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**EFFECTS OF HYDROGEN ON CARBON STEELS AT THE
MULTI-FUNCTION WASTE TANK FACILITY**

ABSTRACT

Concern has been expressed that hydrogen produced by corrosion, radiolysis, and decomposition of the waste could cause "embrittlement" of the carbon steel waste tanks at Hanford. The concern centers on the supposition that the hydrogen evolved in many of the existing tanks might penetrate the steel wall of the tank and cause embrittlement that might lead to catastrophic failure.

This document reviews literature on the effects of hydrogen on the carbon steel proposed for use in the Multi-Function Waste Tank Facility for the time periods before and during construction as well as for the operational life of the tanks. The document draw several conclusions about these effects.

Molecular hydrogen is not a concern because it is not capable of entering the steel tank wall. Nascent hydrogen produced by corrosion reactions will not embrittle the steel because the mild steel used in tank construction is not hard enough to be susceptible to hydrogen stress cracking and the corrosion product hydrogen is not produced at a rate sufficient to cause either loss in tensile ductility or blistering.

If the steel intended for use in the tanks is produced to current technology, fabricated in accordance with good construction practice, post-weld heat treated, and operated within the operating limits defined, hydrogen will not adversely affect the carbon steel tanks during their 50-year design life.

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EFFECTS OF HYDROGEN ON CARBON STEELS AT THE
MULTI-FUNCTION WASTE TANK FACILITY

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EFFECTS OF HYDROGEN ON CARBON STEELS AT THE MULTI-FUNCTION WASTE TANK FACILITY

1.0 INTRODUCTION

1.1 OBJECTIVE

The objective of this study is to determine whether the hydrogen evolved during the 50-year design life of the Multi-Function Waste Tank Facility (MWTF) will be detrimental to the carbon steel plate used in the tank construction.

1.2 BACKGROUND

Most of the waste in tanks at the Hanford Site is believed to evolve hydrogen gas (Garfield 1975) that is released continuously from the waste (see Figure 1). This phenomenon has led to a concern that the hydrogen generated may enter the steel wall of the tank and cause damage that might impair tank function or promote catastrophic failure. The potential sources for the hydrogen are corrosion and radiolytic decomposition of the aqueous waste.

2.0 SUMMARY

Most of the existing waste tanks are believed to evolve hydrogen gas. The interaction of the hydrogen with carbon steel can take many different forms; its exact role in these various modes is not well understood. Nevertheless, a general understanding of the potential effects of hydrogen on the waste tanks requires awareness of these effects even though most do not apply to the MWTF.

If carbon steel, either ASME SA 516 or SA 537, is made to the current technology, fabricated in accordance with good construction practice, post-weld heat treated, and operated within defined operating limits, hydrogen will not affect the carbon steel tanks adversely during their 50-year design life. The reader is referred to the list of references and a recent summary report published by Westinghouse Hanford Company for an in-depth review (see Anantatmula et al. 1994).

3.0 LITERATURE REVIEW

Craig (1987) has defined several modes of hydrogen damage; these are summarized here.

Hydrogen Environment Effects

These effects are important during plastic deformation of ferritic steel in the presence of hydrogen, e.g., from corrosion. They include the

loss in tensile ductility, typically at hydrogen levels in the steel of 0.1 to 10 p/m, and the degradation in flow properties in the presence of low-pressure hydrogen under long-term creep conditions. These effects are most severe at temperatures around 70 °F (20 °C).

Hydrogen Stress Cracking

This effect manifests itself in the form of brittle fracture of a normally ductile steel in the presence of hydrogen. Hydrogen sources include corrosion. It is most severe at temperatures around 70 °F (20 °C), typically when hydrogen content ranges from 0.1 to 10 p/m.

Blistering

This effect is prevalent in low-strength steel that contains laminations or non-metallic inclusions that can be expanded by trapped hydrogen.

Hydrogen Attack

This effect is a high-temperature, internal attack that occurs when steel is exposed to hydrogen for long periods. It is typical at temperatures above approximately 400 °F (200 °C).

Shatter Cracks, Flakes, and Fish Eyes

These are features of forgings, weldments, and castings. They can be caused by water on surface during welding or in electrodes.

Micro-perforation

These effects occur in steel at hydrogen pressures of 30,000 lbf/in² (200 MPa) or higher.

Hydride Formation

This effect occurs only in the presence of certain metals, such as vanadium, niobium, zirconium, titanium, tantalum, and uranium.

Warren (1987) groups the first two effects on this list (hydrogen environment effects and hydrogen stress cracking) under the heading "effect of hydrogen on mechanical behavior of steel" because both are a function of the carbon content and the heat treatment. Raymond (1987) notes that these latter effects, involving the absorption of small amounts of hydrogen that do not react with the metal, are reversible if microcracks have not formed.

Blistering, the third effect defined on the list above, occurs when a lamination or inclusion in the steel traps hydrogen that is diffusing through the steel. The hydrogen enters the void but cannot readily escape. As a consequence, the void expands, causing a bulge or blister that appears on the surface of the steel. Bieffer (1982) also describes a form of blistering called stepwise cracking that can occur in low-strength, low-hardness steel in the presence of numerous small inclusions. This phenomenon requires the presence of inclusions in which hydrogen can collect and form small blisters. If the blisters are sufficiently numerous and close together, then as they

expand, the ligaments between blisters fail and form larger defects that in the long term result in failure that resembles cracking.

Hamburg and Wilson (1989) relate hydrogen-induced cracking to both blistering and embrittlement through the presence of inclusions, particularly Type II inclusions formed by manganese sulfides (MnS) or aluminum oxides (Al_2O_3) based stringers. This type of inclusion is elongated and provides stress risers at its edges. Type I inclusions are more spherical and consequently more resistant to cracking. Type II inclusions containing silicates also tend to be more resistant to cracking.

