A Study of Hydrogen Effects on Fracture Behavior of Radioactive Waste Storage Tanks

Final Report

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by

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A Study of Hydrogen Effects on Fracture Behavior of Radioactive Waste Storage Tanks

Summary

The processing of high-level radioactive wastes now stored at Hanford and Savannah River Laboratories will continue over many years and it will be necessary for some of the liquids to remain in the tanks until well into the next century. Continued tank integrity is therefore an issue of prime importance and it will be necessary to understand any processes which could lead to tank failure. Hydrogen embrittlement resulting from absorption of radiolytic hydrogen could alter tank fracture behavior and be an issue in evaluating the effect of stresses on the tanks from rapid chemical oxidation-reduction reactions. The intense radiation fields in some of the tanks could be a factor in increasing the hydrogen permeation rates through protective oxide films on the alloy surface and be an additional factor in contributing to embrittlement.

The project was initiated in October 1992 for a two year period to evaluate hydrogen uptake in low carbon steels that are representative of storage tanks. Steel specimens were exposed to high gamma radiation fields to generate radiolytic hydrogen and to potentially alter the protective surface films to increase hydrogen uptake. Direct measurements of hydrogen uptake were made using tritium as a tracer and fracture studies were undertaken to determine any alloy embrittlement. The rates of hydrogen uptake were noted to be extremely low in the experimental steels. Gamma radiation did not reveal any significant changes in the mechanical and fracture characteristics following exposures as long as a month. It is highly desirable to investigate further the tritium diffusion under stress in a cracked body where stress-assisted diffusion is expected to enhance these rates. More importantly, since welds are the weakest locations in the steel structures, the mechanical and fracture tests should be performed on welds exposed to tritium with and without stressed crack-fronts.
The project supported three graduate students: Ms. Nevenka Bierny (Materials Science & Engineering), Mr. Stephen Kass (Nuclear Engineering) and Mr. Patrick Markle (Materials Science & Engineering). Mr. Kass completed his Master of Nuclear Engineering (MNE) degree in Dec. 1994 while Mr. Markle completed his Master of Science (MS) degree in June 1995. The above two students did their project/thesis work on different but related topics: Mr. Kass (12/94) - *Radiation Embrittlement and Dynamic Strain Aging in Mild Steels and Armco Iron*, and Mr. Markle (3/95) - *Creep and Creep Crack Growth In A508B Pressure Vessel Steel*. 
1. Introduction

Large carbon-steel tanks at the Savannah River Laboratory in Aiken, South Carolina and the Hanford facility in Richland, Washington are the principal storage containers for the chemical processing solutions that were used in the preparation of weapons grade plutonium. Additional radioactive waste solutions are stored in stainless steel tanks at Idaho Falls, Idaho and in carbon-steel tanks at the West Valley reprocessing facility in New York. Reprocessing operations at these locations have generated solutions of radioactive waste for over forty years and have remained in these waste storage tanks. Initially, the storage tanks were unannealed, single wall carbon steel (A285-B) tanks without any special weld materials; later, additional tanks were constructed with stress relieved, carbon steel (A516-70) double walls. Illustrations of the single and double shelled tanks are included in figures 1.1 (a) and 1.1 (b) respectively. The chemical compositions of the materials used for the single and double walled tanks are shown below in Table 1.1.

Table 1.1
Chemical Compositions (wt %) of Waste Tank Steels

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Cu</th>
<th>Mo</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>A285-B</td>
<td>0.22</td>
<td>0.9</td>
<td>-</td>
<td>0.04</td>
<td>0.03</td>
<td>0.4</td>
<td>0.12</td>
<td>0.3</td>
<td>0.4</td>
<td>balance</td>
</tr>
<tr>
<td>A516</td>
<td>0.20</td>
<td>0.98</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.24</td>
<td>0.03</td>
<td>0.20</td>
<td>0.16</td>
<td>balance</td>
</tr>
</tbody>
</table>

