

Report # DOE/ER/75784-1

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

Progress Report

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I. Introduction

High-level radioactive waste tanks at Savannah River Laboratory and the Hanford Site at Richland Washington contain large quantities of fission product radionuclides that are byproducts of the plutonium processing operations at both sites. As a result of changing process chemistry, the chemical composition of the solutions in the tanks can be complex and includes various combinations of organic complexing agents, inorganic nitrates and nitrites, traces of halides, ferrocyanides and a variety of inorganic salts. The plan for solidification of the wastes anticipates a processing rate of no more than several tanks per year at both sites and it is uncertain when processing will commence. The glass fabrication plant at SRL is completed but not yet operating while the comparable facility at Hanford is yet to be constructed. Waste processing will therefore develop over many years and it will be necessary for the tanks to contain wastes for a considerable time period.

Early tanks were single-shelled and typically fabricated from unannealed A-285 or A-537 carbon steel. Later tanks were double-shelled to improve containment and leak detection and were fabricated from annealed A-516-70 steel which exhibits a lowered tendency to stress corrosion cracking. Tank failure has been observed at both sites, largely with the single-shell tanks, and the tanks have then been pumped dry to prevent continued leaching of radioactivity into the surrounding soil. Table I below summarizes the cumulative failure history to date at both sites.

| | Hanford | SRL |
|----------------------------|---------|-----|
| Single-Shell Tanks (SST's) | 149 | 16 |
| SST's Presumed Failed | 66 | 9 |
| Double-Shell Tanks (DST's) | 28 | 35 |
| DST's Presumed Failed | 0 | 1 |

Given that wastes may have to occupy the tanks for many years before processing, it is important to have a clear understanding of present failure processes and any new corrosion processes that could impact tank lifetime.

A listing of potential corrosion processes includes some processes that have been observed in waste storage tanks.

- Caustic/Low Temperature Embrittlement--Tank pH is typically above pH 12 and early tanks had NDTT temperatures that were quite high so this process has to be considered as a potential failure process.
- Hydrogen Embrittlement--No present confirmation of this failure process currently exists for waste tanks but the literature records many examples of hydrogen effects on fracture behavior for low carbon steels.
- Pitting Corrosion--Corrosion pitting has been observed at SRL on heat exchangers exposed to air above waste tanks. The atmospheric carbon dioxide apparently lowers local pH sufficiently to produce attack.
- Sludge Corrosion--Tank bottoms are routinely covered with sludge which could contribute to localized chemical attack and corrosion failure. Since no means for observing these effects have been identified, sludge corrosion is not confirmed.
- Stress Corrosion Cracking--Nitrate assisted stress corrosion cracking is believe to be the principal corrosion failure process for the single-shell tanks that have failed to date.

The present research is directed towards an examination of hydrogen effects in carbon steels and specifically towards the identification of radiation enhanced hydrogen uptake in steels. The next section describes the research that is planned and now underway.

II. Planned Research

Hydrogen buildup at grain boundaries would be expected to degrade the alloy strength and promote rapid crack growth under stress. Figure 1 represents several processes by which the radiation fields associated with the high level radioactive wastes could increase the permeation of hydrogen into the carbon steels and produce hydrogen embrittlement.

