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**HYDROGEN SULPHIDE STRESS CORROSION CRACKING
IN MATERIALS FOR GEOTHERMAL POWER**

by

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Abstract

Two point bent beam, NACE tensile, C-Ring and DCB stress intensity type specimens were employed to examine a series of steels' SSC resistance in the standard NACE solution and in several modifications pertinent to geothermal environments. Where direct comparisons were possible, the different types of tests qualitatively ranked the alloys in the same order.

Of the commercially available steels that we examined suitable for downhole service, a fine-grained version of 4130 with additional Mo and some Cb appeared to have the highest yield strength "break-point". High purity versions of this and similar type alloys did exhibit somewhat slightly better resistance to SSC. In this class of constructional type steels, those with higher carbon (.20-.30C) and those requiring a higher tempering temperature to achieve a given yield strength appear to be more SSC resistant. These steels all exhibit a 15-20 percent higher yield strength "break-point" at service temperatures near 300-450°F and/or at pH values approaching 7. Several versions of well head equipment type steels with adequate hardenability have demonstrated satisfactory SSC threshold stress values at adequate yield strengths.

The austenitic stainless steels displayed the usual sensitivity to chlorides and cold work. Overaging of several of the age hardenable variety improved the resistance to SSC with only a moderate reduction in strength. Two ferritic stainless steels have shown a higher threshold stress than their commonly employed counterpart.

Examination of C-ring specimens cut from commercially treated casing and tubing clearly indicated the advantages of a tempered martensitic structure and the very real potential for temper embrittlement.

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HYDROGEN SULFIDE STRESS CORROSION CRACKING IN MATERIALS FOR GEOTHERMAL POWER

Introduction

The development of geothermal resources has become a vital facet of the nationwide search for new and increased energy sources (1). One of the major limitations in the full utilization of the various potential energy sites resides in the materials to handle the many hydrogeneous environments associated with most of the promising sources. In this connection one of the most frustrating aspects of this effort is the catastrophic, brittle delayed failure that can occur in many environments, some of which may not appear to be very aggressive from a classical corrosion point of view. This type of environmentally induced failure, often occuring well below conservative design stresses, has generally been termed stress corrosion cracking (SCC) or sulphide stress cracking (SSC) when H_2S is involved. It is well-recognized that, in many instances, hydrogen is involved as an embrittling agent leading to this type of failure.

The sour environment problem was first encountered by the petroleum industry more than 30 years ago (2). The ultimate success of a greatly expanded source of geothermal power, not to mention coal conversion, shale oil, etc., may depend in part on solutions to these same problems. Indeed, a major limitation in the growing energy economy resides in materials to contain, process, and generally handle the various aggressive environments that are encountered (3-10).

Experience in the petroleum industry has often demonstrated that relatively high strength constructional 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 3 ppm in solution. 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 and above (11-19). The hydrogen sulfide acts as a cathodic poison, greatly increasing the amount of hydrogen absorbed from the environment (20-21). In many wells, substantial CO_2 contents result in acidification and pH levels of 3.5 to 5.5 are not uncommon.

In geothermal holes much the same type and even more aggressive environments are often encountered (22-23) and

the associated failures have been recognized for many years in some of the older geothermal fields. As far back as 1960, wells in New Zealand experienced brittle delayed failure in well casing at 80,000 psi yield strength and below (24,25). At this same time it also was indicated that a form of erosion and thermal or 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 hydrogen sulfide induced failures. However, at these low strengths, tubing collapse was encountered and limited the strength of the joints required to compensate for non-axial loading, thermal stresses, etc. In fact, thermal stresses alone can exceed 60,000 psi (26). Near surface earth instability and recent encounters with subsidence further indicate the necessity for higher strength casing, in particular (27,28).

Even at the strength levels generally considered to be safe, greater reliability would be most valuable and help alleviate the drill pipe, casing, and tubing problems.