The compositions of the original solutions in the tanks were known, but subsequent transfers of solutions have made the compositional records of several tanks ambiguous. The tank solutions have complex compositions, and include inorganic nitrates, nitrites, traces of halides, ferrocyanides, and a variety of inorganic salts. The pH of the tank solutions is maintained at approximately 10, and nitrites are added to mitigate the effects of stress corrosion cracking. Only the Savannah River Laboratory site maintains a program to control the chemical conditions within the tanks.
Figure 1.1
Illustrations of (a) Single (top) and (b) Double (bottom) Shelled Tanks
Leaks were noted several years ago in the single wall tanks when tank levels decreased and radioactive nuclides were detected at sampling stations near the waste tanks. Leaking tanks were pumped dry and the remaining solution was transferred to the newer double wall tanks which have proven to be more structurally sound. Leaks have required 100 of the 149 single wall tanks to be emptied. The single wall tank failures were attributed to stress corrosion cracking at the Savannah River and Hanford waste sites. Both storage facilities initiated programs to chemically control the tank contents in an attempt to reduce the amount of stress corrosion cracking. These programs prescribed elevated nitrite concentrations and pH conditions to limit the effect of stress corrosion cracking on the surface of the tanks. Although site personnel believe that these measures have reduced the rate of tank failures, they still consider the single wall tanks to be susceptible to failure in the future.

The double walled tanks were made with greater attention to the selection of the materials, and in most cases were annealed in-situ. Their performance has been satisfactory but the harsh radioactive environment makes the pitting and corrosion process difficult to monitor. A summary of the various tanks and their locations are provided in Table 1.2.

Table 1.2
Status of Waste Storage Tanks

<table>
<thead>
<tr>
<th>Tank Type</th>
<th>Savannah River Lab</th>
<th>Hanford Site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Walled</td>
<td>16</td>
<td>149</td>
</tr>
<tr>
<td>Double Walled</td>
<td>35</td>
<td>28</td>
</tr>
<tr>
<td>Total Storage Tanks</td>
<td>51</td>
<td>177</td>
</tr>
<tr>
<td>Single Walled (Failed)</td>
<td>9</td>
<td>66</td>
</tr>
<tr>
<td>Double Walled (Failed)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

A failed tank does not imply that an unsafe condition exists at the facility in question, since failed tanks are pumped dry to stabilize the radioactive material which exists as a dry sludge in the bottom of the tank. Tank failure does limit the storage capabilities of the sites and there is presently little unused storage capacity to accommodate additional solution storage. There has also been concern about
chemical reactions which may place the integrity of the tanks in jeopardy if the tanks experience an unanticipated load(s). Several tanks are known to generate gaseous mixtures of hydrogen and nitrous oxides.

The Hanford and Savannah River sites anticipate the use of a glassification operation for processing radioactive waste. Both sites have glassification plants planned or under construction; however, these facilities would be able to process only one tank per year per site. The emptying and removal of tanks from service is a lengthy process that will probably not be fully operational for at least ten years. Tank integrity will, therefore, need to be assured for a long time.

The purpose of this discussion is to emphasize the significance and importance of having a solid understanding of the processes and conditions that will lead to potential failure(s) of waste storage tanks. While the tanks appear to be presently stabilized, there is considerable motivation to understand the long term corrosion and failure processes that could compromise tank integrity in the future.

2. Hydrogen Effects

One of the processes that could produce considerable degradation in the structural integrity of the waste tank alloys is the buildup of atomic hydrogen at grain boundaries. Favorable conditions exist for hydrogen adsorption at a crack tip, where the bare metal is not protected by an oxide layer. Rapid diffusion of hydrogen to crack fronts has been known to produce severe embrittlement in many different materials. Hydrogen embrittlement of carbon steels is a well known process that has been the subject of numerous studies and investigations. Embrittlement would not generally be expected under the chemical conditions in which radioactive wastes are stored, however, the radiation environment presents unusual conditions which could alter the normal metallurgical behavior of the alloys.

