0012255

DPST--86-275

DE89 001637

KEYWORDS: WASTE TANK, CORROSION, PITTING, HALIDES, CHLORIDE, pH, Eh, THERMODYNAMICS, INHIBITORS, PRECIPITATE, SLUDGE, IN-TANK PROCESSING

JAN 1991
RECEIVED
EDMC

TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

DPST-86-275

CC: J. K. Okeson, 773-A
W. R. Stevens III, 773-A
E. L. Albenesius, 773-A
M. D. Boersma, 704-T
L. F. Landon, 704-T
C. T. Randall, 704-T
J. M. Congdon, 773-A
R. F. Ondrejcin, 773-A
C. F. Jenkins, 723-A
A. F. Riechman, 723-A
R. A. Corbett, ETC Louvers
S. B. Oblath, 773-A
P. D. d'Entremont, 703-H
GTG (6)
GTG File, 773-A
SRL Records (4), 773-A

TO: M. A. EBRA AND M. J. PLODINEC

FROM: D. F. BICKFORD

FEBRUARY 14, 1986

THERMODYNAMIC MODEL OF WASTE TANK CORROSION WITH IMPLICATIONS TO PITTING DURING IN-TANK PROCESSING, WASHING AND STORAGE

INTRODUCTION

The electrochemical thermodynamics of iron dissolution can be applied to past studies of pitting and general corrosion of carbon steel waste tanks for the storage of radioactive waste. Such studies seek to reproduce in the laboratory the electrochemical conditions existing in waste tanks. The tests employed are either coupon tests in solutions intended to be typical of the environment, or potentiodynamic or potentiostatic tests which impress a voltage on the sample, and measure the resulting electric currents. All types of test samples are microscopically examined for crevice or pitting corrosion. This review discusses the electrochemical processes that occur during such testing. By stating the assumptions which are inherent in such testing, this review seeks to familiarize process engineers and chemists with the conditions favorable for pitting corrosion, and some of the means of controlling it.

Also included is a review of the conditions which exist during the washing and storage of cesium tetraphenylborate, and high aluminum waste. Implications of the model to the chemical control of pitting during these processes are summarized, along with potential alternative methods of controlling the pitting.

CONCLUSIONS AND RECOMMENDATIONS

1) Halides contribute to the pitting seen at or near the water line in coupon tests of washed precipitate. Unfortunately, a chloride specific removal process does not exist in the pH range appropriate for waste tanks. This does however, reemphasize the need for reliable measurements of halide contents in solution for each washed sludge and washed precipitate batch.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

It also indicates the catastrophic effect of concentration gradients resulting from localized evaporation, sludge leaching, etc. As an example, the coupon tests conducted by A. F. Riechman might be interpreted as having pitted as the result of concentration of halides to about 0.05 M, caused by evaporation in the wetted film at the air / water interface.

Addition of calcium may remove harmful fluoride ion from solution in the washed precipitate. Calcium addition is not necessary for washed sludge, since sludge is already saturated with respect to calcium.

2) The washed precipitate slurried in 0.01 M NaOH, and less than 0.01 M nitrite is weakly buffered against drifts in pH and Eh (oxidation/reduction potential). This makes the mixture sensitive to carbon dioxide absorbtion, and decomposition of potassium tetraphenyl borate. Washed sludge is somewhat less sensitive since it contains about 13 wt% hydroxides of transition metals, which tend to buffer both Eh and pH.

3) Initial coupon tests for washed precipitate were conducted at Eh values between -0.1 and +0.1 relative to the standard hydrogen electrode (SHE). The addition of minor redox species as corrosion inhibitors, or to reflect improved understanding of the waste compositions may change this. The effect of radiolytic decomposition of washed precipitate, and the strength of redox buffering by washed sludge are unknown. There is also uncertainty in the tendency for halides to leach out of washed sludge, and lead to increased halide concentrations. It is therefore necessary to directly measure the redox potential, and waste tank potential for existing washed precipitate and washed sludge. It is also desireable to map the pH and soluble chloride content as a function of height in the tank. This will increase the certainty that laboratory tests will be representable of actual conditions. The necessary probes have been ordered, and measurement in the washed precipitate tank is expected within the next month.

4) The addition of oil (e.g. n-parafins) to the waste tank may provide a means of preventing OH- depletion by CO2 absorbtion, and may also disrupt the formation of electrochemical cells at the air / water interface. The direct protective effect of oil on carbon steel may be an additional benefit. Unanswered questions for this approach include: The affect of H2 evolution on tank coil cracking, the stability of oil in radiation fields associated with washed precipitate, the interaction of an organic oil with the aromatic precipitate, and the change in fire safety in the storage tanks. Most of the concerns could be addressed in the next few months, but will need support for radiation and steel cracking studies.

5) Recent coupon tests give the impression that there is a large amount of evaporation, and recondensation in the tanks. Direct observation of the tanks over a range of climatic conditions is necessary to determine if this is true. If it is not true, then

recent coupon tests may have pitted as the result of inhibitor depletion at the water line, in an unrealistic corrosion mode.

6) One method of reducing the tendency of the washed precipitate to pit the waste tank is to remove MgO from the frit fed to the DWPF melter, and add the equivalent amount of Ba(OH)2, Ca(OH)2 and SrO to the washed precipitate. This could be controlled so that it results in no change in the alkali or alkaline earth content of DWPF glass, and therefore has negligible effect on glass quality. The thermodynamic model of glass leaching has been used to indicate what alkaline earth elements could be used, and what their overall effect would be on relative leachability. Calculations indicate that the molar fraction of alkaline earth elements added to the DWPF process could be increased by 50% without a significant change in the leachability. This corresponds to an average M(OH)2 addition rate of 35 M / hour, which is sufficient to maintain the pH above 12 in washed precipitate if the tank purge rate is maintained at the current 350 scfm. With partial carbon dioxide scrubbing of the tank purge gas, higher purge air flow rates could be used. Impact on glass quality, melt rates and melter redox will need to be assessed, but appears reasonable.

7) Phenol, sodium phenolate, boric acid and phenylboric acid are the organic decomposition products most likely to enhance pitting. Aside from the pH shift they cause, it is unlikely that they cause pitting in these solutions. They may increase the tendency to form oxygen occluded cells above the water line, by changing the surface tension of the water, or by physically blocking the diffusion of air to the cell.

8) Washed sludge is saturated with respect to Fe(OH)3 and hydroxides of other transition metals. Since the passivating layer on carbon steel has a similar composition, simulated washed sludge should (as a minimum) be allowed to equilibrate with AFF sludge, or similar substitute for these species. The addition of a small amount of Fe(II) to the simulated washed precipitate may help to establish a passivated layer.

9) Attack of the stainless steel transfer equipment from the waste tank to the DWPF is less likely to occur than pitting in the waste tanks. Should the organic become mixed with other wastes and transferred to the waste evaporators, then the possibility of evaporator tube pitting is increased.

DISCUSSION

In the last twenty years, the use of Pourbaix diagrams for the study of thermodynamic stability of alloys in solution, and the use of potentiodynamic scanning of alloys in solution have become standard methods of investigating aqueous general corrosion, and pitting corrosion [1-3]. The use of Pourbaix diagrams permits the display of the driving force for pitting for all the pH and redox conditions which can exist in solution. Pourbaix diagrams can also indicate the predominant species present in the solution,

and therefore aid in the prediction of conditions of immunity, passivation or general corrosion. Actual corrosion, and pitting in particular, is a dynamic process which can be accelerated or retarded by local conditions which are not characteristic of the average thermodynamic process. For example, the coating of carbon steel with organic materials such as paint or oil does not change overall thermodynamic conditions, but can reduce the rate of corrosion by interfering with the transfer of material.

Figure 1 indicates the region where water is thermodynamically stable. It is plotted against the variables of pH and Eh. Eh is the electrical potential of a sample relative to a standard hydrogen electrode. Eh and pH are related to the oxygen and hydrogen activities in solution, by the decomposition of water, such that $Eh = 1.23 + (0.059/4) \log pO_2 - 0.059\ pH$. Similarly, $Eh = -(0.059/2) \log p(H_2) - 0.059\ pH$. The lowest line in Figure 1 is for iron / magnetite equilibrium. This line is outside of the stability region for water, indicating that at any pH bare iron will tend to react with water to produce hydrogen and ferrous ion or magnetite. Under more oxidizing conditions, iron will corrode to produce hematite and ferric ions.

In the presence of other substances, the fields of phase predominance will shift, and new fields can be added. Figure 2 is the same as Figure 1, except the total dissolved carbonate species is 0.01 molar. Thus, if 0.02 molar sodium hydroxide in contact with iron is allowed to equilibrate with air, it will contain about 0.01 molar sodium carbonate, and if slightly reducing conditons exist, then the pH will drift down to about 10, and a non-protective [6] siderite phase will form on the iron, instead of a protective magnetite or hematite layer. At lower carbonate concentrations, the size of the siderite field is decreased. At higher alkali contents in contact with air, the carbonate concentration will be higher, and the siderite field will be larger.

In addition to pH buffers, there are Eh buffers which control the redox potential of the solutions. Figure 3 indicates the Eh of balanced reactions between several of the redox buffers found in waste. The nitrite and nitrate buffer lines are of particular concern, since nitrite appears to inhibit corrosion in washed precipitate, and nitrate is a major anion in sludge. The effects of the redox buffers can be illustrated by taking the example of Separations Department nitric acid solutions neutralized with sodium hydroxide and fed to the waste tanks. The fresh solution can be expected to have an Eh close to that of the NO_3^- / N_2 buffer line if no nitrite is added. These solutions are highly oxidizing and result in a sufficiently large Eh difference between the average potential of iron in the solution and pits and crevices, that hydrogen can evolve in the pits and result in embrittlement and cracking. The addition of nitrite to the solution lowers the oxidizing strength of the solution, shifting it closer to the NO_3^- / NO_2^- equilibrium line, which decreases the electrical potential for hydrogen evolution.

The net result of Eh and pH on the dissolution of iron or carbon steel is shown in Figure 4, where the Eh/pH diagram is divided into regions of immunity, corrosion and passivation. In the immunity region, there is no thermodynamic driving force for dissolution, and no corrosion occurs. In the corrosion region, there is sufficient driving force for corrosion, and corrosion proceeds. In the passivation region, there is sufficient driving force for corrosion, but the initial corrosion results in the formation of a protective hydrated oxide layer which restricts corrosion to negligible levels. Thus, even though the dissolution of iron is predicted at all pH and Eh conditions, it can be ignored for many conditions in water at pH 10 and higher.