Cotterill (1961) stated the following regarding hydrogen effects on ductility.

- Hydrogen has no significant effect on elastic properties.
- Both of the ductility parameters (elongation and reduction of area) are reduced in proportion to the hydrogen content up to approximately 4.5 p/m (5 cc[STP]/100 g). Above this concentration the ductility has constant, low value.
- The presence of hydrogen in steel does not affect the metal in the unstrained state. The removal of hydrogen from undamaged solid steel before straining ensures full ductility.

Because of the larger size of molecular hydrogen compared to atomic hydrogen, only atomic hydrogen can enter the steel. Generally the most straight-forward method for injecting hydrogen into the steel, and the one mentioned most often in the literature, is corrosion. The next most common method is the use of "high" temperature--above approximately 260 °C (500 °F) or high pressure. The pressure effect is somewhat controversial. There are the effects noted above, such as the degradation in flow properties and loss of tensile ductility indicative of low-pressure hydrogen effects. In contrast is the everyday experience of storing hydrogen at 1,800 lbf/in² (12.4 MPa) in carbon steel cylinders that suggests there is no significant short-term effect up to that pressure at normal ambient conditions.

On the basis of the emphasis put on hydrogen stress cracking and blistering by the previous noted authors, as well as the fact that the other hydrogen effects require temperatures and pressures greatly in excess of MWTF design conditions, only hydrogen stress cracking and blistering will be discussed further. In addition, because practical experience shows that molecular hydrogen H_2 at pressures considerably higher than atmospheric pressure is needed to have an effect at MWTF design temperatures 250 °F (120 °C), only mechanisms that might produce nascent hydrogen (H) will be considered. These mechanisms include corrosion and radiolysis.

3.1 HYDROGEN STRESS CRACKING

Warren (1987) has observed that carbon steel tends to be susceptible to hydrogen stress cracking if it has tensile strength greater than 120 kip/in² (830 MPa) or a hardness greater than Rc 22-23 (Rockwell C 22-23).

Kobrin (1987) also states that hydrogen stress cracking is found only in alloys with a hardness of Rc 22 or greater and implies that it occurs only in acidic media. In addition, he provides data to show that at an ultimate tensile strength less than approximately 130 kip/in² (900 MPa), the quantity of hydrogen present has little effect on ductility. Further, he points out the effectiveness of various impurities in enhancing hydrogen stress cracking, showing them in order of decreasing effectiveness in acid. Arsenic has the greatest effect followed by selenium, tellurium, sulfur, and bismuth. Of all of these impurities, only bismuth is present to any concentration in some of the waste tanks because of the old bismuth phosphate reprocessing method. But, as noted above, these impurities are important only under acid conditions. Kobrin also notes the following.

- Quench-and-tempered treatment results in more resistance to embrittlement than does a normalized-and-tempered treatment.
- The presence of small amounts of oxygen, particularly in the gas phase, can inhibit the entry of hydrogen and subsequent embrittlement.
- Cold-work significantly increases the solubility of hydrogen. In the case of the MWTF, the tanks will be post-weld heat treated after construction, which will reduce the effect.

Anantatmula et al. (1994) have noted that cyanide can assist in promoting hydrogen damage in reducing alkaline environments in the presence of sulfide. Though cyanide is present in Hanford tanks, it is strongly bound as the ferricyanide complex and there is no reported sulfide. In any case, the presence of nitrate and nitrite are expected to inhibit its adverse effects.

Beavers et al. (1987) report that steels with yield strengths below 70 kip/in² (480 MPa) are immune to hydrogen-induced brittle failure or hydrogen stress-corrosion cracking even under the most severe conditions. These authors also note that when there is an influence, hydrogen effects are greater on fracture toughness than on tensile properties.

Hamburg and Wilson (1989) have noted that even in low-strength steel such as A516, Grade 70, hydrogen-induced cracking can originate in the heat-affected zone of welds. Specifically, weldments of steels with greater than 0.22% carbon are sufficiently hard to be susceptible to cracking unless heat treated. Carter and Hyatt (1977) have noted that steel with a carbon equivalent of less than about 0.4% still can be welded without special precautions such as preheating and low-hydrogen electrodes because martensite does not form.

3.2 BLISTERING

Warren (1987) notes that blistering is more prevalent in steel stressed below its yield strength than is embrittlement and that blistering usually is confined to steels of "70-80 ksi tensile strength and Rc 22 or less in hardness." Schuyler (1979) notes, however, that "any low strength carbon steel containing sufficient internal defects" can blister. This contention is repeated by Hamburg and Wilson (1989), who in their study of A516 showed that, in severe conditions (acidic sulfide), stepwise cracking can be a problem even

in low-strength steel. Carter and Hyatt (1977) have pointed out that increases in manganese decrease the resistance to stepwise cracking because of the increased possibility of MnS formation.

Examples of blistering in the field include cases noted by Warren (1987) in which an acidic H₂S medium, with a corrosion rate of about 20 mil/yr (51 μm/y) resulted in blistering in less than approximately 2 years. Both Warren and Schuyler (1979) have reported blistering in 10 to 13 years in hydrofluoric acid systems in the presence of arsenic and sulfide and with a corrosion rate as low as 1 to 2 mil/yr (25 to 50 μm/y). Warren, however, notes that in a sulfuric acid system free of sulfide, limited blistering occurred only after 10 to 15 years even though the corrosion rate was about 30 mil/yr (760 μm/y).

Several conditions can affect susceptibility to blistering. Kobrin (1987) and Schuyler (1979) report that blistering occurs largely in un-hardened carbon steel, with fully killed steels more susceptible than semi-killed steel; Schuyler clarifies this point by noting that the term fully killed should actually be "fine grain practice" steel, i.e., steel that is manufactured to produce small grain sizes. In cases in which steel is being used in operating conditions where blistering is extremely likely, such as in hydrofluoric acid service or in oil and gas pipelines where sulfide is present, calcium may be added to the melt to control the shape of the inclusions, or the steel can be argon blown to purge hydrogen. After construction, the use of PWHT also reduces the potential for blistering by allowing hydrogen picked up during welding to escape.