The consistency of performance depends not only on material strength level but also on environmental factors, some of which may change with time or the manner in which a well is operated. Reliability at higher strength is imperative in much of the ancillary equipment such as well head fittings, valves, pumps, and turbine components, etc. Indeed, similar limitations on useful strength level exist even in the higher alloyed classes of materials including stainless steels, Inconel, Monel, and others. However, in these alloys, the specificity of the environment with regard to temperature range for sensitivity or influence of chloride concentration generally is different than that for the constructional steels. In general, the sensitivity increases at the higher temperature (~400-600°F) and higher chloride concentrations. Indeed, failure in these alloys appears to be more related to chloride stress cracking than to SSC, particularly at the higher temperatures.

Since it is generally accepted that cracking in sour environments involves hydrogen embrittlement, particularly for the constructional steels, it may be of value to outline some of the parallelism of behavior between SSC and brittle delayed failure induced by cathodically charged hydrogen (29-32). Both will exhibit an incubation time for crack

initiation, discontinuous crack propagation, preferred crack nucleation at crevices, notches or pits, similar temperature ranges of sensitivity, similar fracture appearance, a critical threshold stress for failure, a generally low stress intensity factor ($K_{I_{SCC}}$) and increased sensitivity to failure as the yield strength is raised (33-34).

Of particular interest in these applications 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 several hundred °F for the constructional type alloys. Of course, this range is also sensitive to many other parameters such as the environment, stress state and strength level (21, 35-38). The critical temperature limits correspond with those at which hydrogen can be mobile (39). Also of significance is the relation between the threshold stress for failure and the Y.S. This threshold 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. 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 as the temperature is raised (40).

The incubation time is of some relevance to the behavior of geothermal materials, especially for above-ground components. 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.

Engineering application of materials in these sour environments, particularly for down hole use, demands an evaluation of the threshold stress in terms of the percent of the yield strength for currently available steels and relevant geothermal environments. In addition, the development of materials resistant at higher yield strengths and thus higher 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 (41,43).

For the available constructional steels, the behavior in sour oil well and similar environments has been quite thoroughly explored. Although there are many similarities

of environment in oil or gas and geothermal wells, potential geothermal sources present a much wider spectrum of variation in the environment; for example, the broad range of chloride contents and of pH in some of these environments (44,45).

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., may not serve on a technical and/or economic basis for much of the rest of the installation, such as well head fittings, valves, pumps, bolts, and ancillary 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. overaging), threshold stress, maximum safe strength level, etc., have not been systematically determined particularly with respect to the relevant geothermal environments. Indeed, recent studies have indicated unexpected failure behavior in some of these alloys which are currently under intense study (46-48).

Methods and Materials

Types of Tests:

Essentially, four different types of mechanical tests have been employed in this program. A two point type bend specimen, loaded to approximately 100% of the design yield strength, provided a simple early screening test (49). Aside from the advantage of low cost and simplicity, there is virtually no crevice corrosion. However, extreme care must be exercised in loading, since any plastic flow will reduce the calculated applied stress. Fig. 1a shows an example of a no-fail and a fail result. The glass inserts shown were employed only for the higher temperature autoclave runs to avoid coupling with iron. The normally used non-metallic fixtures could not withstand the higher temperatures. This test yields data on what we have termed the "break-point", that is, a yield strength value which will not sulphide stress crack when loaded to 97-100 percent of its yield strength in the standard and/or modified NACE solution (50). The bend type test was ideally suited for screening and multiple testing to evaluate metallurgical, chemical and processing changes designed to improve SSC.

Since a substantial portion of this study involved materials for casing, tubing and other down hole applications a C-ring type test, widely employed in the petroleum industry, was adopted (13,51). Here, a series of rings cut from commercially heat treated casing and tubing were examined and stressed to approximately 100% of their yield strength. Fig. 2 illustrates how the C-ring was loaded and the stress calculated by the deflection method. With the use of calipers an accuracy of approximately one percent in the stress is attainable. The loading bolts, nuts, washers, etc., were protected from the solution by the use of RTV102 silicone rubber. These rings were also tested with a standard Charpy V notch, except that the notch depth was only 10% of the wall thickness. The stress was calculated on the reduced wall. It should be appreciated that on this basis there had to be substantial cold work developed at the notch root when it was loaded.

