IS 4742
UC 90

Alloy Evaluation for Fossil Fuel Process Plants (Liquefaction)

Quarterly Report for

Period

1 January, 1980 through 31 March, 1980

C. M. Woods and T. E. Scott

AMES LABORATORY

Iowa State University

Ames, Iowa 50011

April 15, 1980

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY
UNDER CONTRACT NO. W-7405-Eng-82, & NUMBER WPAS-AA-60-03-01

FOREWORD

This report covers work performed during the period 1 January, 1980 through 31 March, 1980. The work was funded by the Office of Advanced Research and Technology under the Assistant Secretary for Fossil Energy and was monitored by R. A. Bradley, Manager of Fossil Energy Materials Projects at Oak Ridge National Laboratory. The report was prepared by Charles M. Woods and T. E. Scott of the Mechanical Properties Section in the Metallurgy and Ceramics Division at the DOE-Ames Laboratory, Ames, Iowa.

The work was performed under the direction of Dr. Scott as principal investigator assisted by: C. M. Woods, S. Shei, C. V. Owen and L. K. Reed.

ABSTRACT

A potential drop vs. crack growth calibration curve for dynamically loaded compact tension specimens of A387-74A-Gr.22-Cl.2 steel was established. Fatigue crack growth rates (da/dN) were determined for a wide variation of stress intensity range values (ΔK). Testing was done in moist air ($\sim$ 30% RH) at ambient temperature and pressure. Near-threshold to rapid crack growth stages were examined.

Corrosion specimens of A387-74A-Gr.22-Cl.2 steel were exposed to a coal slurry environment at 800°F, 4000 psig total pressure for 24, 48, 72 and 240 hours. Corrosion scale growth rates and micrographs of the scale region are presented.

OBJECTIVE AND SCOPE

The objective of this program is to evaluate the mechanical properties of liquefaction process plant "dissolver" vessel materials in a "dissolver" vessel environment including coal slurry and pressurized hydrogen gas at temperatures up to 800°F. Originally, the intent was to test at 900°F but we soon learned that above 850°F (455°C) gasification is ignited giving coke and methane. Consequently, all runs originally indicated as 900°F will be run at 800°F to assure there are no excursions above the critical gasification ignition temperature.

Specifically, the degradation of notched-bar and smooth-bar tensile samples of 2 1/4 Cr - 1 Mo will be monitored as a function of exposure time and stress in the "dissolver" vessel environment. Compact tension specimens will be used to monitor the degradation of fracture properties in the "dissolver" vessel environment.

Progress Summary

I. Fracture Mechanics Tests

A. Procedure and Results:

An electropotential measurement system for monitoring crack growth in dynamically loaded compact tension specimens was constructed. The system incorporates an SCR-Norbatron constant current power supply with a Keithley Model 174 digital multimeter interfaced to a Keithley Model 750 printer (Fig. 1). Excitation current to the specimen is switched on and off by means of a battery driven relay. This enables potential drop measurements across the crack to be made at preset intervals with the excitation current

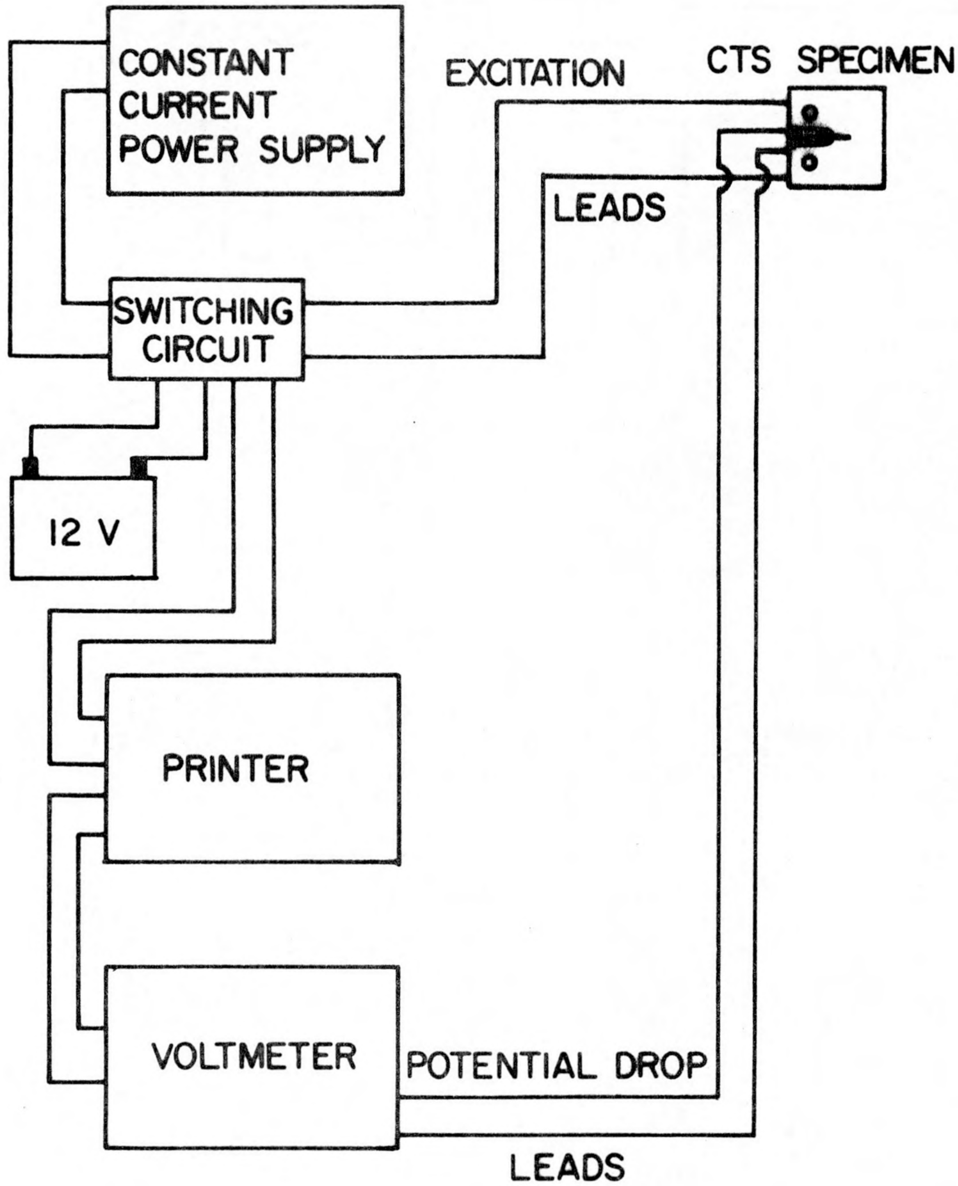


Fig. 1: Block Diagram of Electropotential Measurement System.

both on and off. The difference between the two measurements is taken as the true potential drop across the crack. This allows elimination of thermal potentials and other transients. The relay is activated by a Darlington transistor switching circuit that has been appropriately interfaced with a switching circuit in the printer. The printer circuit switches from lo to hi and back to lo again as the printer cycles through a double print phase. The printer can be cycled every 2 to 120 seconds depending on the time increment desired for making the potential drop measurement. The excitation current is 5 amps. The sensitivity of the multimeter is ±0.1 μV which corresponds to a resolution of crack growth of ∿ ±0.5 mils. The system stability has been determined to be better than ±0.2 μV per day after warm-up which gives a resolution of better than ±1.0 mil of crack growth increment. Calibration of the crack growth measurement system will be subsequently described.