The intense radiation fields that have been associated with decaying radioactive species continuously generate hydrogen and hydroxyl free radicals that react to form gaseous hydrogen and hydrogen peroxide. The combination of continuous production of atomic hydrogen and the exposure of the internal tank wall oxide layers could alter the normal permeation behavior of the surface oxide. It is possible that these oxide layers are altered in such a way that increases the access of atomic hydrogen to the bulk metal. The research literature has little information on
the effects of radiation fields in promoting hydrogen adsorption. However, it is generally assumed that the destruction of the protective oxide surface layers would lead to rapid hydrogen uptake. It is plausible that the unique chemical environment associated with stored wastes, in conjunction with the radiation field would alter the hydrogen uptake rates and the subsequent embrittlement. The research issues discussed here are illustrated in Fig. 2.1.

Hydrogen Effects

1. Can Radiation Fields Produce Accelerated Hydrogen Uptake?

A. Free Radical Formation:

    Hydrogen Permeation

\[ H_2 \Rightarrow H^\cdot + H^\cdot \]

\[ H_2O \Rightarrow H^\cdot + OH^\cdot \]

In Radiation Fields

\[ H^\cdot + H^\cdot \Rightarrow H_2 \]

\[ \cdot OH + \cdot OH \Rightarrow H_2O_2 \]

B. Breakdown of Oxide Protective Films

2. If Accelerated Hydrogen Uptake Occurs, Will Substrate Fracture Behavior be Degraded?

Figure 2.1
Issues Related to Hydrogen Effects
In this study, samples of steels commonly used in waste tanks were placed in aqueous solutions which contained a known amount of tritium and were subsequently exposed to a gamma ray field of approximately 40,000 rads/hr. This dose rate is approximately ten times those encountered in the waste tanks. The hydrogen adsorption and the consequent mechanical properties of the samples were examined to determine if the gamma rays had any effect on hydrogen migration and subsequent fracture properties.

3. Experimental Methods

This section provides a description of the experimental techniques and procedures that were employed in this research. It includes a description of the materials that were tested, their chemical compositions, microstructures, and tensile properties of unirradiated specimens. Details are provided on the technique used to irradiate the specimens, procedures used to determine the amount of tritium diffusion and its effect on mechanical properties of the steel. Methods and procedures for sample fabrication, performance of the tensile tests and data recording are also included.

3.1 Materials

3.1.1 Chemical Composition

Three different steels were considered in this research: A516gr70, AISI 1020, and A354 steel. Their chemical compositions are included in Table 3.1. The 1020 steel was acquired from Duke Power Company (courtesy Mr. Ray McCoy) while the A516gr70 and A354 steels were procured from HUB Incorporated.

3.1.2 Optical Metallography

Microstructures of unirradiated A516 steel, AISI 1020 steel, and A354 steel are shown in figures 3.1 (a), 3.1 (b) and 3.1 (c). All of these materials are categorized as hypoeutectoid steels, meaning their carbon contents are less than 0.77 weight percent. The light grains in each micrograph are the primary alpha iron phase (ferrite) and the dark areas are pearlite. Pearlite is a microconstituent in steel which has a lamellar structure of alternating layers of ferrite and cementite (Fe3C). Average grain sizes for these four steels range between 20 and 40μm.
Table 3.1
Chemical Composition (wt %) of Experimental Steels

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Cu</th>
<th>Mo</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>A516</td>
<td>0.20</td>
<td>0.98</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.24</td>
<td>0.03</td>
<td>0.20</td>
<td>0.16</td>
<td>balance</td>
</tr>
<tr>
<td>1020</td>
<td>0.20</td>
<td>0.40</td>
<td>0.10</td>
<td>0.04</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>balance</td>
</tr>
<tr>
<td>A354</td>
<td>0.55</td>
<td>1.65</td>
<td>0.6</td>
<td>0.04</td>
<td>0.04</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>balance</td>
</tr>
</tbody>
</table>

