

MATERIALS RESEARCH AND EVALUATION
FOR GEOTHERMAL CORROSION ENVIRONMENTS

Progress Report
for Period December 15, 1975 - December 15, 1976

A. R. Troiano and R. F. Hehemann

Case Western Reserve University
Cleveland, Ohio 44106

December 1976

Prepared for

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT EY-76-S-02-2602

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *ie*

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

1. In terms of stress corrosion cracking resistance in sour brines, a recently developed modified 4135 steel has exhibited a design yield strength advantage of approximately 10,000 psi over the standard 4130 (Y.S.=110,000 psi) widely employed for casing, production tubing, etc.
2. For a specified strength level, resistance to SCC is improved by higher tempering temperatures in heat treating, giving rise to an approach to new alloy design for constructional type steels. Preliminary results indicate that improvements over the modified 4135 can be achieved.
3. Increasing test temperature reduces the susceptibility to SSC in the constructional steels thus moderately raising the useful strength level; but immunity cannot be achieved. On the other hand, susceptibility of the highly alloyed materials increases with increasing temperature, at least up to 425°F.
4. Increasing salt concentration from 5%-20% did not appear to increase susceptibility to SCC.
5. Of the higher strength, corrosion resistant materials, MP35N has shown outstanding resistance to general corrosion and SCC. However, recent reports indicate that certain conditions related to anisotropy may cause SCC.
6. An age hardenable austenitic alloy, A-286, is susceptible to SSC in the fully aged condition (190 KSI) at 325°F and 425°F. Susceptibility is greatly reduced by over-ageing to a still respectable strength level of 155 KSI.

HYDROGEN SULFIDE STRESS CORROSION CRACKING IN MATERIALS FOR GEOTHERMAL POWER

R. F. Hehemann and A. R. Troiano
Department of Metallurgy and Materials Science
Case Western Reserve University

Catastrophic brittle delayed failure can occur in many environments, some of which may not appear to be very aggressive from a straight corrosion point of view. This type of environmentally induced failure, often occurring well below standard conservative design stresses has generally been categorized as stress corrosion cracking (SCC). It is well recognized that in many instances hydrogen is involved as an embrittling agent leading to this type of failure and constituting a definite limitation on the use of available materials.

The highly developed petroleum industry presents some of the most critical examples of these problems. The ultimate success of a greatly expanded source of geothermal power encounters, in many cases, much the same type of problems. Indeed, a major limitation in the growing energy problem resides in materials to contain, process, and generally handle the various aggressive environments that are encountered⁽¹⁻⁴⁾.

It has been realized for many years that relatively high strength constructional type steels will crack in "sour" environments. Such an environment has been characterized as one that contains damaging amounts of H_2S which can be as low

as .001 atmosphere.* This is based on the susceptibility to cracking of normally employed oil well casing and tubing steels in the 80,000 psi yield strength range (N-80) and above (P110)⁽⁵⁻¹⁰⁾. Indeed, as little as 0.1 ppm H_2S has produced failure in laboratory tests. The H_2S acts as a cathodic poison, dissociating to allow hydrogen absorption into the metal and the formation of FeS at the surface⁽¹¹⁾. Accompanying CO_2 results in acidification and pH levels of 3 to 4 are not uncommon.

In geothermal holes much the same type and even more aggressive environments are often encountered⁽¹²⁾ and the associated failures have been recognized for some years in some of the older geothermal power fields. As far back as 1961, wells in Waireki, New Zealand experienced brittle delayed fracture in well casing at 80,000 psi yield strength and below⁽¹³⁾. At this same time it also was indicated that a form of thermal corrosion fatigue was encountered due to the "unclean" nature of geothermal steam, particularly damaging to pumps, turbines, and ancillary equipment.

Other experience with geothermal wells indicated that 55,000 psi yield strength was the maximum safe strength allowable in terms of H_2S induced failures. However, at these low strengths, tubing collapse was encountered and limited the strength of the joints required to compensate for non-axial

* At ambient temperature this is equivalent to approximately 3 ppm in solution.

loading, thermal stresses, lack of complete cementing, etc. (14). Higher strength steels are also clearly necessary for bursting and collapse resistance where even thermal stresses alone can exceed 60,000 psi⁽¹⁵⁾.

Even at the levels generally considered to be a safe maximum Y.S., greater reliability would be most valuable and help alleviate the drill pipe, casing, and tubing problems. The consistency of performance is not only a material strength level variable but also is dependent upon environmental factors, some of which may change with time or the manner in which the wells are operated. Reliability at still higher strength is imperative in much of the ancillary equipment such as well head fittings, valves, pump components, bolts, sub-surface equipment, such as down hole pumps for geothermal wells, etc. Indeed, similar limitations on useful strength level exist even in the higher alloyed classes of materials such as stainless steels, Inconels, Monel, etc. as indicated in a number of recent conferences. However, in these alloys, the specificity of the environment may not completely correspond to that involved in the constructional type steels.