Compact tension specimens (CTS) (Fig. 2) were prepared from a 0.75 inch thick hot rolled plate of A387-74A-Gr.22-Cl.2 steel. The starter notch was machined perpendicular to the rolling direction (ASTM specification E-399, L-T type specimen). The surface of the specimens was mechanically polished to 600 grit. Two specimens were precracked to a total crack length, 'a' (as measured from the load line to the tip of the precrack), of 0.85 and 1.33 inches respectively using an MTS-series 810 electrohydraulic test system. The precracking was done in load control. The frequency was 20 Hz. and the loading was sinusoidal in a tension-tension mode with the minimum load controlled at 10% of the maximum load. The maximum load criterion was derived as shown in the following analysis. The ASTM E-399 fatigue precracking procedure requires that —

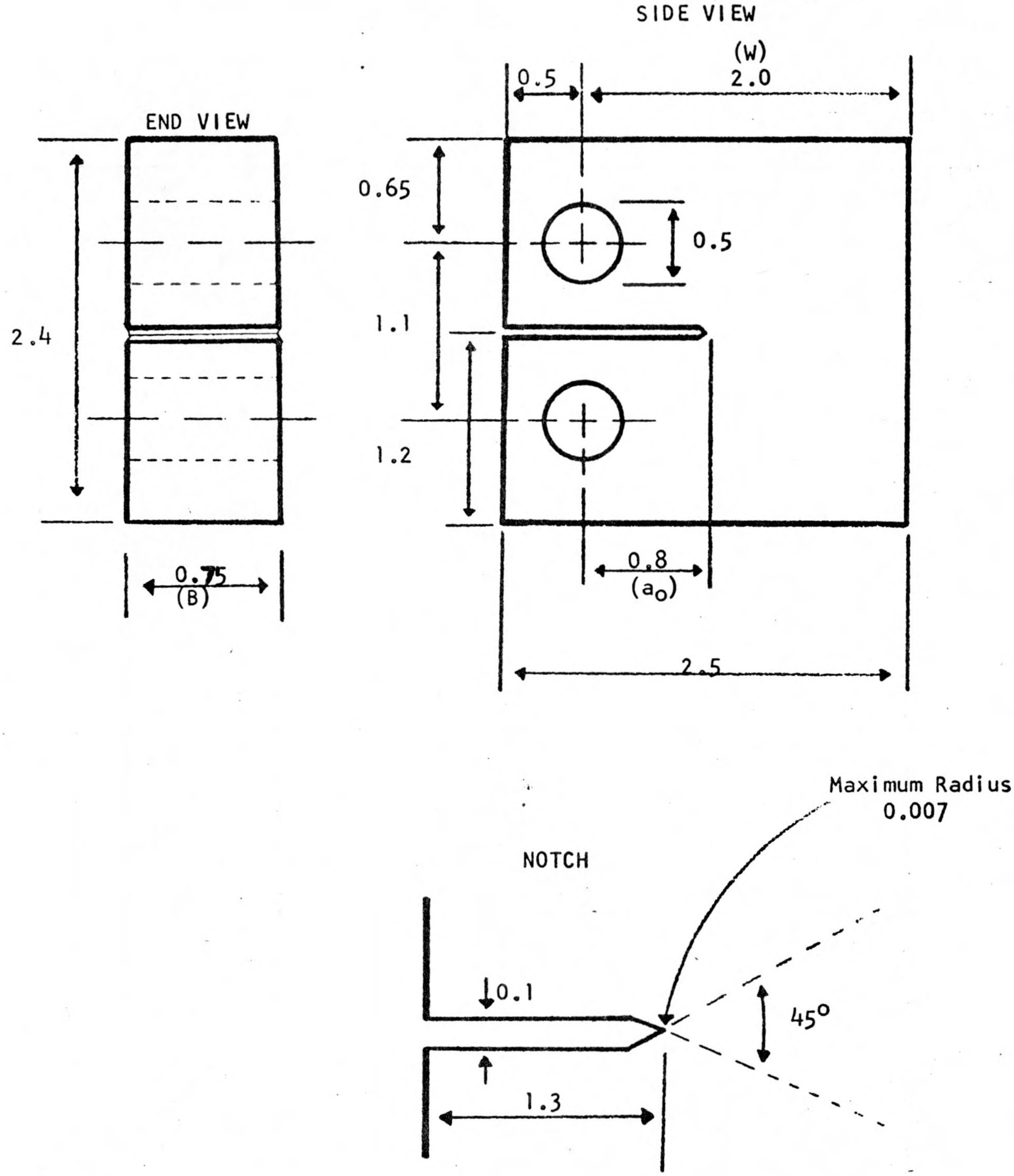


Fig. 2: 2 1/4 Cr-1 Mo Compact Tension Specimen. All dimensions are in inches.

$$K_{f\ max} \leq 0.002\ E\sqrt{in}\ .$$

However for the CTS, K_f is given by —

$$K_f = (P/B\sqrt{a})\ f(\frac{a}{W})\ .$$

Rewriting the preceding equation in terms of maximum load gives —

$$P_{max} = \frac{K_{f\ max}(B\sqrt{a})}{f(a/w)}\ .$$

Inserting the ASTM E-399 condition for $K_{f\ max}$ as given above leads to the maximum load criterion —

$$P_{max} \leq 0.002\ E\ (\frac{B\sqrt{a}}{f(a/w)})\ ,$$

where, $K_{f\ max}$ = maximum stress intensity of the fatigue cycle

E = Young's modulus

P = load

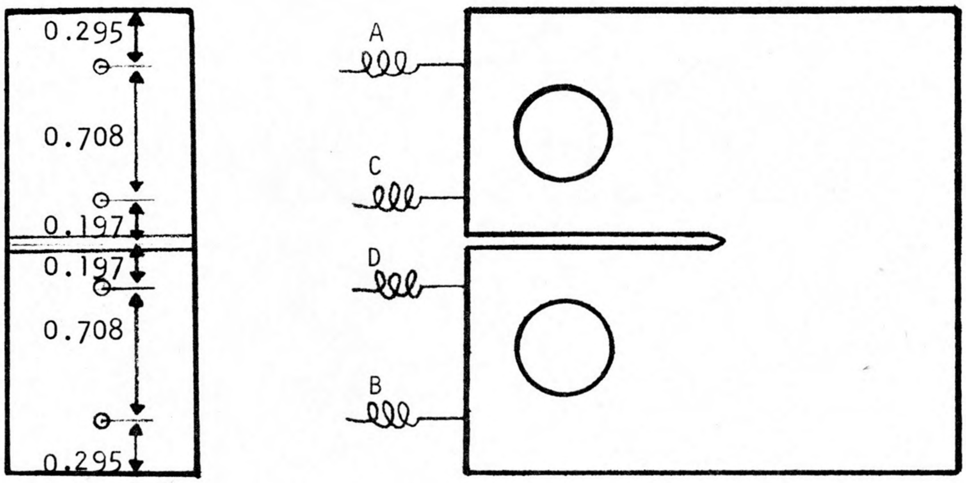
B = specimen thickness

a = crack length

$f(a/w)$ = measure of the compliance of the specimen .