The addition of chloride or other halides to the water can result in pitting. Pitting is rapid localized corrosion under conditions where the majority of the metal surface is behaving as if it were immune. Figure 5 shows how the addition of 0.01 molar chloride ion to the solution changes the shape of the passive region. In the region of perfect passivity, pitting neither initiates nor propagates. In the region of imperfect passivity pitting is not initiated, but existing pits can propagate. Figure 6 shows how the passive region is further reduced when the chloride concentration is increased to 0.1 molar. The circle with a dot in it at pH 3.5 and Eh -0.2 is the approximate condition in a pit or crevice corroded region. The low Eh is the result of the evolution of hydrogen during iron dissolution in the pit. The low pH occurs when chloride diffuses into the pit and stabilizes a relatively high hydrogen ion concentration. Chloride ion is attracted by the electrical field set up between the pit and metal in contact with the bulk solution. Once the pit is established, corrosion will continue as long as the electrical potential is maintained, and species are permitted to move through the opening. Thus, increasing the pH of the bulk solution makes it more difficult to pit, because it makes it more difficult for local corrosion to stabilize the necessary electric potential. Other species can inhibit pitting by raising the potential or pH in the pit, or interfering with the transfer of material through the pit. Polarization scans conducted by A. F. Riechman all indicated that the Eh in washed precipitate and washed sludge is between -0.1 and +0.1 volt. Pitting occured in the samples at pH 9.3, but not in the samples at pH 12. This is indicated by the X's and OK's on Figure 6. Since Riechman's starting solutions were less than 0.01 M chloride, this could be interpreted as indicating that the evaporation of water in the wetted film at the air / water interface resulted in a local chloride content to about 0.05 M, resulting in pitting near the water line.

The pitting proceeds as the result of an electrochemical cell. Figure 8 shows how the passive and immune regions are enlarged for iron in chloride free solutions by the addition of different oxidizing species to the solutions. The usefulness of such inhibitors is being investigated by J. W. Coogdon and R. F. Ondrejcin.

APPLICATION TO WASHED PRECIPITATE STORAGE

There continues to be a concern that the storage of washed potassium tetraphenyl borate precipitate may result in the pitting of carbon steel waste tanks at or near the interface of the air and liquid [17-19]. The first test solutions considered contained only about 0.01 M NaOH to buffer the pH, and about 0.02 molar nitrite to buffer the Eh. In such a case it is easy to see that the pH may be considerably lower, and the Eh may be drastically different in the wetted film existing on the iron above the surface of the washed precipitate. In the case of solution in equilibrium with the washed precipitate, a small and reasonable deviation, such as 0.3 volts, is likely to extend into the pitting region. Once this occurs, conditions inside the pits can rapidly approach the conditions for pitting in Figure 6. This tendency would be increased if the organic precipitate provides a film resistant to penetration by air.

Low inhibitor levels, in combination with halides in the washed sludge and precipitate make coupon tests and tank operations sensitive to the effects of evaporation and condensation. For instance, if water evaporates, condenses and runs down the tank wall or test coupon, it will leave water low in pH and inhibitors at the surface of the water. Halides may migrate to the area more rapidly than the inhibitors, and a concentration cell may be set up which is favorable for pitting. It is therfefore necessary to determine how much condensation may occur in the waste tanks, for a range of climatic conditions. Coupon tests should then simulate those conditions.

Tests on DWPF melter offgas solutions recycled to the waste farm indicate that 0.01 M OH- is not sufficient to prevent general corrosion or pitting of carbon steel waste tanks. However, an increase in OH- to 0.5 M results in the development of a protective layer which is resistant to abrasion and attack by concentrated acids [22]. Thus, pH control is probably the surest way of controlling pitting.

Table 1 represents one approach at determining which chemical species can be suspected of contributing to pitting in washed precipitate. It consists of general corrosion rates of carbon steel in various commercially pure solutions. For the most part the solutions are at a concentration of 10%, but data for 100% pure chemicals are shown where more dilute data was not available, or where there is limited solubility. There is a general trend for the organics to become more aggressive as they are more oxidized in the sequence: 1) hydrocarbon (e.g. toluene), 2) alcohol (e.g. ethanol), 3) aldehyde (e.g. formaldehyde), 4) acid (e.g. acetic, formic or benzoic acids). The acids cause direct dissolution of iron, but their salts with alkali or alkaline earth metals are generally not aggressive to carbon steel. Exceptions to this are oxalic acid salts, and sodium phenate (phenolate) resulting from the reaction between phenol and sodium hydroxide. Thus, it appears that the only organic

likely to directly contribute to corrosion is phenol.

Table 2 is similar to Table 1, but includes more inorganic species, and also addresses the question of attack of the stainless steel transfer lines and waste evaporators. Just as in Table 1, there is not much evidence that direct attack will occur. However, should any of the organics become trapped under salt deposits in the waste evaporators it is possible that the combination of high halogen concentration and a reducing agent at temperatures above the boiling point of water will result in pitting.

In the absence of chlorides or other halides, the passive region is large, and there is much reduced tendancy to pit. Ion exchange resins are available to reduce the the chloride level to the ppb range, but are not effective at the pH of neutralized waste [23].

With washed precipitate, the solution will not provide a strong reservoir of Eh or pH control. Localized variations in potential can be expected because of local composition differences (e.g. manganese sulfide inclusions or breaks in the mill scale) resulting in localized attack. Once the pH has dropped below about 10.3, the precipitation of $FeCO_3$ could stabilize the environment around a pit, tending to sustain or accelerate the corrosion. Another way of looking at this is that once the pH is permitted to drift into the bicarbonate field of stability, then it becomes relatively easy for local conditions to drop in pH to the bicarbonate/carbonic acid buffer (pH = 6.5), which makes it easier to maintain conditions in the pit favorable for pitting.

Just as in pH buffering, it is likely that a small number of species are providing Eh buffering. Dependent upon the exact ratio of nitrate to nitrite, the buffering probably shifts between the NO_3/N_2 line and the NO_2/NH_4^+ line.

Radiation can be expected to cause a shift in both pH and Eh. Radiolysis of air produces nitric acid and ozone, which will tend to oxidize and lower the pH of the solution. In typical waste tank solutions, the overall reaction is reducing rather than oxidizing, and conversion of nitrate to nitrite can occur at the rate of 4.7 X 10E-14 mole NO_2^- / liter-joule of waste heat [9]. In the case of irradiated washed precipitate this is probably a minimum value, since the irradiation products of the organic portion of the slurries should be more reducing than comparable irradiations of inorganic salt solutions. Thus, with a range of waste activity during the first few years equivalent to 0.06 and 0.29 watts/gallon [24], conversion is from 2 x 10E-9 to 9.5 x 10E-9 moles nitrite per month, which is negligable. Radiolysis of the organic could produce nascent hydrogen, which would be a reducing agent. In the irradiation of aromatic compounds this is much less of a concern than in the radiation of saturated organics, which more easily lose their hydrogen [26]. The rate of such production has not been estimated, but is not expected to be signifigant for aromatics in the bulk solution. The effect may become important where layers of organic phase contact the steel

tanks with a minimum of solution present. In these areas there will be a tendency for reduction under the film, leading to anodic conditions. The exact nature of the film created by the organic is unknown, but increase in the Ca or Mg content of the solution may cause it to curdle, much like soap in hard water, changing its tendancy to create an airtight film, and also changing the rate at which ions can diffuse through the precipitate.

Radiolysis of TPB has also been shown to cause a lowering of pH. This is because of the production of phenol, which is acidic in an alkaline environment, and phenylboric acid. As a gross approximation, this can be seen as the decomposition of a monovalant salt to yield three monovalant acids, and one divalant acid and one alkali ion. Thus, the net increase in unbalanced functional acid groups can be considered to be one mole of acid for each mole of phenol produced, and one net mole of unbalanced acid for each mole of phenyl boric acid produced. Under average conditions, the rates of evolution per liter of average slurry are 0.25 g/l/month phenol, and 0.17 g/l/month phenylboric acid [25]. This is equivalent to an average depletion of 0.0042 molar hydroxide per month from radiolysis.

The pH is also reduced because of consumption of hydroxide by reaction with carbon dioxide in the air [21]. About 75% of the carbon dioxide in the air used to purge the tanks is absorbed by fresh caustic in the tanks. This results in an average hydroxide depletion rate of 0.0064 molar hydroxide per month for a 100% full waste tank. For waste tanks that are less than full, the surface area for contact is unaffected, but the solution volume is reduced. Therefore, the rate of hydroxide reduction by carbon dioxide is inversely proportional to the tank level, and for a 10% full tank the rate is 0.064 molar per month. Consideration has been given to scrubbing of carbon dioxide from the incoming air to slow the loss of hydroxide [27]. A simpler, less expensive, and perhaps more effective method may be to float an oil layer on the top of the mixture, to provide a barrier to carbon dioxide transport.

Based upon the previous discussion, it is desireable to buffer both the pH and Eh of washed precipitate. Recent work by B. A. Hacker indicates that part of the alkali content in the frit an be removed, and additional sodium hydroxide added. This is sufficient to increase the pH buffering capacity by a factor of about 1.6. Clearly, this is in the right direction, but a factor of ten or more would be preferable. An additional possible source of hydroxide is a similar change in the location of the addition of the alkaline earths currently in the frit, possibly combined with an overall increase in their content in the glass. The DWPF Basic Data Report shows 1.93 lb/hr MgO in the fresh frit slurry to the SME and 0.95 lb/hr MgO in spent can decon slurry to the SME. If this were diverted to the 596 lb/hr water flow in the precipitate slurry to the precipitate reactor, then this would increase hydroxide molarity by 2 x 0.12 molar, or 0.24m OH-. Obviously, this would not be in solution, but with the addition

of equivalent Ca(OH)2 or MgO, the overall buffering capability would increase by this amount.

By adjusting the amount and species of alkaline earth elements used, it is probably possible to maximize the pH of the washed precipitate, without adversely affecting glass durability or processing. A thermodynamic model exists for predicting the rate of glass dissolution as a function of glass composition [29]. Recently, C. M. Jantzen and I used this model to estimate the amount of alkaline earth elements that could be added to the glass while keeping the glass quality similar to that for Frit 165 glasses. The model also permits the investigation of the tradeoffs between various alkaline earth elements. The optimum results have about 50% higher alkaline earth concentration than normal. This is reasonable, since Frit 131 contained twice the MgO content of Frit 165, together with more alkali. This would need to be neutralized with formic acid in the precipitate reactor, which would increase the formic acid going to the melter by 2 x 0.119 lb mole/hr formic acid, or 11 pounds per hour. This is 57% of the amount currently flowsheeted to the SRAT, and is sufficient to cause concern about redox problems in the melter. It is probably not necessary to go that high, however, to reach the desired effect. Table 3 indicates the pH of a stock solution based upon BDR washed precipitate composition (but without precipitate), combined with various concentrations of alkaline earths. These experimentally determined values indicate that pH as high as 12.5 is readily achieved using the alkaline earths, without affecting DWPF glass quality.

The thermodynamic leaching model uses the total free energy of hydration as a measure of the rate of dissolution. It is indicated as "DELTA G" in Tables 4-7. Important structural parameters are the amount of excess silica available to stabilize the protective gel layer on the glass, and the fraction of non-bridging oxygen atoms in the glass structure. The amount of excess silica is proportional to the "Excess Si" value in the tables. The fraction non-bridging oxygens is labeled "NBO". Table 4 summarizes these values for typical simulated waste glasses, as an indication of what values appear to be satisfactory. Tables 5-7 indicate compositions with modified alkaline earth contents that are similar to average sludge glass made with Frit 131, an early acid hydrolysis glass, and an acid hydrolysis glass developed by C. M. Jantzen to be similar to Frit 165, respectively. The modified Alkaline earth glasses were computed by removing the MgO from the frits, and subtituting 0.7 x Wt. of MgO as CaO, and 0.9 x Wt. of MgO as both SrO and BaO. The resulting glasses have negligable shifts in the parameters, when compared to the corresponding shifts caused by sludge variation.