Figure 3.1
Optical Micrographs of A516 (a), 1020 (b) and A354 (c) Steels
3.1.3 Mechanical Properties of Unirradiated Iron and Steel

Mechanical characteristics of the unexposed steels were evaluated for subsequent comparison with the samples exposed to hydrogen and radiation. Tensile tests were performed on a closed loop Instron servohydraulic tensile testing machine (as described later) at ambient temperature and at a strain rate of \(1 \times 10^{-4} \text{s}^{-1}\). The mechanical properties of these archive materials are summarized below in Table 3.2.

**Table 3.2**  
**Mechanical Properties of Unirradiated Steel Specimens**

<table>
<thead>
<tr>
<th>Material</th>
<th>Test Temp. (K)</th>
<th>0.2% Offset Yield Stress (MPa)</th>
<th>UTS (MPa)</th>
<th>Uniform Strain (%)</th>
<th>Total Strain (%)</th>
<th>Strain Hardening Exponent (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020</td>
<td>295</td>
<td>289</td>
<td>441.4</td>
<td>16.0</td>
<td>20.8</td>
<td>0.280</td>
</tr>
<tr>
<td>A516</td>
<td>295</td>
<td>325</td>
<td>525</td>
<td>16.5</td>
<td>24.0</td>
<td>0.262</td>
</tr>
<tr>
<td>A354</td>
<td>295</td>
<td>344</td>
<td>480</td>
<td>0.166</td>
<td>12.0</td>
<td>0.243</td>
</tr>
</tbody>
</table>

3.2 Radiation Arrangement

3.2.1 Sample Irradiation

A capped aluminum container (2" diameter and 3" high), was fabricated to hold the Charpy (three-point bend) and tensile specimens while in the gamma cell. The photographs of the container are included in figure 3.2 while a schematic of the container is shown in figure 3.3.
Figure 3.2
Photographs of Aluminum Container for Gamma Irradiation
A fitting was machined into the cap of the aluminum container to accommodate a thermocouple which was used to control and monitor the temperature during irradiation. A relief valve was also placed on the cap of the container (at the center) to vent any pressure that may have built up during high temperature exposures. Three-point bend and tensile specimens were placed in the aluminum container with a 20 ml solution that included a tritium tracer. Specimens were sealed in the container and irradiated in a Co-60 gamma cell at room temperature, 80°C and 100°C.

A Gamacell model 220, manufactured by Atomic Energy of Canada Ltd., was used for all sample exposures. Gamma dose rates were determined using the following decay rate provided by the manufacturer:

\[ d = 9.58 \times 10^5 \cdot e^{-(\ln 2)(t - t_0)/526} \]
where, \( d \) is the gamma dose in rads/hr, \( t_0 \) is May 29, 1970 and \( t \) is the date of use. All gamma irradiations performed in this study were on the order of 45000 rads/hr.

The Gammacell 220 is a Cobalt-60 irradiation chamber that is designed for use in an unshielded room. The unit consists of an annular source permanently enclosed within a lead shield, a cylindrical drawer and a drive mechanism to move the drawer up or down along the center line of the source. The drawer has a chamber to carry samples to be irradiated from outside the shield to the source. Samples approximately six inches in diameter and eight inches in height can be accommodated in the chamber. Electrical and mechanical connections can be introduced into the sample chamber through an access tube in the upper portion of the drawer. A photograph and diagram of the gamma cell are included in figures 3.4 and 3.5 respectively.