The smooth tensile specimen adopted by NACE for testing in sour environments was also used (52). This type of test provided data on both the threshold stress; that is, the percent of Y.S. below which SCC will not occur in 30 days and the break-point value of the Y.S. Fig. 1b shows the type of test unit employed. The stress is applied by loading

a calibrated proof ring. The container surrounding the tensile specimen will allow the continuous flow of gas and/or liquid test environment through inlet and outlet ports. The recently adopted NACE Standard TM-01-77 describes this test in detail.

Finally, a double canterlever beam (DCB) type specimen was employed to obtain threshold stress intensity values, $K_{I_{SSC}}$ below which a crack will not grow to catastrophic failure. This value is a material property for a given environment and hence can be used as a quantitative measure of resistance to sulfide stress cracking. The fracture mechanics specimen is shown in Fig. 3. A complete discussion of the DCB technique and a detailed evaluation of sulfide stress cracking resistance in low alloy steels have been published by Heady (53). Sulfide stress cracking resistance is described in terms of the critical stress intensity for environmentally induced slow crack growth ($K_{I_{SSC}}$). This test apparently is highly sensitive to a steel's sulfide cracking resistance, since large variations in cracking resistance have been observed among the same type of low alloy steels such as 4130 supplied by different producers. A significant scatter band resulted for 3130 when $K_{I_{SSC}}$ was plotted as a function of hardness or strength (53).

Environments:

The primary test environment was the standard NACE solution for sour environments which is a deaerated aqueous solution of 5% NaCl, 0.5% acetic acid saturated with a continuous flow of H_2S (52). 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. On the other hand, geothermal environments vary widely and no one solution can serve for total evaluation. Thus, the NACE solution was modified to encompass chloride concentrations of 0, 1, 5, and 20% pH levels from 3 to 7 and temperatures up to 425°F.

In the early phases of the program the recommended procedure of continuous purging with H_2S for the full 30-day test duration was adopted. However, later it was observed that specimens that failed at ambient temperature did so within the first 10 - 12 days. Thus, except for the most promising materials, bent beam tests were generally terminated after 14 days. This was done for the constructional type steels only. The split ring and tensile specimens were allowed to run the full recommended 30 days and 15 days was sufficient for all crack growth to occur in the

DCB tests.

At the higher temperatures employing a pressure vessel, continuous purging with H_2S was not possible. However, this did not pose a problem, since it is a closed system previously deaerated and substantial concentration of H_2S was evident in the environment after 30 days. Dessicators were employed to contain the solution for tests at ambient temperature and autoclaves for tests at $212^{\circ}F$ and higher.

The available tank H_2S has approximately 300 ppm of oxygen. 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 much above ambient were conducted in autoclaves. The oxygen effect was minimized by prepurging the H_2S through scrap iron in the NACE solution.

Materials:

A wide range of alloys have been examined both with standard commercial treatments and metallurgical structures as well as composition variations which may potentially

enhance performance. Their compositions are listed in Tables 1, 2, and 3. The bent beam specimen has yielded data for several of the common commercial alloys in the standard NACE solution that were qualitatively quite consistent with data in the literature. In short, the two point bend specimen was capable of the same rank ordering of the alloys as other types of tests such as simple tensile, C-rings, etc. Naturally, the absolute values may not be expected to match. Many factors contribute to this, not the least of which is the different stress states developed by different types of specimens.

The heat treatments were as commercially recommended or reasonably adjusted for the experimental steels and were conducted in a purified nitrogen atmosphere at controlled temperatures. For the constructional steels, in particular, extra precautions were taken to avoid decarburization during both the normalizing and austenitizing treatment. This was vitally important for the bent beam specimens. The constructional steels were quenched for martensite and tempered at the appropriate temperature to attain the desired strength. A few tests involved normalized and tempered treatments as indicated in the appropriate table or graph. In some cases where producers have supplied test specimens, heat treatment

and mechanical properties were furnished.