In addition to the more obvious macroscopic form of blistering, the phenomenon also can occur on a smaller scale. Stepwise cracking, described earlier, is a specialized form of blistering that, according to Biefer (1982), does not occur unless the hydrogen content is > 0.8 p/m and only if the H₂S concentration is greater than 100 p/m. He further notes that in tests with steels susceptible to stepwise cracking, i.e., steels containing numerous Type II inclusions, no such cracking was observed at a pH of 6. On the other hand, both those steels susceptible to stepwise cracking as well as steels normally resistant to it were capable of being cracked if the pH were dropped sufficiently low, e.g., to a level of approximately 3. This fact implies a very strong dependence on pH for hydrogen entry into the steel, with immunity to stepwise cracking at pH values greater than 6 even for steels normally susceptible to this kind of cracking. Indeed, Kobrin (1987) corroborates these and earlier statements with the observation that both blistering and stepwise cracking are limited to acid systems in which a poison, such as sulfur, is present.

Complementary tests performed at the Savannah River Site (see Donovan 1974 and Springer 1979) using artificial laminations (pillows made by welding two plates together), showed neither swelling nor significant corrosion after 13 years in Tank 15 or 18 years in Tank 16, both of which contained alkaline nitrate/nitrite solutions similar to those at Hanford.

4.0 DISCUSSION

4.1 EFFECTS OF OPERATING LIMITS AND CONDITIONS

In the previous sections, characteristics of the various hydrogen effects, including those on operating limits, have been listed. The following discussion describes the effects of these limits, the operating conditions expected for the MWTF, and sources of hydrogen.

According to Cotterill (1961), the solubility of hydrogen at 1 atm (0.1 MPa) in steel is small at the tank-operating temperatures expected. On the basis of Cotterill's data, expectations are that the solubility will be approximately 0.01 p/m even at the design temperature of 250 °F (120 °C) (see Figure 2). Warren (1987), Figure 3, adds that the diffusivity of hydrogen through steel also decreases with decreasing temperature; this phenomenon, combined with that of decreased solubility, results in a greatly decreased permeability at lower temperatures. Consequently any hydrogen entering the steel under normal operating conditions will be slow to diffuse through the steel.

The data of Darken and Smith (1977) (see Figure 4) show that because the amount of hydrogen expected to penetrate the steel is low, the influence of corrosion on hydrogen effects should be slow at the pH level for normal tank operations if the corrosion reaction continues to involve the production of hydrogen in accordance with the reaction $H^+ + e^- = \frac{1}{2}H_2$. In the alkaline conditions found in the waste tanks, the reaction is expected to be $H_2O + e^- = \frac{1}{2}H_2 + OH^-$, which, according to Burns is approximately 10^9 times slower than $H^+ + e^- = \frac{1}{2}H_2$. Thus the production rate of hydrogen, and therefore its permeation through the surface, is expected to be much slower than suggested by Figure 4, which is based on acid media.

As several discussions, e.g., Cotterill (1961) and Carter and Hyatt (1977), point out, if equilibrium exists with a 1 atm (0.1 MPa) hydrogen pressure external to the steel and if transfer of hydrogen into the steel were reversible at the void surfaces, then the pressure within a void, defect, or inclusion in the metal would also equal 1 atm (0.1 MPa). The work of Harries and Broomfield (1963), however, suggests that the transfer of H_2 into steel does not occur easily below approximately 260 °C (500 °F) and that, if sufficient hydrogen enters the steel, void pressures greater than 1 atm (0.1 MPa) may result.

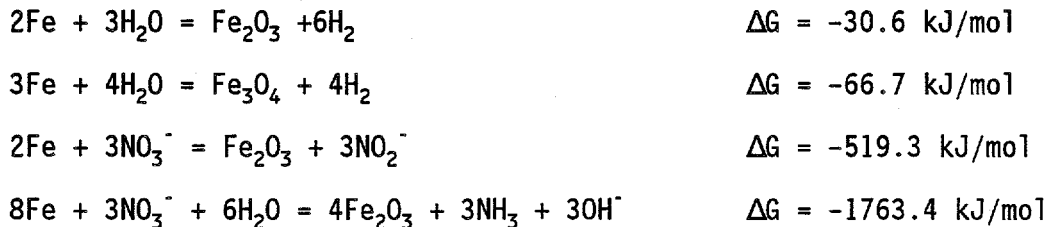
The remainder of this discussion examines possible sources of hydrogen and their production rates in the waste tanks.

4.2 SOURCES OF HYDROGEN

There are several potential sources of hydrogen in the waste tanks: corrosion, radiolysis of the aqueous waste, and chemical or radiolytic decomposition of the organic components in the waste.

4.2.1 Corrosion

The corrosion mechanism of the tank steel in alkaline nitrate/nitrite waste generally is believed to involve oxygen or some oxygenated species rather than hydrogen. The actual corrosion reactions that occur in the waste are unknown. Several possibilities exist:



All of these reactions are viable because the Gibbs functions are exothermic. However, the first two have significantly smaller driving forces. The reaction that actually occurs will be a function of the reaction kinetics and will have to be determined experimentally.

A corrosion reaction that uses $\text{H}^+ + \text{e}^- = \frac{1}{2}\text{H}_2$ as the cathodic reaction depends directly on the hydrogen ion concentration. For every unit increase in pH, the H^+ concentration, and therefore the corrosion rate, will decrease by a factor of 10. Most of the literature detailing hydrogen problems discusses environments of about pH 4. The MWTf tanks are to be held at a pH > 12 in the presence of oxidizing components. Consequently, on the basis of pH alone, hydrogen production should be approximately nine orders of magnitude smaller than those reactions in which hydrogen effects are noted.