APPLICATION TO WASHED PRECIPITATE STORAGE

Unlike the washed precipitate, washed sludge contains a vast supply of Eh and pH buffering species, in the form of precipitated hydroxides of alkaline earth and transition metals with absorbded anions. During storage the dilute inhibited water

will seek equilibrium with the sludge, and final solution concentrations will be controlled by the sludge. It is likely that since the sludge is saturated with $Fe(OH)_3$, that there will be so much iron present in the solution that mildly passivating conditions will assure a protective layer. Since additional nitrite is not expected to adversely affect sludge processing in the DWPF, additional nitrite could be added to this waste. Major shifts in the alkali content are not quite as restrictive as for washed precipitate, because of volumetric flow rate differences, but cannot be ignored.

APPLICATION TO IN-TANK PROCESSING

Testing to date has concentrated on the storage of dilute solutions. It must be remembered that the waste processing tanks will see a range of solution concentrations between those levels which will be stored and the concentrated solutions added to the tanks for washing. Thus, testing of washed sludge or precipitate is not adequate to assure the prevention of pitting in the processing tanks. Once the conditions for prevention of pitting in the storage tanks are assured, it is probable that the intermediate concentrations will also be found to be safe.

REFERENCES

[1] M. Pourbaix, Lectures on Electrochemical Corrosion, Plenum Press, New York (1973).

[2] M. Pourbaix, Atlas D'Equilibres Electrochemiques, Gauthier-Villars, Paris (1963).

[3] M. Pourbaix, "The Electrochemical Basis For Localized Corrosion, Localized Corrosion, NACE (1974).

[4] R. M. Garrels and C. L. Christ, Solutions, Minerals and Equilibria, Harper & Row, New York (1965).

[5] M. Whitfield and D. Jagner, Marine Electrochemistry, John Wiley & Sons, New York (1981).

[6] J. M. West, Electrodeposition and Corrosion Processes, D. Van Nostrand & Co., London (1965).

[7] Electrochemical Corrosion Testing, F. Mansfield and U. Bertocci, eds., ASTM 04-727000-27 (1981).

[8] Corrosion Data Survey, N. E. Hamner, compiler, NACE (1974).

[9] R. S. Ondrejcin,"Nitrite Ingrowth and Stress Corrosion Characterization of Tank 11H Supernate", DPST-75-507, November 25, 1975.

[10] A. F. Riechman,"Method for Caustic Addition During Tank 42 Demonstration", DPST-81-499, June 23, 1981.

[11] A. F. Riechman,"In-Tank Sludge Processing Chemical and Temperature Limits on Waste Tank Contents During Tank 42 Demonstration", DPST-81-552, July 21, 1981.

[12] A. F. Riechman,"In-Tank Sludge Processing Revised Chemical and Temperature Limits on Waste Tank Contents During Tank 42 Demonstration", DPST-82-510, May 6, 1982.

[13] A. F. Riechman,"Salt Decontamination Demonstration: Inhibitor Limits for Water Additions and Steel Corrosion by Salt Film", DPST-82-1007, November 15, 1982.

[14] A. F. Riechman,"Foaming During Salt Decontamination: Corrosion Considerations", DPST-82-816, September 23, 1982.

[15] A. F. Riechman,"In-Tank Processing: Program to Develop Technical Standards for Removal of Alumina from Sludge", DPST-83-443, April 14, 1983.

[16] A. F. Riechman,"In Tank Precipitation Corrosion Results", DPST-82-801, September 2, 1983

[17] A. F. Riechman,"CsTPB Precipitate Processing: Corrosion Test Results", DPST-83-925, October 17, 1983.

[18] A. F. Riechman,"Integrated Program for Salt Decontamination: Prevention of Water Line Corrosion", DPST-83-947, October 26, 1983.

[19] A. F. Riechman and R. E. Eibling,"In-Tank Processing: Program to Study Vapor Space Corrosion Above Solutions Containing Tetraphenylborate", DPST-84-890, December 12, 1984.

[20] A. F. Riechman,"In-Tank Processing: Inspection Results for Tanks 42H and 48H", DPST-85-471, May 7, 1985.

[21] D. T. Hobbs,"Hydroxide Depletion in Dilute Supernates Stored in Waste Tanks", DPST-85-861, October 10, 1985.

[22] D. F. Bickford and R. A. Corbett,"DWPF Corrosion Testing Database", DPST-85-956, December 30, 1985.

[23] J. P. Bibler, private communication.

[24] L. F. Landon, private communication

[25] D. D. Walker, private communication

[26] R. E. Eibling, private communication

[27] D. T. Hobbs, private communication

[28] A. F. Riechman, private communication.

[29] M. J. Plodinec, C. M. Jantzen, and G. G. Wicks, "Stability of Radioactive Waste Glasses Assessed from Hydration Thermodynamics," Mat. Res. Soc. Symp. Proc. Vol 26 (1984).

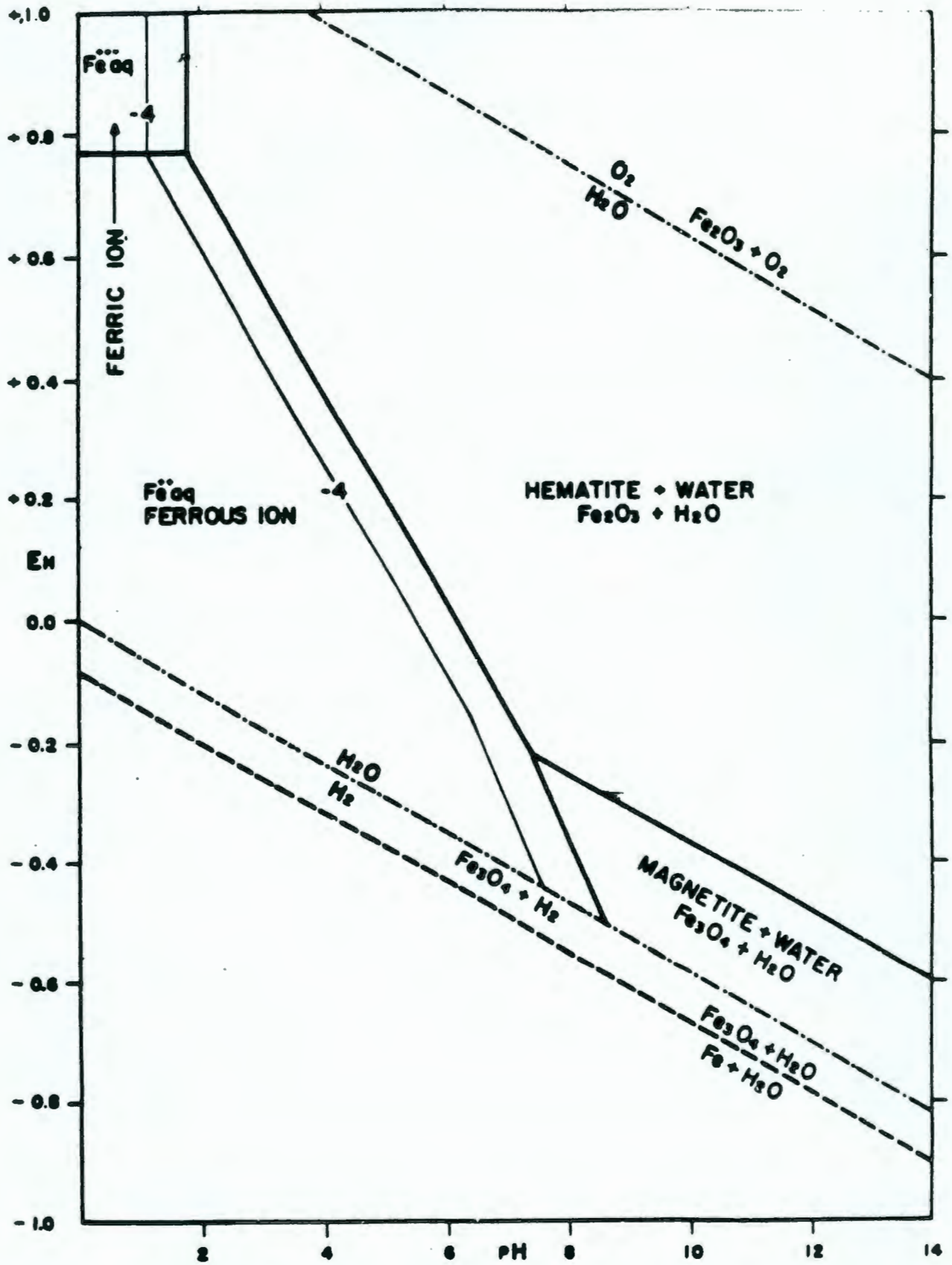

FIGURE 1: Composite diagram showing stability fields of hematite and magnetite in water. Fields of ions are designated where total activity of dissolved species are $> 10^{-6}$. Fields of ions are labeled with dominant species. Contour of log [dissolved species] = −4 is included to show slope of activity change. Plot at 25 °C and 1 atmosphere total pressure. [4]