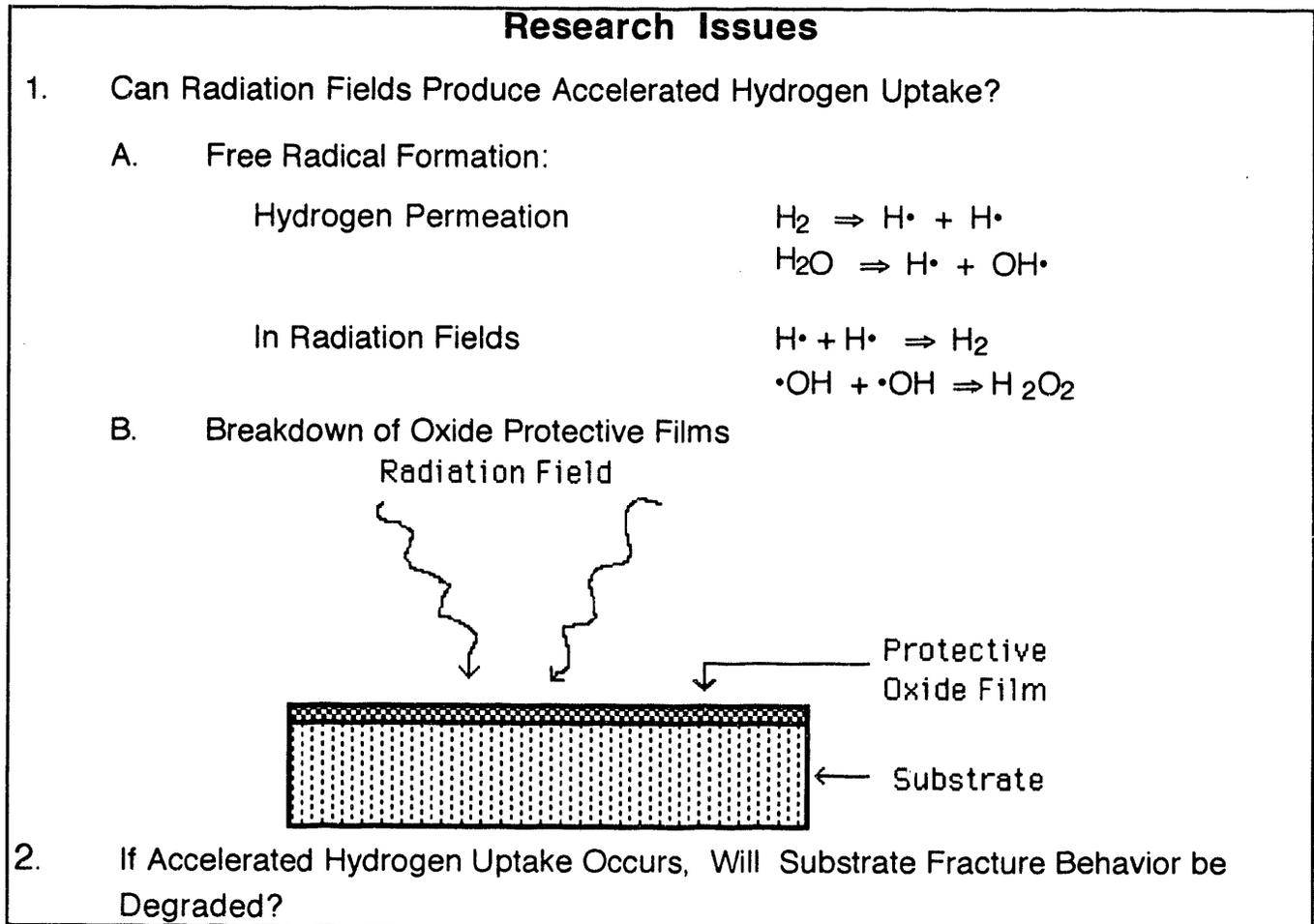


Figure 1
Processes for Radiation Enhanced Hydrogen Uptake in Carbon Steels

Hydrogen permeation occurs as atomic hydrogen with the dissociation process typically occurring at the alloy surface. Radiation generates free-radical atomic hydrogen which could lead to increased concentrations of atomic hydrogen at alloy surfaces. This in turn, could increase the driving force for hydrogen diffusion into the alloy.

The thin, adherent oxide film on an alloy surface is generally regarded as the principal barrier to hydrogen dissolution in the metal. Figure 2 shows hydrogen concentrations as a function of depth following the injection of tritium into 304 stainless steel alloy surfaces as measured by electropolishing and liquid scintillation counting at the our facility. This work predates the present studies with A 516 steel. The clear buildup of tritium in the oxide surface layers is evident from the plots.

