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MATERIALS RESEARCH AND EVALUATION FOR GEOTHERMAL CORROSION ENVIRONMENTS

Progress Report
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MASTER

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ABSTRACT

Bent beam and self-stressed specimens have been employed and shown to give results consistent with other types of specimens as reported in the literature. All tests have been conducted in the standard NACE, H_2S environment for initial screening and then in a 20% NaCl modified NACE solution.

Among the higher strength corrosion resistant alloys, K Monel at 135 ksi Y.S. did not fail in either environment at temperatures up to 425°F stressed at the Y.S. Age hardenable A286 failed at 325°F when stressed to the 190 ksi Y.S., but did not fail when stressed to an overaged Y.S. of 135 ksi. A new NiCoCrMo age hardenable alloy heat treated to 220 ksi Y.S. and stressed to this value did not fail in either environment at temperatures up to 420°F. Also, this material was substantially "brighter" after the tests than either the K-Monel or A286.

As we examine the first year's work plan, as might be expected we are slightly behind schedule in some areas and ahead of schedule in others. Specifically, a complete and current file of pertinent literature has been compiled. This includes not only the rather limited information dealing with materials' problems in geothermal power systems but also the voluminous literature involving material behavior in sour deep oil and gas well environments which are quite similar to those encountered in geothermal holes.

Two autoclaves, one Hastalloy and one Inconel 600 have been purchased and are operating at temperatures up to 425°F. Other non-pressurized systems for handling the environment have been developed and are operating.

The particular environment for the early screening tests is the NACE standard solution for sour environments which is a completely deaerated aqueous solution of 5% NaCl, 0.5% acetic acid saturated with H_2S. This solution has been widely used for evaluating materials in sour environments and thus there is a vast storehouse of information on almost all commercially available alloys with standard treatments. Geothermal environments vary widely and no one solution can serve for total evaluation. However, those material situations that successfully pass the standard solution are then subjected to a modified NACE solution with 20 percent NaCl, which is likely to be more aggressive for many alloys and certainly will better match the high chloride contents of most geothermal holes.

The use of H_2S is a dangerous business at best and many precautions must be taken, some of which involve substantial expense. The situation is difficult enough with mature and trained personnel and with students even greater and continued vigilance is necessary.

Screening tests for both the commercial constructional and high strength corrosion resistant alloys are in progress at both ambient and elevated temperatures. These alloys have been furnished largely by Armco Steel Corporation, a subcontractor, who not only supplies the alloys but characterizes them and fabricates them into forms suitable for the preparation of test specimens.

Test specimens have been mostly of the two point bend type, usually loaded to 100 percent of the design yield strength. The use of this type of test is illustrated in Fig. 1. One advantage of this test aside from its simplicity and the relatively low cost type of specimen rests in the fact that there is virtually no crevice corrosion.

Another type of test specimen to be increasingly employed in future tests of the more promising alloys is the self-stressed type bend specimen shown in Fig. 2. Clearly, this configuration is susceptible to crevice problems which can be circumvented by protecting the crevice from the environment. However, this test is particularly interesting because it will allow a semi-quantitative measure of the influence, if any, of environment exposure for specimens that do not fail in the NACE adopted standard of 30 days exposure.

Obviously, 30 days is arbitrary but tests must end in a reasonable time to gather any substantial amount of data. In Fig. 2A the unexposed specimen was compressed in the arrow direction until a crack was observed. Specimen B had been exposed 32 days in the NACE solution at ambient temperature without failure. However, it is evident that it had lost much of its toughness, as indicated by the reduced deformation it could sustain prior to the incidence of cracks. At this time no one can say whether or not this indicates impending failure at longer exposure times. An interesting question which should be examined further but is somewhat outside our immediate objectives.

One of the major problems with sour environments is the limitation on usable alloy strength. It is well known that for constructional type steels, the susceptibility to H_2S environments increases dramatically as one exceeds yield strengths of 80-90,000 psi, and even at these low strengths complete reliability does not exist. Thus, as indicated in the original proposal, perhaps the single most important objective of this study is to evaluate the use of existing commercial as well as newly designed alloys at higher yield strengths or even at moderate levels with greater reliability.

Commercial or near commercial materials currently on hand and under study include 4120, 4130, 4140, 4135 (climax modified), 410, 431, 440, A286 stainless, K Monel 500, and MP35N.

Although the data are not complete enough to allow a systematic listing in tabular form, several tentative but significant features are beginning to emerge. The most necessary early determination is that our bend type specimens are yielding data for commercial alloys in the standard NACE solution at ambient temperatures that are completely consistent with the literature particularly with respect to strength and applied stress. Specifically, steels 410, 440, and 431, which represent petroleum industry attempts to achieve strengths above the 80-90,000 psi level, all failed in our bend tests at higher strength levels as they have with other types of test specimens including simple tensile, notched bend, bent tubing, etc., specimens. Tentatively, and in accordance with our screening procedure these alloys will not be further examined in our geothermal type environment.