These factors, together with the observation by Kobrin (1987) that small amounts of oxygen, at least in the gas phase, inhibit hydrogen entry into steel, suggest that with the oxidizing species present in the MWTf tanks, little atomic hydrogen will be available. Indeed, in early work, McCright (1977) noted that nitrate ions react readily with nascent hydrogen even at high corrosion rates, an observation strongly suggesting that hydrogen will not be available to enter the steel nor be evolved as gaseous hydrogen. More recent work by Meisel et al. (1993) notes that the nitrite, which is present in the waste in large quantities, actually acts as the most efficient getter for atomic hydrogen whereas the nitrate actually reacts with the solvated electron which forms additional nitrite. Both observations lead to the same conclusion even though different mechanisms are cited. McCright as well as Potter (1961) notes that in alkaline solutions a cathodic potential must be applied to effect hydrogen entry into the steel. For these reasons, the concentration of corrosion-produced hydrogen at the steel surface is expected to be small.

Anantatmula et al. (1994) have pointed out that there is no quantitative way to determine the role of potential on the effective pressure (concentration) of the hydrogen at the surface. Subramanian (1981) shows, however, that in the worst-case kinetics, a fast discharge of the H^+ and a slow combination into H_2 which will promote hydrogen entry into the steel, the equation is identical to the Nernst Equation found in MacInnes (1939). Consequently, as shown in the appendix, the maximum hydrogen pressure expected in the MWTf tanks from corrosion is approximately 0.4 lbf/in² (2.5 kPa).

Thus, because of the low equilibrium pressure, the quantity of hydrogen entering the steel will be minuscule. A comparison of the equivalent corrosion rate to data reported by Warren (1987) indicates that these small corrosion rates are of no consequence.

4.2.2 Radiolysis of Aqueous Waste

According to Burns et al. (1983), the formation of H from water is 0.61 atoms per 100 eV. If the dose rate is 1,000 rad/h (10 Gy/h), then approximately 2×10^{11} atoms/s of H per gram of water will be produced. Burns et al. also give the rate constant for $H + H = H_2$ as 10^7 cm³/mol's. More recent work by Meisel et al. (1993) shows that atomic hydrogen is rapidly consumed by nitrite at a rate at least two orders of magnitude faster than the self-combination rate. Therefore, at steady state, the production rate equals the depletion rate; consequently the maximum steady-state hydrogen flux at the steel surface is estimated at 2×10^9 atoms/cm²sec. Thus, the amount of hydrogen that can enter the steel by radiolysis of water is much smaller than that expected from corrosion.

4.2.3 Secondary Radiation Effects

A review of the waste stored in the tank farms shows that many tanks contain organic compounds. Concerns about hydrogen led to recent sampling of the waste in tank 241SY101 tank and the analysis of the sample for organics. The analyses found the sodium forms of ethylenediaminetetraacetic acid, nitroso-iminodiacetic acid, nitrilotriacetic acid, citric acid, succinic acid, and ethylenediaminetriacetic acid. At Argonne National Laboratory (ANL), samples made of similar solutions containing these organics were irradiated and analyzed. After heating the irradiated sample, ANL found that approximately ten times as much hydrogen had been produced as was produced as in the heated, non-irradiated sample (Meisel et al. 1993). Similar results were found by Ashby et al. (1994). In addition, because the chelants degrade under the radiation field in the tanks, the concentrations of these organics will drop to half their original concentration in less than 1.5 years at an assumed dose rate of 1,500 rad/h (15 Gy/h) and the concentrations of the degradation products will rise commensurately. However, recent testing shows that radiolytic degradation products are significantly more efficient in the thermal generation of H₂ than the original chelants.

Although they are numerous and possibly prolific producers of H₂, the reactions (Meisel et al. 1993) described do not produce nascent H atoms.

5.0 CONCLUSIONS

Review of the literature leads to the following conclusions about the effects of hydrogen on the carbon steel from which the MWTf tanks are to be constructed. These conclusions are based on the assumptions listed at the end of this section.

- **Effects of hydrogen before and during tank construction** - Any hydrogen picked up in the steelmaking process will be largely removed during normalization. The hydrogen that accumulates from corrosion during construction will be eliminated during the post-weld heat treatment (PWHT) performed at 1,100 °F (≈590 °C) for a minimum of 1 hour.
- **Effects of hydrogen during the 50 years of tank operation** - Because of the low strength of the steel, hydrogen stress cracking is not considered a significant factor.

Blistering is not likely at tank operating conditions; these conditions include a $\text{pH} \geq 12$ and the presence of nitrate and other oxidizing species. Blistering does not occur except in acid systems. However, even if a corrosion reaction were postulated to provide sufficient nascent hydrogen to reach the wall, and if blistering, including stepwise cracking, were to occur, it is estimated that from 25 to 50 years might pass before it appeared. This estimate is substantiated by work performed at Savannah River Laboratory (Donovan 1974, Springer 1979) indicating that detectable blistering was not measurable in similar wastes for approximately 20 years.

For a number of reasons, the effects of hydrogen therefore are judged to be negligible over the 50-year operating life proposed for the tanks.

- The type of steel to be used will not be particularly susceptible to hydrogen effects.
- No significant hydrogen is expected to be produced in the nascent form that would be harmful.
- Even if hydrogen were produced and a mechanism postulated to charge it into the steel, the type of steel and the operating conditions are such that no significant effect is expected over the life of the tanks.

Therefore either A516, Grade 70, or A537, Grade Class I, carbon steel is satisfactory and no special requirements are necessary. The assumptions on which these conclusions are based include the following.