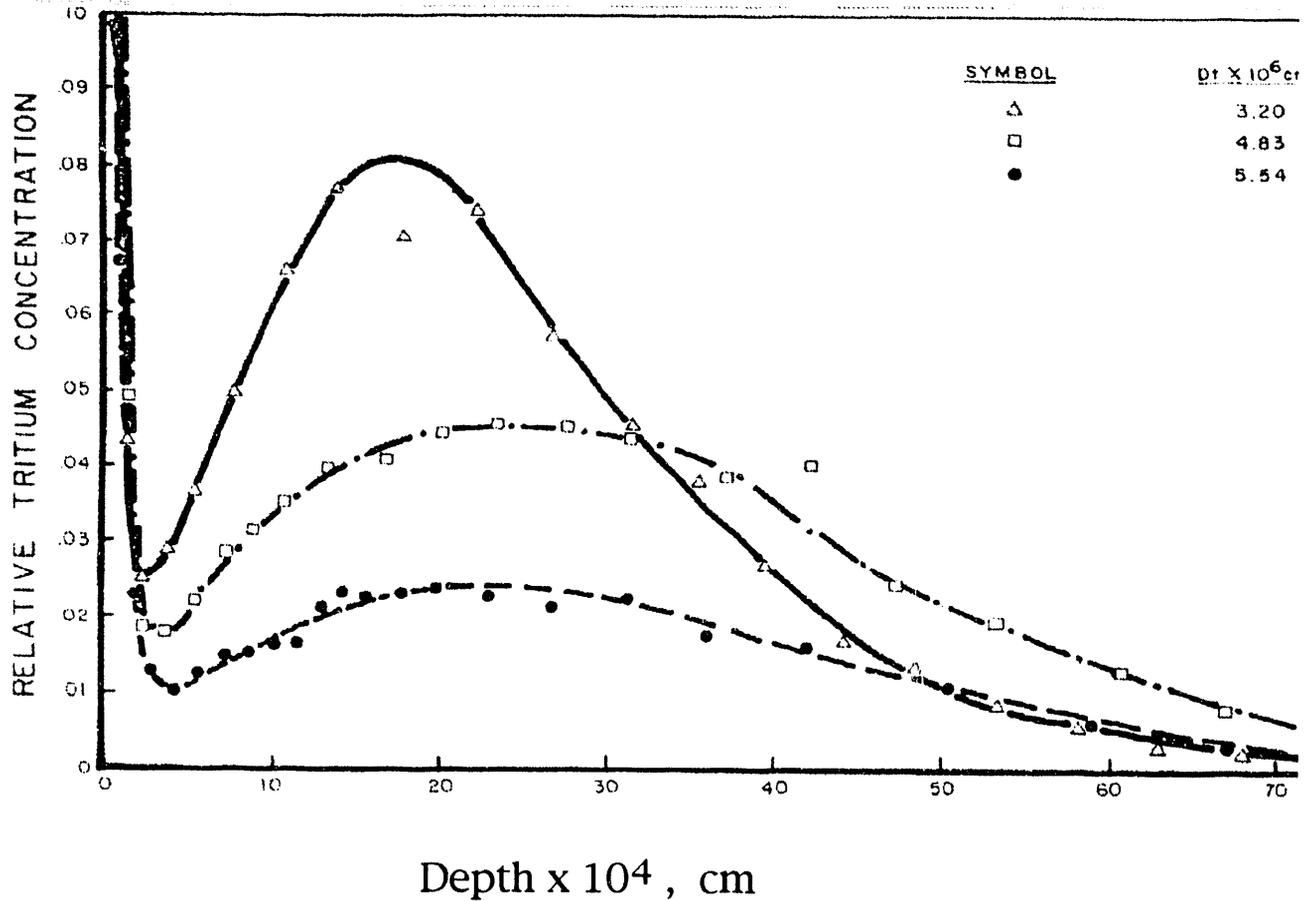


Figure 2
 Tritium Concentration Versus Depth for 304 Stainless Steel.
 High Concentrations at Specimen Surface Show Hydrogen Trapping in Surface Film.
 (J. H. Austin, et al., *J. Nucl Mat.* 48:307-316 (1973))

The high gamma ray and beta particle fields produced by the fission products might be expected to alter the permeability characteristics of the films to allow greater uptake of hydrogen. Radiation therefore could accelerate the uptake of hydrogen and the onset of hydrogen embrittlement by the two processes described.

