NRL Report 7264

Investigations of Selective Interactions of the Iron/Aqueous Sodium Chloride System

Part 1 - The Adsorption of Chloride Ion by Alpha-Iron(III) Oxide in Sodium Chloride Solutions Saturated by Oxygen at 30°C

T. A. KOVACINA AND D. L. VENEZKY

Inorganic Chemistry Branch
Chemistry Division

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NAVAL RESEARCH LABORATORY
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13. ABSTRACT

A radioisotope procedure was used to investigate the chloride ion adsorption characteristics of crystalline α-iron (III) oxide in dilute sodium chloride (^{36}Cl-labeled) solutions at 30°C. The adsorption of the chloride ion was found to be pH dependent, i.e., hydroxyl ions in solution also competed for the active sites on hydrated α-iron (III) oxide surfaces. The chloride ion was preferentially adsorbed in the solution pH range of approximately 2 to 4, while hydroxyl ion adsorption was favored in the pH range above 4 to approximately 9. Only a small fraction of the total surface area determined by the BET method was found active for chloride adsorption in an acid environment.

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This is an interim report; work on the problem is continuing.

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INVESTIGATIONS OF SELECTIVE INTERACTIONS OF THE IRON/AQUEOUS SODIUM CHLORIDE SYSTEM

Part 1 - The Adsorption of Chloride Ion by Alpha-Iron (III) Oxide in Sodium Chloride Solutions Saturated by Oxygen at 30°C

INTRODUCTION

The presence of the chloride ion in an aqueous environment and its role in the stress corrosion cracking mechanism of various metals and alloys have been the subject of much disagreement among investigators (1) in the field of corrosion science. The basis for this disagreement undoubtedly lies in the complexity of the corrosion process which implies a multiplicity of interactions and/or similar competitive reactions between the various components of the system. A more meaningful approach may be to characterize potential interactions and then study them individually under conditions where model reactions take place in a less complicated environment than the overall system.

For example, recently an investigation was initiated at NRL to study specific chemical and physical processes of the iron/aqueous sodium chloride system. One important process isolated from the more complicated system was ion-exchange between crystalline iron (III) oxide and dilute aqueous sodium chloride solutions. The purpose of the present work was to study the anticipated weak affinity for the chloride ion by iron (III) oxide, the most predominant thermodynamically stable oxide formed when iron is exposed to aqueous solutions at normal atmospheric conditions. Although γ-iron (III) oxide would be the oxide species actually formed under the corrosion conditions of current interest, α-iron (III) oxide was substituted in the current investigation because of its ready availability in very high purity. Chlorine-36 isotope, also readily available, possessed the practical nuclear characteristics and high specific activities (disintegrations per unit time per unit mass) required for extremely low limits of detection.

EXPERIMENTAL PROCEDURE

Reagents

The uses of high-purity reagents were stressed in the current study to prevent extraneous ions from influencing the ion-exchange and adsorption characteristics of α-Fe_2O_3. The α-Fe_2O_3 (United Mineral and Chemical Corporation) was 99.999% pure and was used without further purification. The specific surface area of the α-Fe_2O_3 was approximately 11 m^2/g as determined by BET analyses of N_2 adsorbed at -196°C. Single crystals of optical-grade NaCl were also used without further purification. Chlorine-36 (half-life, 3×10^5 yr; beta emitter, 0.7 Mev) was obtained as aqueous NaCl solution (Amersham/Searle Corporation).

Apparatus

The pH was monitored in the solution by a combination glass electrode (Sargent-Welch Scientific Company) and an electrometer (Keithley 610A). The electrode and electrometer were calibrated with standard buffer solutions of pH values 4,7, and 10 (Beckman). A standard curve was used to translate the electrode potential readings into pH values of the bulk solutions.

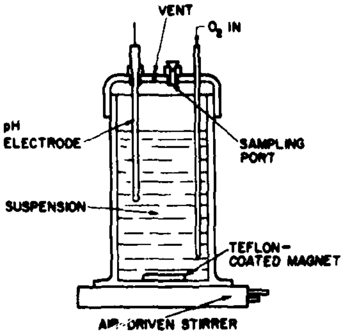

Fig. 1 - Polyethylene adsorption cell

A methane gas-flow counter with a 1.7-mg/cm^2 aluminum window was used to determine the activity of the residue from evaporated NaCl solutions.

The adsorption cell used in this investigation consisted of a polyethylene container (Fig. 1) fitted with a bubbler tube, ports for sampling and venting, and a port for the glass electrode. An air-driven submersible magnetic stirrer (Bromwell Scientific) was found convenient to drive the Teflon-coated stirring bar in the adsorption cell. The temperature of the various solutions was maintained at 30° ± 0.02°C by a constant-temperature bath.