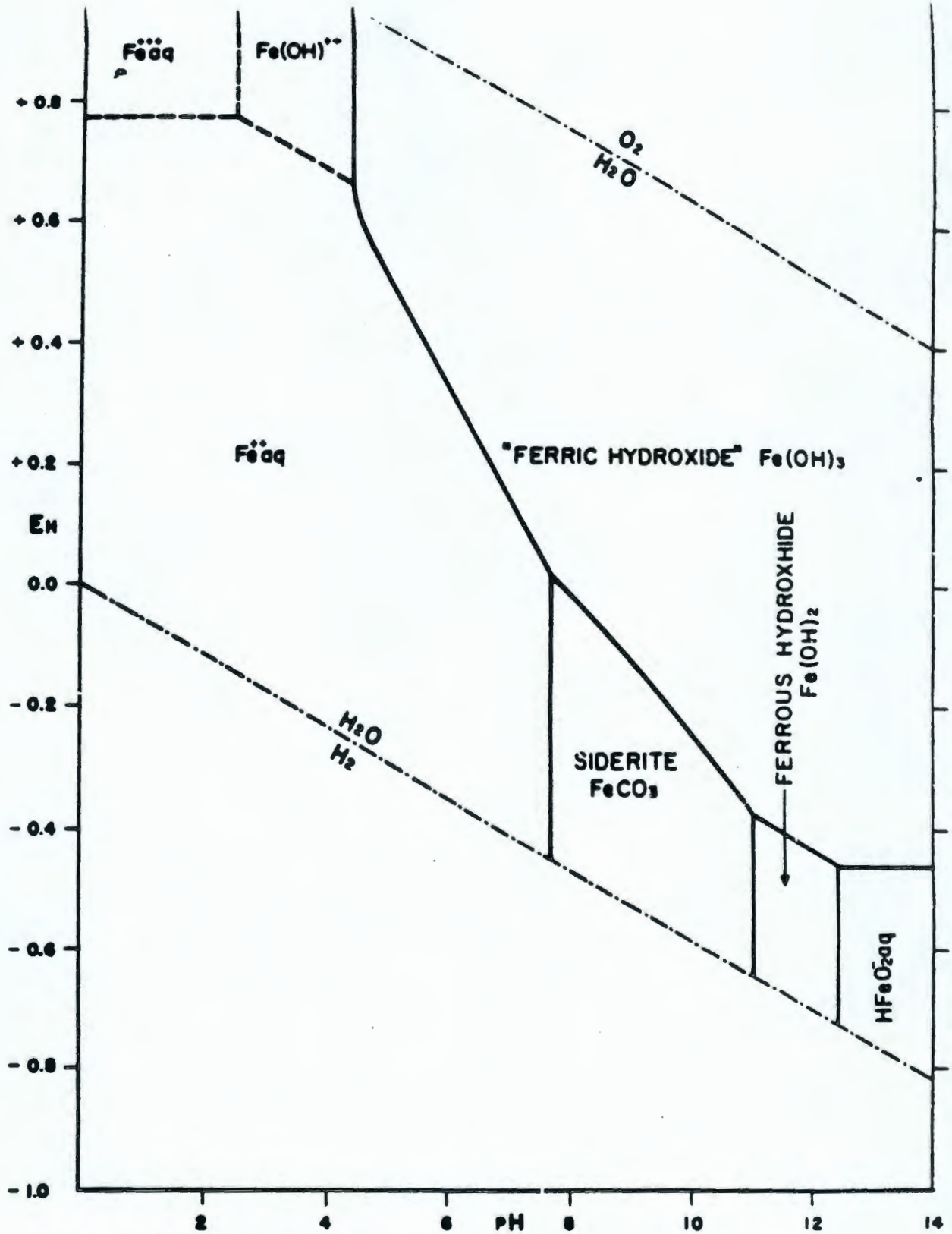

FIGURE 2: Diagram showing the relations among the metastable iron hydroxides and siderite at 25 °C and 1 atmosphere total pressure. Boundary between solids and ions at total activity of dissolved species = 10^{-6}. Total dissolved carbonate species = 10^{-2}. Dashed lines are boundaries between fields dominated by the labeled ion. [4]

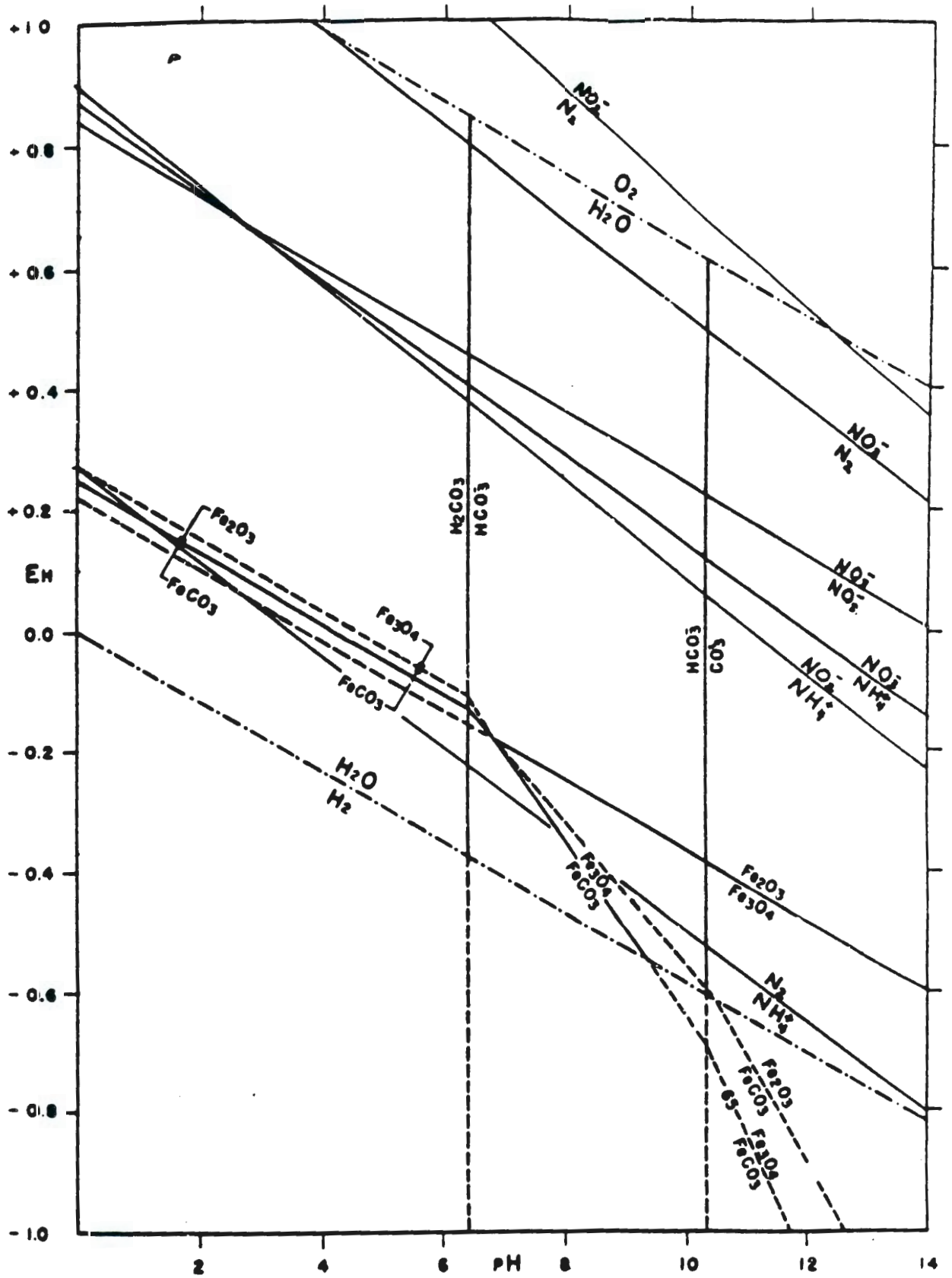

FIGURE 3: REDOX BUFFERS IN WASTE TANK SOLUTIONS [4,5]

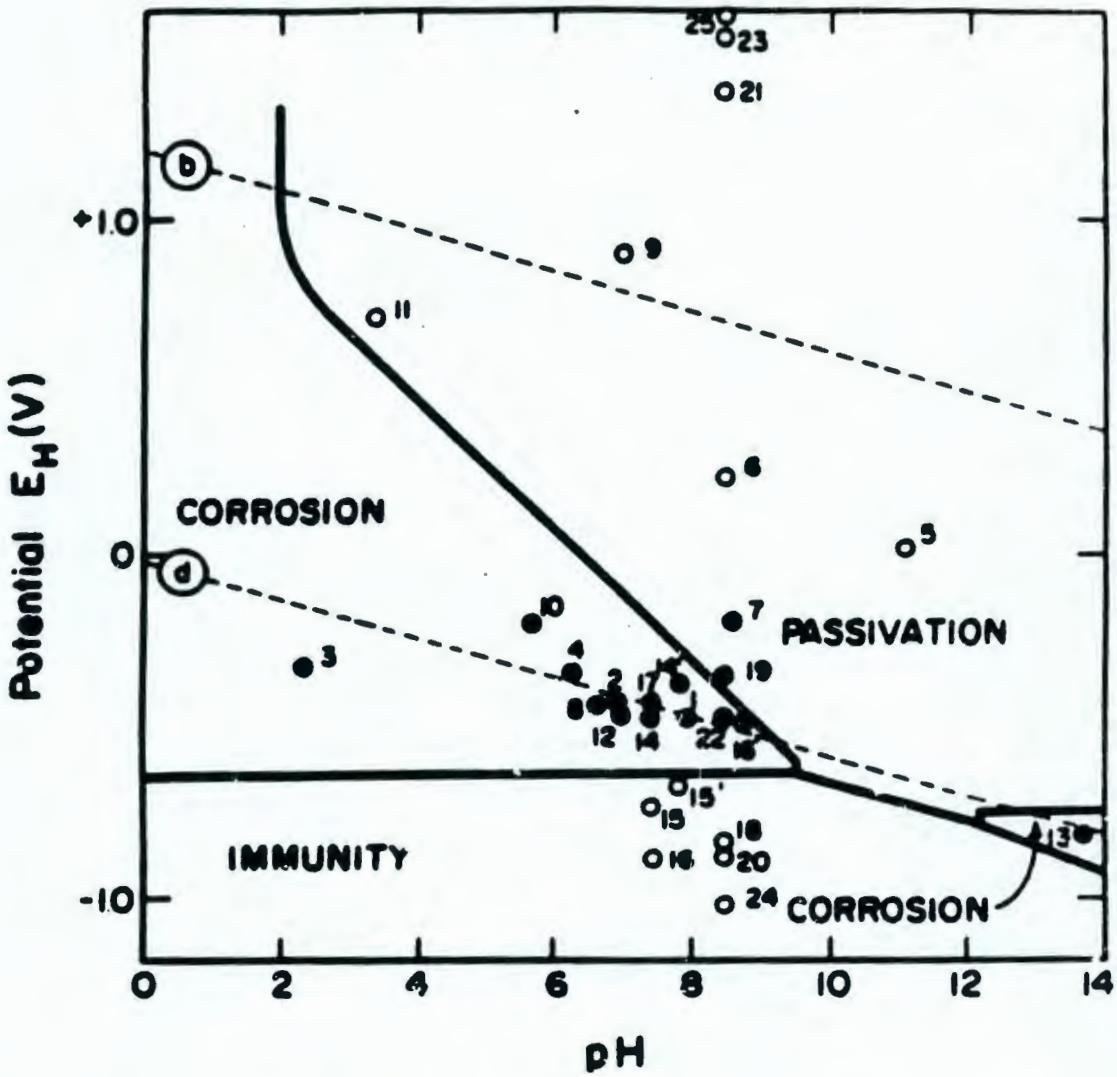

FIGURE 4: CORROSION, PASSIVIATION AND IMMUNITY REGIONS FOR IRON [1]