The 41XX series alloys and particularly 4130 is widely considered by the petroleum industry as the best available alloy for down hole tubing, etc., at strength levels only slightly above the 80-90,000 psi level with a moderate degree of reliability. Again our bend tests fall in line with the literature. However, the lower carbon variety 4210, not considered to any extent in the literature, tentatively seems to offer some potential for reliability at 100-110,000 psi yield strength. This is currently under further examination.

Most recently, a modified semi-commercial version of 4130 developed by Climax has been put into the program. Early tests by Climax appear to indicate an advantage of approximately 10-15% in yield strength over the standard 4130 with conventional quench and temper heat treatments. Very preliminary bend tests, appear to confirm this for the standard NACE solution at ambient temperature. This study continues and will be extended to our modified NACE solution.

Among the higher strength corrosion resistant alloys, K Monel 500 treated to 135-140,000 psi yield strength, has been tested at ambient, 325° and 425°F temperatures for 32-34 day exposures stressed at 100% of the Y.S. for the standard NACE environment without failure. In addition, of particular interest, is the fact that no failure was observed after 34 days at 425°F in the goethermal modified environment (20% NaCl). Although the rather limited literature on this alloy does not indicate failure in the NACE solution, there are several unofficially reported field service failures in sour wells.

The age-hardenable austenitic stainless steel, A286, exhibited increased resistance to sulphide cracking when overaged to a reduced but still very respectable strength level as the data in Fig. 1 indicate. Additional preliminary data appears to indicate a similar resistance at 420°F for the 20% NaCl modified environment. This study continues as rapidly as possible under the limitations of 30 day exposures and two small autoclaves.

Perhaps the most exciting material examined to date is a newly developed and not yet commercial, non-ferrous, age-hardenable, stainless alloy designated MP35N. This alloy, with a nominal composition of 35Ni, 35 Co, 20 Cr, and 10 Mo, was originated by Du Pont, and further developed by

Latrobe Steel (now Timken). Fully aged, it has the potential of attaining yield strengths in excess of 250,000 psi. The alloy is currently under intense study by the petroleum industry and as far as we can determine no one has observed failure in the standard NACE solution with a wide variety of different types of tests. Our experience is the same. Specifically in our tests, this alloy heat-treated to 220,000 psi Y.S. and stressed at 100% of this value gave no evidence of failure after 32-34 day exposures at temperatures up to 420°F in both the standard and our modified geothermal NACE solution. Indeed, after exposure even at the highest temperature, the specimens emerged relatively bright as compared to the K Monel and A286.

In terms of the development of possible new alloys, particularly of the constructional type, we are slightly ahead of our work plan. Specifically, some four new experimental heats of steel have been made, characterized, and fabricated by Armco Steel into forms suitable for specimen preparation.

One set of 3 experimental alloys is designed to evaluate the influence of carbon content in 3% Cr-1%Mo alloys which allow relatively high tempering temperatures to attain moderately high strengths. The other heat of steel represents a compromise analysis between the above and the standard 4130.

In addition, the electron microscopy substructure studies have been initiated both in our laboratory and at Armco.

In this respect, Armco has been particularly active. These and additional data will be presented in the next progress report where it may be possible to establish a relation, if any, between SCC and substructure as the SCC data become available. Finally, Armco has initiated fracture mechanics testing on one of the experimental alloys, employing the Shell-Heady type specimen.

Communication with our subcontractor, Armco Steel has been excellent involving at least 6 fact-to-face meetings of key personnel and frequent phone conferences and correspondence. In addition, personal contacts including visits have been made to Shell and Exxon in Houston, Texas, and EIC, Inc. in Newton, Massachusetts. In particular, the contacts with Shell and Exxon have been most valuable. We would like to especially mention Drs. Greer and Kane at Exxon and Drs. Kochera and Heady at Shell. Also Dr. Radd at Continental Oil has expressed interest and offered assistance. In order to further implement the utilization plan, these types of contacts will be continued and extended, particularly to some of the West Coast establishments such as Magma Power Corporation, Bechtel Corporation and Pacific Gas and Electric, etc.

Over the last year, since the inception of this program, the principal investigators have distributed their time as follows:

Prof. A. R. Troiano, Responsible Investigator

25% Academic, contributed by University as cost sharing

25% Summer

Prof. R. F. Hehemann, Co-principal Investigator

25% Academic

50% Summer

No substantial change over the remainder of the contract period is contemplated except that Prof. Troiano will spend 50% of his time next summer as originally budgeted.