P_{max}, for each of the two specimens, was chosen as the greatest value of load that satisfies the inequality at 'a' equal to 0.85 and 1.33 inches respectively.

Excitation current was applied by attaching copper leads to two threaded holes positioned one on each side of the notch at the notch end of the specimen (Fig. 3). The holes were drilled and tapped at the center of the thickness dimension (B) at 0.295 inches in from the outer edge of the specimen. Potential drop measurements were made by attaching leads to two



A & B - Excitation Leads

C & D - Potential Drop Leads

All dimensions in inches

Fig. 3: 2 1/4 Cr-1 Mo Compact Tension Specimen showing position of excitation and potential drop leads.

threaded holes, one on each side of the notch, positioned at the center of the thickness dimension and 0.197 inches out from the notch center (Fig. 3).

Each specimen was cycled in load control at 20 Hz. for ΔK values never exceeding 40 ksi $\sqrt{in}$. ΔK was calculated as follows:

$$\Delta K = (P_{max} - P_{min}) \frac{f(a/w)}{B\sqrt{a}}$$

where,

P_{max} = maximum load of fatigue cycle

P_{min} = minimum load of fatigue cycle .

The load cycling was stopped after each 10 μV change ($\sim$ 3 μV for the second specimen) in the potential drop measurement and the crack size was measured on the surface of the sample. A plot of Va/Va_0 vs a/a_0 is presented in Fig. 4 for both specimens. It is apparent that the curve is linear, reproducible and independent of initial crack length. The slope of the calibration curve is shown to be 0.861.

Fatigue crack growth rates (da/dN) were determined as a function of stress intensity range (ΔK) in moist ($\sim$ 30%RH) air at ambient temperature and pressure. A compact tension specimen was precracked to a total crack length of 0.85 inches using the procedure outlined above. The precracked specimen was then cycled at 20 Hz. in load control at a ΔK value of 10 ksi $\sqrt{in}$. The loading was sinusoidal with P_{min} controlled at 10% of P_{max} ($R=0.1=P_{min}/P_{max}$). The loading was carried out until the crack growth rate was detected to be uniform over moderate periods of time. This assured that the plasticity ahead of the crack due to the precracking procedure would not affect the determination of the stress intensity threshold (ΔK_{TH}).

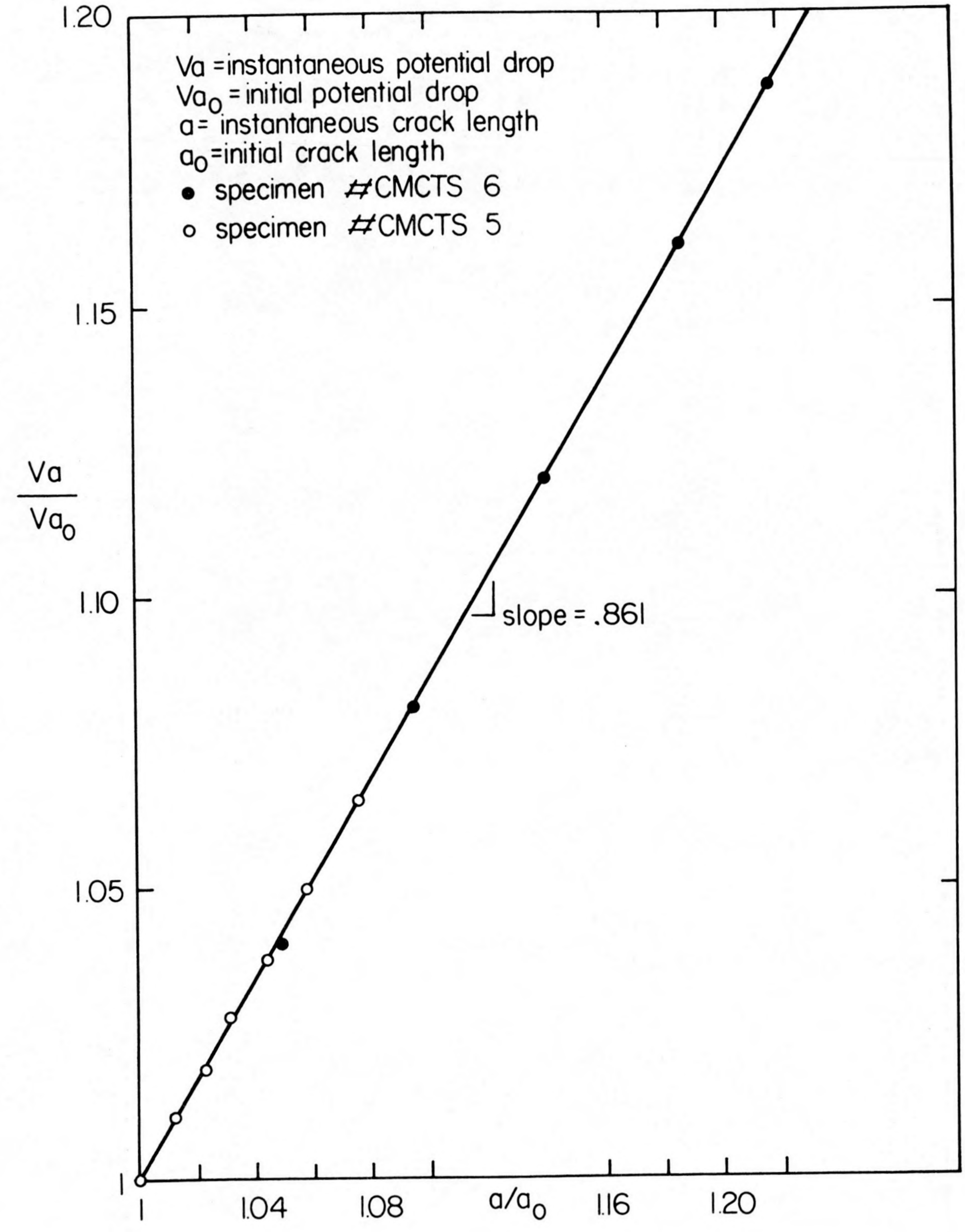


Fig. 4: Normalized potential drop vs. crack growth calibration curve for 2 1/4 Cr-1 Mo, .75T- Compact Tension Specimen.

The stress intensity range was decreased in 10% increments until crack growth could not be detected in 2 x 10^5 cycles. Since the resolution of the crack growth measurement system is ∿ ±1 mil, this corresponds to a crack growth rate of 5 x 10^{-9} in./cycle. This was termed the stress intensity threshold. ΔK_{TH} was determined to be 8.5 ksi $\sqrt{in}$ in moist air at ambient temperature and pressure. Fatigue crack growth rates were then determined for ΔK values ranging from threshold to ∿ 40 ksi $\sqrt{in}$. The results were plotted as log da/dN vs log ΔK (Fig. 5).

II. Corrosion Tests

A. Procedure:

Cylindrical corrosion specimens (Fig. 6) were prepared from longitudinal (parallel to the rolling direction) sections of the plate. One group each of 4 specimens was placed in a pressure vessel and subjected to one of the following exposures: 24, 48, 72 or 240 hours in a coal slurry and hydrogen gas environment at 4000 psig pressure at 800°F. The coal slurry was a blend of 35 volume percent of -100 mesh Kentucky bituminous (Proximate Analysis, wt.pct.: Moisture, 6.1; Ash, 15.5; Volatile Matter, 36.3; Fixed Carbon, 42.1) and 65 volume percent solvent. The sulfur content of the coal was 5.53 wt.pct. The solvent was centrifuged Synthoil product (Ash free wt.pct.: Organic benzene insols, 3.3; asphaltenes, 32.3; Oils, 64.4) from PERC Run FB-61 made from the coal described above. The coal and solvent were graciously supplied by Paul M. Yavorsky of PERC. The slurry was prepared by mixing the fine coal in the solvent which, because of its high viscosity (161 SSF at 180°F) at room temperature, was preheated to 110°F.