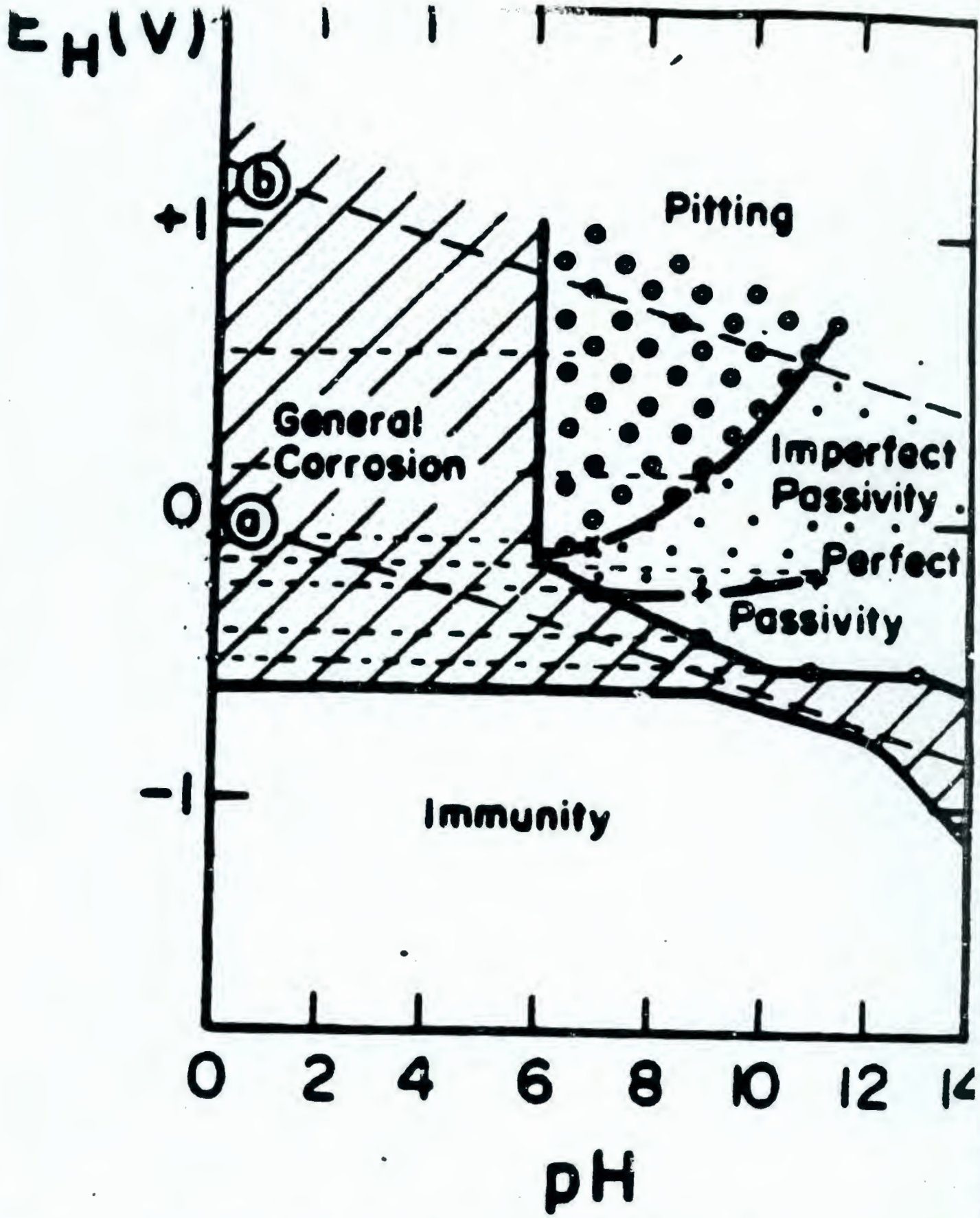

FIGURE 5: SIZE REDUCTION OF PASSIVE REGION FOR IRON WITH 0.01 M Cl-

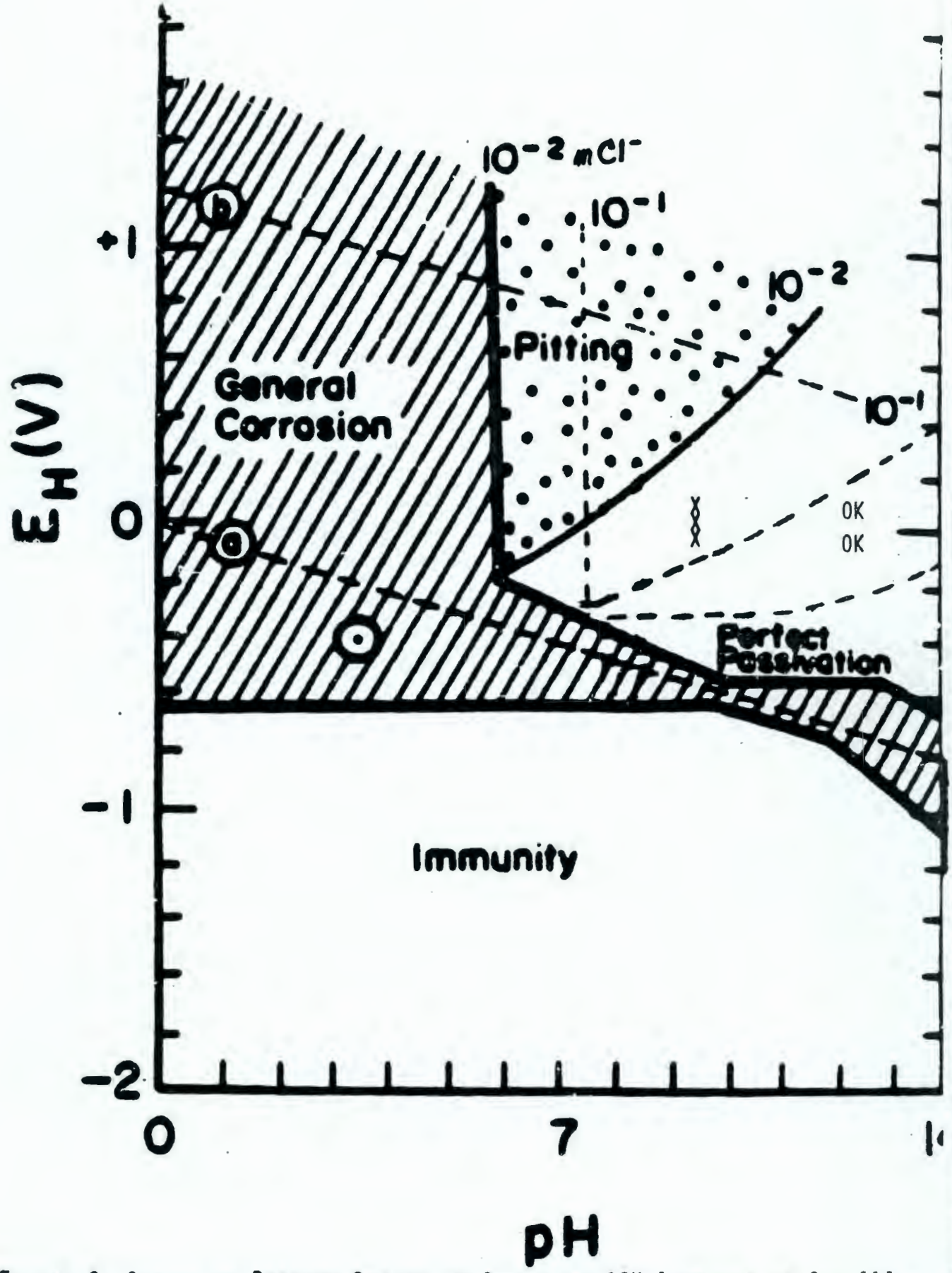

FIGURE 6: CHANGE OF PASSIVE REGION OF IRON WITH 10X INCREASE OF Cl^- [11]

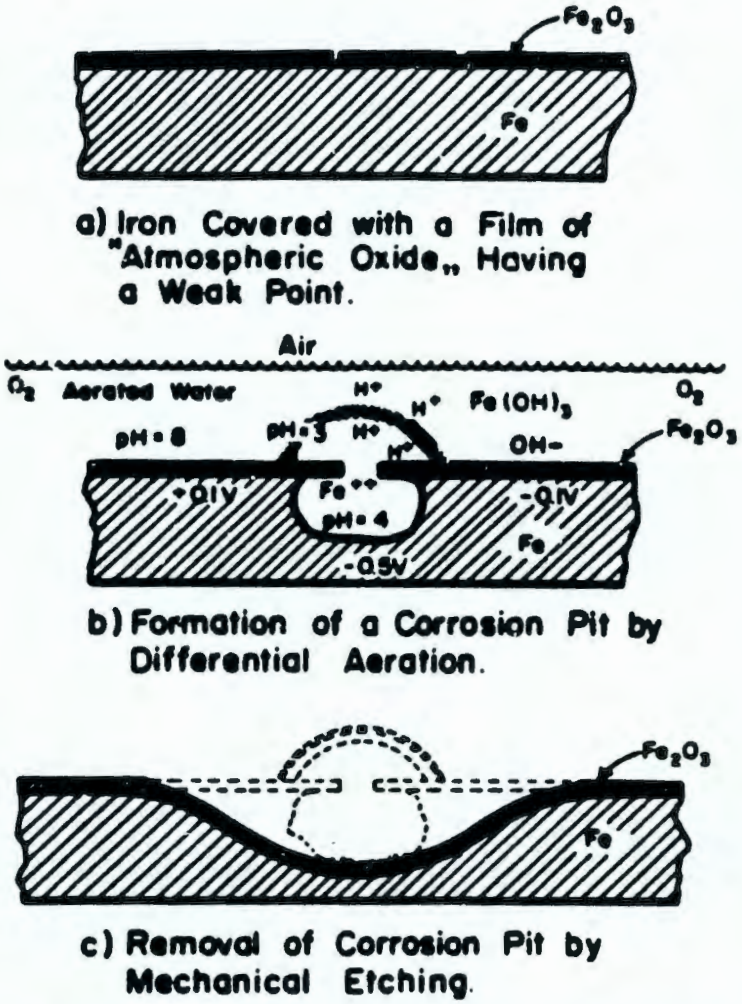

FIGURE 7: Corrosion pits formed on iron: (a) iron covered with a film of "atmospheric oxide" having a weak point; (b) formation of a corrosion pit by differential aeration; and (c) removal of corrosion pit by mechanical etching.