High temperature gamma radiation exposures were made to enhance hydrogen diffusion into the steel which may result in changes in the mechanical properties of these materials. Standard heating tape was wrapped around the circumference of the aluminum canister and was connected to a 120V variable power supply through a thermocouple and a Barber Coleman temperature controller. The desired temperature was set on the temperature controller which opened and closed the circuit to the power supply (and the heating tape) depending on how far the thermocouple temperature was from the desired set point. Tensile samples were irradiated in distilled water to 80°C and in silicone oil to 100°C. Silicone oil was used for the high temperature irradiations to minimize the pressure build up in the aluminum container during prolonged exposure times.
Figure 3.4
Photograph of the Gamma Cell
Figure 3.5
Detailed Diagram of the GAMACELL 220

GAMACELL 220
GENERAL DIMENSIONS
3.3 Sample Preparation and Testing

Tensile specimens were fabricated from the three different grades of steel used for this study: A516gr70, AISI 1020, and A354. Three point bend specimens were made from A516gr70 only. The three point bend samples were used to measure the diffusion coefficient of hydrogen in the steel. To accomplish this, the specimens were exposed in gamma cell while immersed in a solution that contained tritium. After gamma ray exposure, layers of the steel sample were removed via electropolishing. The electropolish solution was then counted in a liquid scintillator counter to measure the tritium activity as a function of polish depth. Tensile specimens were fabricated to determine the effect of gamma rays on mechanical properties at room and elevated temperatures. Samples were immersed in distilled water (without a tritium tracer) and silicone oil (for high temperature irradiations), irradiated and then examined for changes in the mechanical properties such as ductility, yield strength, and ultimate tensile strength. An apparatus was also designed and constructed to irradiate three point bend samples under loaded conditions. A photograph of this apparatus is shown in figure 3.6. The original idea was to examine the effect of stress concentration at the crack front in enhancing the migration of hydrogen (stress-induced diffusion) into the material and subsequent embrittlement of the steel.

Figure 3.6
Photograph of Jig for Gamma Irradiation under Load
4.3.1 Sample Preparation

Three point bend specimens were machined from a block of A516gr70 steel in accordance with the diagram shown in figure 3.7. A hole was tapped into the top of the sample to accommodate a screw, which was attached to the positive lead of a power supply for electropolishing. These specimens were placed into the aluminium container with 2 ml of tritiated water. The tritiated solution was prepared from a stock solution of 1-4 Dioxene with an activity of 1.5x10^5 dpm/ml. The activity of the tritium solution placed in contact with the steel samples and exposed in the gamma cell varied from 0.5 to 50 μCi/ml. A A516 steel sample was placed in the aluminum canister with the notch facing down into the tritiated water, ensuring that only one face was exposed to the tritium. The aluminum container, with the steel sample and tritiated water, was placed in the gamma cell and was exposed for times ranging from five days (4.8 Mrad) to 25 days (24 Mrad). The three point bend specimens were used to determine the diffusion coefficient of hydrogen in the steel.

Figure 3.7
Three-Point Bend Specimens

Tensile specimens were fabricated from blocks of A516, AISI 1020, and A354 steels in accordance with the diagram provided in figure 3.8. These specimens were placed into the aluminum container with 20 ml of distilled water for room temperature and 80°C irradiations. High temperature irradiations (100°C) used silicone oil in place of water to reduce the amount of liquid lost from evaporation.
The tensile specimens were used to determine the mechanical property changes in the steel samples following gamma ray exposures. Tritium tracers were not placed in the water or oil solutions since these samples were not used to determine hydrogen diffusion gradients or concentrations into the steel.

Figure 3.8
Drawing of Tensile Specimens

3.3.2 Sample Testing

3.3.2.1 Tritium Tracer Measurement

A516 steel samples were placed in a tritiated solution and were irradiated in the Gammacell 220 to a specific gamma ray dose. The three point bend samples were removed from the aluminum container after irradiation and were prepared for electropolishing and liquid scintillation counting to determine the concentration of tritium in the steel, as a function of depth, after exposure to gamma rays. The dimensions of each irradiated steel sample were measured with a micrometer, attached to a 2/56" x 1.25" screw, using gloves and tweezers, and placed into an
electrolytic solution with a piece of stainless steel (also attached to a 2/56" x 1.25" screw). This arrangement is illustrated in figure 3.9.