Classical hydrogen embrittlement delayed failure exhibits many characteristics of environmentally induced stress corrosion cracking⁽¹⁶⁻¹⁸⁾. Since it is generally accepted that cracking in sour environments involves hydrogen embrittlement, particularly for the constructional type steels, it may be

instructive to outline some of the parallelism of behavior. Both will exhibit an incubation time for crack initiation, discontinuous crack propagation, preferred crack nucleation at crevices, notches, pits, etc., similar temperature ranges of sensitivity, similar fracture appearance, a critical threshold stress for failure, a generally low stress intensity factor ($K_{I_{SCC}}$)^(19,20), and increased sensitivity to failure as the yield strength is raised.

Of particular interest to the problem at hand are the temperature range of sensitivity and the threshold stress. The temperature range is generally considered to span the region from approximately minus 50°F to plus 300°F for the constructional type (body-centered cubic) alloys. It must be appreciated that this range is sensitive to many other parameters such as the environment and the strength level^(21,23). These temperature limits correspond with those at which hydrogen can be mobile and yet not so high as to preclude the accumulation of the critical concentration for failure⁽²⁴⁾. Also of significance is the relation between the threshold stress for failure and the Y.S. This critical stress rises as the Y.S. is reduced until eventually it becomes equal to the Y.S. Below this strength, brittle delayed failure will not occur⁽²⁵⁾. This, of course, accounts for the present limitations of 80,000-100,000 psi yield strength at ambient temperatures. This threshold stress is also sensitive to temperature and increases with rising temperature.

The incubation time is of some relevance to the behavior of geothermal materials especially with above-ground installations. The incubation time marks the line between reversible and permanent damage and as such provides the basis for dehydrogenation cycles for equipment involving hydrogenous environments.

Environmental induced failure (SCC) as compared to hydrogen pick-up in processing usually involves the additional complications of an inexhaustible supply of hydrogen and the complexities of changing surface and environment in terms of hydrogen absorption. Proposed solutions to this problem can take many different directions. Obviously one approach is to systematically establish the limits of confidence for a given set of circumstances in terms of material and environmental conditions for established or recently developed alloys. Clearly another approach involves attempts to develop materials with higher threshold stress values, either static or dynamic, for the specific environmental conditions related to geothermal holes.

For the available alloy constructional type steels, the behavior in sour oil well and similar environments has been quite thoroughly explored. Although there are many similarities of environment in oil-gas and geothermal wells, potential geothermal holes present a much wider spectrum of variation in the environment; for example, the very high chloride contents and broad range of pH in these environments.

The development of materials resistant at higher yield strengths and threshold stress values is of prime concern. There is an increasing awareness of the role of metallurgical structure. It is now generally appreciated that fine structures with uniform carbide distributions such as tempered martensite are more resistant to hydrogenous environments than the more coarse structures such as ferrite-pearlite mixtures (normalized structures) in constructional type steels, all other things equal⁽²⁶⁻²⁸⁾.

Many different types of materials are necessary to meet the requirements of a complete geothermal power system. For the most part, steels suitable for casing, tubing, etc., will not serve for much of the rest of the installation, such as well head fittings, valves, pumps, bolts, and ancilliary equipment. Often, more highly alloyed and corrosion resistant materials are employed. In terms of the available alloys, particularly the age hardenable and corrosion resistant types such as austenitic stainless steel, Inconel, Stellites, K-Monel, A-286, MP35N, etc., the limits of confidence in terms of heat treatment (e.g., overageing), threshold stress, maximum safe strength level, etc., have not been systematically determined particularly with respect to the relevant geothermal environments.

For the most part, these more highly alloyed materials have face-centered cubic structures as compared to the

body-centered cubic structure of the constructional steels. There are several vital differences that should be appreciated in assessing the response to a geothermal environment. The F.C.C. alloys are not notch sensitive, generally more subject to chloride induced pitting and most significantly exhibit a substantially slower rate of hydrogen diffusion which raises the temperature range for failure which is dependent upon the influence of diffusible (mobile) hydrogen.

Essentially, this communication represents a progress report on studies to evaluate performance of alloys in geothermal power systems. This includes not only commercially available alloys with standard treatments but also manipulation of the metallurgical structures and/or designed composition modifications. The petroleum industry has accumulated and made available a vast storehouse of data involving performance of virtually all commercially available alloys in a sour environment. Much but not all of these data are relevant to geothermal environments which apparently exhibit a wider range of varying aggressive situations.

Experimental

The test specimens were mostly of the two point bend type, usually loaded to 90-100 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 critical crevice corrosion. On the other hand, extreme care must be exercised in loading the specimen since any plastic flow will reduce the calculated applied stress. Of course, any permanent set on removal from the test jig will indicate some overstressing. The specimens' dimensions were generally 4" x .5" x .035" and in all cases cut with the long direction parallel to the rolling direction.

The "self-stressed" type of bend test specimen was employed for some of the early tests as illustrated in Fig. 2 (29). The difficulty in circumventing crevice corrosion caused us to drop its use, at least during the early screening procedures. However, it is particularly interesting since 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.