Two samples of each group were immersed in the coal slurry, which was

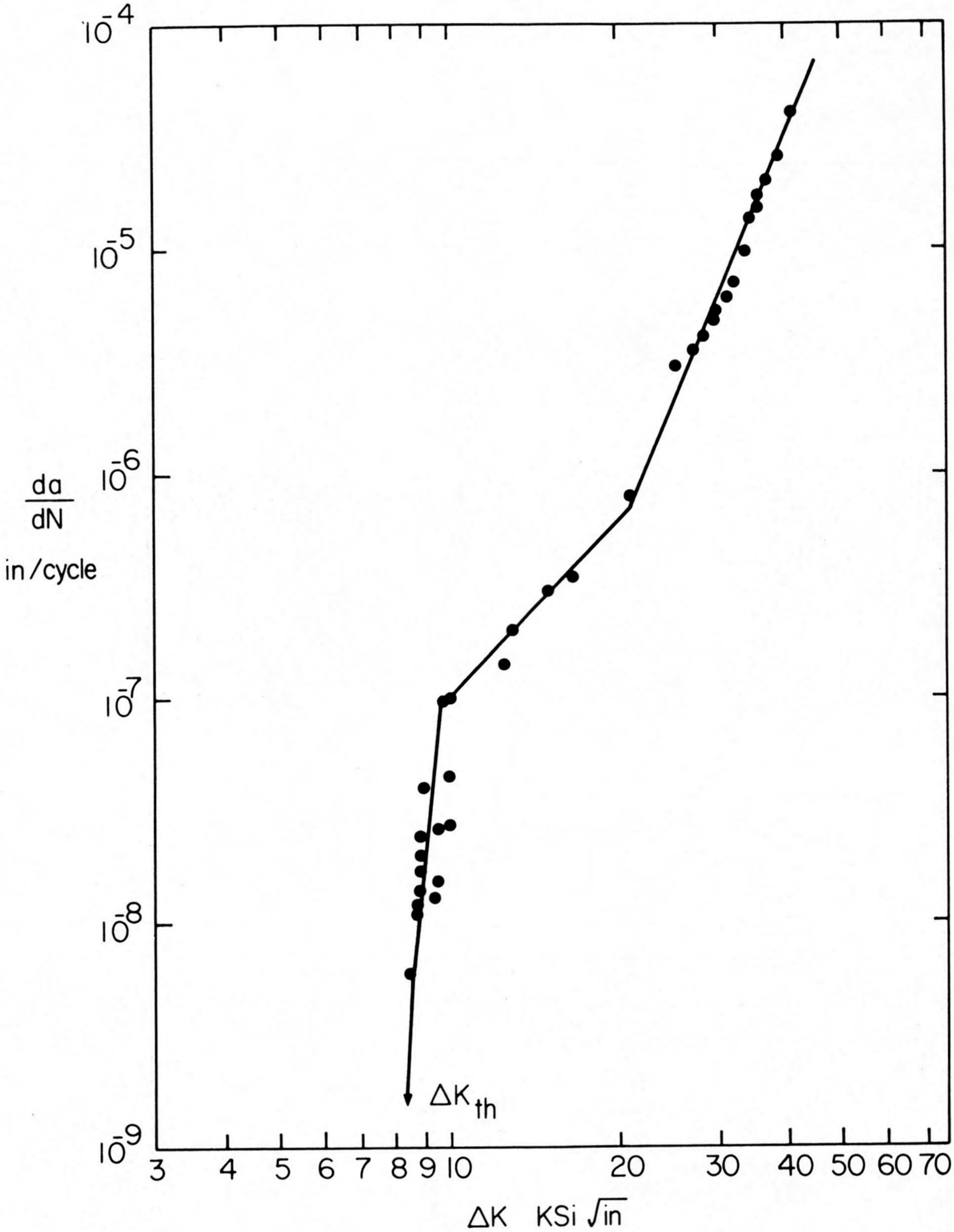


Fig. 5: Fatigue crack growth rate curve for 2 1/4 Cr-1 Mo steel in moist air (~30% R.H.) at ambient temperature and pressure.

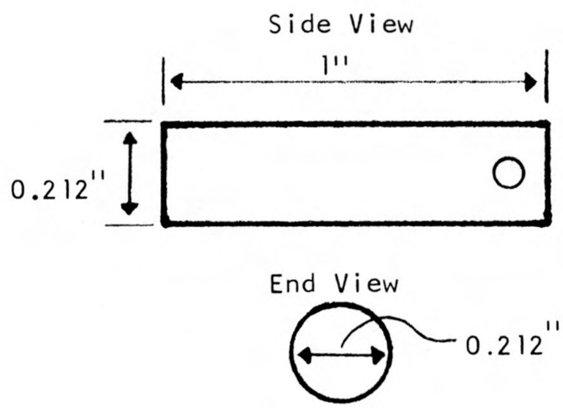


Fig. 6: 2 1/4 Cr-1 Mo Steel Corrosion Specimen.

contained inside a 304 stainless steel can, and the remaining two samples were suspended in the gaseous phase above the slurry. The can was then placed inside one of the specially designed H_2 pressure vessels for subsequent pressure and temperature equilibration. The samples were exposed to conditions given above during which time the total pressure was controlled within ± 100 psig of the required pressure. The temperature fluctuations were ± 10°F.

At the end of each exposure the samples were removed from the pressure vessel, cleaned with acetone and mounted in conducting Bakelite. The samples were then ground and polished to Linde B (.05 micron particle size Al_2O_3). Care was taken to keep the sample surface parallel to the Bakelite base. The scale thickness was then microscopically measured. The measurements were done on the ends of the samples to assure measurement of a perpendicular cross section. Six measurements of each specimen were made at random and the values for each two like specimens (i.e. gas phase or slurry immersion exposures) were averaged. Micrographs were then made of each set of samples.

B. Results:

Results of the corrosion tests are given in Figs. 7 through 13. A linear plot of scale thickness vs. exposure time (Fig. 7) shows what appears to be a parabolic growth rate curve. However, when the data are plotted as scale thickness vs log time (Fig. 8) the result is a straight line. The scale thickness of a smooth-bar tensile specimen immersed in the slurry and exposed to the same exposure conditions for 856 hours falls on the log t vs thickness line for the specimens that were suspended in the slurry gases.