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. The stainless steels were examined in both the low strength annealed condition and after strengthening by cold work. The C-ring test specimens were all cut from commercially heat treated casing or tubing. It should be appreciated that not all of these steels were designed for use in sour environments.

Results and Discussion

Bent Beam Tests

Constructional Steels:

The superior resistance to SSC of tempered martensite compared with normalized (ferrite-pearlite) structures has placed a premium on hardenability. This is particularly true considering the difficulty of thru quenching long sections of tubing or the increased wall thickness at upset joints (54). Thus, the Cr/Mo steels, for example, have

become favored over the more economical Mn or Mn/Mo grades. Here, 4130 with its well-documented behavior in sour environments has been chosen as a reference material.

Since several thousand tests are involved it is not feasible to tabulate every test item in a series of tables. Rather, Table 4 indicates the nature of the raw data obtained for a steel of considerable interest. Specifically, this Table indicates the manner in which the 0.2% offset yield strength "break-point" is obtained; that is, the highest value of the yield strength which survives the sour environment when loaded to approximately 100% of its yield strength. Also shown is the influence of chloride concentration at the indicated pH values. For example, for this steel, these data would indicate an average "break-point" at a yield strength of approximately 122 ksi, relatively independent of the chloride concentration. Also indicated is the slightly lower pH of the 20% chloride environment which rises about 1 point pH during the run as shown. Tables 5-14, inclusive, summarize this type of data for the bent beam type tests at both ambient and elevated temperatures. Some of the early results of this study have been published and are integrated into this report (50).

Table 5 shows the break-points for a variety of steels. Of the commercially available steels, the modified 4135 appears to have a 10 percent higher break-point than the standard 4130, approximately 122 ksi compared to 110 ksi. The modified analysis varies from the standard primarily in a higher molybdenum content and the addition of columbium (55). At this time, this still appears to be the best commercially available steel we have examined in terms of strength level and resistance to chloride containing sour environments. The very low breakpoint for the 4340 steel emphasizes the deleterious influence of nickel in constructional steels exposed to sour environments.

V1312 and V1313 are vacuum melted experimental steels more or less designed on the model of the modified 4135 but with lower carbon and sulphur; both of which are known to generally improve resistance to fracture. Table 5 indicates that these steels are somewhat better than the standard 4130 but do not quite match the higher carbon modified version. One possible reason may be the lower carbon content. It is interesting to note that the sulphur in these two steels was substantially lower than for the modified 4135 (.004 vs .010%). On the other hand, the Mn, Si, and P contents were at normal levels and these elements may play a decisive role

in the response of these steels to hydrogenous environments.

It is quite well-established that lower carbon contents normally enhance resistance to brittle failure for the constructional type steels. The 4118 and 4123 together with the other steels represent an attempt to determine whether the enhanced resistance to brittle fracture under atmospheric conditions carries over to sour environments---clearly, it does not!

At this time, it is instructive to recognize that the lower carbon steels require a lower tempering temperature to attain the same strength level as one of higher carbon. In this connection, there is some evidence to indicate that the tempering temperature per se required to attain a given strength level may be a significant factor in resistance to sour environments (55-57). In fact, this effect may extend beyond the influence of carbon, also including some of the alloying elements, particularly those which enhance resistance to softening on tempering. More specifically, the higher the tempering temperature required to attain a given strength the more resistant the steel, particularly at the strength levels of interest. A comparison of 4118 with 4135 modified clearly illustrates this. At 5% NaCl, 4118 has a break-point of less than 110 ksi obtained by tempering at 1075°F. On

the other hand, 4135 modified gave a break-point value of 122 ksi. However to obtain this value of 122 ksi, it was necessary to temper at 1275°F. The phenomenon of temper embrittlement, to be discussed later, may be responsible for this beneficial effect of the higher tempering temperature. The lower tempering temperatures are known to promote brittle behavior.

The 2 1/4Cr-1Mo steels at both the .20 and .30 carbon levels represent steels of substantial high hardenability for heavy sections such as well head equipment, valve bodies turbine housings, etc. (18,58). It is apparent that the sour environment break-points are quite respectable in terms of the other steels examined and present realistic values of SSC resistance at acceptable strength levels for these applications.