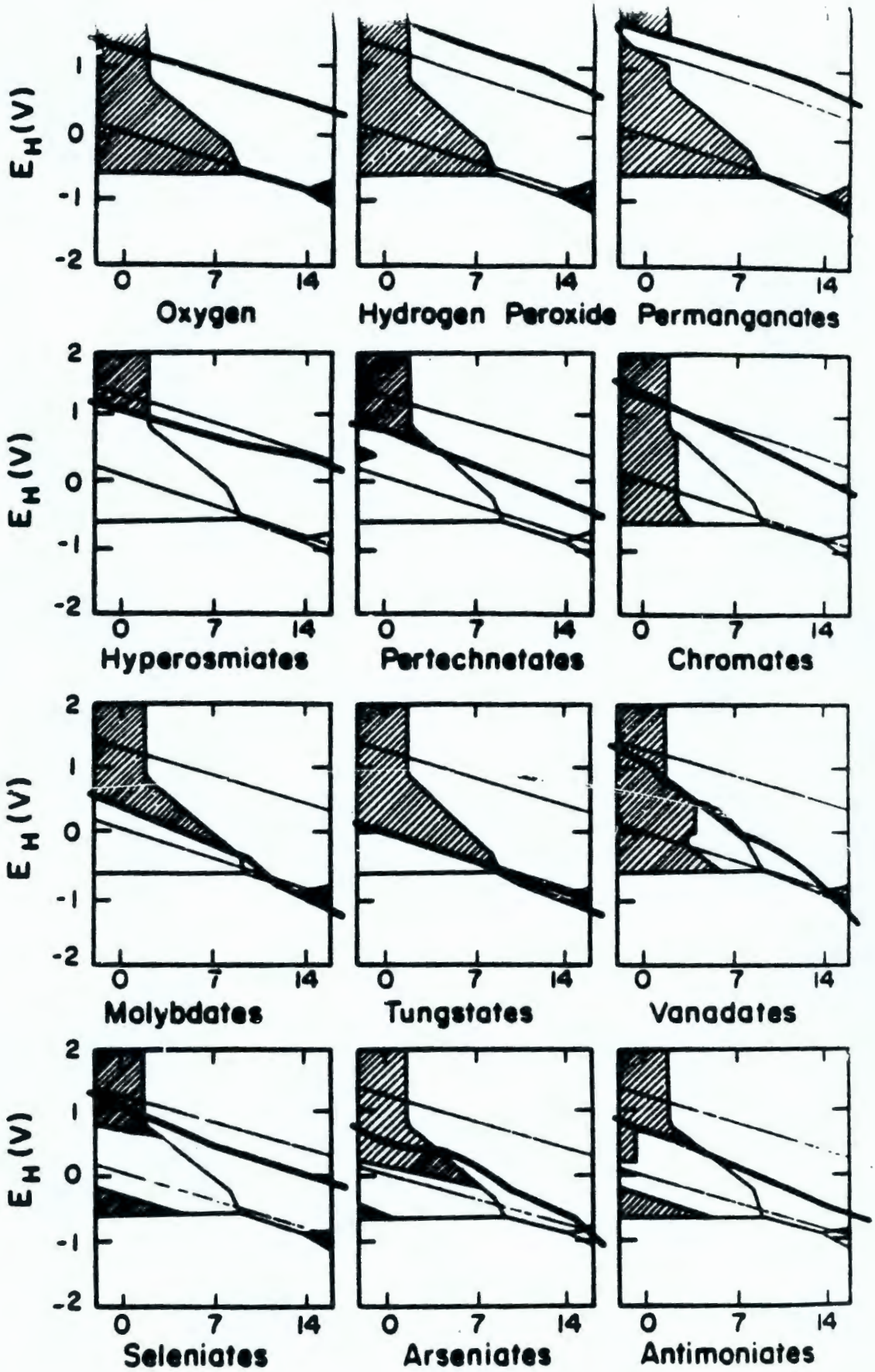

FIGURE 8: DECREASE OF CORROSION REGIONS WITH THE ADDITION OF OXIDIZERS [

TABLE 1
RELATIVE RATES OF ATTACK OF ORGANIC SPECIES ON CARBON STEEL*
(ALL REAGENTS AT 10% UNLESS NOTED OTHERWISE)
DFB 12/85

	CARBON STEEL 25°C	CARBON STEEL 75°C
(GREATER THAN 50 MILS PER YEAR)		
ACETIC A. (AERATED,10-100%)	CH3COO-H	$CH3COO-H$
ACETIC A. (NO AIR)	$CH3COO-H$	$CH3COO-H$
BENZALDEHYDE	C6H5-CHO	$C6H5-CHO$
BENZOIC ACID	Ph-COOH	$Ph-COOH$
CALCIUM OXALATE	Ca=OOCCOO	$Ca=OOCCOO$
CARBONIC ACID	HO-COOH	
FATTY ACIDS & Na SALTS	R-OOH	R-OOH
FORMALDEHYDE	H-CHO	H-CHO
FORMIC ACID	H-COOH	H-COOH
GLYCEROL (100%) + NaCl		(CH2OH)2CHOH
HYDRAZINE (20%)	H2N-NH2	$H2N-NH2$
NITROPHENOL	C6H4(NO2)OH	
OXALIC ACID	$H-OOCCOO-H$	$H-OOCCOO-H$
POTASSIUM OXALATE	K-OOCCOO-K	$K-OOCCOO-K$
SORBOSE	C6H6(OH)6	$C6H6(OH)6$
**********		
(20 TO 50 MILS PER YEAR)		
BENZAMIDE (100%)		$PhCONH2$
BENZYL ACETATE (95%)		H3CCOOCH2Ph
BENZYLPHENOL (100%)	PhCH2C6H4OH	GREATER THAN 20
OLEIC ACID (100%)	C17H33COO-H	C17H33COO-H
#SODIUM PHENATE	C6H5O-Na	C6H5O-Na
STEARIC ACID (100%)	CH3(CH2)16COO-H	CH3(CH2)16COO-H
**********		
(LESS THAN 20 MILS PER YEAR)		
#BENZENE	$C6H6$	$C6H6$
#BENZENE (100%)	C6H6	C6H6
BENZIDINE (100%)	NH2C6H4-C6H4NH2	NH2C6H4-C6H4NH2
BENZIL (100%)	PhCO-COPh	PhCO-COPh
BENZOIN (100%)	PhCO-CH(OH)Ph	PhCO-CH(OH)Ph
BENZONITRILE (100%)	C6H5-CN	C6H5-CN
BENZOYLBENZOIC ACID (100%)	PhCOC6H4COO-H	PhCOC6H4COO-H
BENZYL BENZOATE (100%)	Ph-COOCH2-Ph	Ph-COOCH2-Ph
CALCIUM ACETATE	CH3COO-Ca-OOCCH3	CH3COO-Ca-OOCCH3
#CALCIUM CARBONATE	COOO=Ca	COOO=Ca
CALCIUM STEARATE	(CH3(CH2)16COO)2=Ca	(CH3(CH2)16COO)2=Ca
#MAGNESIUM CARBONATE	COOO=Mg	$COOO=Mg$
METHANOL	CH3OH	CH3OH
PALMITIC ACID (100%)	C15H31COO-H	
#POTASSIUM CARBONATE	COOO=K2	COOO=K2
SODIUM BENZOATE	PhCOO-Na	PhCOO-Na
(SODIUM PHENYLFORMATE)		
SODIUM FORMATE	Na-COOH	Na-COOH
#XYLENE (100%)	C6H4Me2	C6H4Me2
#SODIUM BICARBONATE	HCOOO-Na	HCOOO-Na
**********		
(LESS THAN 2 MILS PER YEAR)	*	
BENZYL ACETATE (100%)	MeCOOCH2Ph *	
POTASSIUM ACETATE	CH3COO-K *	CH3COO-K
AMMONIUM HYDROXIDE	NH4-OH *	NH4-OH
ACRYLIC ACID (100%)	CH2=CH-COOH **********	
AMMONIUM NITRATE	NH4-NO3	NH4-NO3
BENZYL ALCHOHOL	PhCH2OH	
BENZYL AMINE (100%)	PhCH2NH2	LESS THAN 20
ETHANOL	C2H5-OH	C2H5-OH
HYDRAZINE (decomposes)	H2N-NH2	H2N-NH2
#NITROBENZENE (100%)	C6H5NO2	C6H5NO2
NITROPHENOL (100%)	C6H4(NO2)OH	C6H4(NO2)OH
#PHENOL (90%)	C6H5-OH	C6H5-OH
POTASSIUM FORMATE	Na-COOH	Na-COOH
SODIUM ACETATE (20%)	CH3COO-Na	CH3COO-Na
#SODIUM CARBONATE	COOO=Na2	COOO=Na2
#TOLUENE (100%)	C6H5CH3	C6H5CH3

$ $ INDICATES INFERRED VALUES. *DATA FROM NACE CORROSION DATA SURVEY
# SPECIES ANTICIPATED IN WASHED PRECIPITATE

TABLE 2

RELATIVE RATES OF ATTACK OF PRECIPITATE HYDROLYSIS SPECIES ON CARBON AND AUSTENITIC STAINLESS STEELS*

(ALL REAGENTS AT 100 UNLESS NOTED OTHERWISE)