The proposed research plan consisted of an investigation of the effects of gamma radiation on hydrogen uptake and measurement of the deformation to fracture of irradiated and unirradiated specimens. The planned experimental sequence is:

1. Survey literature on radiation effects on carbon steels and the past research on hydrogen embrittlement in these alloys.

2. Develop baseline of stress to fracture for unirradiated A-516 steel using three point bend tests. Figure 3 shows a schematic of the three-point test equipment and a typical load-displacement run.

3. Expose samples to Co-60 gamma ray dose rates in the range 10^6 - 10^7 rads absorbed dose during specimen immersion in pH 12 solution and repeat three point bend tests. The absorbed doses correspond to a number of years of fission product exposure but are less than life-time absorbed doses for the highest activity tanks.

4. Expose samples to gamma rays in solutions tagged with tritium and electropolish layers from the specimen following irradiation to establish the tritium profile in the specimen. This technique establishes the concentration gradient and helps confirm accelerated hydrogen accumulation.

5. Expose stressed samples to gamma rays during solution exposure. Samples will be loaded to a stress in the plastic region by three point loading during irradiation.

6. Repeat measurements at elevated temperatures (80°C) to more closely duplicate tank environments.

7. If hydrogen uptake is observed, evaluate effects of using a *fissium* solution and of altering the solution pH. Each condition duplicates conditions that could be produced in tanks.

8. Use autoradiography or proportional counting to confirm hydrogen buildup at the crack tip during deformation (sample under stress).

The expectation at the beginning of the program was that items 1 to 4 would be carried out during the first year and the remaining items would be the focus for the second year of investigation.

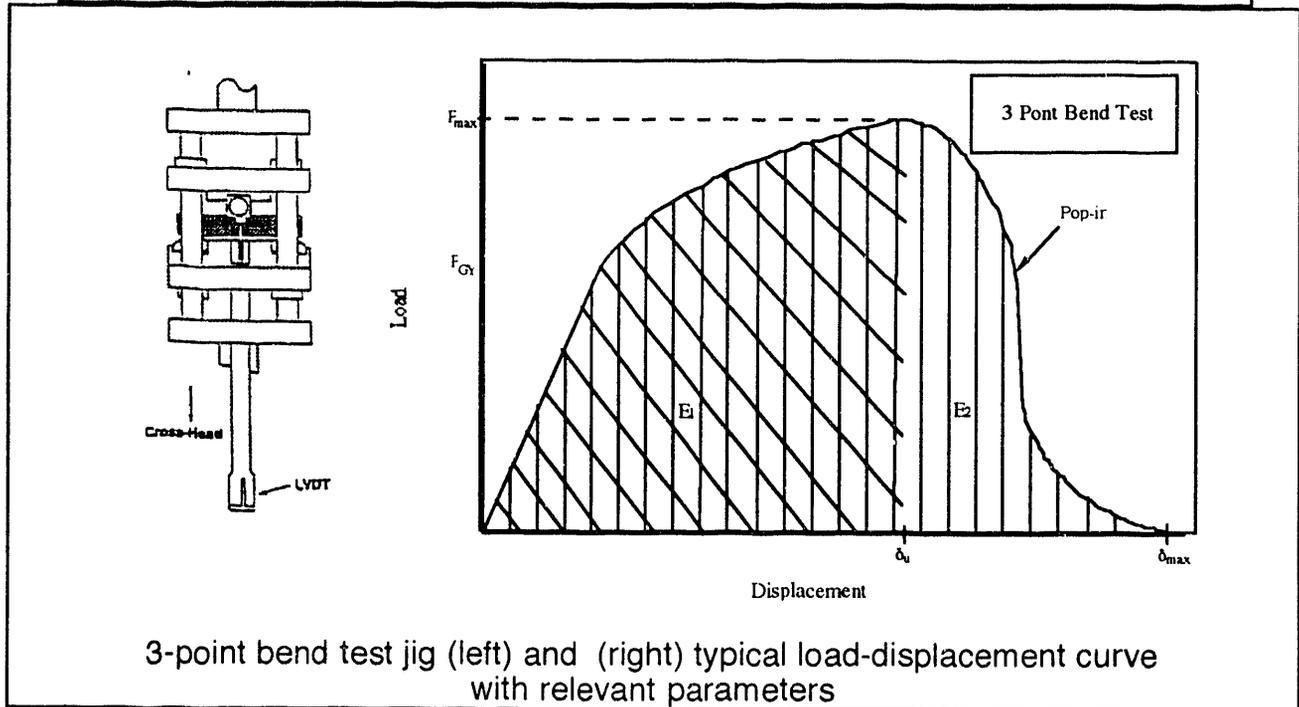
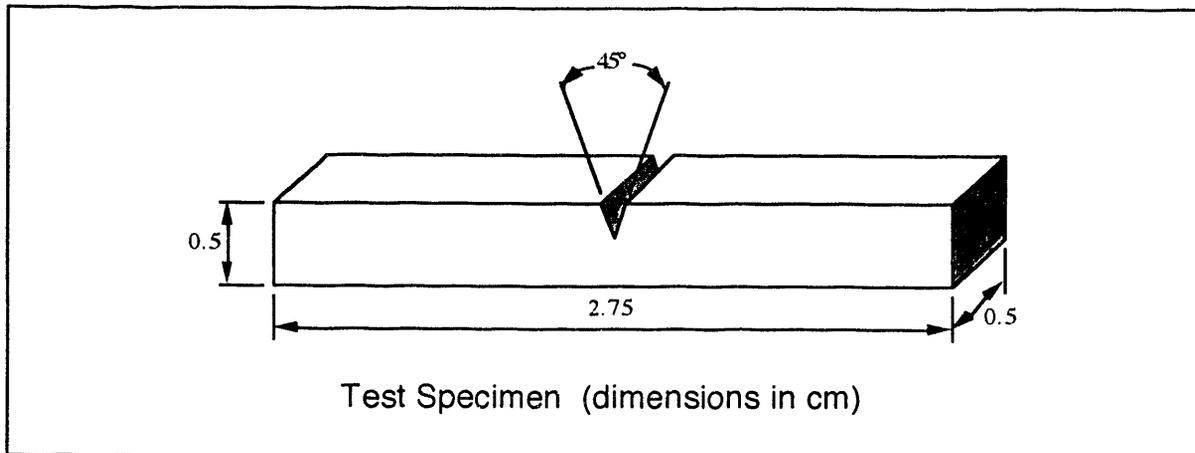