The V1397 (high purity 4130) and the 4135 Modified (high purity) are two steels of rather special interest. As indicated, each of them represent a vacuum melted high purity steel with the basic analysis of their commercial counterpart. Although the purity is obviously outside of regular commercial feasibility, the idea was to examine the influence of inclusion content, type, distribution,

as well as sulphur, phosphorus, manganese, silicon, etc. These factors known to influence fracture characteristics in normal environments and several studies have indicated some influence in sour environments (59-63). Comparing in Table 5 the standard 4130 with its high, virtually inclusion-free counterpart, it is apparent that the V1397 steel enjoys a substantial advantage over its commercial counterpart. Indeed, the modified 4135 which exhibited the best break-point of any steel examined also showed substantial improvement in the high purity version to give the highest value of bent beam break-point observed in the entire study. The obvious implication is that at least some of these factors are significant and perhaps may be beneficially controlled without the necessity for super purity. Indeed, very low sulphur is most certainly commercially feasible today and modern steel making practice offer opportunities for controlled inclusion types, etc.

The influence of chloride concentration on cracking in sour environments has been open to some question particularly for the constructional type steels. Examination of Table 6 clearly reveals that the higher chloride concentrations are not detrimental and may even be slightly beneficial. To the extent that the hydrogen pickup results from corrosion, the

inhibitive effect of chlorides above 1% in these steels can account for this behavior (63). This result is particularly relevant to the development of the Imperial Valley, and similar high chloride geothermal resources.

In the constructional type steels it is well-known that the resistance to hydrogen embrittlement and SSC increases substantially as the temperature is raised. The data of Table 7 are quite consistent with this indicating a significant improvement in resistance to SSC at higher exposure temperatures. Break-points of 140 ksi or slightly higher are apparent and again essentially independent of chloride concentration. The improvement appears also to be independent of the temperature above 215°F. Isolated tests at 325°F were quite consistent with this view.

Although exposure at elevated temperatures does provide improvement, contrary to common belief, there apparently is no complete immunity; there still is a critical yield strength break-point which can not be exceeded. In other words, one can not use very high strength steels on the assumption that SSC is not operative at the more elevated temperatures. However, this type of data is significant in that it can provide at least semi-quantitative design guidelines to match temperature changes with depth. This phenomenon is

merely a manifestation of the influence of temperature on the critical yield strength for hydrogen induced brittle delayed failure (35,40).

It is well-recognized that the threshold stress for failure decreases as the pH is lowered, particularly at pH values less than 4-5 (13), this in turn can limit the yield strength break-point as indicated in the introduction. The data of Table 8 illustrates the improvement in the critical (break-point) yield strength at pH values close to neutral. At ambient temperature and pH values of 2.5-4, yield strength break-points of 110 ksi-122 ksi were indicated as compared to approximately 140 ksi at pH 6-7. Solutions initially started at pH 6.0 rather quickly settled at 6.5 as did those initially started at 7.

Here again, contrary to common belief, a near neutral pH does not provide immunity. Indeed, SSC has been observed at pH 12. However, quite similar to the effect of elevated exposure temperatures it does quite substantially raise the critical yield strength for SSC. Just as in the case of higher down hole operating temperatures, this phenomenon provides greater reliability for those steels that may be operating marginally.

Bent Beam Tests (Continued)

Corrosion Resistant Alloys

A286

Many of the corrosion resistant alloys are based on face-centered cubic structures and may be expected to exhibit greater susceptibility to SSC at temperatures significantly above ambient. The age-hardenable austenitic stainless steel A-286 behaves in this manner. When fully aged to 190 ksi (16 hrs.-1200°F) there was no failure at 215°F. On the other hand, testing at 325 and 425°F in both 5 and 20% chloride modified NACE solution produced failure. However, the 30 day-215°F exposure did indicate some loss of basic ductility in other tests. At this time, there is no way of knowing whether or not this loss of ductility indicated impending failure at some longer exposure time; a basic problem in any of these accelerated tests.