**Figure 3.9**
Electro-Polishing Apparatus for Surface Removal

Proper combinations of current, voltage and polish solution were determined after many weeks of experimentation. The sulfuric/phosphoric acid electrolyte, 0.694 A and 4V provided conditions for a constant and even polishing rate across the face of the three point bend specimen. This polishing rate was determined to be 115 microns/min. After each polish, 2 ml of the polish solution were removed and placed into a 20 ml liquid scintillation counting vial. The steel specimen was removed from the solution, cleaned and measured with a micrometer to determine the amount of material removed from the surface. A new electrolyte solution was prepared and the steel specimen was placed back into the solution for additional polishing. Five to six polishes were performed on each steel sample to produce a hydrogen concentration profile of the specimen. A liquid scintillation cocktail was prepared for each vial which contained 2 ml of the polish solution and 18 ml of the liquid scintillator, Scintiverse II. These vials were counted in Packard 4430 Liquid...
Scintillation Counter along with known standard and background solutions. The standard solution was prepared using a 2 ml solution of tritium known to have 1.11x10^6 dpm and 18 ml of Scintiverse II, and the background solution was prepared using 20 ml of Scintiverse II. Three counting windows were programmed into the liquid scintillation counter. Since tritium emits an 18 keV beta particle, the first, second and third windows were set for 0-19 keV, 2-19 keV and 19-1 keV respectively. The vials containing the polish solution, the standard sample, and the background sample were counted three times for an hour each to obtain good counting statistics. The number of counts per minute for each vial was determined by averaging the three values obtained from the liquid scintillator (since each vial was counted three times).

3.3.2.2 Tensile and Three-Point Bend Testing

Tensile specimens of A516, AISI 1020, and A354 steels were used to determine the effect of gamma radiation on the mechanical properties of the steel specimens. Tensile specimens were fabricated in the NCSU Nuclear Engineering Machine Shop from forged plates of each particular material. The samples were 1.55 inches long with a 0.5 inch gage section. Grips were fabricated from tool steel and were used to hold the samples while performing the uniaxial tensile tests. The grips were 35 mm long and 16 mm wide with a notch and hole to accept the connecting rods and pins respectively. A detailed diagram of the grips is included in figure 3.10. Tensile tests were performed on an Instron model 1350 servo-hydraulic testing machine with a 1010-AF load cell. A mounting frame was used to prevent from bending the tensile specimens while being placed in the Instron machine. The upper connecting rod was attached to the load cell and the lower connecting rod was attached to the movable piston on the Instron machine.

Load-elongation curves were obtained from a Hewlett Packard 7004B X-Y chart recorder that read the output voltage for load and displacement from the Instron machine. Three to four measurements were made along each dimension and averaged. Tensile tests were performed at a constant strain rate of 1x10^-4 s^-1 at ambient test temperature.
Figure 3.10
Grip Arrangement for Tensile Tests

- upper connection rod
- tensile grip
- mounting frame
- tensile specimen
- hexa-sew hole of 1.6 mm dia
- lower connection blade

44.5 mm
4. Results and Discussion

4.1. Tritium Diffusion

Two solutions were evaluated for the electropolishing of carbon steel specimens. A glycerine-nitric acid based solution exhibited low polish rates and substantial pitting of the specimens. A solution consisting of 50% phosphoric acid, 50% sulfuric acid produced polishing rates of several mils per hour and a smoother specimen finish. This solution was selected for the polishing experiments. Aliquots of tritium tagged solution were added to the polish solution and counted in a liquid scintillation counter using a Scintiverse-II cocktail. The phosphoric-sulfuric acid lowered the counting efficiency from approximately 45% (pure water) to 20% (polish solution) but it was possible to liquid scintillation count the tritium by directly adding the polish solution to the scintillation cocktail.