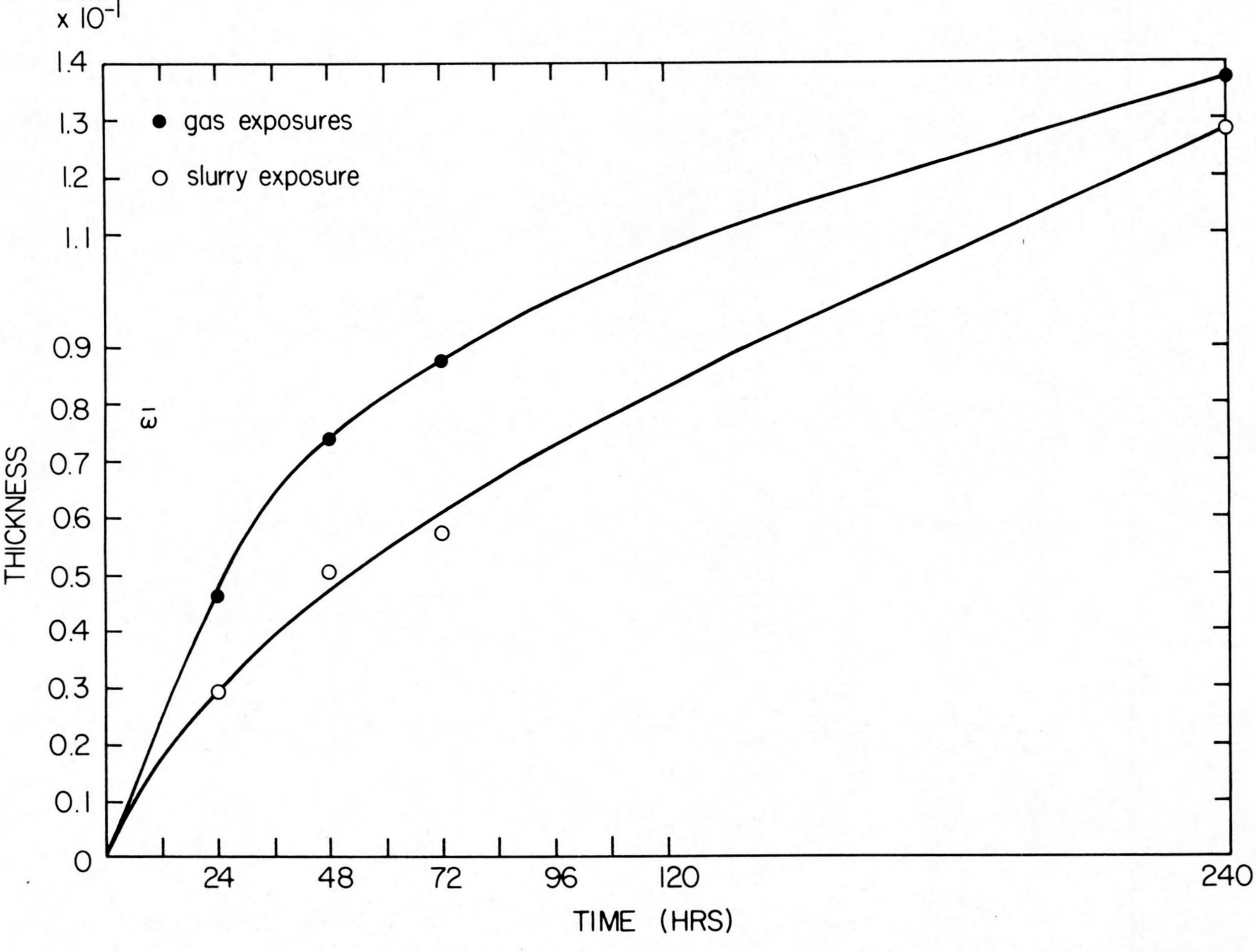


Fig. 7: Surface scale thickness vs. time plot for 2 1/4 Cr-1 Mo steel exposed to a coal slurry-H_2 environment at 800°F and 4000 psig total pressure.

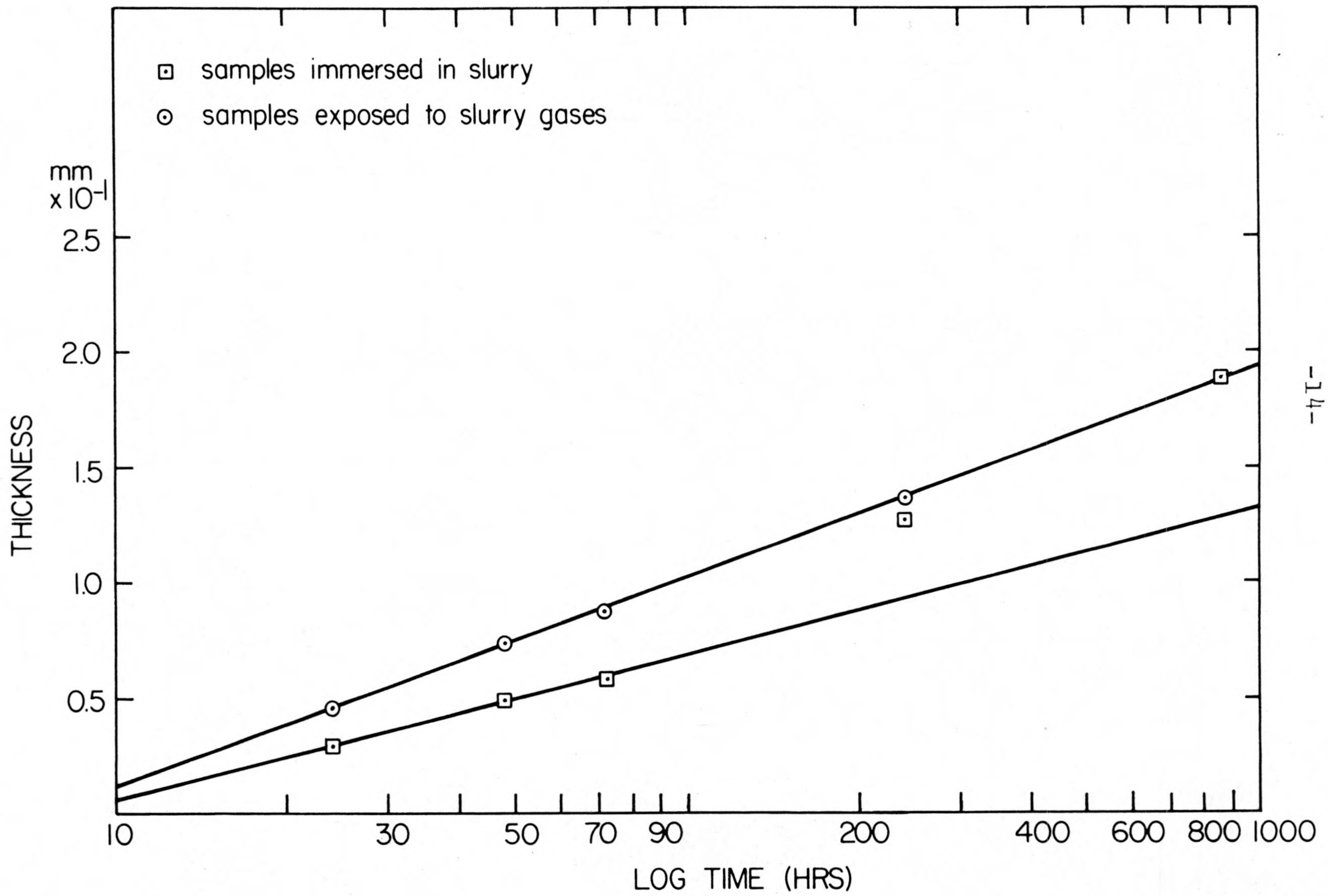


Fig. 8: Surface scale thickness vs. log time plot for 2 1/4 Cr-1 Mo steel exposed to a coal slurry-H_2 environment at 800°F and 4000 psig total pressure.