- The tanks will be constructed of either normalized A516, Grade 70, or A537, Grade Class I, carbon steel.
- The steel will be prepared in accordance with fine grain practice.
- The tanks will be constructed by welding.
- The steel will be preheated before welding if the ambient temperature is less than 50 °F (10 °C), and standard procedures will be used to ensure the use of low-hydrogen welding electrodes.
- After construction the tanks will be post-weld heat treated at a minimum temperature of 1,100 °F (590 °C) for an hour at temperature and then air cooled.
- The final hardness of the steel will be $< \text{Rc } 22$.

- Moving the tanks from the site at which the post-weld heat treatment takes place to their final location will not cause any significant stress to accumulate in the tanks.
- The waste composition will remain within the range specified by the Hanford technical specifications (Groth 1993).
- The operating temperature of the tanks will not exceed the design temperature of 250 °F (120 °C).
- Radiation dose rates will not exceed 1,000 rad/h (10 Gy/h) of combined α , β , or γ radiation.

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Figure 1. Internal Hydrogen Environments in Carbon Steel Waste Tanks.

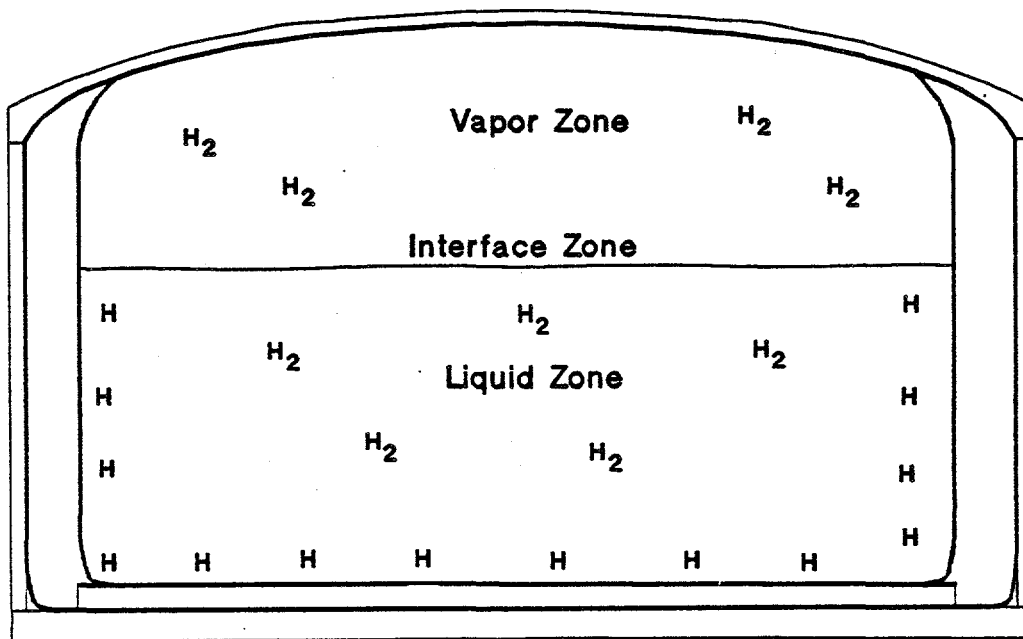


Figure 2. Hydrogen Solubility in Steel.