Figure 3
Schematic of Test Specimen and Three-Point Displacement Apparatus
with Typical Test Curve

III Results to Date

A misunderstanding on the starting date for the project lead to a delay in the research initiation. The project authorization was received from DOE in August 1992 and a call was then placed to DOE to establish the expected project start date. The project co-PI (Elleman) was informed that the project would likely start in January 1993 and this date was used as a guideline in the recruiting of students to work on the

project. On approximately October 10, notification was received through the University that the project had been initiated on September 30. Since the students were not available until the beginning of the year to work at the expected level, the work to date reflects closer to three months of activity rather than six months. The project is proportionately underexpended and it is hoped that some recovery of the missing time can be obtained by hiring the two research students on a full-time basis during the coming summer.

A. Literature search A detailed literature search on hydrogen effects in carbon steels has been completed. Much of this work was done in conjunction with a related project through Los Alamos to investigate literature results on corrosion processes in carbon steels and was pre-existing at the time of initiation of the DOE project.

B. Baseline Fracture Tests The test equipment portrayed in Figure 3 was used to establish load versus failure curves for notched A 516 test specimens. A typical experimental result is given in Figure 4. A pre-existing data base of load-failure curves has been established for A-516 specimens but it is anticipated that additional curves will be run to obtain a comparison of this data base with the current specimens.