Overaging (16 hrs.-1300°F) to obtain a Y.S. of 155 ksi did not fail in the 5% NaCl solution. In the 20% NaCl solution only one of three specimens cracked but pitting was evident in all three. This appears to be more than a simple strength level effect since under-aging to similar strength

levels exhibited failure in all cases. Although not examined systematically, reference to Table 9 indicates a greater sensitivity to higher chloride concentrations for A286 in contrast to the behavior in constructional type (BCC) steels. Of course, it has long been appreciated that austenitic type stainless steels are sensitive to environments containing appreciable amounts of chloride.

K Monel

K Monel 500, treated to 140 and 170 ksi yield strengths has resisted cracking in both the 5% and 20% NaCl, H₂S environments (Table 10). This agrees with the rather limited literature on this alloy indicating resistance to SSC in the standard NACE solution. However, there are several unofficially reported service failures in sour wells. Also, there is evidence that this alloy can be subject to hydrogen embrittlement under rather specific conditions (32). In order to examine further the potential susceptibility of this alloy to a hydrogenous environment a number of experiments were conducted under the same general conditions as reported in Table 10, but coupled with steel for 30-34 days. No failures or other evidence of deterioration was observed.

MP35N

Much attention has been focused recently on a highly corrosion resistant non-ferrous, age-hardenable alloy, MP34N (47,48,65). This alloy has not only demonstrated excellent corrosion properties but also resists pitting and until recently was believed to be completely immune to SSC at yield strength levels up to 250 ksi.

It is evident in Table 11 that at the high strength levels SSC can occur at ambient temperatures when coupled with iron; in short, under cathodic charging (46). Indeed, aging at almost any temperature below approximately 1300°F will produce failure when coupled to iron or otherwise cathodically charged. Pertinent conferences and a recent comprehensive publication clearly indicate this and extend the phenomenon to some of the Inconels and Hastalloys (47, 66).

The data of Table 11 are consistent with those being compiled in many laboratories. It is apparent that no failures occurred in the 30 day tests in the NACE solutions at all temperatures when not coupled to iron or otherwise cathodically charged. This was true for both the 5 and 20 percent chloride solutions. As recent studies have indicated,

coupling to iron and testing at ambient temperature in acid or NACE solution produces failure quite readily. However, testing at 215°F, even when coupled, did not yield failure.

Most of the tests were conducted with the transverse orientation which usually is a direction of lesser resistance to cracking. However, as expected, it is possible to get failure in the longitudinal orientation; for example, the 50% HCl acid environment tests listed in Table 11. This is probably merely a question of degree and severity of the environment. The concept of the beneficial effect of over-aging with only slight loss of strength as indicated in our studies on A286 (Table 9) shows promise for the MP35N alloy. A limitation on the maximum aging temperature involves recrystallization following the necessary cold work prior to aging (46).

Table 12 gives the results of a series of special tests conducted at 425°F. The primary difference between these tests and those presented in Table 11 resides in the fact that the autoclaves were charged with the H₂S and/or Argon at a pressure of 75 ksi at ambient temperature resulting in a pressure-temperature relation approaching somewhat more of what may be encountered in service. As indicated in the table, no failure was observed under any of the four conditions,

each of which was examined in quadruplicate.

It was interesting to note that in this alloy, treatments which appeared to result in greater sensitivity to SSC did not influence the excellent tensile and ductility properties of the alloy. In short, tensile testing in a normal atmosphere is incapable of predicting performance in a sour environment.

The 300 series austenitic stainless steels are not generally considered to be high strength alloys but can be substantially strengthened by cold work. Table 13 for 304 indicates that in the annealed condition there was no failure at ambient temperature and without chloride. This was true even when given an embrittling treatment at 1200°F. On the other hand, after strengthening by cold work, failure was encountered above 1% NaCl, even at pH 6.5. Also, at all elevated temperatures and all chloride concentrations failure was evident.

The more highly alloyed 310 data are presented in Table 14. At ambient temperature there does appear to be greater resistance to SSC than for 304 when both are in the cold worked condition. Indeed, failure occurred only with the maximum 20% NaCl condition. Just as with 304, failure

was observed at all elevated temperatures.

