture.

The hot ring in the radioautograph is an edge effect. It may be due to the large pressure applied to the spacers (and imbedded O-rings) to prevent leakage from the cells. The increased local pressure in the paint at the ring may alter its structure enough to permit increased penetration by the lanthanum. It was determined that the spacer and O-rings had little tendency to adsorb the lanthanum.

5.2 ADSORPTION BY TiO_2

The results of lanthanum adsorption by TiO_2 are more easily interpreted than are the results for lanthanum adsorption by paint. Equilibrium was attained rapidly, permitting accurate determination of the isotherm in two regions of different adsorption mechanism, as shown in Fig. 14. As with the paint, adsorption follows the Freundlich relation. The values of n are 1.0 in the lower concentration region and 0.8 above a solution concentration of 3×10^{-6} g La/cc, both values being independent of inert electrolyte concentration. The values of k for the 1.0 N NaCl curve are 2.1 cc/g TiO_2 in the low concentration region and 0.16 cc/g TiO_2 in the higher region. Both values of k are larger by a factor of 1.9 for the 0.1 N NaCl curve - i.e., lanthanum adsorption by the TiO_2 decreases with increasing inert electrolyte concentration at the pH (2.7) of this experiment. This is shown also by the high La concentration specific adsorption data plotted in Fig. 15. The variation of pH in this data is indicated and shows that adsorption decreases with increasing pH.

Using the value of $\Sigma = 6000$ cm^2/g TiO_2, obtained from microscopic examination of the particles, gives $\Gamma = 3.5 \times 10^{-4}$ C for the low concentration region of the 1.0 N NaCl curve. This, in turn, gives a value of $\Gamma = 10^{-9}$ g La/cm^2 for lanthanum adsorption at the break in the 1.0 N NaCl curve. This represents about 0.1 % of a close-packed surface monolayer - a good indication of a transition from chemical to physical adsorption. The extremely small adsorption by TiO_2 compared to that of paint indicates that TiO_2 is not primarily responsible for the adsorption of lanthanum by paint.

The pH data in Table 11 shows that TiO_2 reacts slowly with acidic and basic solutions (hydrolyzes) just as the paint does.

CHAPTER 6

CONCLUSIONS

Although adsorption of lanthanum by Navy paints and by TiO_2 was by no means fully characterized, the following results were obtained:

1. Lanthanum adsorption by the paint goes essentially to completion for concentrations of adsorbed lanthanum less than about 3×10^{-6} g/cm^2. This is more than enough capacity to adsorb all the important gamma-emitters from seawater fallout (including the radioinert quantities of these elements naturally obtained from the seawater), assuming they would adsorb to the same extent as lanthanum (they obviously do not, based on the results of contamination-decontamination studies,[1] although it should be worthwhile to determine how many of them would).

2. Lanthanum adsorption by the TiO_2 is minimal, indicating that TiO_2 is not a primary adsorbent in the paint. It should be worthwhile to investigate the adsorption behavior of other paint components to see whether, indeed, there are any single components which are largely responsible for the adsorption behavior of paint.

3. Lanthanum adsorption by TiO_2 is very rapid; lanthanum adsorption by paint may be rapid, although it could not be determined in these tests because of diffusion control in the apparatus used.

4. Both the paint and the TiO_2 hydrolyze very slowly compared to the rate of lanthanum adsorption. This indicates that adsorption by both is determined by the initial pH of a contaminating solution since pH changes due to hydrolysis will be slow.

5. Desorption of lanthanum from paint will not occur without scrubbing and/or the use of chemical agents to strip it from the paint.

Some deficiencies in the work herein reported have been indicated, and suggestions for conducting more informative experiments have been made. The major limitation was the failure to obtain equilibrium in the paint adsorption tests. Overcoming this problem would require a radical modification in apparatus but obtaining equilibrium data would allow verification of the correct isotherm, an important step in characterizing the adsorption.

If future operational requirements indicated that further work was necessary, the first step in a continuation of this type of investigation would be the studying of other paint components to determine if the overall adsorptive properties of paint can be minimized by acceptable changes in paint composition. Complete determination of the adsorption behavior of the individual fission product elements and paint components should permit one of the following: (1) Development of a nonadsorptive paint (or at least one that adsorbs very little.) (2) Discovery of a highly effective chemical decontaminating agent. (3) Discovery of a means of saturating the adsorption capacity of paint prior to contamination.

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APPENDIX

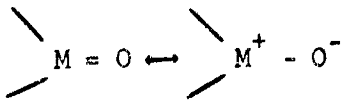
SOLID-LIQUID ADSORPTION REACTIONS

The importance of surface charge in adsorption reactions can be understood by considering the electric phenomena occurring at the solid-liquid interface. Any of the surface reactions involving ionic species can modify the existing charge distribution at the interface. When the solid acquires a surface charge through some adsorption reaction, a counter charge builds up in the solution immediately adjacent to the solid.