Essentially two different environments have been employed. One is the standard NACE solution for sour environments which is a 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 appear promising with the standard solution are then subjected to a modified NACE solution with 20 percent instead of 5% NaCl, which will better match the high chloride contents of many geothermal holes.

For both environments, the recommended tentative procedure of continuous purging with H_2S for the full 30 day tests was adopted⁽³⁰⁾. For the higher temperatures employing a pressure vessel, continuous purging with H_2S was not possible. However, this does not pose a problem, since it is a closed system, previously deaerated, and substantial concentration of H_2S is evident in the environment after 30 days.

The standard available tank H_2S has approximately 300 ppm oxygen according to the supplier. In those tests where a continuous flow of H_2S was employed, the influence of this oxygen was quite apparent in the relatively low but definite corrosion in the 30 day tests at ambient temperature and seriously affected tests near the boiling temperature of the solution. Consequently, tests at the boiling point and higher were conducted in autoclaves. Steps are being taken to reduce this oxygen concentration.

A wide range of alloys are under examination both with standard commercial treatments and metallurgical structures and composition variations which may potentially enhance performance. Their nominal compositions are listed in Table I. The beam specimen has yielded data for commercial

alloys in the standard NACE solution at ambient temperatures that are completely consistent with the literature. For example, steels 410, 431, and 440, which represent industry attempts to achieve improved corrosion resistance with strengths above the present general limits, all failed at the higher strength levels just as they had with many other types of test specimens, including simple tensile, notch bend, bent tubing, etc. These particular steels will not be further considered in this report.

All heat treatments were performed in a purified nitrogen atmosphere at controlled temperature. For the constructional steels in particular, extra precautions were taken to avoid decarburization during both the normalizing and austenitizing treatment. All constructional steels were quenched for martensite and given a single temper at the appropriate temperature to attain the desired strength as indicated in the tables. The age-hardenable alloys all required prior cold work to attain their optimum yield strength levels. Generally, these materials were received in the cold worked condition. Our ageing treatments were designed to produce under-aged, fully aged, and over-aged conditions.

Results and Discussion

It will be convenient to consider the performance of the constructional steels and of the more corrosion resistant materials separately.

Constructional Steels

The superior resistance to SSC of tempered martensitic compared with pearlitic structures has placed a premium on hardenability. This has favored Cr/Mo steels over the more economical Mn or Mn/Mo grades. In this program, 4130 with its well-documented behavior in sour environments has been chosen as a reference material and its resistance to SSC is shown in Table II.

With the unnotched beam samples employed in this study, 4130 is resistant at ambient temperatures to SSC at a yield strength level of 110 KSI and lower. Variable performance is exhibited at intermediate strength levels and failure consistently occurs at strengths of 128 KSI and above.

It is well known that the resistance of the BCC structure to hydrogen embrittlement improves significantly as the temperature is raised. Thus, at 212°F and above, failure has not been observed at yield strength levels as high as 138 KSI. Higher strength levels are currently under study in order to

determine the maximum strength for resistance to SSC as a function of temperature.

The performance of the modified 4135 steel is presented in Table III. As has been shown by others, this composition is somewhat more resistant to SSC than the standard 4130 and exhibits a yield strength advantage of the order of 10 KSI^(31,32). This yield strength advantage while of interest per se, may have a greater significance. Specifically, it should provide greater reliability at a given strength level such as 110 KSI compared to that of standard 4130 steels. As for the standard 4130, the resistance to cracking of this modified 4135 steel improves significantly as the test temperature is increased.

In general, the resistance to SSC of both the standard 4130 and the modified 4135 steels in the 20% NaCl solution was comparable or perhaps slightly superior to that in the 5% NaCl solution. The possibility that this may result from similar or slightly reduced corrosion rates in the 20% NaCl solution is being further examined, since the chloride ion is reported to act as a corrosion inhibitor.

Despite the dominant influence of strength level on resistance to hydrogen embrittlement and SSC, it is evident that microstructural and compositional details also exert a significant affect and can be manipulated to optimize useable strengths and reliability. Lower carbon content is known to enhance toughness significantly, and its influence on sulphide SCC is currently under study.

Preliminary results indicate that carbon contents much below 0.3% are detrimental to the SSC resistance. For example, Table IV demonstrates that the threshold strength level of a 4118 steel is significantly below that for 4130 and similar results have been obtained on a 0.2C-2 Cr-0.75 Mo steel (Table V) as well as an 0.1C-3 Cr-1.0 Mo steel (Table VI).

Tempering temperature appears to be the primary factor responsible for the influence of carbon content on the useable strength level. There is evidence to indicate that resistance to SSC at a given strength level improves as the tempering temperature is raised⁽³¹⁾. Thus, the poor performance of the 4118 steel compared to that of 4130 appears to be associated with the relatively lower tempering temperatures required to achieve comparable strength levels in the two steels.