DPB 1/86

	CARBON STEEL 25°C	CARBON STEEL 75°C	S. STEEL 25°C	S. STEEL 75°C	S. STEEL 100 OR 125°C
(LESS THAN 2 MILS PER YEAR)					
CALCIUM FLUORIDE			Ca-F2	Ca-F2	Ca-F2
BENZYL ALCOHOL	PhCH2OH		PhCH2OH	PhCH2OH	PhCH2OH
MAGNESIUM SULFATE	Mg-SO4	Mg-SO4	Mg-SO4	Mg-SO4	Mg-SO4
NITROPHENOL (100%)	C6H4(NO2)OH	C6H4(NO2)OH	C6H4(NO2)OH	C6H4(NO2)OH	C6H4(NO2)OH
OZONE	OOO		OOO		
POTASSIUM FORMATE	Na-COOH	Na-COOH	Na-COOH	Na-COOH	Na-COOH
SODIUM CARBONATE	COOO=Na2	COOO=Na2	COOO=Na2	COOO=Na2	COOO=Na2
SODIUM NITRATE	Na-NO3	Na-NO3	Na-NO3	Na-NO3	Na-NO3
SODIUM NITRITE	Na-NO2	Na-NO2	Na-NO2	Na-NO2	(Na-NO2)
(LESS THAN 20 MILS PER YEAR)					
BENZENE (100%)	C6H6	C6H6	*(C6H6)	C6H6	(C6H6)
PALMITIC ACID (100%)	C15H31COO-H		*C15H31COO-H	C15H31COO-H	C15H31COO-H
SODIUM SULFATE (20%)	Na2-SO4	Na2-SO4	*Na2-SO4	Na2-SO4	
(20 TO 50 MILS PER YEAR)					
BENZYL ACETATE (95%)		H3CCOOCH2Ph			
BORIC ACID	B(O-H)3	B(O-H)3	*B(O-H)3	B(O-H)3	B(O-H)3
CALCIUM SULFATE	Ca-SO4	Ca-SO4	*Ca-SO4	Ca-SO4	Ca-SO4
CALCIUM SULFITE	Ca-SO3	Ca-SO3	*Ca-SO3	Ca-SO3	Ca-SO3
SODIUM THIOSULFATE	C6H5O-Na	C6H5O-Na	*C6H5O-Na	C6H5O-Na	C6H5O-Na
SODIUM SULFITE	Na2-SO3	Na2-SO3	*Na2-SO3	Na2-SO3	Na2-SO3
STEARIC ACID (100%)	CH3(CH2)16COO-H	CH3(CH2)16COO-H	*CH3(CH2)16COO-H	CH3(CH2)16COO-H	CH3(CH2)16COO-H
(GREATER THAN 50 MILS PER YEAR)					
ACETIC ACID (AERATED)	CH3COO-H	(CH3COO-H)	*CH3COO-H	CH3COO-H	CH3COO-H
BORIC ACID (20%)	B(O-H)3	B(O-H)3	*B(O-H)3	B(O-H)3	B(O-H)3
CARBONIC ACID	HO-COOH		*HO-COOH	HO-COOH	HO-COOH
FATTY ACIDS & Na SALTS	R-COOH	R-COOH	*R-COOH	R-COOH	R-COOH
FORMALDEHYDE	H-CHO	H-CHO	*H-CHO	H-CHO	
HYDRAZINE (20%)	H2N-NH2	(H2N-NH2)	*H2N-NH2	H2N-NH2	H2N-NH2
NITRIC ACID	H-NO3	H-NO3	*H-NO3	H-NO3	H-NO3
SORBITOL	C6H6(OH)6	(C6H6(OH)6)	*C6H6(OH)6	C6H6(OH)6	C6H6(OH)6
ACETIC A. (AERATED,20-90%)	CH3COO-H	(CH3COO-H)	CH3COO-H	CH3COO-H	CH3COO-H
BENZALDEHYDE	C6H5-CHO	(C6H5-CHO)	C6H5-CHO	C6H5-CHO	C6H5-CHO
BENZOIC ACID	Ph-COOH	(Ph-COOH)	Ph-COOH	Ph-COOH	Ph-COOH
CALCIUM OXALATE	Ca=OOCCOO	(Ca=OOCCOO)	Ca=OOCCOO	Ca=OOCCOO	Ca=OOCCOO
GLYCEROL (100%) + NaCl		(CH2OH)2CHOH	(CH2OH)2CHOH	(CH2OH)2CHOH	(CH2OH)2CHOH
HYDROGEN PEROXIDE (20%)	H2O2	(H2O2)	H2O2	H2O2	H2O2
MAGNESIUM SULFITE	MgSO3	(MgSO3)	MgSO3	MgSO3	MgSO3
POTASSIUM OXALATE	K-OOCCOO-K	(K-OOCCOO-K)	K-OOCCOO-K	K-OOCCOO-K	K-OOCCOO-K
SODIUM CHLORIDE	NaCl	(NaCl)	NaCl	NaCl	NaCl
SULFUROUS ACID	H2-SO3	(H2-SO3)	H2-SO3	H2-SO3	(H2-SO3)
ACETIC A. (NO AIR)	(CH3COO-H)	(CH3COO-H)	CH3COO-H	CH3COO-H	CH3COO-H
ACETIC A. (AERATED,60-100%)	CH3COO-H	(CH3COO-H)	CH3COO-H	CH3COO-H	CH3COO-H
SULFURIC ACID (AERATED)	H2-SO4	(H2-SO4)	H2-SO4	H2-SO4	H2-SO4
FORMIC ACID	H-COOH	H-COOH	H-COOH	H-COOH	H-COOH
HYDROCHLORIC ACID	H-Cl	H-Cl	H-Cl	H-Cl	H-Cl
HYDROFLUORIC ACID	H-F	H-F	H-F	H-F	H-F
NITROPHENOL	C6H4(NO2)OH				
NITROUS ACID	(H-NO2)	(H-NO2)	H-NO2	H-NO2	(H-NO2)
OLEIC ACID (95%)			C17H33COO-H		
OZONE (WET,20%)	OOO				
SODIUM HYDROXIDE (50%)		Na-OH			
SULFURIC ACID (NO AIR)	H2-SO4	(H2-SO4)	H2-SO4	H2-SO4	H2-SO4
OXALIC ACID	(H-OOCCOO-H)	(H-OOCCOO-H)	H-OOCCOO-H	H-OOCCOO-H	H-OOCCOO-H
(20 TO 50 MILS PER YEAR)					
OLEIC ACID (100%)	C17H33COO-H	C17H33COO-H	C17H33COO-H	C17H33COO-H	C17H33COO-H
BENZAMIDE (100%)		(PhCONH2)	PhCONH2	PhCONH2	PhCONH2
BENZYLPHENOL (100%)	PhCH2C6H4OH	GREATER THAN 20*	PhCH2C6H4OH	PhCH2C6H4OH	PhCH2C6H4OH
(LESS THAN 20 MILS/YEAR)					
BENZENE	(C6H6)	(C6H6)	C6H6	C6H6	C6H6
BENZIDINE (100%)	NH2C6H4-C6H4NH2	NH2C6H4-C6H4NH2	NH2C6H4-C6H4NH2	NH2C6H4-C6H4NH2	NH2C6H4-C6H4NH2
BENZIL (100%)	PhCO-COPh	PhCO-COPh	PhCO-COPh	PhCO-COPh	PhCO-COPh
BENZOIN (100%)	PhCO-CH(OH)Ph	PhCO-CH(OH)Ph	PhCO-CH(OH)Ph	PhCO-CH(OH)Ph	PhCO-CH(OH)Ph
BENZONITRILE (100%)	C6H5-CN	C6H5-CN	C6H5-CN	C6H5-CN	C6H5-CN
BENZOYLBENZOIC ACID (100%)	PhCOC6H4COO-H	PhCOC6H4COO-H	PhCOC6H4COO-H	PhCOC6H4COO-H	PhCOC6H4COO-H
BENZYL BENZOATE (100%)	Ph-COOCH2-Ph	Ph-COOCH2-Ph	Ph-COOCH2-Ph	Ph-COOCH2-Ph	Ph-COOCH2-Ph
CALCIUM ACETATE	CH3COO-Ca-OOCCH3	CH3COO-Ca-OOCCH3	CH3COO-Ca-OOCCH3	CH3COO-Ca-OOCCH3	
CALCIUM CARBONATE	COOO=Ca	COOO=Ca			
CALCIUM HYDROXIDE	HO-Ca-OH	HO-Ca-OH	HO-Ca-OH	HO-Ca-OH	HO-Ca-OH
CALCIUM NITRATE	NO3-Ca-NO3		NO3-Ca-NO3	NO3-Ca-NO3	NO3-Ca-NO3
CALCIUM STEARATE	(CH3(CH2)16COO)2=Ca	(CH3(CH2)16COO)2=Ca	(CH3(CH2)16COO)2=Ca	(CH3(CH2)16COO)2=Ca	(CH3(CH2)16COO)2=Ca
CARBONIC ACID	HO-COOH				
HYDROGEN PEROXIDE	H2O2	H2O2	LESS THAN 2	H2O2	H2O2
MAGNESIUM CARBONATE	COOO=Mg	(COOO=Mg)	COOO=Mg	COOO=Mg	COOO=Mg
MAGNESIUM HYDROXIDE	HO-Mg-OH	HO-Mg-OH	HO-Mg-OH	HO-Mg-OH	HO-Mg-OH
MAGNESIUM NITRATE	NO3-Mg-NO3	NO3-Mg-NO3	NO3-Mg-NO3	NO3-Mg-NO3	NO3-Mg-NO3
METHANOL	CH3OH	CH3OH	CH3OH	CH3OH	CH3OH
POTASSIUM CARBONATE	COOO=K2	COOO=K2	COOO=K2	COOO=K2	COOO=K2
POTASSIUM HYDROXIDE	K-OH	K-OH	K-OH	K-OH	K-OH
POTASSIUM NITRATE	K-NO3	K-NO3	K-NO3	K-NO3	K-NO3
POTASSIUM NITRITE	K-NO2	K-NO2	K-NO2	K-NO2	K-NO2
SODIUM BENZOATE	PhCOO-Na	PhCOO-Na	PhCOO-Na	PhCOO-Na	PhCOO-Na
(SODIUM PHENYLFORMATE)					
SODIUM FORMATE	Na-COOH	Na-COOH	Na-COOH	Na-COOH	Na-COOH
(LESS THAN 2 MILS PER YEAR)					
BENZYL ACETATE (100%)	NaCOOCH2Ph		NaCOOCH2Ph	NaCOOCH2Ph	LESS THAN 2
POTASSIUM ACETATE	CH3COO-K	CH3COO-K	CH3COO-K	CH3COO-K	CH3COO-K
SODIUM HYDROXIDE	NaOH	NaOH	20 TO 50	GREATER THAN 50	
CALCIUM CHLORIDE	Ca-Cl2	Ca-Cl2	Ca-Cl2	Ca-Cl2	Ca-Cl2
ETHANOL	C2H5-OH	C2H5-OH	C2H5-OH	C2H5-OH	C2H5-OH
PHENOL (90%)	C6H5-OH	C6H5-OH	C6H5-OH	C6H5-OH	C6H5-OH
SODIUM ACETATE (20%)	CH3COO-Na	CH3COO-Na	CH3COO-Na	CH3COO-Na	CH3COO-Na
ACRYLIC ACID (100%)	CH2=CH-COOH		CH2=CH-COOH	CH2=CH-COOH	
BENZYL AMINE (100%)	PhCH2NH2	LESS THAN 20	PhCH2NH2	PhCH2NH2	PhCH2NH2

( ) INDICATES INFERRED VALUES. *DATA FROM NACE CORROSION DATA SURVEY

TABLE 3
pH WHEN STOCK SOLUTION SIMULATING WASHED PRECIPITATE IS COMBINED WITH VARIOUS ALKALI AND ALKALINE EARTHS

Reagant	Initial pH	2 Week pH*
0.6 M Na_2CO_3	11.26	10.50
0.6 M KOH	12.84	12.55
0.007m Na_2CO_3 + 0.0049 M $CaCO_3$	10.45	9.13
0.3 M Li_2CO_3	10.96	9.99
0.007 M Li_2CO_3 + 0.12 M $Ba(OH)_2$	12.07	12.01
0.3 M SrO	12.28	12.19
0.3 M $Ba(OH)_2$	12.51	12.26
0.3 M $CaCO_3$	10.28	9.17
0.3 M MgO	10.44	9.42
0.3 M Na_2CO_3	11.16	9.91
0.3 M $Ca(OH)_2$	11.96	11.82
0.04 M $NaNO_3$	12.00	9.54

* air bubbled through the mixtures for 2 weeks, with Pt/10% Rh catalyst present during the last 3 days.

TABLE 4
THERMODYNAMIC AND STRUCTURAL PARAMETERS FOR MODIFIED GLASSES

GLASS	DELTA G	FREE Si	NBO
131HiAl	-5.1		
131HiFe	-8.5		
165 Black Frit	-5.0		
165 Minimelter	-5.4		
165 TNX Melter	-5.3		
165HiAl	-3.7		
165HiFe	-6.6		
131TDS (AH131)	-6.6	0.92	0.60
131TDS MOD A.E.	-6.8	0.94	0.60
AH8 "Plodglass"	-5.8	1.200	0.40
AH8 MOD A.E.	-5.9	1.384	0.50
AH10	-4.8	1.48	0.47
AH10 MOD A.E.	-5.0	1.66	0.47