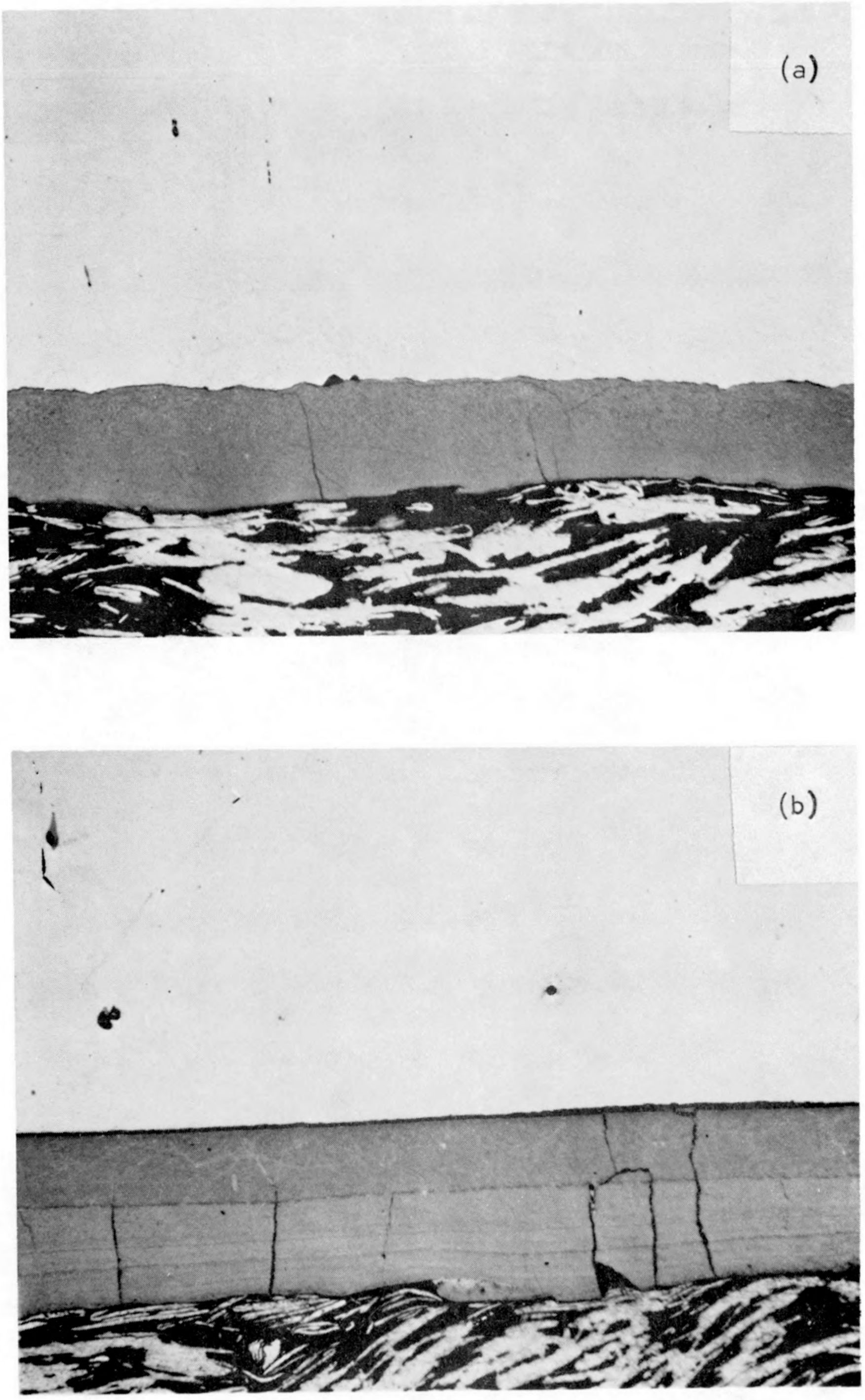


Fig. 9: Surface scale region of 2 1/4 Cr-1 Mo steel exposed to a coal slurry-H_2 environment at 800°F, 4000 psig pressure for 24 hours. a.) Immersed in slurry. b.) Suspended in gas phase. (500X)

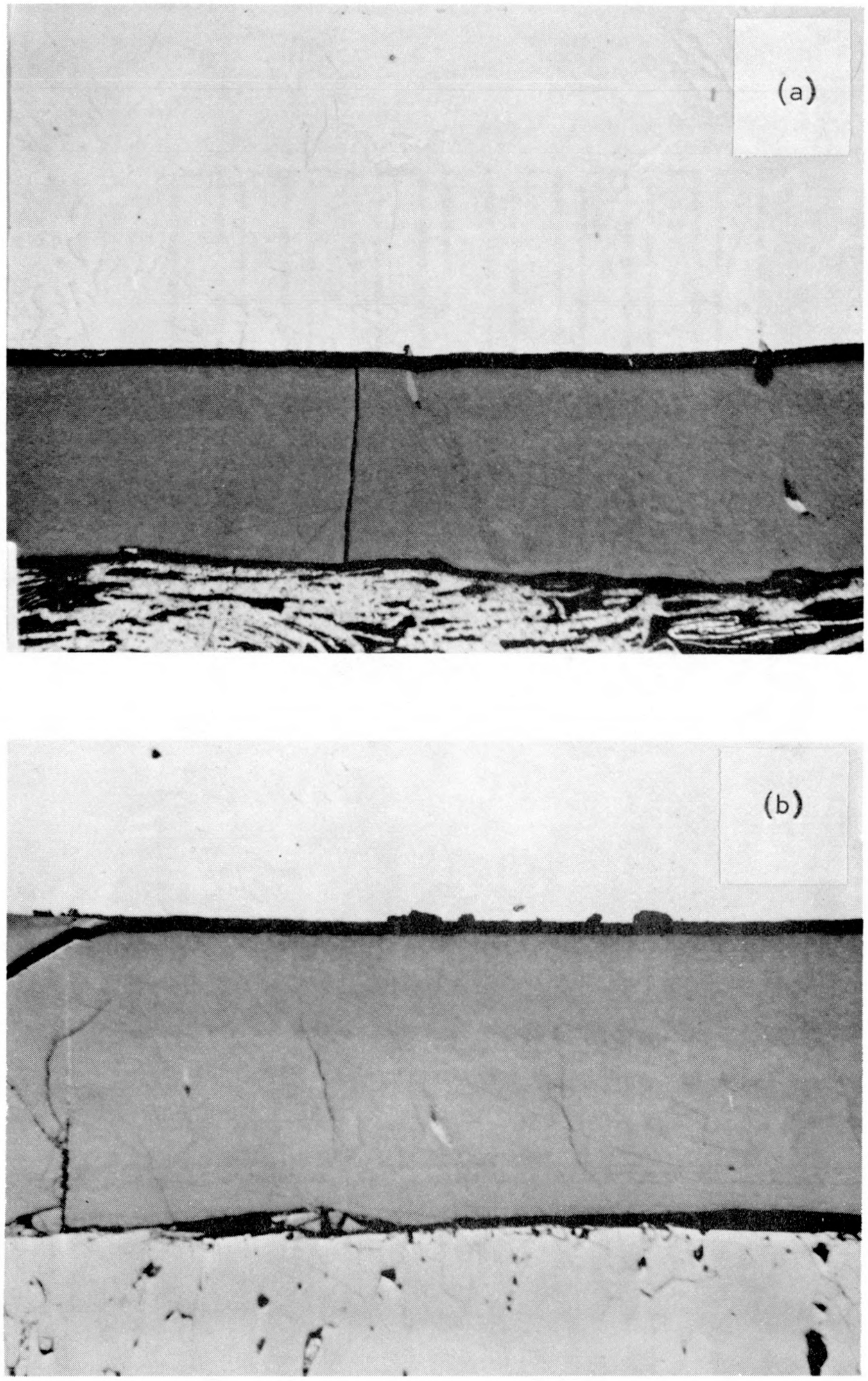
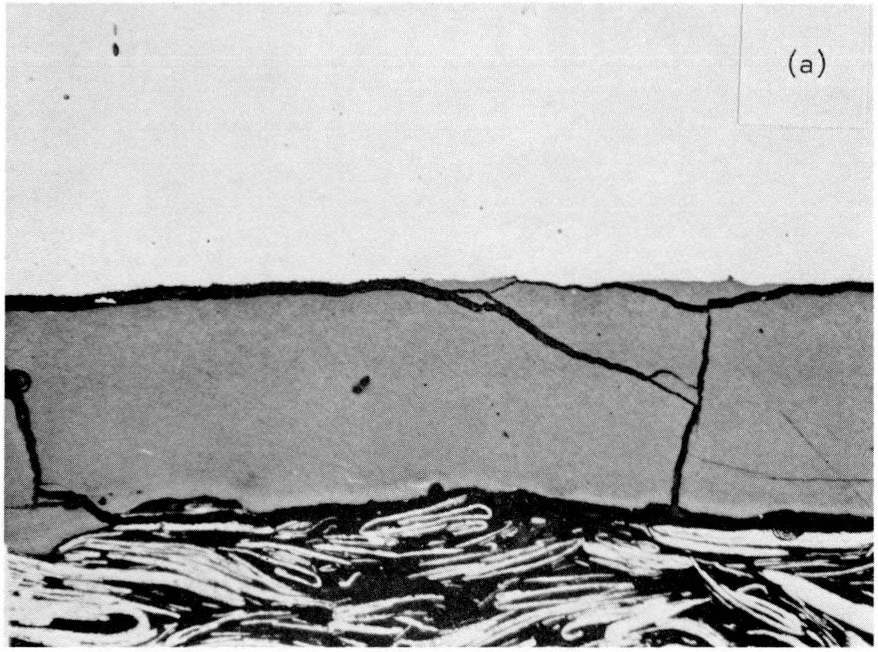