Procedure

Approximately 300 ml of the radioactive solution containing a known Cl^- concentration was transferred to the adsorption cell, purged with O_2, and equilibrated at 30°C for a period of at least 2 hours. This time was sufficient for O_2 saturation of the solution and for elimination of CO_2 as indicated by the resultant equilibrium pH of approximately 7. One ml of the labeled solution for initial specific activity determination of Cl^- was withdrawn using a polyethylene pipette and processed as follows:

1. A 500-μl volume of the solution was transferred, using a pyrex pipette, to a stainless-steel counting planchet (1-1/4 in. in diameter with a 1/16-in. raised lip).

2. To prevent hydrolysis of NaCl and loss of ^{36}Cl activity during subsequent evaporation, the solution was made basic with 1 to 2 drops of 1% NaOH solution. Distilled H_2O was carefully added dropwise until the cross section of the planchet was covered.

3. The solution, after being evaporated under an infrared heating lamp, produced a uniform solid deposit of closely spaced concentric rings over the surface of the planchet.

4. The activity of the solid sample was determined.

A weighed amount of α-Fe_2O_3 (1 gram) was then introduced into the solution (300 ml) through the sampling port of the apparatus (Fig. 1), and timing of the adsorption experiment was begun. The purging of the system with O_2 that was first passed through a water bubbler maintained at 30°C was continued throughout a given run to prevent reduction of Fe(III) in solution or in the solid α-Fe_2O_3. The rapidly stirred suspension was sampled periodically using a syringe and a polyethylene pipette (1 ml). The sample was filtered through a 0.1-μ porosity filter disk (Gelman, type AM-9), which was supported in a stainless-steel chimney, and the specific activity was determined, as above, on the filtrate collected in a 10-ml polyethylene test tube. The pH of the solution was continuously monitored throughout the course of a typical experiment.

RESULTS

Radioactivity Calculations and Corrections

The procedure described for the continuous adsorption experiments resulted in observed specific activities which required rigorous correction before meaningful comparisons for adsorption/desorption determinations were possible; the uncorrected specific activity of the solution consistently increased with both time and frequency of sampling. The increased specific activity of the solution, caused by a Cl^- concentration effect, was attributed to solvent depletion resulting from two principal sources. First, significant evaporative losses were sustained in the O_2-saturated solution by the continuous gas purging over extended periods of time. The average evaporation rate was determined from the difference between the initial and final volumes (corrected for sampling) in the adsorption cell divided by the length of the experiment. In a typical run, the calculated evaporation rate varied between 0.2 and 0.3 ml per hour at the O_2 flow rates used (300 cc/min).

Second, continuous sampling of suspensions of α-Fe_2O_3 of high specific surface can have a latent concentration effect on the solution with respect to Cl^-. For example, under conditions initially favoring adsorption, a relatively small fraction of the total oxide surface containing adsorbed Cl^- is removed from the system in a single sampling (the estimated equivalent of <0.2 mg of original Fe_2O_3 added, or only 0.02%), while at the same time a significant quantity of solution containing less than the original concentration of Cl^- is removed. In dilute solutions, such sampling is essentially equivalent to removal of pure solvent. Subsequently, under conditions favoring desorption, the release of adsorbed Cl^- may result in a solution having a Cl^- concentration considerably higher than the original solution, depending on the previous sampling frequency.

In such continuous adsorption experiments using radioactive solutions which approach infinite dilution and contain suspended solid adsorbents, the cumulative volume loss of solvent due to both sampling and evaporation must be taken into account. Corrections must be made before the specific activities of such solutions can be accurately determined at any time during the run and before meaningful comparisons with initial values can be made. In dilute solutions, the cumulative amount of solute permanently lost from the system in small samples will be rather insignificant and can be neglected in the specific activity determinations. Consequently, the observed specific activity of the solution should essentially be a direct function of the integral solvent loss from the aforementioned sources, and the corrected specific activity should be closely estimated by the following mathematical expression:

$$A_t = B_t \frac{C - (D_t + E_t)}{C} ,$$

where A_t and B_t are the corrected and observed specific activities of the solution at time t, respectively; C is the initial volume of solution in the cell; D_t is the integrated volume loss of the solvent because of evaporation; and E_t is the integrated volume loss of the solvent due to sampling. The observed specific activities were corrected using the above formula.

Cell and Electrode Adsorption

The adsorption of Cl^- by the surfaces of the polyethylene cell and glass electrode was investigated by contact with a 3.7×10^{-4} M NaCl solution in the same geometric arrangement and pH range as those used in α-Fe_2O_3 runs. The data in Table 1 were normalized for convenience and plotted in Fig. 2. A slight tendency for adsorption by

Table 1
Change in Specific Activity of 3.7 × 10^{-4}M Sodium Chloride Solution in Contact with the Combined Surface Areas of the Polyethylene Cell and the Glass Electrode at 30°C

Elapsed Time (hours)	pH of Solution	Specific Activity* of Solution (counts/min/ml)
0.0	6.9	41,118
0.5	2.9†	-
1.0	2.9	40,878
1.25	11.6‡	-
1.75	11.6	40,482
2.0	3.0†	-
2.5	3.0	41,260
2.7	9.5‡	-
3.2	9.5	40,010
19.25	9.5	41,282
25.3	2.3†	-
25.8	2.3	41,556

*Corrected.
†pH adjusted with $HClO_4$.
‡pH adjusted with NaOH solution.