A516 LOAD-DISPLACEMENT AT 300K

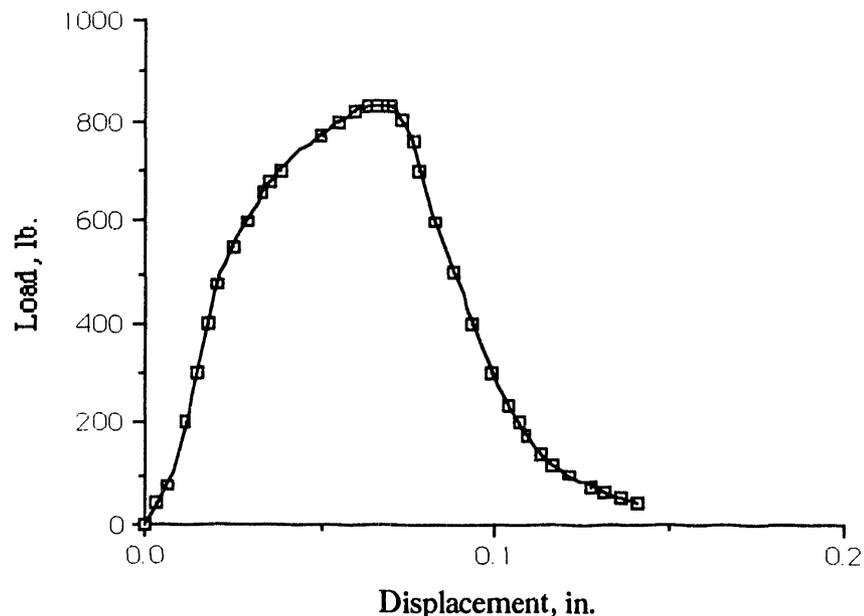


Figure 4
Experimental load-displacement curve for A516 steel

C. Sample Electropolishing 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.

D. Direct Sample Counting A 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.

E. Fracture Behavior of Irradiated Specimens Four specimens were irradiated in solution to an accumulated dose of 3.24×10^6 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. A second series of specimens that will be exposed to an accumulated dose of 2.52×10^7 rads are currently in the gamma source and will be tested over the next several weeks.

F. Tritium Uptake Measurements The first experiment to expose specimens to solutions containing tritium tracer during irradiation is currently underway. The specimen will be exposed to an accumulated dose of 8.4×10^6 rads, the specimen layers removed by electropolishing and the tritium concentrations in the removed layers measured. The tritium concentration in solution is $50 \mu\text{Ci/ml}$, which is about the lowest concentration at which it would be possible to measure hydrogen uptake. The experiment will help to establish whether higher specific activity tritium will be required

in future experiments.

In addition to the liquid scintillation counting of the polished layers, the specimen will be placed in the windowless proportional counter after each layer is removed and the polished surface counted. This will allow detection of the tritium atoms that are trapped in the newly forming oxide surface film and provide an alternate means for establishing the tritium profiles in the specimens.