In addition to microstructure, the type, size and number of non-metallic inclusions, particularly sulfides, can influence the mechanical properties significantly. In order to explore this, two vacuum melted versions of the modified 4135 analysis have been prepared. The analyses of these steels are compared with that of the Climax modified 4135 in Table VII. Heat V 1312 essentially matches the Climax material except for reduced carbon and sulfur contents. In heat V 1313, a V addition has been substituted for the Nb addition.

The SSC resistance of these steels as well as that of a commercial 4123 pipe is presented in Table VIII. Although the data are still somewhat limited, it appears that the performance of these steels is comparable to that of the Climax version. Specifically, at ambient temperatures, all three steels resist cracking at strengths below approximately 125 KSI. This is further confirmed by fracture toughness tests currently in progress on steels V 1312 and V 1313. K_{ISCC} for the two vacuum melted steels is comparable to that reported by the Climax Molybdenum Corporation for the modified 4135 steel.

Further improvement in toughness and perhaps resistance to SCC may be expected from reduction in the Mn and Si contents. A vacuum melted heat of standard 4130 has been prepared from high purity stock in order to attain very low concentrations of Mn, Si and S. This steel exhibits exceptional resistance to SSC (Table IX) with susceptibility arising at yield strengths in excess of 130 KSI.

Corrosion Resistant Alloys

A limited number of higher strength corrosion resistant alloys are currently under study. Many of these are based on FCC structures and may be expected to exhibit maximum susceptibility to SSC at temperatures significantly above the ambient. The age hardenable austenitic stainless steel,

A-286, appears to perform in this manner as shown in Table X. While the fully aged condition (16 hours at 1200°F) was resistant at 212°F, it failed when tested at 325°F in the NACE solution and at 425°F in the 20% NaCl solution.

Although A-286 did not fail at 212°F or lower, it did suffer substantial ductility loss as revealed by compression of self-stressed samples after exposure (Fig. 2). In Fig. 2A, the unexposed specimen was compressed in the direction of the arrow until a crack was observed. Specimen B had been exposed for 30 days in the NACE solution at ambient temperature without failure. However, it is evident that it had lost much of its ductility, as indicated by the reduced deformation it could sustain prior to the incidence of cracks.

This loss of ductility may not necessarily indicate impending failure. Indeed, low strength steels will exhibit loss of ductility resulting from hydrogen but will not exhibit brittle delayed failure.

As with the constructional steels, microstructural details influence the performance of this age-hardenable alloy at a given strength level. Thus, when over-aged (16 hours at 1300°F) to a still respectable strength level of 155 KSI the alloy is resistant to cracking in both the NACE solution at 325°F and in the 20% chloride solution at 425°F. This does not appear to be simply a strength level effect since under-ageing (1 hour at 1150°F) to essentially the same

strength level results in susceptibility, at least at 425°F, in the 20% chloride solution.

Much attention has been devoted recently to a newly developed non-ferrous, age-hardenable alloy - MP35N⁽³³⁾. This alloy exhibits excellent resistance to general and to pitting corrosion and, as shown in Table XI, has been resistant to SSC in both the NACE and the 20% chloride environments. In fact, an additional sample, not reported in Table XI was exposed for a total of 90 days in the NACE solution (30 days at 325°F and 60 days at 425°F) with no apparent corrosion and complete resistance to cracking. This outstanding performance generally confirms that reported in the literature*.

K Monel 500, treated to 140 and to 170 KSI strength levels has resisted cracking in both the standard and the modified NACE solutions (Table XII). This agrees with the rather limited literature on this alloy indicating resistance to SSC in the NACE solution; however, there are several unofficially reported service failures in sour wells.

While generally not considered as high strength alloys, the 300 grade austenitic stainless steels also are of potential interest for use in geothermal environments. As indicated in Table XIII several of these have resisted SSC at 325°F

* As a word of caution, however, it has been shown recently that cracking can be induced in MP35N by galvanic coupling to a more active metal such as iron⁽³⁴⁾.

in both the annealed and higher strength conditions achieved by cold work.

In general, susceptibility of these austenitic alloys, including A-286, to chloride SCC increases as the concentration of the chloride ion is increased. The oxygen content of the solution also appears to be of significance with regard to the cracking resistance in these solutions. Thus, the influence of temperature, salt concentration and oxygen concentration on the cracking resistance of the austenitic steels is under further study.

Conclusions

1. For the constructional steels of interest for casing, tubing and other applications, the modified 4135 analysis exhibits a strength advantage of approximately 10 KSI over the standard 4130 analysis. This should also improve reliability when employed at strength levels below its maximum (approximately 120 KSI) for resistance to SSC.
2. For a specified strength level, resistance to SCC is improved at higher tempering temperatures. This appears to provide a lower limit on the carbon level for optimum resistance to SSC.
3. Increasing salt concentration from 5% to 20% does not appear to increase susceptibility to SSC.
4. Of the higher strength, corrosion resistant materials, MP35N has shown outstanding resistance to general corrosion and has not suffered SSC in these tests. Recent reports, however, indicate that certain specific conditions may cause SCC.