The progress made thus far would not have been possible without the help of Armco Steel Corporation extending well beyond the limits of their contractual obligations. In this connection we wish to mention the cooperation of Drs. John Peterson and Peter Moroz, Jr. as well as Dr. Robert Boni, Director, Metallurgical R and D.

Many others, too numerous to list, have offered advice and assistance.

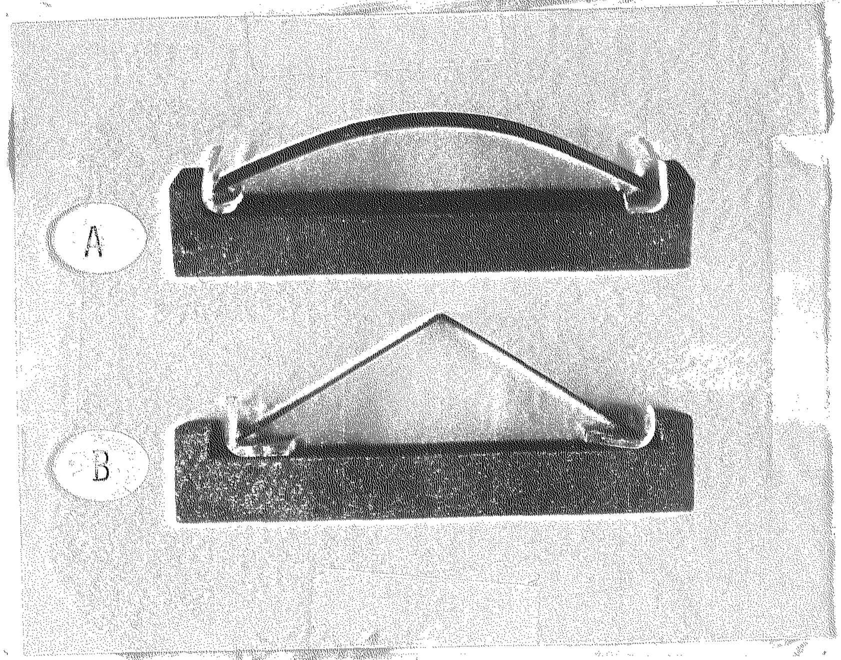

Fig. 1. A286 Standard NACE solution.
34 days, 325°F, Stressed at 100% of Y.S.
A. Overaged to 135,000 psi Y.S.
B. Fully aged to 190,000 psi Y. S.

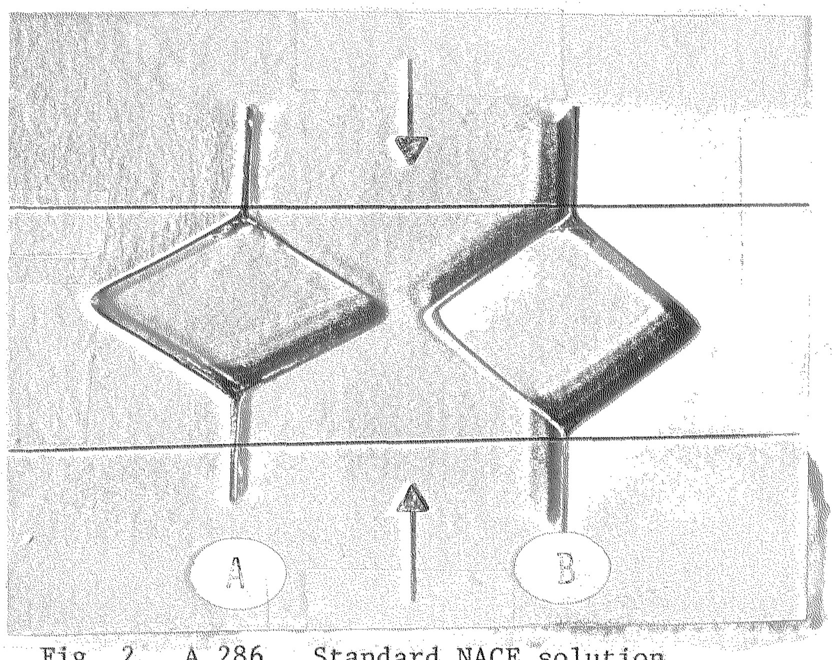

Fig. 2. A 286 Standard NACE solution.
190,000 psi Y.S. 32 days ambient temperature
Stressed at 90% Y.S.
A. Not exposed. Compressed to initial cracking
B. Exposed to environment but no failure

Note: Reduced ability to be compressed before cracking (∿40%)