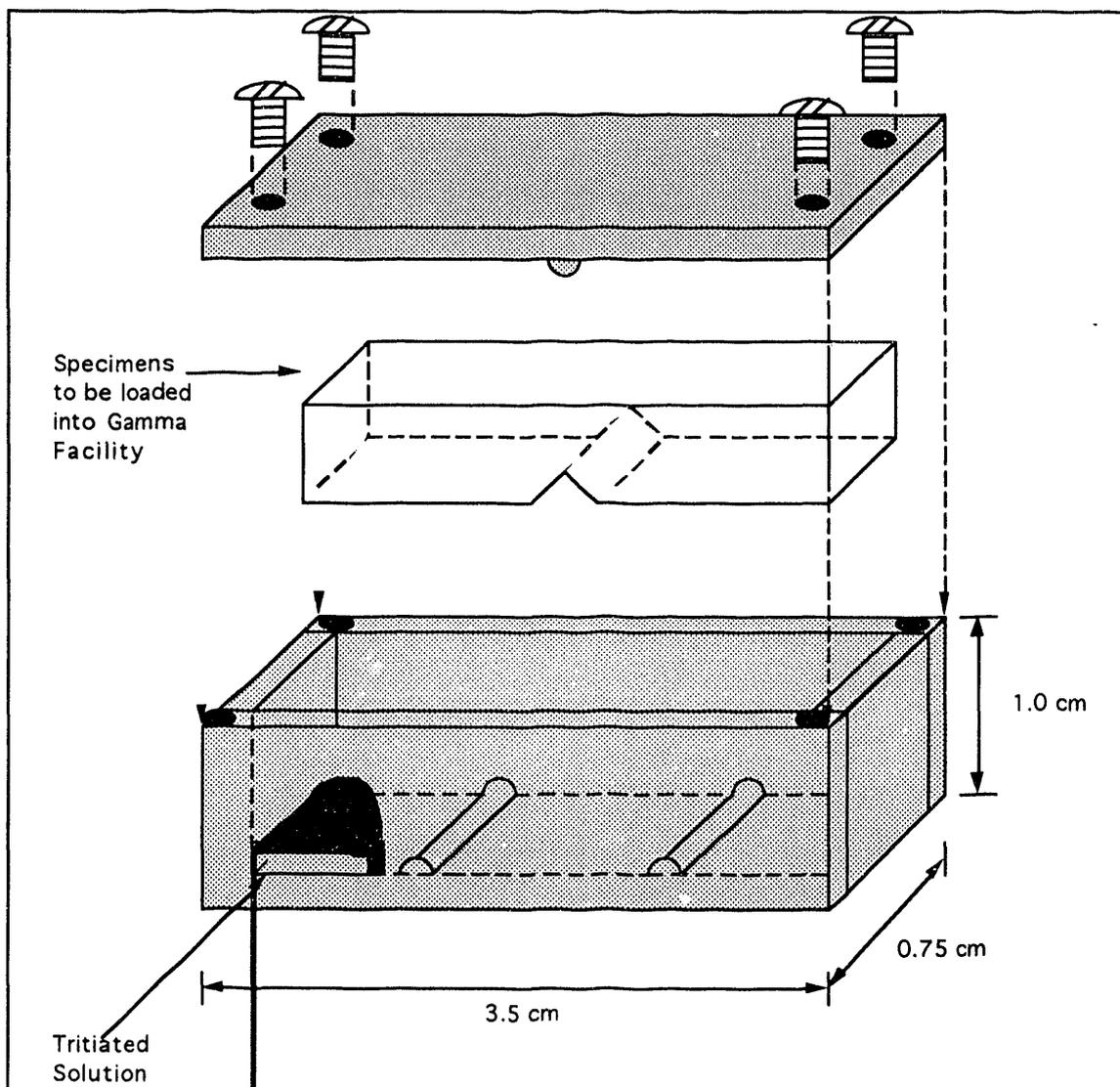


Figure 5

Design of holders for exposure of stressed samples

G. Irradiation and tritium-measurement of stressed-samples The fracture tests of the as-received samples clearly indicated that precracking of the notched specimens is required to reduce the load required for exposing stressed samples to tritiated solutions and gamma radiation. Figure 5 depicts the design of the holders for

tritium and radiation exposures of the stressed samples. In addition, the precracking of the 3-point bend samples will have uniform (sharp) crack fronts which are expected to yield more consistent fracture data. Thus plans are made to fatigue-precrack the 3-point samples prior to diffusion, irradiation and fracture studies (following essentially similar procedures as were previously developed at NCSU for studies on radiation embrittlement of pressure vessel steels).

IV Conclusions and Discussion

The results to date are too preliminary to draw any specific conclusions on radiation effects on hydrogen uptake. The fracture measurements made with specimens irradiated to absorbed doses of 3.24×10^6 rads did not show a change in yield strength but this dose is below the lifetime radiation exposures for tank alloys and the experiments were run at room temperature, a more restrictive condition for hydrogen uptake than is encountered by the tanks. What has been established to date is that the experimental methods for measuring the hydrogen gradients appear to be satisfactory and it will be necessary to conduct additional measurements before conclusions can be drawn.

Although the project was started only 5 months ago, good progress could be made mainly because we already have some of the required materials (A516 steel), hard-ware for fracture testing and the necessary facilities for gamma radiation exposure and also since we could identify 2 (of the 3) highly motivated students immediately at the commencement of the project. We anticipate many data and results within the next 10 to 12 months which should direct us to the future studies which are relevant for the understanding of the hydrogen effects on waste-tank steels.

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