5. An age hardenable austenitic alloy, A-286, is susceptible to SSC in the fully aged condition (190 KSI) at 325°F and 425°F. Susceptibility is greatly reduced by over-ageing to a strength level of 155 KSI but not by under-ageing to a comparable strength level.
6. For the constructional steels, increasing test temperature reduces the susceptibility to SSC substantially thereby increasing the strength level that is resistant to cracking. Susceptibility of the highly alloyed materials, on the other hand, increases with increasing temperature, at least in the range up to 425°F.

Acknowledgements

This program constitutes a cooperative effort between the Armco Steel Corporation, Middletown, Ohio and the Metallurgy Department, Case Western Reserve University. The very substantial contribution of Armco Steel Corporation is gratefully acknowledged. The entire program has been supported by ERDA.

References

1. R. N. Tuttle, "Deep Drilling - A Materials Engineering Challenge", Shell Development Company, Bellair Research Center Publication, #BRC-EP-630, Houston, Texas, 1973. See also Materials Performance, February, 1974.
2. T. Marshall and A. Tombs, "Delayed Fracture of Geothermal Bore Casing Steels", Aus. Corros. Eng'g, 13, 9, 2-8, 1969.
3. Basil Wood, "Basis of Selection of Materials for Geothermal Schemes", UNESCO, Geothermal Energy, Paris, 1973.
4. K. C. Youngblut, "Materials Selection - Coal Gasification Pilot Plant", Materials Protection and Performance, p. 33, Dec. 1973.
5. C. N. Bowers, W. J. McGuire and A. E. Wiehe, "Stress Corrosion Cracking of Steel under Sulphide Conditions", Corrosion, Vol. 8, p. 333, 1952.
6. R. S. Treseder and T. M. Swanson, "Factors in Sulphide Corrosion Cracking, Corrosion, 24, 31, 1968.
7. J. F. Bates, "Sulphide Cracking of High Yield Strength Steels in Sour Crude Oils", Materials Protection, p. 33, Jan. 1969.
8. E. H. Phelps, "Stress Corrosion Behavior of High Yield Strength Steels", Proc. 7th World Petroleum Congress, Elsevier Publishing Company, Ltd., p. 201, 1967.
9. J. L. Battle, T. V. Miller, and M. E. True, "Resistance of Commercially Available High Strength Tubular Goods to Sulphide Stress Cracking", Materials Performance, June, 1975.
10. D. S. Burns, "Laboratory Test for Evaluating Alloys for H₂S Service", Materials Performance, Jan. 1976.
11. P. Bastien and Amiot, "Mechanism of the Effect of Ionized Solutions of H₂S on Iron and Steel", Comptes Rendus, Vol. 235, p. 1031, 1952.
12. H. C. Helgeson, "Geologic and Thermodynamic Characteristics of the Salton Sea Geothermal System", Amer. Jour. of Sci., 266, p. 129, 1968.

13. P. K. Forster, T. Marshall, and A. Tombs, U.N. Conf. on New Sources of Energy, Rome, 1961. See also Aust. Corrosion Eng'g., Vol. 6, p. 306, 1962.
14. J. H. Smith, "Casing Failures in Geothermal Bores at Wairekei", Geothermal Energy, Vol. 3, U.N. Conf., p. 254, 1961
15. A. C. L. Fooks, "The Development of Casings for Geothermal Boreholes", Ibid.
16. A. R. Troiano and J. P. Fidelle, "Hydrogen Embrittlement in Stress Corrosion Cracking", Magistrale Lecture, International Conference Hydrogen in Metals, Paris, France, June 1972. See also ART Keynote Lecture, Ref. No. 18.
17. C. F. Barth, E. A. Steigerwald and A. R. Troiano, "Hydrogen Permeability and Delayed Failure of Martensitic Steels", Corrosion, Vol. 25, p. 353, 1969.
18. J. Papp, R. F. Hehemann, and A. R. Troiano, "Hydrogen Embrittlement of High Strength FCC Alloys", ASM, CMU Conference, Seven Springs, Pennsylvania, September 1973, ASM Confer. Vol. 1973.
19. E. A. Steigerwald, "Delayed Failure of High Strength Steel in Liquid Environments", Proc. Am. Soc. Testing Materials, Vol. 60, p. 750, 1960.
20. L. M. Dvoracek, "Sulphide Stress Corrosion Cracking of Steels", Corrosion, Vol. 26, p. 177, 1970.
21. W. Beck, E. J. Jankowsky and P. Fischer, "Hydrogen Stress Cracking of High Strength Steels", Naval Air Development Center, Rept. No. NADC-MA-7140, 1972.
22. J. B. Greer, "Factors Affecting the Sulphide Cracking of High Strength Steels", Materials Performance, Vol. 14, 11-22, 1975.
23. R. D. Kane and J. B. Greer, "Sulphide Stress Cracking of High-Strength Steels in Laboratory and Oil Field Environments", Jour. Petroleum Tech., AIME, Oct. 1976. Preprint SPE 6144.