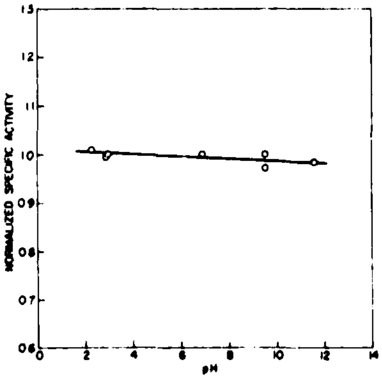

Fig. 2 - pH dependence of the specific activity of 3.7 × 10^{-4}M NaCl solution contacted by the polyethylene cell and the glass electrode. The activity data were normalized to 41,115 counts/min/ml.

the polyethylene walls and the Jena U glass electrode was observed as the solution pH was increased above that of the original solution (pH ≈ 7). Consequently, some ^{36}Cl must have been adsorbed under the initial equilibrium conditions but desorbed at lower pH values where the normalized activities were greater than 1. The results indicated that Cl^- was adsorbed preferentially by the polyethylene cell and/or electrode at high OH^- concentrations. Allowances for these slight effects were made, where necessary, in runs using suspended α-Fe_2O_3; the normalized corrected activity of the solution of a known pH was divided by the normalized activity at the corresponding pH value given in Fig. 2. For adsorption values observed in the systems studied below approximately pH 4, the correction was negligible; however, in the pH region above 6, the correction was used.

Effect of Chloride Ion Concentration on Adsorption

When excess α-Fe_2O_3 is added to O_2-saturated NaCl solutions at approximately pH 7, the hydrogen ion concentrations increase by three orders of magnitude (10^{-7} to 10^{-4}M, Table 2). The new equilibrium pH value (4.3) appeared to be independent of Cl^- concentration over the range 1×10^{-1}M to 5.5×10^{-4}M. Depletion of Cl^- from solutions containing 1×10^{-3}M and 5.5×10^{-4}M NaCl is shown in Figs. 3 and 4, where the normalized corrected activities decreased rapidly to a minimum and then slowly increased to a higher value. The depletion appeared to be directly related to the adsorption of Cl^- from solution by the solid α-Fe_2O_3; a slower desorption process (increased specific activity of solution) followed the adsorption. The rate of adsorption appeared to be inversely related to the NaCl concentration—the 5.5×10^{-4}M NaCl solution (Fig. 4) showed a more rapid rate of adsorption than the 1×10^{-3}M solution (Fig. 3). This phenomenon may reasonably be explained by an increase in Fe (III) solubility as a function of Cl^- concentration due to the formation of soluble iron-chloride complexes. Subsequent hydrolyses of these complexes would result in an increased concentration of soluble iron-hydroxo complexes, which would also compete for Cl^-. The lower rate of Cl^- adsorption observed in the more concentrated solutions is consistent with the assumed competitive reaction between the complex-Cl^- association and Cl^- adsorption by the Fe_2O_3 surface. Figures 3 and 4 also showed that the amount of adsorption at the estimated minimum point of the curve was directly proportional to the NaCl concentration. However, the data did not allow a quantitative determination of the adsorption dependence on the Cl^- concentration.

When the concentration was increased to 1×10^{-2}M NaCl or higher, an unexpected result was observed; the Cl^- content of the solution appeared to be increased above the original concentration when the normalized corrected activities were plotted with respect to time (Fig. 5 and 6). The increase in activity reached a maximum and then approached the original value (1.0). The height of the maximum appeared to depend on the NaCl concentration, but the rate of reaching the maximum and returning to what approached the original activity appeared independent of concentration.

The apparently anomalous activities exhibited by the 10^{-2}M and 10^{-1}M NaCl solutions could also be reasonably explained by an increase in Fe (III) concentration by the formation of soluble iron-chloride complexes. Consequently, the solution removed from the suspensions for analysis might have contained an unfavorable amount of soluble Fe (III), which could have caused irregularities in the activities by selfscattering during the counting. As the solutions aged, the iron-chloride complexes could have hydrolyzed and/or formed aggregates that precipitated Fe (III) from solution, thus decreasing the Fe (III) concentration to its original value and preventing interference with the activity measurements.

For measuring Cl^- activities, the solutions with Cl^- concentrations 10^{-3}M or lower, having high specific activities of Cl^-, were most sensitive to detection of adsorption and least sensitive to interference from iron solubility. Conversely, the commensurately lower specific activities of the more concentrated chloride solutions, 10^{-2}M and greater, apparently were not sufficiently sensitive to detect the low adsorption capacity of α-Fe_2O_3 because of the interference of soluble Fe (III) in the measurements.