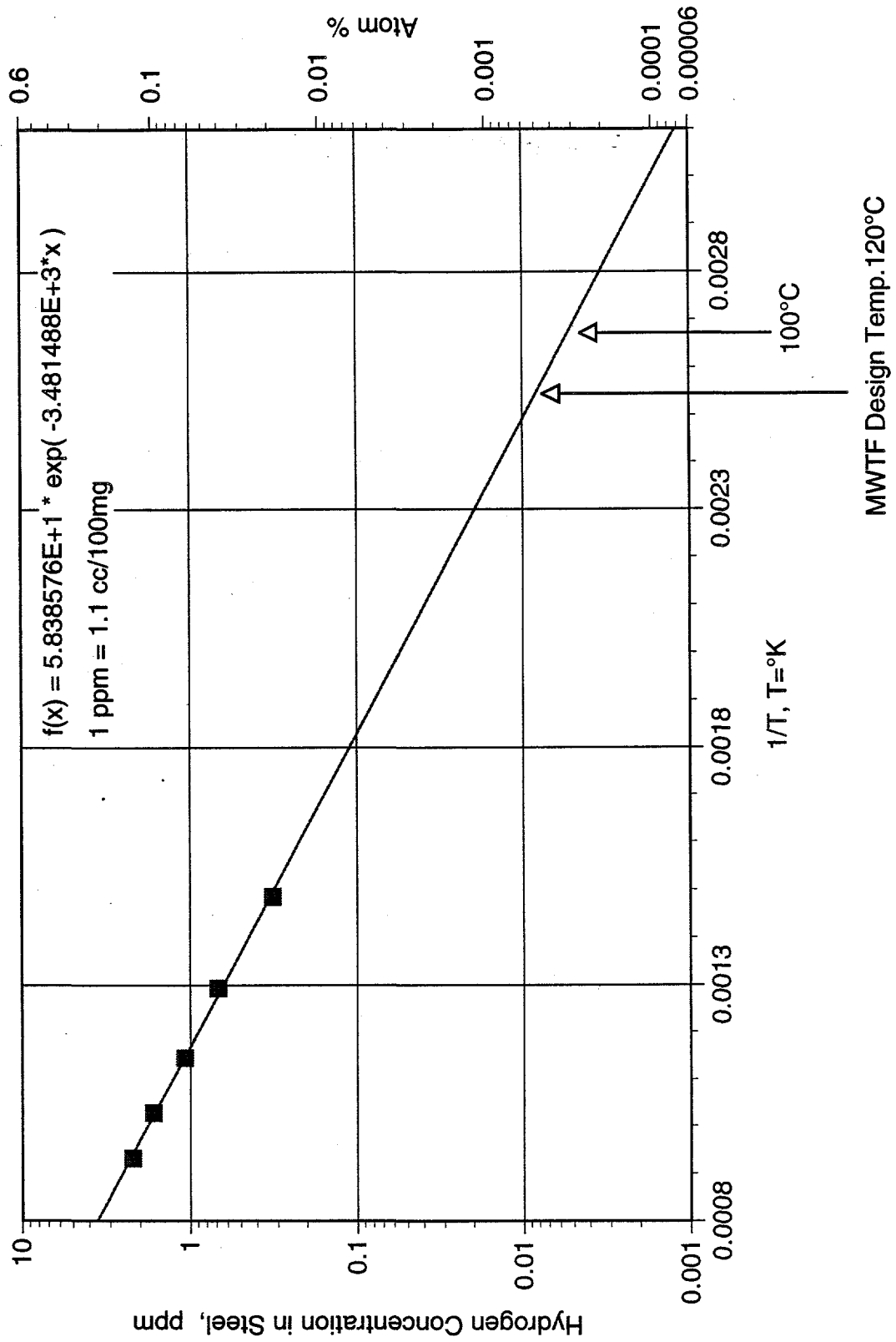


Figure 3. Transport of Hydrogen Through Steel.

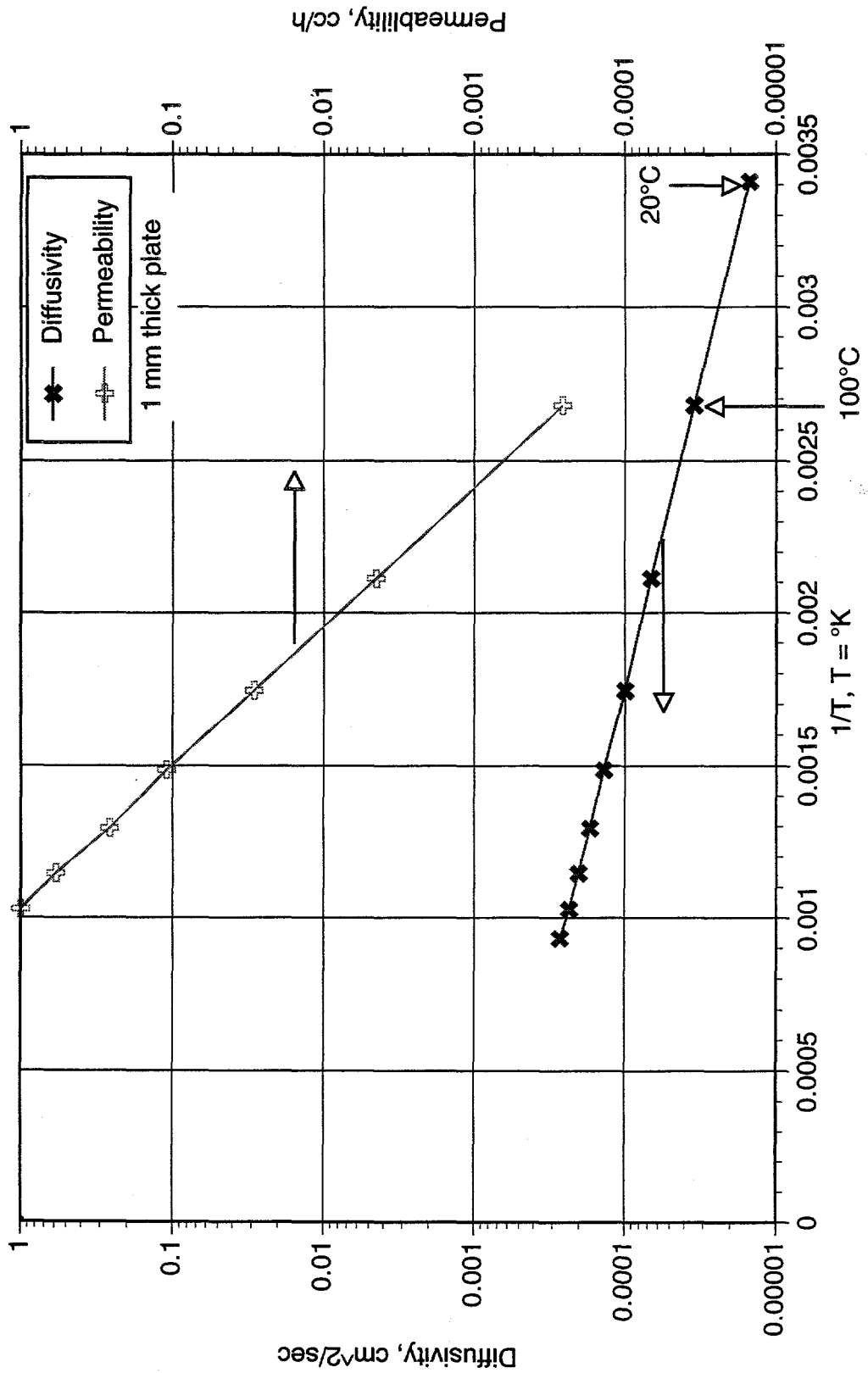
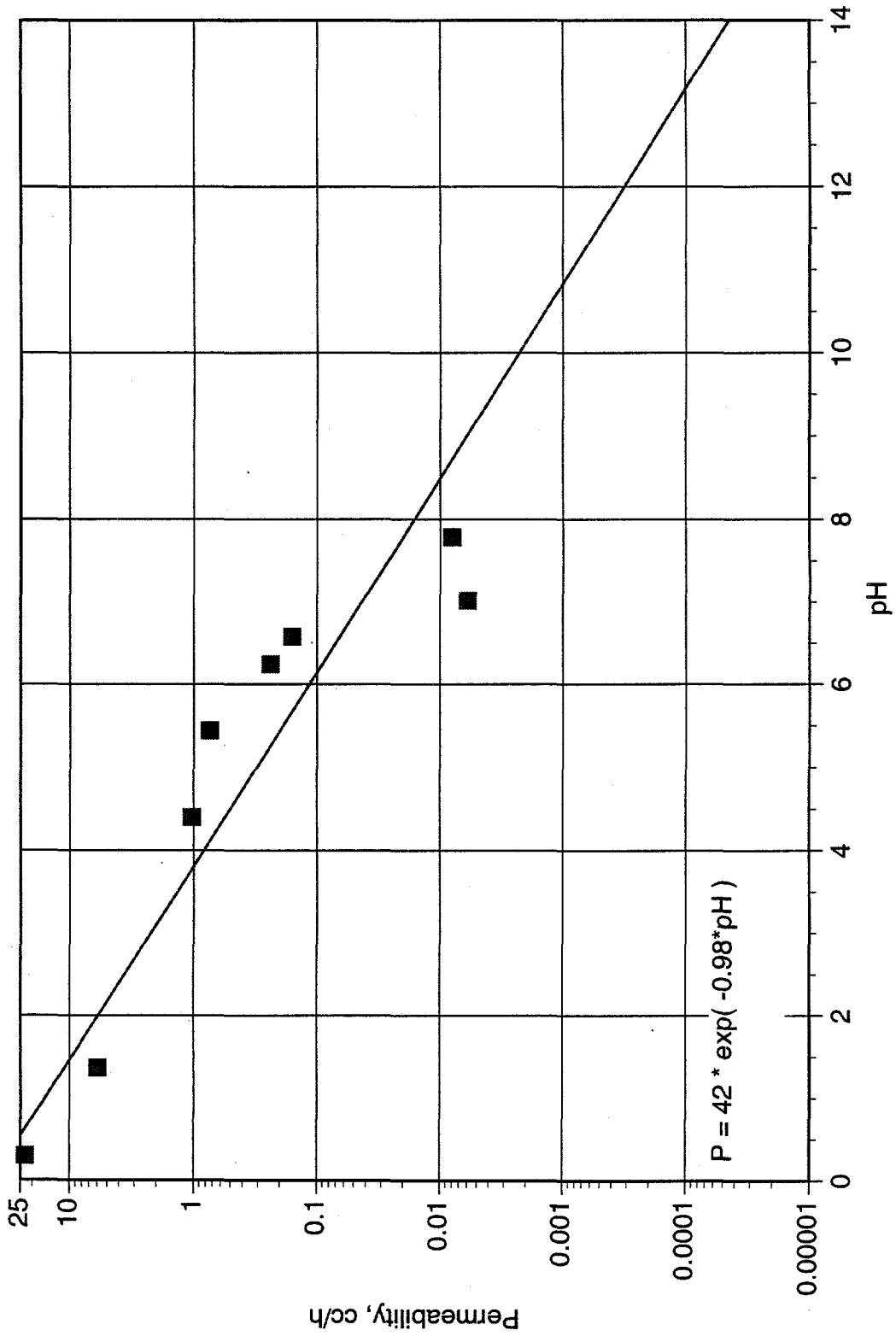