24. A. R. Troiano, "The Role of Hydrogen and Other Interstitials in the Mechanical Behavior of Metals", Edward DeMille Campbell Memorial Lecture, Trans. ASM, Vol. 52, p. 54, 1960.
25. M. F. McGuire, A. R. Troiano and R. F. Hehemann, "Stress Corrosion of Ferritic and Martensitic Stainless Steels", Corrosion, Vol. 29, p. 268, 1973.
26. W. M. Cain and A. R. Troiano, "Steel Structure and Hydrogen Embrittlement", Petroleum Engineer, Vol. 37, p. 5, May 1965.
27. E. Snape, "Roles of Composition and Microstructure in Sulphide Cracking of Steel", Corrosion, Vol. 24, p. 261, 1968.
28. E. Snape, "Sulphide Stress Corrosion of Some Medium and Low Alloy Steels", Corrosion, Vol. 23, p. 154, 1967.
29. G. J. Geimerl and D. N. Braski, "Materials Research and Standards", ASTM, January, 1965.
30. "Evaluation of Metals for Resistance to Sulphide Stress Cracking at Ambient Temperature", Proposed NACE Standard T-11-9 Procedure, January 15, 1975.
31. J. B. Grobner, D. L. Sponseller, and W. W. Cias, "Development of Higher Strength H_2S Resistant Steels for Oil Field Applications", Materials Performance, June, 1975.
32. L. M. Dvoracek, "High Strength Steels for H_2S Service", Materials Performance, May, 1976.
33. J. P. Stroup, A. H. Bauman, and A. Simkovich, "Multiphase MP35N - An Alloy for Deep Sour Well Service", Materials Performance, June, 1976.
34. Private Communication, P. R. Rhodes, Shell Development Co., Houston, Texas.

The nominal analyses of the alloys considered in this report are given in Table I below:

TABLE I

<u>Designation</u>	<u>C</u>	<u>Cr</u>	<u>Mo</u>	<u>Cb</u>				
4118	0.20	0.50	0.15	-				
4130	0.30	1.0	0.20	-				
4135 mod.*	0.35	1.0	0.75	.04				
2 Cr-0.75 Mo	0.20	2.0	0.75	.03				
3 Cr-1.00 Mo	0.10	3.0	1.0					

	<u>Ni</u>	<u>Cr</u>	<u>Ti</u>	<u>Mn</u>	<u>Mo</u>	<u>V</u>		
A-286	25	15	2	1.5	1.3	0.3		

	<u>Ni</u>	<u>Cr</u>	<u>Al</u>	<u>Fe</u>	<u>Ti</u>	<u>Mn</u>		
K Monel	65	30	3	1.0	0.50	0.50		

	<u>Ni</u>	<u>Co</u>	<u>Cr</u>	<u>Fe</u>	<u>Mo</u>	<u>Ti</u>	<u>Cb</u>	<u>Al</u>
MP35N	25	35	20	9	7	3	0.6	0.2

	<u>C</u>	<u>Mn</u>	<u>Cr</u>	<u>Ni</u>				
301	.08	1.0	17.5	7.5				
304	.08	1.5	19	9				
310	.08	1.5	25	20				

* Developed by Climax Molybdenum Corporation.

TABLE IISulfide Stress Cracking of 4130 Steel

<u>Test Temp.-°F</u>	<u>Tempering Temp.-°F*</u>	<u>Y.S. KSI</u>	<u>No. Failed No. Tested</u>
<u>5% NaCl (NACE Solution)</u>			
Ambient	1100	138	1/1
	1150	128	4/4
	1200	123	2/3
	1250	119.5	2/3
	1300	107.5	0/2
212	1100	138	0/1
	1500	128	0/3
	1200	123	0/2
	1250	119.5	0/2
325	1150	128	0/1
	1200	123	0/1
	1250	119.5	0/2
<u>20% NaCl</u>			
Ambient	1200	123	1/2
	1250	119.5	0/3
212	1200	123	0/1
	1250	119.5	0/1
325	1150	128	0/1
	1200	123	0/1
425	1100	138	0/1
	1150	128	0/1
	1200	123	0/1

* 1650°F, 1/2 Hr, A.C.; 1550°F, 1/2 Hr, W.Q.;
Temper 1/2 Hr, A.C.

TABLE IIISulfide Stress Cracking of Modified 4135 Steel

<u>Test Temp.-°F</u>	<u>Tempering Temp.-°F*</u>	<u>Y.S. KSI</u>	<u>No. Failed No. Tested</u>
<u>5% NaCl (NACE Solution)</u>			
Ambient	1200	138	5/5
	1250	125	5/8
	1275	116	0/4
	1300	110	0/4
212	1150	150	1/1
	1200	138	0/1
	1250	125	1/3
	1300	110	0/2
325	1200	138	0/3
	1250	125	0/2
<u>20% NaCl</u>			
Ambient	1200	138	2/2
	1250	125	2/3
	1300	110	0/1
212	1250	125	0/1
	1300	110	0/1
325	1150	150	0/1
425	1250	125	0/1

* 1750°F, 1 Hr, A.C.: 1650°F, 1/2 Hr, O.Q.;
Temper 2 Hrs, A.C.