Table 2
Effect of Concentration on the Specific Activities of Sodium Chloride Solutions in Contact with α-Iron (III) Oxide at 30°C

Concentration of NaCl Solution (moles/liter)	Elapsed Time (hours)	pH of Solution	Specific Activity* of Solution (counts/min/ml)
1×10^{-1}	0.0	7.0	14,372
1×10^{-1}	0.5	4.3†	15,306
1×10^{-1}	1.0	4.3	14,754
1×10^{-1}	26.3	4.3	16,144
1×10^{-1}	48.4	4.3	14,329
1×10^{-1}	71.3	4.3	14,259
1×10^{-2}	0.0	7.0	35,474
1×10^{-2}	1.0	4.3†	36,228
1×10^{-2}	4.0	4.3	36,829
1×10^{-2}	21.3	4.3	36,579
1.1×10^{-3}	0.0	6.9	13,898
1.1×10^{-3}	1.0	4.3†	13,167
1.1×10^{-3}	20.3	4.3	10,637
1.1×10^{-3}	44.0	4.3	11,567
1.1×10^{-3}	67.1	4.3	11,260
5.5×10^{-4}	0.0	6.9	49,107
5.5×10^{-4}	0.53	4.3†	45,997
5.5×10^{-4}	1.53	4.3	40,786
5.5×10^{-4}	19.42	4.3	43,703

*Corrected
†pH adjustment on the addition of 1 g α-Fe_2O_3 to 300 ml of solution.

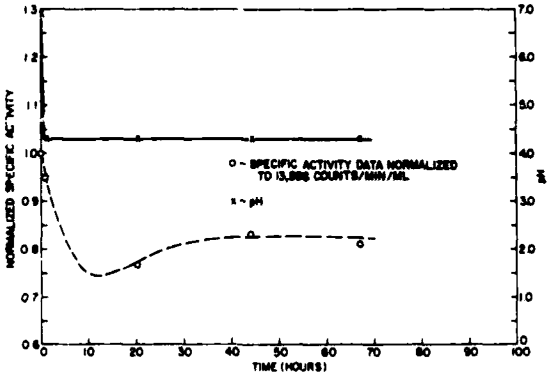

Fig. 3 - Changes of specific activity and pH of 1×10^{-3}M NaCl solution (initially neutral) upon equilibration with α-Fe_2O_3 solid

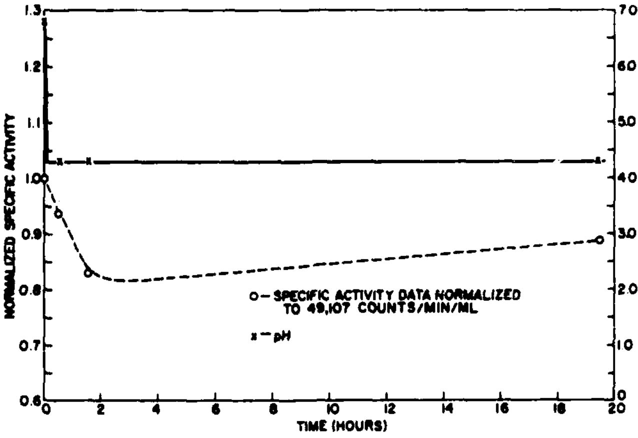

Fig. 4 - Changes of specific activity and pH of 5.5×10^{-4} M NaCl solution (initially neutral) upon equilibration with α-Fe_2O_3 solid

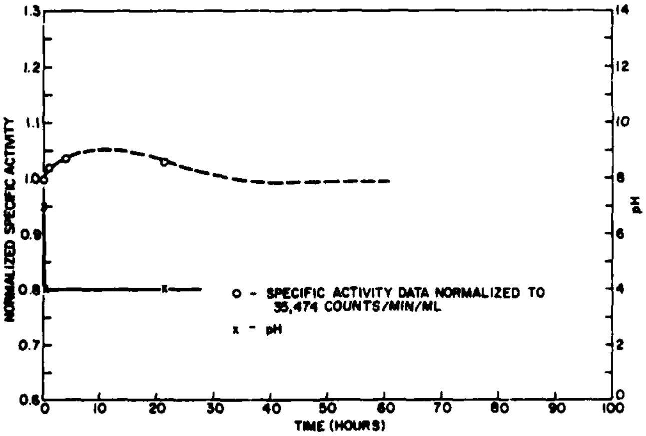

Fig. 5 - Changes of specific activity and pH of 1×10^{-2} M NaCl solution (initially neutral) upon equilibration with α-Fe_2O_3 solid