As pointed out, in addition to the liquid scintillation counting of the polished layers, windowless proportional counter with a pulse height discriminator window to screen noise pulses was assembled to count exposed samples directly. The counter was calibrated with a purchased metal hydride tritium source (Amersham Corp.) and a satisfactory counting plateau was obtained. Specimens were soaked in tritiated water solution, rinsed lightly, and counted in the proportional counter. The counting rate was low enough to indicate that little tritium absorbed in the oxide film to produce an undesirable counting background for the tritium uptake studies.

The hydrogen diffusion experiments yielded the activity versus depth which are related to the diffusion coefficient, D,

\[ A = A_0 \exp(-x^2/4Dt) . \]

Here, \( A \) is the counts/min. Thus semi-log plots of the activity versus square of the depth [\( \log(A) \) vs \( x^2 \)] should follow straight lines with slopes from which \( D \) can be evaluated.

Typical data obtained are shown in Fig. 4.1 to 4.3 for various time periods exposed to different total doses: sample #2 (27 Mrad), #3 (13 Mrad) and #4 (16 Mrad). There is a lot of scatter in the data, and straight lines are drawn through log vs square-of-depth. The slopes of these lines yield \(Dt\) from which the diffusion
coefficient of tritium in A516 was estimated. From \( \ln(\text{activity}) \) vs time, the diffusion rates were calculated, 
\[
D = 9.71 \pm 2.03 \times 10^{-8} \text{ cm}^2/\text{hr} \ (\text{or} \ 2.7 \times 10^{-11} \text{ cm}^2/\text{sec}).
\]
These are very small values compared to published data of hydrogen diffusion in steels.

Figure 4.1
Depth Profile from A516 Sample #2
Irradiation Time = 600.1 hrs

Figure 4.2
Depth Profile A516 Sample #3
Irradiation Time = 288.15
Unfortunately, limitations in the budget did not permit evaluation of depth profiles as a function of temperature. Modifications to the gamma-cell are required for high temperature study. However, mechanical properties were evaluated following \( \gamma \)-radiation exposures at higher temperatures with no tritium tag. The work performed to date, however, does clearly indicate that the experimental approach is appropriate for the proposed study. The original plan of investigating the hydrogen uptake at crack front in 3-point bend specimens under load could not be undertaken.

![Figure 4.3](image)

**Figure 4.3**
Depth Profile from A516 Sample #4
Irradiation Time = 366.18 hrs

\[ y = 216.55 \times 10^{(-3858.5x)} \quad R^2 = 0.635 \]

4.2. Effect of \( \gamma \)-Radiation on Mechanical Properties

Tensile tests were performed at room temperature on various steel samples following exposure to \( \gamma \)-radiation in the gamma cell. No consistent results were obtained. Changes in the strength and ductility were nominal, and in many cases they are within the experimental scatter.

4.2.1. A516 Gr 70 Steel

Figures 4.4 to 4.8 show \( \sigma-\epsilon \) curves for the unirradiated versus those following exposures at 100 °C to various times or total doses upto 20 Mrad. We did not find any consistent behavior of either the strength or the ductility, both uniform and total elongations.
Figures 4.4 and 4.8
Stress-Strain Curves for A516 Gr 70 Steel - Effect of Exposure to γ-Radiation
Figure 4.9 depicts the effect of dose on fracture strain at 100 °C (in silicone oil bath) and the strains ranged from about 25% for the as-received to about 19% at 15 Mrad while it increased at the highest dose used, namely 20 Mrad. The corresponding data on yield and tensile strengths are shown in Fig. 4.10; within the scatter normally noted for these steels, the variations are regarded as negligible. Similar trends are noted at room temperature also, and Figures 4.11 and 4.12 document these data. Experiments were performed at 80 °C also (Figures 4.13 and 4.14).