TABLE 5

				GLASS ID=	AH131	28DAY	DPSTN =	E37249 +		
				MODIFIED ALK. EARTH				E37250		
	ELEMENT	GRAV	OXIDE	NORM OXIDE	M.W.	MOLE	NORM OXIDE	COMPONENT	FREE ENERGY	NBO
	WT%	FACTOR	WT%	WT%		FRACTION	MOLE %	FREE ENERGY	HYDRATION	
Al2O3		1.8895	4.2800	4.2860	101.9600	0.0418	2.7543	3.0400	0.0837	-0.0551
CaO		1.3992	1.8721	1.8835	56.0794	0.0334	2.2008	-18.1180	-0.3547	0.0440
Fe2O3		1.4297	8.8900	8.9442	159.6922	0.0557	3.6898	15.5000	0.5888	-0.0734
FeO		1.2865	2.4000	2.4148	71.8464	0.0334	2.2021	-14.8090	-0.3217	0.0440
MgO		1.6583	0.0000	0.0000	40.3114	0.0000	0.0000	-13.8880	0.0000	0.0000
MnO		1.2912	2.6200	2.6360	70.9374	0.0369	2.4347	-14.8710	-0.3621	0.0487
Na2O		1.3480	13.5900	13.6728	61.9790	0.2193	14.4544	-28.8150	-4.1850	0.2891
Li2O		2.1525	4.1000	4.1250	29.8774	0.1372	9.0482	-22.7400	-2.0571	0.1809
NiO		1.2728	0.9800	0.9880	74.7094	0.0131	0.8647	-14.3470	-0.1241	0.0173
SiO2		2.1393	44.6600	44.9322	60.0848	0.7433	48.9981	5.5900	0.9449	0.0000
Cr2O3		1.4816	0.0000	0.0000	151.9974	0.0000	0.0000	37.3600	0.0000	0.0000
B2O3		3.2201	10.5800	10.6445	69.6204	0.1520	10.0178	-9.9300	-0.9948	0.0000
UO2		1.1344	0.0000	0.0000	270.0388	0.0000	0.0000	-6.8000	0.0000	0.0000
SrO		1.1828	1.3480	1.3542	103.6194	0.0130	0.8583	-24.4000	-0.2089	0.0171
ZrO2		1.3508	0.3800	0.3822	123.2188	0.0029	0.1928	45.1000	0.0869	0.0077
TiO2		1.6680	2.0200	2.0323	79.8988	0.0253	1.6668	15.9900	0.2665	0.0667
K2O		1.2048	0.0000	0.0000	94.2034	0.0000	0.0000	-41.7350	0.0000	0.0000
Cs2O		1.0802	0.0600	0.0604	281.8094	0.0002	0.0140	-48.8200	-0.0068	0.0003
Sb2O3		1.1970	0.0000	0.0000	291.4982	0.0000	0.0000	0.0000	0.0000	0.0000
P2O5		2.2910	0.0000	0.0000	141.9370	0.0000	0.0000	-53.6200	0.0000	0.0000
Nd2O3		1.1680	0.3800	0.3822	336.4782	0.0011	0.0705	-28.3200	-0.0200	0.0021
BaO		1.1165	1.2960	1.3039	153.3394	0.0085	0.5572	-30.5700	-0.1703	0.0111
PbO		1.0772	0.0000	0.0000	223.1900	0.0000	0.0000	-6.8100	0.0000	0.0000
SUMS			99.3941	100.0000		1.5170	100.0000		-6.8344	0.6008
ppm(Si)	42.10	48.30						SUM+pH Si	-7.0505	
NLI(Si)=	20.17	23.14	TEST=	MCC-1,DI				SUM+pH B	-7.8565	
ppm(B)	7.86	8.97	TIME=	28 DAY				pH =	9.64	
NLI(B) =	23.92	27.30	SA/V =	0.1CM-1						

TABLE 6

GLASS ID= AH8 28DAY DPSTN = E37249 +

PLODGLASS MODIFIED ALK.EARTH E37250

	ELEMENT WT%	GRAV FACTOR	OXIDE WT%	NORM OXIDE WT%	M.W.	MOLE FRACTION	NORM OXIDE MOLE %	COMPONENT FREE ENERGY	FREE ENERGY HYDRATION	NBO
Al2O3		1.8895	4.4400	4.4855	101.9600	0.0435	2.9209	3.0400	0.0868	-0.058
CaO		1.3992	1.7818	1.7797	56.0794	0.0314	2.1070	-16.1160	-0.3396	0.042
Fe2O3		1.4297	8.8900	8.9811	159.6922	0.0557	3.7341	15.5000	0.5788	-0.074
FeO		1.2865	2.4000	2.4248	71.8464	0.0334	2.2407	-14.6090	-0.3273	0.0448
MgO		1.6563	0.0000	0.0000	40.3114	0.0000	0.0000	-13.8880	0.0000	0.0000
MnO		1.2912	2.6200	2.6468	70.9374	0.0369	2.4774	-14.8710	-0.3684	0.0495
Na2O		1.3480	9.9500	10.0520	61.9790	0.1605	10.7684	-28.8150	-3.1029	0.2154
Li2O		2.1525	3.2000	3.2328	29.8774	0.1071	7.1842	-22.7400	-1.8337	0.1437
NiO		1.2728	0.9800	0.9900	74.7094	0.0131	0.8799	-14.3470	-0.1262	0.0178
SiO2		2.1393	47.7700	48.2595	60.0848	0.7950	53.3288	5.5900	1.3838	0.0000
Cr2O3		1.4818	0.0000	0.0000	151.9974	0.0000	0.0000	37.3600	0.0000	0.0000
B2O3		3.2201	10.0600	10.1631	69.6204	0.1445	9.6924	-9.9300	-0.9625	0.0000
UO2		1.1344	0.0000	0.0000	270.0388	0.0000	0.0000	-6.8000	0.0000	0.0000
SrO		1.1828	1.2020	1.2143	103.6194	0.0118	0.7781	-24.4000	-0.1899	0.0158
ZrO2		1.3508	0.0000	0.0000	123.2188	0.0000	0.0000	45.1000	0.0000	0.0000
TiO2		1.6680	1.3000	1.3133	79.8988	0.0163	1.0914	15.9900	0.1745	0.0437
K2O		1.2048	3.2000	3.2328	94.2034	0.0340	2.2785	-41.7350	-0.9509	0.0458
Cs2O		1.0602	0.0600	0.0608	281.8094	0.0002	0.0143	-46.8200	-0.0067	0.0003
Sb2O3		1.1970	0.0000	0.0000	291.4982	0.0000	0.0000	0.0000	0.0000	0.0000
P2O5		2.2910	0.0000	0.0000	141.9370	0.0000	0.0000	-53.6200	0.0000	0.0000
Nd2O3		1.1660	0.0000	0.0000	336.4782	0.0000	0.0000	-28.3200	0.0000	0.0000
BaO		1.1165	1.1520	1.1638	153.3394	0.0075	0.5039	-30.5700	-0.1541	0.0101
PbO		1.0772	0.0000	0.0000	223.1900	0.0000	0.0000	-8.8100	0.0000	0.0000
SUMS			98.9858	100.0000		1.4908	100.0000		-5.9363	0.4952
ppm(Si)	42.10	40.30						SUM+pH Si	-5.9752	
NL1(Si)=	18.85	18.05	TEST=	MCC-1,DI				SUM+pH B	-6.1948	
ppm(B)	6.35	6.17	TIME=	28 DAY				pH =	8.83	
NL1(B) =	20.33	19.75	SA/V =	0.1CM-1						

TABLE 7

				GLASS ID=	AH10 28DAY		DPSTN =	E37249 +		
		MODIFIED ALK. EARTH			ALK DEP			E37250		
	ELEMENT	GRAV	OXIDE	NORM OXIDE	M.W.	MOLE	NORM OXIDE	COMPONENT	FREE ENERGY	NBO
	WT%	FACTOR	WT%	WT%		FRACTION	MOLE %	FREE ENERGY	HYDRATION	
Al2O3		1.8895	4.4400	4.4867	101.9600	0.0435	2.8661	3.0400	0.0871	-0.0573
CaO		1.3992	1.7360	1.7542	56.0794	0.0310	2.0374	-18.1160	-0.3284	0.0407
Fe2O3		1.4297	8.8900	8.9834	159.8922	0.0557	3.6640	15.5000	0.5679	-0.0733
FeO		1.2865	2.4000	2.4252	71.8464	0.0334	2.1988	-14.6090	-0.3212	0.0440
MgO		1.6583	0.0000	0.0000	40.3114	0.0000	0.0000	-13.8880	0.0000	0.0000
MnO		1.2912	2.6200	2.6475	70.9374	0.0369	2.4309	-14.8710	-0.3815	0.0486
Na2O		1.3480	6.7500	6.8209	61.9790	0.1089	7.1679	-28.8150	-2.0654	0.1434
Li2O		2.1525	4.4800	4.5271	29.8774	0.1499	9.8689	-22.7400	-2.2442	0.1974
NiO		1.2728	0.9800	0.9903	74.7094	0.0131	0.8633	-14.3470	-0.1239	0.0173
SiO2		2.1393	52.2500	52.7991	60.0848	0.8898	57.2342	5.5900	1.6681	0.0000
Cr2O3		1.4818	0.0000	0.0000	151.9974	0.0000	0.0000	37.3600	0.0000	0.0000
B2O3		3.2201	7.5000	7.5786	69.6204	0.1077	7.0902	-9.9300	-0.7041	0.0000
UO2		1.1344	0.0000	0.0000	270.0388	0.0000	0.0000	-6.8000	0.0000	0.0000
SrO		1.1828	1.2020	1.2146	103.6194	0.0116	0.7635	-24.4000	-0.1863	0.0153
ZrO2		1.3508	0.0000	0.0000	123.2188	0.0000	0.0000	45.1000	0.0000	0.0000
TiO2		1.6680	1.3000	1.3137	79.8988	0.0163	1.0709	15.9900	0.1712	0.0428
K2O		1.2048	3.2000	3.2336	94.2034	0.0340	2.2357	-41.7350	-0.9331	0.0447
Cs2O		1.0602	0.0600	0.0608	281.8094	0.0002	0.0140	-46.8200	-0.0068	0.0003
Sb2O3		1.1970	0.0000	0.0000	291.4982	0.0000	0.0000	0.0000	0.0000	0.0000
P2O5		2.2910	0.0000	0.0000	141.9370	0.0000	0.0000	-53.6200	0.0000	0.0000
Nd2O3		1.1660	0.0000	0.0000	336.4782	0.0000	0.0000	-28.3200	0.0000	0.0000
BaO		1.1165	1.1520	1.1641	153.3394	0.0075	0.4945	-30.5700	-0.1512	0.0099
PbO		1.0772	0.0000	0.0000	223.1900	0.0000	0.0000	-8.8100	0.0000	0.0000
SUMS			98.9800	100.0000		1.5194	100.0000		-4.9333	0.4737
ppm(Si)	38.00	38.40						SUM+pH Si	-4.9731	
NL1(Si)=	15.56	14.90	TEST=	MCC-1,DI				SUM+pH B	-5.1968	
ppm(B)	4.02	3.88	TIME=	28 DAY				pH =	8.84	
NL1(B) =	17.28	16.57	SA/V =	0.1CM-1						

TABLE 8

ALKALINE EARTH HYDROXIDE REQUIREMENTS [27]
(TO MAINTAIN pH $\geq$ 12)

CASE	@1.67 yr. (mole/hr.)	@8 yr.
1000 scfm/400 ppm CO2	35.5	50.6
1000 scfm/100 ppm CO2	20.3	34.6
500 scfm/400 ppm CO2	25.5	40.6
500 scfm/100 ppm CO2	17.3	30.0
No CO2/Radiolysis Only	15.2	30.0

ELEMENT	FRIT	MELTER FEED (mole/hr.)	GLASS
Mg	21.7	39.6	34.8
Ca	0	17.1	17.0
Sr	0	0.62	0.61
Ba	0	8.7E-4	8.7E-4