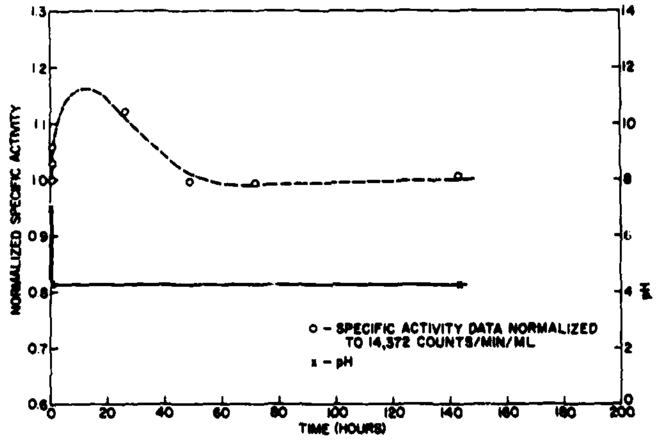

Fig. 6 - Changes of specific activity and pH of 1×10^{-1} M NaCl solution (initially neutral) upon equilibration with α-Fe_2O_3 solid

Chloride Ion-Hydroxyl Ion Competition

Competition between the Lewis bases, Cl^- and OH^-, for active sites on the hydrated α-Fe_2O_3 was studied by disturbing the equilibrium pH (approximately 4), which was established after adding α-Fe_2O_3 to a 5.5×10^{-4}M NaCl solution (Fig. 4). Variation in the pH of the system was accomplished by adding 50% NaOH solution or concentrated perchloric acid (Fig. 7, 8, and 9).

After the first addition of NaOH to the suspension, a gradual decrease in pH was observed from an initial pH value of 5.9. However, the specific activity of the solution increased sharply at first and then slowly decreased (Fig. 7). A similar phenomenon was observed when two additional portions of NaOH solution were added to increase the pH of the system to approximately 7.4 from an apparent equilibrium pH of 4.7 and then from 6.7 to 8.1. In each case, the final observed specific activity was always greater than the initial activity, while the final equilibrium pH of the solution was always less than the initial value. This observation suggests that chloride ions are released from the α-Fe_2O_3 surface and are replaced by hydroxyl ions as the pH is increased. The normalized activities of solutions above pH 9 or below pH 3 (Fig. 9) rapidly reached an equilibrium value while the pH remained relatively constant. In the pH region above 9, no detectable competition occurs between the two Lewis bases for sites on the solid surfaces of the suspended α-Fe_2O_3.

Because the Jena U glass electrode used was reportedly (2) unaffected by Na^+ interference below a pH of approximately 10, the observed pH drifts were attributed to the removal or "abstraction" of OH^- from solution, that is, a reduction in pH. To corroborate the conclusion that the decrease in pH was not caused by either increased ionic strength of the solution or increased Na^+ concentration when the pH was increased, a separate experiment was run in which the OH^- concentration of a 5.5×10^{-4}M NaCl solution, without α-Fe_2O_3 added, was increased by NaOH addition. No pH drift was noted over a 24-hour period.

The variation of the normalized activity with pH is shown in Fig. 10. The normalized activities in the pH range 6 to 12 were corrected for the cell and electrode adsorption as described earlier. Figure 10 also shows the results after the manipulation of the pH by

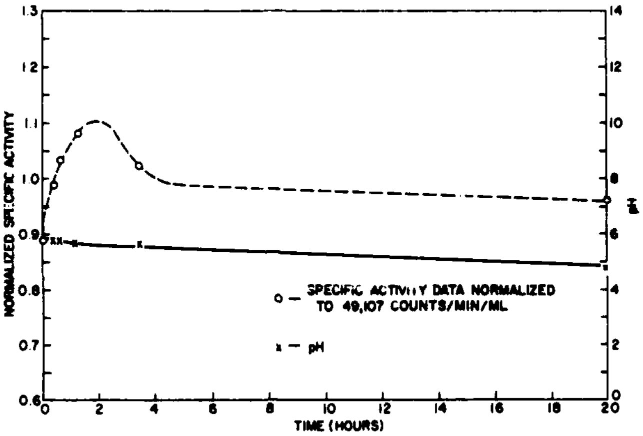

Fig. 7 - Changes of specific activity and pH of 5.5×10^{-4} M NaCl solution (pH = 5.9, initially) upon equilibration with α-Fe_2O_3 solid

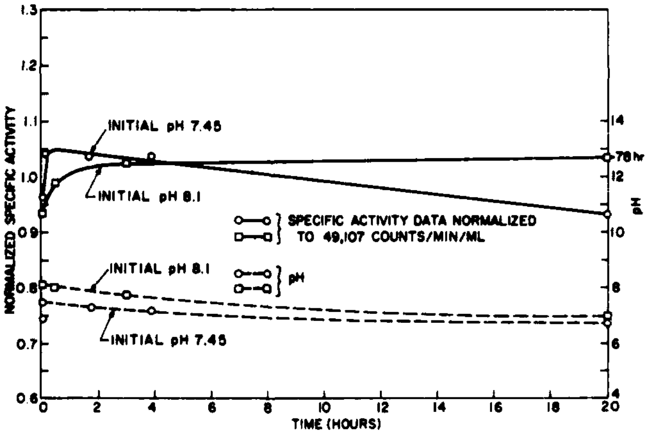

Fig. 8 - Changes of specific activities and pH's of 5.5×10^{-4} M NaCl solutions (pH of 7.45 and 8.1, initially) upon equilibration with α-Fe_2O_3 solid