TABLE IVSulfide Stress Cracking of 4118 Steel

<u>Test Temp.-°F</u>	<u>Tempering Temp.-°F*</u>	<u>Y.S. KSI</u>	<u>No. Failed No. Tested</u>
	<u>5% NaCl (NACE Solution)</u>		
Ambient	1000	120	1/1
	1050	108	1/2
	1100	95	0/3

* 1/2 Hr, 1650°F, A.C.; 1/2 Hr, 1550°F, W.Q.;
Temper 1 Hr, A.C.

TABLE VSulfide Stress Cracking of 2 Cr-0.75 Mo Steel

<u>Test Temp.-°F</u>	<u>Tempering Temp.-°F*</u>	<u>Y.S. KSI</u>	<u>No. Failed No. Tested</u>
<u>5% NaCl (NACE Solution)</u>			
Ambient	1200	130	2/2
	1250	118	1/1
	1300	105	0/4
<u>20% NaCl</u>			
Ambient	1300	105	0/1

* 10 Min. 1750°F, A.C.; 10 Min. 1650°F, W.Q.;
Temper 1 Hr, A.C.

TABLE VISulfide Stress Cracking of 3 Cr-1.0 Mo Steel

<u>Test Temp.-°F</u>	<u>Tempering Temp.-°F*</u>	<u>Y.S. KSI</u>	<u>No. Failed No. Tested</u>
<u>5% NaCl (NACE Solution)</u>			
Ambient	1150	154	1/1
	1200	130	1/1
	1250	115	1/1
	1130	100	0/2

* 10 Min. 1750, A.C.; 10 Min. 1650, W.Q.;
Temper 1 Hr, A.C.

TABLE VII

Analysis of 41XX Steels

	<u>Armco</u>		<u>Climax Molybdenum</u>	
	<u>V1312</u>	<u>V1313</u>	<u>Commercial 4123</u>	<u>4135</u>
C	0.26	0.26	0.23	0.33
Mn	0.50	0.52	0.84	0.86
Si	0.21	0.22	0.36	0.28
S	0.005	0.004	0.016	0.015
Al	0.027	0.023	-	0.067
Cr	1.01	1.01	0.93	1.08
Mo	0.78	0.78	0.20	0.83
Nb	0.038	<.005	-	0.054
V	<.005	0.058	-	-

TABLE VIII

SSC Susceptibility of 41XX Type Steels*

<u>Steel</u>	<u>Test Temp.-°F</u>	<u>NaCl Conc.-%</u>	<u>Tempering Temp.-°F</u>	<u>Y.S. KSI</u>	<u>No. Failed No. Tested</u>
V1312	Ambient	20	1200	136.5	1/1
	Ambient	20	1250	116	0/1
	212	5	1200	136.5	0/1
	425	20	1200	136.5	0/1
V1313	Ambient	20	1200	143	2/2
	Ambient	20	1250	125.5	0/1
	212	5	1200	143	1/1
	325	20	1250	125.5	0/1
	425	20	1200	143	1/1**
4123	Ambient	20	1150	131	2/2
	Ambient	20	1200	123	1/1
	Ambient	20	1250	119.5	0/1
	212	5	1150	131	0/1
	325	20	1150	131	0/1

* - Ten day tests

** - Cracked but did not fail completely

TABLE IXSSC Susceptibility of Very Low Sulfur 4130 Steel*

<u>Test Temp.-°F</u>	<u>NaCl Conc.-%</u>	<u>Tempering Temp.°F</u>	<u>Y.S. KSI</u>	<u>No. Failed No. Tested</u>
Ambient	20	1040	145	1/1
		1100	138	1/1
		1150	136	0/1
		1200	128	0/1
		1250	123	0/1
212	5	1150	136	0/1
325	20	1200	128	0/1

* Ten day tests

TABLE XSulfide Stress Cracking of A-286 Steel

<u>Test Temp.-°F</u>	<u>Ageing Treatment</u>	<u>Y.S. KSI</u>	<u>No. Failed</u> <u>No. Tested</u>
<u>5% NaCl (NACE Solution)</u>			
212	16 Hrs-1200°F	190	0/1
325	16 Hrs-1200°F	190	1/1
	16 Hrs-1300°F	155	0/1
<u>20% NaCl</u>			
425	16 Hrs-1200°F	190	3/4
	1 Hr -1150°F	165	1/1
	16 Hrs-1300°F	155	0/2*

* An additional sample tested without deaeration of the solution exhibited small cracks.

TABLE XISULFIDE STRESS CRACKING OF MP35N

<u>Test Temp.-°F</u>	<u>Y.S. KSI</u>	<u>No. Failed No. Tested</u>
----------------------	-----------------	----------------------------------

5% NaCl (NACE Solution)

Ambient	220	0/1
425	220	0/1

20% NaCl

425	220	0/2*
-----	-----	------

* One sample tested without deaeration.