Figure 4. Permeability as a Function of pH.



APPENDIX - Calculations on Hydrogen Effects on Carbon Steel

ANALYTICAL CALCULATIONS

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Subject Calculations on Hydrogen Effects on Carbon Steel
 Originator J. R. Divine Date 12/15/94
 Checker L. D. Blackburn *L.D. Blackburn* Date 1-12-95

Selected Chemical Reactions^a

Species	ΔG°
Fe, H ₂	0
H ₂ O _(l)	-237.2 kJ/mol
OH ⁻	-157.3
NO ₂ ⁻	-37.0
NO ₃ ⁻	-111.3
NH ₃ (aq)	-26.6
Fe ₂ O ₃	-742.2
Fe ₃ O ₄	-1015.5

2Fe + 3H ₂ O = Fe ₂ O ₃ + 6H ₂	$\Delta G = -30.6$
0 -237.2 -742.2 0	
3Fe + 4H ₂ O = Fe ₃ O ₄ + 4H ₂	$\Delta G = -66.7$
0 -237.2 -1015.5 0	
2Fe + 3NO ₃ ⁻ = Fe ₂ O ₃ + 3NO ₂ ⁻	$\Delta G = -519.3$
0 -111.3 -742.2 -37	
8Fe + 3NO ₃ ⁻ + 6H ₂ O = 4Fe ₂ O ₃ + 3NH ₃ (aq) + 3OH ⁻	$\Delta G = -1763.4$
0 -111.3 -237.2 -742.2 -26.6 -157.3	

^a Data from Bard, A. J., R. Parsons, and J. Jordan, 1985, *Standard Potentials in Aqueous Solution*, Marcel Dekker, New York, New York.

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Subject Calculations on Hydrogen Effects on Carbon Steel
 Originator J. R. Divine Date 12/15/94
 Checker L. D. Blackburn *L. D. Blackburn* Date 1-12-95

H₂ Production from Corrosion

$$E = E^\circ - (RT/F) \ln [(H_2)^{1/2}/(H^+)]$$

$$= E^\circ - 0.059 \text{ pH} - 0.03 \log P_{H_2}$$

$$\text{pH} \geq 12$$

The most negative value of E for waste solutions^b is $-0.94 V_{SCE}$

$$\therefore E \geq -0.94 V_{SCE} = -0.66 V_{SHE}$$

Therefore, substituting

$$-0.66 = 0 - 0.059(12) - 0.03 \log P_{H_2}$$

solving

$$0.048 = -0.03 \log P_{H_2}$$

$$\log P_{H_2} = -1.6$$

$$\therefore P_{H_2} = 0.025 \text{ atm} \approx 0.4 \text{ psi} = 2.5 \text{ kPa}$$

At 100 °C, the solubility of hydrogen in steel at one atmosphere pressure is $\approx 0.005 \text{ p/m}$. Therefore, if Sievert's Law^c is obeyed, the solubility at 2.5 kPa hydrogen pressure is about 0.0008 p/m.