Fig. 10: Surface scale region of 2 1/4 Cr-1 Mo steel exposed to a coal slurry-H_2 environment at 800°F, 4000 psig pressure for 48 hours. a.) Immersed in slurry. b.) Suspended in gas phase. (500X)



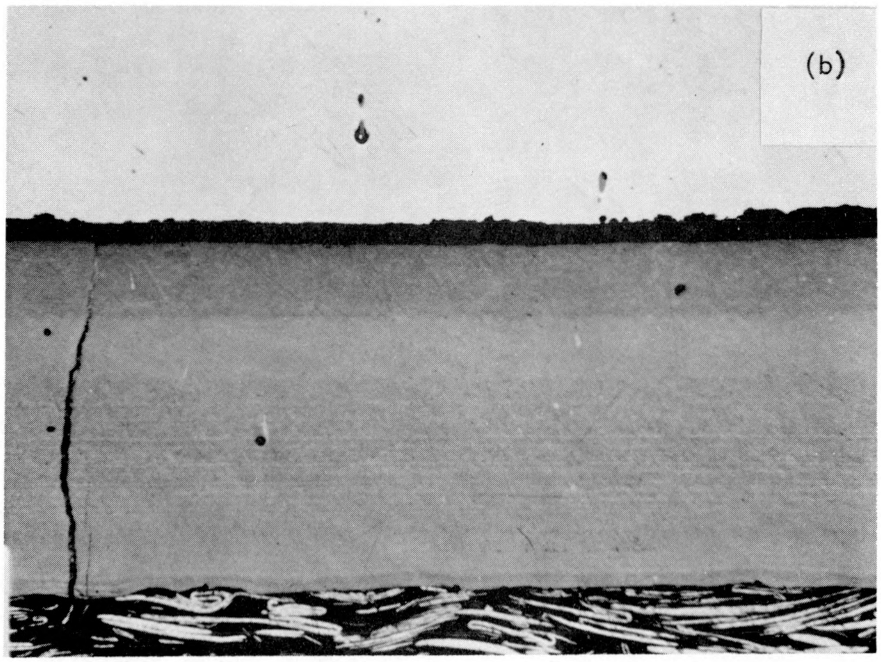


Fig. 11: Surface scale region of 2 1/4 Cr-1 Mo steel exposed to a coal slurry-H_2 environment at 800°F, 4000 psig pressure for 72 hours. a.) Immersed in slurry. b.) Suspended in gas phase. (500X)