TABLE XIISulfide Stress Cracking of K Monel

<u>Test Temp.-°F</u>	<u>Ageing Treatment</u>	<u>Y.S. KSI</u>	<u>No. Failed No. Tested</u>
<u>5% NaCl (NACE Solution)</u>			
Ambient	8 Hr, 1000°F/F.C. to 900°F/W.Q.	170	0/1
325	16 Hr, 1100°F/F.C. to 900°F/A.C.	140	0/1
425	16 Hr, 1100°F/F.C. to 900°F/A.C.	140	0/2
<u>20% NaCl</u>			
425	8 Hr, 1000°F/F.C. to 900°F/W.Q.	170	0/1
	16 Hr, 1100°F/F.C. to 900°F/A.C.	140	0/2

TABLE XIIISulfide Stress Cracking of Austenitic Stainless Steels

<u>Test Temp.-°F</u>	<u>Steel</u>	<u>Condition</u>	<u>Y.S. KSI</u>	<u>No. Failed</u> <u>No. Tested</u>
<u>5% NaCl (NACE Solution)</u>				
325	301	30% C.W.	160	0/1
	304	Annealed	40	0/1
		30% C.W.	130	0/1
	310	Annealed	30	0/1
		30% C.W.	70	0/1

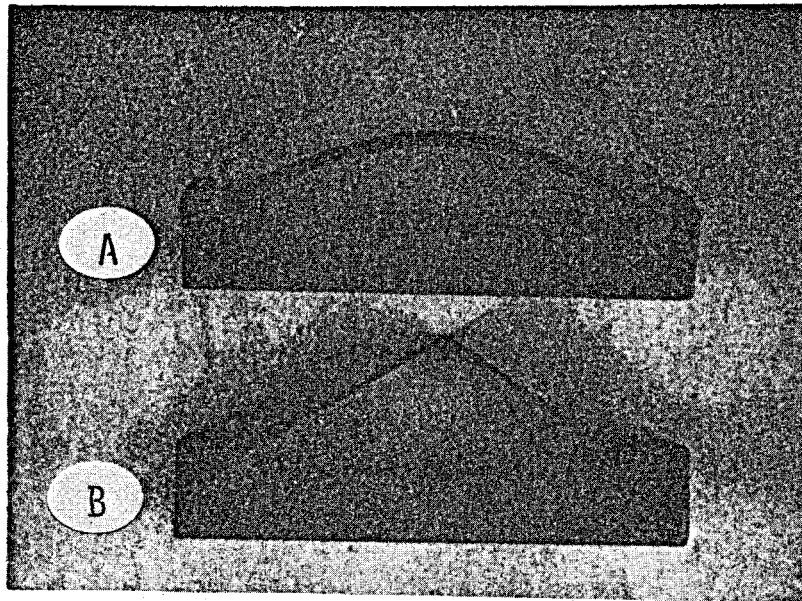


Fig. 1. A286 Standard NACE solution.
34 days, 325°F, Stressed at 100% of Y.S.
A. Overaged to 135,000 psi Y.S.
B. Fully aged to 190,000 psi Y.S.

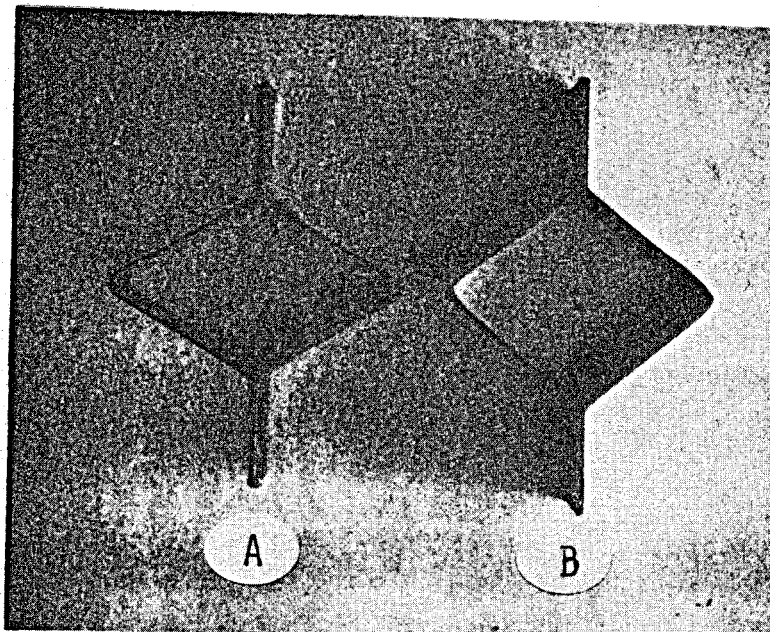


Fig. 2. A 286 Standard NACE solution.
190,000 psi Y.S. 32 days ambient temperature
Stressed at 90% Y.S.
A. Not exposed. Compressed to initial cracking
B. Exposed to environment but no failure

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