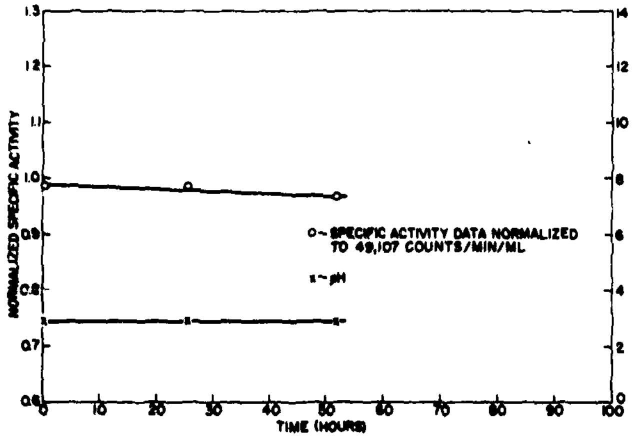

Fig. 9 - Changes of specific activity and pH of 5.5×10^{-4} M NaCl solution (pH = 2.9, initially) upon equilibration with α-Fe_2O_3 solid

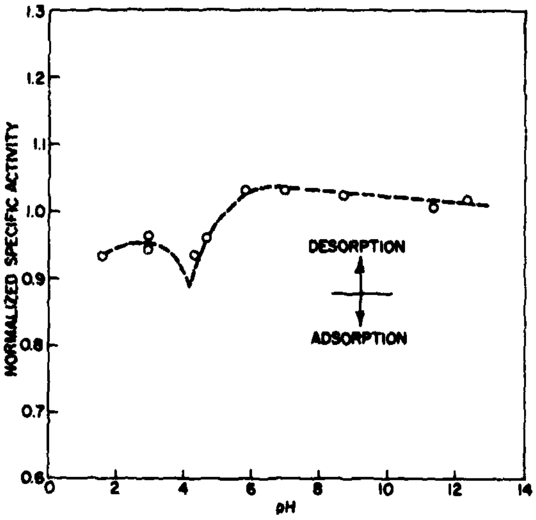

Fig. 10 - Relationship between specific activity and pH of 5.5×10^{-4} M NaCl solution in contact with α-Fe_2O_3 solid for 0.5 hr. The specific activity data were normalized to 49,107 counts/min/ml.

adding perchloric acid and then NaOH. A specific activity minimum (maximum Cl^- adsorption by α-Fe_2O_3) occurred at a pH of approximately 4, and then the activity appeared to level off below pH 3. The maximum value of the activity (little, if any, Cl^- adsorbed by α-Fe_2O_3) was reached at approximately pH 6 and above.

DISCUSSION

Surface Hydrolysis of Iron (III) Oxide

When excess α-Fe_2O_3 is added to either O_2-saturated distilled H_2O or NaCl solution, the increased H^+ concentration is ascribed to the acid nature of Fe_2O_3. A two-step process (3) may be postulated for the reaction; the surface is first hydrated and is then followed by dissociation of the hydroxides formed on the surface. The steps may be generalized as shown in the equations below:

1. Hydration of the surface:

$$Fe_2O_3 + H_2O \rightarrow 2FeOOH, \text{ and/or} \qquad (A)$$

$$Fe_2O_3 + 3H_2O \rightarrow 2Fe(OH)_3 \qquad (B)$$

2. Dissociation of hydroxylated surface:

$$FeOOH + H_2O \rightleftharpoons FeO_2^- + H_3O^+, \text{ and/or} \qquad (C)$$

$$Fe(OH)_3 + H_2O \rightleftharpoons H_2FeO_3^- + H_3O^+ \qquad (D)$$

$$H_2FeO_3^- + H_2O \rightleftharpoons HFeO_3^{2-} + H_3O^+ \qquad (E)$$

$$HFeO_3^{2-} + H_2O \rightleftharpoons FeO_3^{3-} + H_3O^+ \qquad (F)$$

The release of protons in the dissocation of the hydrated α-Fe_2O_3 results in an induced electrical surface charge which now becomes important from an ion-exchange viewpoint, depending on the composition of the solution in which the oxide is suspended. Equations C and D show that the surface potential of the suspended oxide will depend on the concentration of H^+ in solution in equilibrium with the hydrated Fe_2O_3. Consequently, the charge on the surface of Fe_2O_3 can be modified by varying the pH of the solution in which the oxide is suspended, and the resulting surface, so modified, can attract (or adsorb) either cations or anions from solution. Parks and de Bruyn (3) recently reported that the surface charge distribution of α-Fe_2O_3 is positive in acidic and negative in basic media, with the zero point of charge occurring at approximately pH 8.5. This surface potential/environmental effect (3) may qualitatively be illustrated by the following types of equilibria:

3. Reaction of surface hydroxides in acid:

$$FeOOH + H_3O^+ \rightleftharpoons FeO^+ + 2H_2O, \text{ and/or} \qquad (G)$$

$$Fe(OH)_3 + H_3O^+ \rightleftharpoons Fe(OH)_2^+ + 2H_2O \qquad (H)$$

$$\mathrm{Fe(OH)_2^+ + H_3O^+ \rightleftharpoons Fe(OH)^{2+} + 2H_2O} \qquad \text{(I)}$$

$$\mathrm{Fe(OH)^{2+} + H_3O^+ \rightleftharpoons Fe^{3+} + 2H_2O} \qquad \text{(J)}$$

4. Reaction of surface hydroxides in base:

$$\mathrm{FeOOH + OH^- \rightleftharpoons FeO_2^- + H_2O}, \text{ and/or} \qquad \text{(K)}$$

$$\mathrm{Fe(OH)_3 + OH^- \rightleftharpoons H_2FeO_3^- + H_2O} \qquad \text{(L)}$$

$$\mathrm{H_2FeO_3^- + OH^- \rightleftharpoons HFeO_3^{2-} + H_2O} \qquad \text{(M)}$$

$$\mathrm{HFeO_3^{2-} + OH^- \rightleftharpoons FeO_3^{3-} + H_2O} \qquad \text{(N)}$$

Adsorption of Chloride Ion by Alpha-Iron (III) Oxide

On the basis of the above postulated ionized surfaces of hydrated Fe_2O_3, anionic adsorption would be expected to occur in acidic solutions and cationic adsorption in basic solutions. Corroboration of the former case was indicated by the data shown in Fig. 10 for Cl^-. The minimum specific activity of solution at pH approximately 4 indicated the preferred association of Cl^- with the positive hydrated surface of Fe_2O_3. The predominant surface species at this pH is assumed to be $Fe(OH)_2^+$. Below pH 4, the specific activities leveled off at slightly higher values than the minimum observed activity and may be due to the competition between the charged surface of the Fe_2O_3 for ClO_4^-, and/or H^+ in solution for Cl^-. Although the magnitude of the positive surface charge is expected to increase with decreasing pH, the increased H^+ concentration (and ClO_4^-) in solution may prevent a further increase in Cl^- adsorption by the solid.

Above pH 6, little if any Cl^- adsorption was indicated. This suggests that under our experimental conditions, the surface area of the oxide is composed of either neutral species and/or negatively charged species. Parks and de Bruyn (3) have reported that the zero point of charge of α-Fe_2O_3 occurred at a pH of approximately 8.5. The discrepancy between our pH value of approximately 6 and 8.5 may be attributed to experimental conditions and should be further investigated. In any event, for values of the pH above the zero point of charge where a negative surface charge is expected, cation rather than anion adsorption should occur. The slight decreasing slope of the curve (Fig. 10) above pH 7 may be attributed to a double-layer effect caused by the adsorption of Na^+ on the solid surface and then the attraction of this new surface for Cl^- in solution.

The Cl^- adsorption observed for the 5.5×10^{-4}M and 1.1×10^{-3}M NaCl solutions containing an excess of α-Fe_2O_3 at pH approximately 4 was recalculated in terms of micrograms of Cl^- per gram of Fe_2O_3 and plotted as a function of time in Fig. 11. The rate of adsorption in both cases initially appeared to be identical while the slower desorption process took place between 7 and 12 hours later, depending on the concentration. Comparison of the relative magnitudes of Cl^- adsorbed after a sufficient period of aging (20 to 50 hr) indicated a direct, although qualitative, relationship between Cl^- concentration and amount of adsorption. For example, from Fig. 11, after 25 hr, approximately 1.8 micrograms Cl^- per gram Fe_2O_3 had been adsorbed from a 5.5×10^{-4}M NaCl solution, and approximately 8.6 micrograms per gram Fe_2O_3 from a 1.1×10^{-3}M NaCl solution. The amount of adsorption increased approximately fivefold when the concentration of NaCl in solution was doubled.