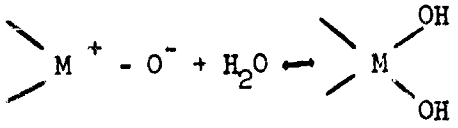
The ionic species responsible for establishing this electrical double layer (i.e., transferring charge to the solid) are called potential-determining ions. These ions are unique for each solid compound in contact with aqueous solution.[4] For ionic solids, they are the ions constituting the crystal lattice (e.g., Ba^{++} and $SO_4^{=}$ for $BaSO_4$). For most insoluble oxides, they are H^+ and OH^- because the pH controls the extent of surface ionization (hydrolysis). Figure 1 shows how the electric potential varies across the double layer when a surface has acquired a negative charge through adsorption of potential-determining anions and has then adsorbed cations (not potential-determining). The charge-balancing ions in the diffuse layer (called counter ions) are not unique for any solid.

Conditions resulting in the absence of a double layer (called the zero point of charge - ZPC) are of interest because they permit adsorption to be studied independently of the effects of the charged surface. For a solid whose potential-determining ions are H^+ and OH^-, the pH (i.e., concentrations of potential-determining ions) resulting in the ZPC depends on the relative basic and acidic properties of the solid.[4] For instance, strongly amphoteric oxides such as Al_2O_3 and Fe_2O_3 should have their ZPC near pH 7. Acidic oxides such as SiO_2 have their ZPC at $pH < 7$. Basic oxides such as Ag_2O and MgO have theirs at $pH > 7$.

Much work has been done in investigating the surface reactions of metal oxides with aqueous solutions.[5-7] The hydrolysis reactions for these systems are considered by most investigators as follows: When a dry metal oxide surface is placed in contact with aqueous solution, some of the surface oxygen will break a bond, producing an active group.

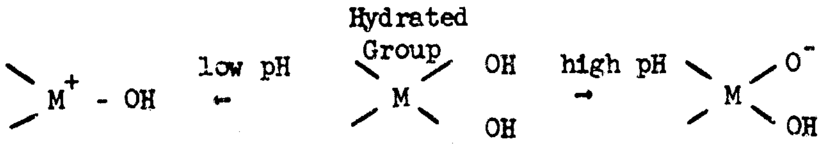


M is any metal at the solid surface (shown in these examples with a valence of +4). Depending upon pH and the properties of the metal, some fraction of these active groups will adsorb water (undergo surface hydration).



The hydrolysis reaction, which similarly depends on pH and the properties of the metal, resulting in a surface charge, may take place through either dissociation of some of the hydrated groups (A) or adsorption by some of the active groups (B).

(a)



(b)

The two mechanisms are at present experimentally indistinguishable. The pH ranges referred to are relative to the pH of the ZPC, where the surface densities of both charged groups are equal (the charge densities may or may not be zero).

The adsorption of ions (other than the potential-determining ions) and charged colloidal particles generally will be governed by the surface charge and the number of active groups (sites). In addition, the adsorption of a particular ionic species will depend on its solution concentration and on its properties (e.g., valence, effective radius) and the properties of any other ions competing for adsorption sites. Generally adsorption increases with ionic charge and concentration of the adsorbed species.

Some investigators have studied the adsorption of ions via the zeta potential (ζ). The zeta potential is the electrical potential between the non-flowing liquid film adjacent to a solid surface and the bulk liquid moving past the surface. It is determined through electrophoresis, electroosmosis or streaming potential measurements. Early investigators considered ζ to be identical to Ψ_δ (the potential drop across the diffuse liquid layer - see Fig. 1).[3] The assumption that $\zeta = \Psi_\delta$ requires the slipping or shear plane to be at the distance δ (the plane of fixed charges). Actually, this plane is located slightly beyond δ, indicating that $\Psi_\delta > \zeta$. While some determinations of ζ and Ψ_δ indicate good agreement for the adsorption of monovalent ions, ζ is considerably less than Ψ_δ for bi- or trivalent ions. More recent investigators have found empirically a relation between the surface potential and ζ, namely $\zeta = 0.55 \Psi_0$, rather than a close relation between ζ and Ψ_δ.[3] However, multivalent ions charged oppositely to the surface can be so strongly adsorbed that ζ may be even of opposite sign from Ψ_0. Experiments[9] using corundum (Al_2O_3) as the solid showed that the adsorption of multivalent ions (as long as they are not potential-determining) can change the sign of ζ, whereas the adsorption of monovalent ions can change only the magnitude of ζ slightly.

Uni-univalent salts that are inactive with respect to the solid surface are called inert or indifferent electrolytes. Although these electrolytes do not directly affect the surface by being preferentially adsorbed, they can affect the adsorption of other species by changing the dielectric properties of the solution (as a result of ionic strength) and, consequently, the charge distribution. Since they affect adsorption only via the surface charge, they will not affect adsorption at the ZPC of the solid.

Unless adsorbed species can react directly with the hydrated or unaltered surface groups, chemical adsorption will be limited to active groups such as those shown above. Therefore, the extent of chemical adsorption on metal oxides may not be more than a small fraction of a single layer immediately adjacent to the solid surface. For example, the density of ionizable sites on thoria (ThO_2) in aqueous solution was determined to be slightly less than one site per 1000 $Å^2$.[7] This represents about 0.1 % of a saturated surface layer for monatomic species. Similarly, ion exchange is restricted to certain types of active sites. Physical adsorption, however, can occur at inactive sites and in layers removed from the solid surface.

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(over)

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2. Paints

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III. Title
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13. ABSTRACT

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