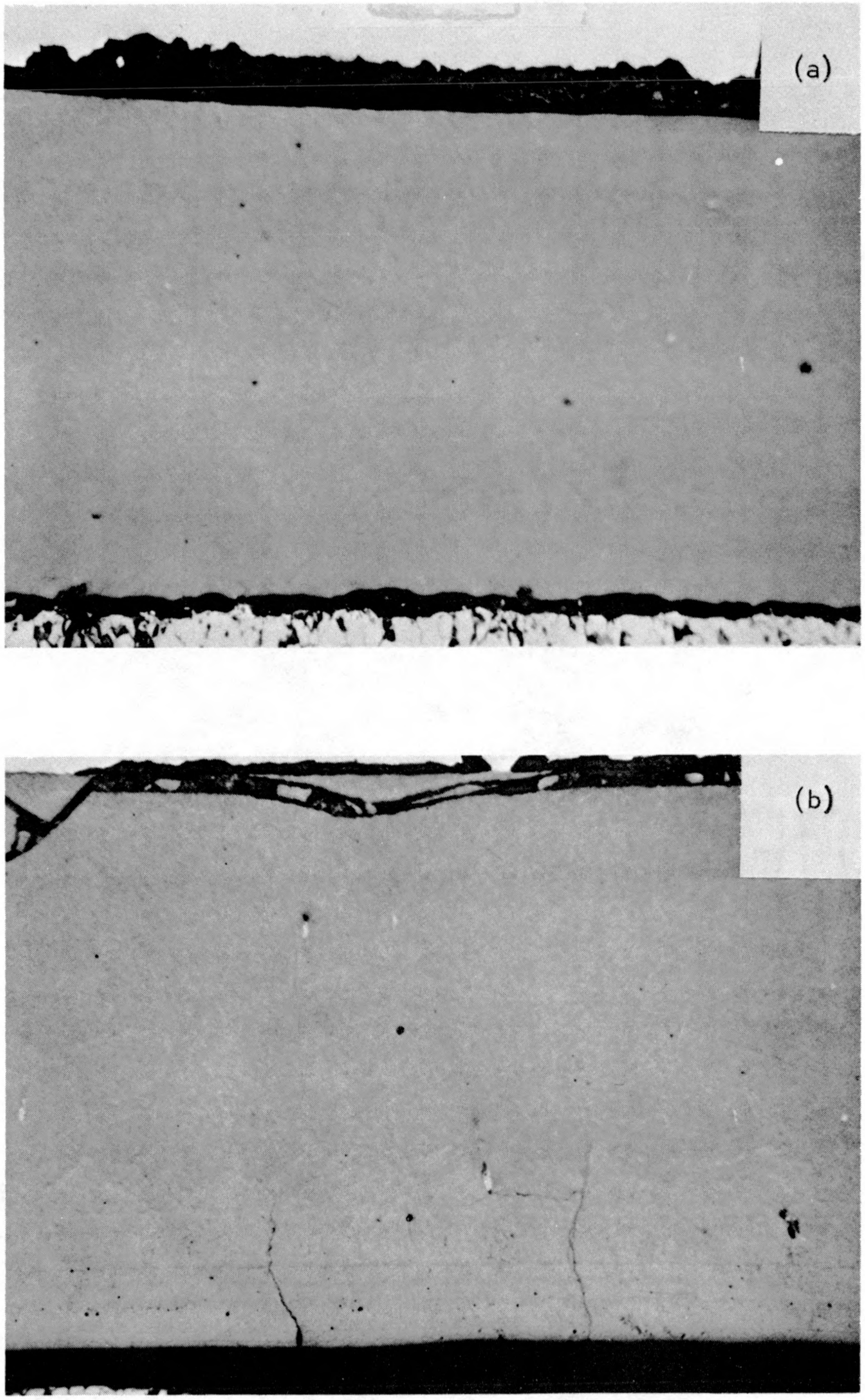


Fig. 12: Surface scale region of 2 1/4 Cr-1 Mo steel exposed to a coal slurry-H_2 environment at 800°F, 4000 psig pressure for 240 hours. a.) Immersed in slurry. b.) Suspended in gas phase. (500X)

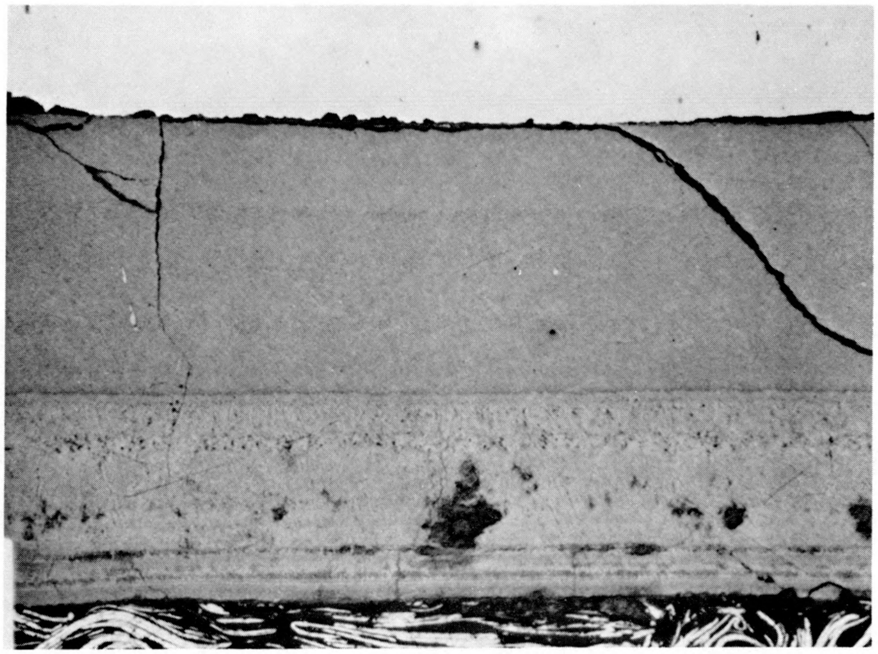


Fig. 13: Surface scale region of 2 1/4 Cr-1 Mo steel exposed to a coal slurry-H_2 environment at 800°F, 4000 psig pressure for 240 hours. The specimen was suspended in the slurry gas phase. Different regions of scale composition can be seen. (500X)

Also, the 240 hour slurry immersed samples show scale growth only slightly less than the 240 hour suspended samples whereas the 24, 48, and 72 hour tests show markedly slower scale formation rates in the slurry phase than in the slurry gas phase (Fig. 8).

It has been our experience that during the course of the first 168 hours of 800°F exposures to the coal slurry environment, the slurry undergoes marked changes as the heavy viscous portions of the slurry react with the hydrogen to form lighter fractions. These light fractions cause an increase in pressure above the upper pressure control point and get vented off via the pressure release system. After about 168 hours the system stabilizes and remains reasonably constant in pressure. What is then present is a mixture of slurry gases, H_2, some light liquids and coke. Therefore, for the short time exposures, the mobility of the corrosive species is probably hindered by the heavy viscous fractions of the slurry and results in slower scale formation rates. As the viscous fractions are converted to light fractions, the mobility of the corrosive species increases which results in an increase in the scale formation rate approaching that in the gaseous phase. The scale formation rate is seen to be a logarithmic function of the exposure time in both phases (Fig. 8).

WORK FORECAST

Fatigue crack growth studies in hydrogen are presently underway. Crack growth studies under static and dynamic loading will be performed in the coal slurry gaseous environment. Scaling studies at lower temperatures will be performed to see the results of the heavy viscous environment on scale formation rates. Electron microprobe analyses will be completed on all exposures run to date to map out scale composition as a function of exposure time.

Distribution List for Technical Reports

Name and Address

S. J. Dapkunas (2)
Department of Energy
Div. of Planning and Systems Engineering
Mail Stop C-156 (GTN)
Washington, D.C. 20545

R. A. Bradley, Manager (4)
Fossil Energy Materials Project
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

S. J. Schneider (2)
National Bureau of Standards
Department of Commerce
Washington, D.C. 20234

E. E. Hoffman, Chief (1)
Energy Materials and Systems Branch
Oak Ridge Operations Office
Department of Energy
P. O. Box E
Oak Ridge, TN 37830

Richard Schorr (1)
Battelle Columbus Lab
505 King Avenue
Columbus, OH 43201

R. P. Wei (1)
Lehigh University
Center for Surface and Coatings Branch
Bethlehem, PA 18015

Dilip Bhandarkar (1)
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

D. Canonico (1)
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

Technical Information Center (245)
Department of Energy
Oak Ridge, TN 37830

J. Slaughter (1)
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

W. J. Lochmann (1)
The Ralph M. Parsons Co.
100 West Walnut Street
Pasadena, CA 91124

G. Sorell (1)
Exxon Research and Engineering Company
P. O. Box 101
Florham Park, NJ 07932

William E. Erwin (1)
Engineering Department
Standard Oil Company of California
P. O. Box 1272
Richmond, CA 94802

G. Catus (1)
109 Office & Laboratory
Ames Laboratory
Iowa State University
Ames, IA 50011

R. Fisher (2)
321 Spedding
Ames Laboratory
Iowa State University
Ames, IA 50011

T. Scott (5)
126 Metals Development Building
Ames Laboratory
Iowa State University
Ames, IA 50011

Charles M. Woods (10)
204 Metals Development Building
Ames Laboratory
Iowa State University
Ames, IA 50011

Burton Gleason (10)
201 Spedding
Ames Laboratory
Iowa State University
Ames, IA 50011