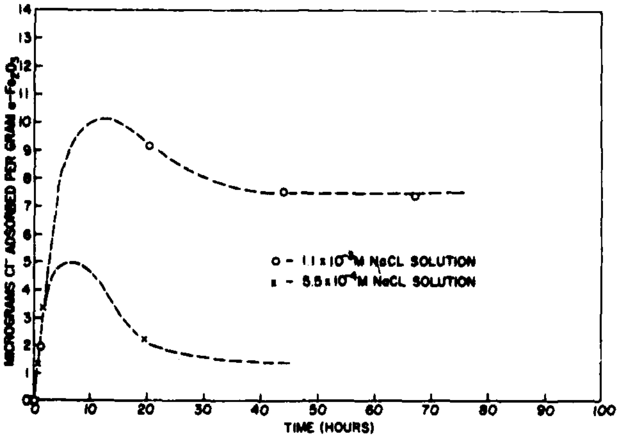

Fig. 11 - Effect of concentration of solution on amount of Cl^- adsorbed by α-Fe_2O_3 solid

The maximum amount of Cl^- that could be adsorbed on the α-Fe_2O_3 surface was calculated from the 11 m^2/g surface area of the solid. Assuming that the ionic radius of Cl^- is 1.81 Å, the theoretical area that would be covered by one atom is 10.3 $Å^2$. Thus, 1.07×10^{20} chloride ions should completely cover the area of the solid in a monolayer. In this work, 10 micrograms of Cl^- per gram α-Fe_2O_3 was the largest amount of adsorption observed; this amount corresponded to approximately 1.7×10^{17} chloride ions or 1.75×10^{18} $Å^2$ of surface covered. This relatively small area of coverage by the apparently small amount of chloride ions could be explained by the assumption that not all of the area determined by the BET method was active. By gradually increasing the Cl^- concentration of an aqueous suspension of α-Fe_2O_3 at a pH of approximately 4, we hope to be able to determine a saturation number for the Cl^- adsorption from the solution by the solid (under the conditions reported) in a manner similar to the BET method using N_2 at -196°C.

Although our adsorption data are not complete, the significance of solid Fe_2O_3 in the overall corrosion mechanism of an iron/aqueous solution system at atmospheric conditions may be anticipated. Irrespective of its origin, the presence of an oxide (either as contaminant or primary corrosion product on the metal surface) may be an important factor controlling the chemical reactivity of the system. For example, the reaction rate may be limited by the diffusion of both H_2O and Cl^- through the oxide film. When the innermost layers of oxide become hydrated, acid conditions may prevail as when α-Fe_2O_3 was added to H_2O or NaCl solution. The induced positively charged surface at the advancing hydration front would provide the driving force (i.e., adsorption of Cl^-) for diffusion of Cl^- toward the metal/oxide interface. The solid and/or liquid phase diffusion would depend on the porosity of the film. The underlying metal may eventually react with the hydrochloric acid produced as a result of dissociated hydroxyl groups of the hydrated oxide in the presence of Cl^- and the corrosion cycle repeated.

The postulated reaction mechanism advanced for the corrosion of the iron/aqueous sodium chloride system is tokenly supported by a recent study of Brown et al. (4) in which an aluminum and a steel alloy were both investigated under essentially our same conditions. Localized pH measurements varied between approximately 3.5 and 3.8 at the solid/liquid interfaces of the aluminum and steel alloys, respectively, and 6.5 in the bulk solution. The reported pH values near the solid/liquid interfaces could possibly be explained by the hydrolysis of Al_2O_3 and Fe_2O_3 (formed as corrosion products) in much the same manner as that postulated for α-Fe_2O_3 in the current study. Because Al_2O_3 is a slightly stronger acid than Fe_2O_3, a somewhat lower pH value in the case of the aluminum alloy would be expected. Similar investigations of various crystalline metal oxides in contact with aqueous NaCl solutions would constitute a valuable aid in predicting the compatibility of such corresponding metal component systems.

CONCLUSIONS

The current study showed that chloride ions are adsorbed by Fe (III) oxide most prevalently at approximately pH 4. The adsorption in acid solution indicated a positive surface potential on the oxide, formed by the initial reaction of water with the solid surface to form hydroxides which subsequently hydrolyze. The chloride adsorption qualitatively appeared to depend on the chloride ion concentration in solution—fivefold increase in adsorption for an approximately twofold increase in concentration. Under the experimental conditions described, only a small fraction of the total surface area determined by the BET method was found active for chloride adsorption. Two possible causes for the discrepancy are that water molecules surrounding the chloride ions would make the effective ionic radii much larger than the crystal radii, and, second, not all of the surface area determined by the BET method would be active toward chloride ion adsorption, which is limited to certain sites having a positive charge distribution.

When the pH of the environment surrounding the solid α-iron (III) oxide was increased, competition between hydroxyl ions and chloride ions for sites on the oxide was suggested by both an increase in chloride content of the solution and a slow decrease in pH of the solution in which the α-iron (III) oxide was suspended. Above pH 6, little, if any, chloride appeared to adsorb on the α-iron (III) oxide; however, the slight decrease in activity observed may be caused by a double-layer effect due to sodium ion adsorption in a region where the surface charge on the solid is assumed to be negative.

The experimental approach described in the current investigation should be generally amenable to any sparingly soluble oxide in contact with water or aqueous solutions. The results of such adsorption studies will be fundamentally important to the elucidation of the role that chloride ion, or any other ions, plays in reactions occurring in aqueous solution in contact with a solid phase.

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