Figure 4.9
Effect of Dose (at 100 °C) on Room-Temperature Fracture Strain (A516 Steel)

![Fracture Strain vs Dose](image)

Figure 4.10
Effect of Dose (at 100 °C) on Room-Temperature Yield and Tensile Strengths

![Stress vs Dose](image)
Figure 4.11
Effect of Dose on Fracture Strain at 25 °C (A516 Steel)

Figure 4.12
Effect of Dose on Yield and Tensile Strengths at 25 °C (A516 Steel)
Figure 4.13
Effect of Dose (at 80 °C) on Room-Temperature Fracture Strain (A516 Steel)

Figure 4.14
Effect of Dose (at 80 °C) on Room-Temperature Tensile Strength (A516 Steel)
4.2.2. A354 Steel

Tests were performed on A354 steel (Table 3.2) following exposure in the gamma cell at 100 °C. Again, since no discernible changes were noted following room-temperature exposure with and without tritium tag, we first wanted to examine the relatively high temperature exposure effects. The intention here was to eventually develop a system to expose the materials to tritiated solution at higher temperatures so that higher rates of tritium uptake could take place. Figures 4.15 and 4.16 show the dose effects on ductility and strength, and essentially similar (as per A516 steel) are observed.

Figure 4.15
Effect of Dose (at 100 °C) on Room-Temperature Fracture Strain (A354 Steel)

Figure 4.16
Effect of Dose (at 100 °C) on Room-Temperature Yield and Tensile Strengths
4.2.2. 1020 Steel

Tests were performed on 1020 steel (Table 3.2) following exposure in the gamma cell at 100 °C. Again, no discernible changes were noted in the fracture strains (Figure 4.17). As depicted in Fig. 4.18, both the yield and tensile strengths increased at the initial exposure following which they both decreased with increased dose. However, the changes are not significant - with a maximum of 50 MPa.
5. Closure

As noted in section 4.1, no significant uptake of tritium was noted in the tritium-tag experiments. Limited amount of 3-point bend tests performed also revealed no discernible changes in the load-displacement curves. As described in the interim report, specimens were irradiated in solution to an accumulated dose of 3.24x10^6 rads and three point bend tests were performed. The results obtained appeared to be generally consistent with the results for unirradiated specimens and no modification in fracture strength was obtained. Later, a second series of specimens were exposed to an accumulated dose of 2.52x10^7 rads which also did not reveal any differences. Thus, most of the mechanical property evaluations were made using tensile tests.

Majority of the time was spent on getting chemical experiments performed using tritiated water exposures. The studies on tritium diffusion under stress of cracked specimens could not be taken up due to the discontinuity of the NEER project in 1994; only no-cost extensions helped in getting the students complete their master's degree research. It is highly desirable to investigate further the tritium diffusion under stress in a cracked body where stress-assisted diffusion is expected to enhance these rates. More importantly, since welds are the weakest locations in the steel structures, the mechanical and fracture tests should be performed on welds exposed to tritium with and without stressed crack-fronts.

Mr. Kass completed his MNE (master of nuclear engineering) project by investigating dose rate effects and his project work resulted in a technical paper which is included in the Appendix. Very interesting and new results were obtained by comparing the mechanical properties following exposures to total (fast + thermal) neutron radiation versus only fast (using Cd-wrapped) neutron radiation. Effect of grain size on the strength following these exposures revealed non-negligible effects of low-energy neutrons on radiation hardening of steels. Inclusion of thermal neutrons along with fast resulted in further decrease in the source hardening with a slight increase in the friction hardening which revealed a critical grain size below which exposure to total (fast and thermal) neutron spectrum resulted in a slight reduction in the yield stress compared to the exposure to only fast neutrons. This is the first time such a grain size effect is reported and this is shown to be consistent with known radiation effects on friction and source hardening terms along with the observation that low-energy neutrons have a nonnegligible effect on the mechanical

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properties of steels. In ferritic steels, however, despite their small grain size, exposure to total neutron spectrum yielded higher strengths than exposure to only fast neutrons. This behavior is consistent with the fact that the source hardening is small in these alloys and radiation effect is due only to friction stress.

6. Bibliography


Appendix removed for separate processing

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