To estimate the hydrogen flux through the steel surface, note that $0.0008 \text{ p/m} \approx 0.0008 \text{ cc H/100g Fe}$.

$$8 \times 10^{-4} \text{ cc H/100g Fe} = 8 \times 10^{-6} \text{ cc H/g Fe}$$

$$\rho_{Fe} = 7.86 \text{ g/cc}$$

$$\text{Therefore, } S = (8 \times 10^{-6} \text{ cc H/g Fe})(7.86 \text{ g Fe/cc Fe}) = 6.3 \times 10^{-5} \text{ cc H/cc Fe}$$

^b From J. H. Payer, E. S. Kolic, and W. K. Boyd, *Corrosivity of Solutions from Evaporation of Radioactive Liquid Waste*, a final report to Atlantic Richfield - Hanford Corporation, May 4, 1977, Battelle Columbus Laboratory, Columbus, Ohio.

^c $\sqrt{p} = k S$, where p = pressure, k = constant, and S = solubility.

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Subject Calculations on Hydrogen Effects on Carbon Steel
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Fick's Law states the flux N is given by

$$N = D \Delta c / \Delta x$$

where D is the diffusivity of H in steel

Δc is the concentration difference at the inner and outer surfaces of the steel,

and

Δx is the steel thickness

Warren gives $D = 3.5 \times 10^{-5} \text{ cm}^2/\text{s}$

$$\Delta x = \frac{3}{4}'' = 1.9 \text{ cm}$$

$$\begin{aligned} \Delta c &= C_{\text{INNER}} - C_{\text{OUTER}} = C_{\text{INNER}} - 0 = C_{\text{INNER}} \\ &= 6.3 \times 10^{-5} \text{ cc H/cc Fe} \end{aligned}$$

$$\begin{aligned} N &= 1.5 \times 10^{-5} (6.3 \times 10^{-5}) / 1.9 \text{ cm} \\ &= 1.16 \times 10^{-9} \text{ cc H/cm}^2 \text{ sec} \\ &= (1.16 \times 10^{-9} \text{ cc H/cm}^2 \text{ sec}) (1 \text{ mol H} / 22414 \text{ cc H}) \\ &= 5.2 \times 10^{-14} \text{ mol H/cm}^2 \text{ sec} \\ &= (5.2 \times 10^{-14} \text{ mol H/cm}^2 \text{ sec}) (6.023 \times 10^{23} \text{ atoms/mol}) \\ &= 3.1 \times 10^{10} \text{ atoms/cm}^2 \text{ sec} \end{aligned}$$

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Subject Calculations on Hydrogen Effects on Carbon Steel
 Originator J. R. Divine Date 12/15/94
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H₂ Production from Radiolysis of Water

$$G_H = 0.61 \text{ atoms/100 eV}$$

Assume dose rate = 1,000 rad/h = 10 Gy/h = 10 J/kg h = 6.2x10¹⁶ eV/gh

$$(1 \text{ Gy} \equiv 1 \text{ J/kg}) \quad (1 \text{ eV} \equiv 1.602 \times 10^{-19} \text{ J})$$

$$1 \text{ mol} = 6.0 \times 10^{23} \text{ atoms (Avogadro's \#)}$$

$$G_H = 0.0061 \text{ atoms/eV}$$

∴ for each g of water (neglect density)

$$6.2 \times 10^{16} (0.0061) \text{ atoms/h} = 1.1 \times 10^{11} \text{ atoms/sec are produced}$$

$$\approx 10^{11} \text{ atoms/sec cc} = 1.66 \times 10^{-13} \text{ mol/sec}$$

For the reaction $H + H = H_2$, the reaction constant is $k = 10^7 \text{ cm}^3/\text{mol sec}$

If the reaction with nitrite is two orders of magnitude faster, then k can be set equal to $10^9 \text{ cm}^3/\text{mol sec}$.

$$dH/dt = -k H^2 + 1.66 \times 10^{-13} \text{ mol/cc sec}$$

At steady state $dH/dt = 0$

$$\therefore kH^2 = 1.66 \times 10^{-13} = 10^9 H^2$$

$$\therefore H^2 = 1.66 \times 10^{-22}$$

$$H = 1.3 \times 10^{-11} \text{ mol/cc}$$

$$= 7.8 \times 10^{12} \text{ atoms/cc} = \text{steady state concentration}$$

From B. E. Conway, "Electrochemical Data," Elsevier, New York, 1952, a typical D for ions is about $2 \times 10^{-5} \text{ cm}^2/\text{sec}$. Therefore, if the bulk concentration of H is $7.8 \times 10^{12} \text{ atoms/cc}$ and it is assumed the concentration at the steel surface is zero (i.e., all atoms are instantly and totally absorbed), then the Δc over the diffusion length is $7.8 \times 10^{12} - 0 = 7.8 \times 10^{12} \text{ atoms/cc}$. Without having a good understanding of the hydrodynamics, calculation of a diffusion layer is not possible. However, if it is assumed a 0.1 cm layer of corrosion product then by Fick's Law, the flux is

$$F = D \Delta c / \Delta x$$

$$= 2 \times 10^{-5} \text{ cm}^2/\text{s} (7.8 \times 10^{12} \text{ atoms/cm}^3) / 0.1 \text{ cm} \approx 15.6 \times 10^8 \approx 2 \times 10^9 \text{ atoms/cm}^2 \text{ s}$$