As might be expected, the austenitic stainless steels demonstrated greater sensitivity at the higher chloride concentrations and at the elevated temperatures even in the absence of oxygen. Strengthening by cold work also increased the sensitivity to SSC.

NACE Tensile Tests

Break-points

A limited number of tests on several selected alloys were examined to check break-points by the NACE tensile method. The rate at which these data can be accumulated is limited by the fact that only one data point per run can be obtained (see Fig. 1b). Tables 15, 16 and 17 list the results for the high purity 4135 modified, the 2 1/4Cr-1Mo-.19C and a similar lower carbon cast variety. The results in Tables 14 and 16 are of particular interest since they allow a direct comparison of the break-points obtained on precisely the same material by the tensile and bent beam tests. For example, a value of around 94 ksi is indicated for the Modified 4135 (high purity) by the tensile method, this is in

the same general range of values as recently obtained by others (67). On the other hand, the bent beam test gave a value near 126 ksi (see Table 5)---approximately 32 ksi difference in break-points. A similar comparison for the 2 1/4Cr-1Mo-.19C steel yields a difference of approximately 36 ksi. The data of Tables 15, 16, and 17 are also plotted in Figs. 3, 4 and 5 and indicate the type of scatter obtained in these tests.

The difference in break-points by the two methods is significant and real. Although only the two steels were matched precisely for the two types of tests, general comparisons of the data of Table 5 with tensile data in the literature for similar type steels also yield substantial differences and in all cases the tensile values are much lower.

It is fully appreciated that any loss of thickness by corrosion on the relatively thin bend specimens would tend to reduce the actual applied stress as compared to a similar loss of section in the tensile specimen. To evaluate this possibility, periodic checks of section loss were made, particularly for the two steels discussed above. These measurements were made at the end of the run and converted to a stress difference of about 5 ksi where the maximum

observed was equivalent to less than 10 ksi. It is concluded that the observed difference between the two tests is real and substantial.

This is not an inconsequential observation. These types of tests are conducted to evaluate a materials resistance to sour environments and to provide some design guidelines. Although no one test can provide data for every variation of service, virtually no service conditions involve pure tensile stress. It would appear that a test involving a complex stress state (in our bent beam specimen, biaxial stress) would be more likely to anticipate service conditions. This is particularly true when an embrittling phenomenon may be involved.

Several factors account for the difference in break-point values. The fact that the bend test produces higher values than the tensile test by 20 to 30 percent is suggestive of a major input from the stress state parameter. If the transverse tension induced into the surface of the bend specimen has its normal strengthening effect, then it is quite logical that higher values of circumferential stress would be required to produce a circumferential strain equivalent to the longitudinal strain in the tension test piece at its break-point. In short, although we think in terms of stress, strain is

the critical parameter. This aspect of the study is being pursued.

Duplex (austenite and ferrite) stainless steels generally are considered to exhibit improved stress corrosion cracking in chloride environments. The several test results in Table 18, in as far as they go, appear to substantiate this. Even in a boiling, saturated NaCl, no failure occurred in 30 days. The 55 ksi Y.S. is quite respectable for an austenitic stainless steel. Obviously, additional tests should be conducted.

Threshold Stress

The NACE Standard TM-01-77 describes the method in which the threshold stress should be determined and the data presented. The results of such tests are presented in Figure 6-10, inclusive. Figures 6 and 7 give the threshold stress values for cast 8620 at 80 and 92 ksi Y.S. It appears in both cases that the no-fail value is approximately 75 percent of the Y.S. However, the data for the 92 ksi Y.S. treatment indicates quite some scatter near the 75 percent value as compared to the lower Y.S. material. On this basis, the 80 ksi Y.S. treatment with a threshold stress of 75 percent or a stress of 60 ksi should provide a more realistic design

figure.

The curve of Fig. 8 exhibits a threshold stress of about 75 percent or slightly higher for an AOD cast 8630 at 85 ksi Y.S. or a stress of 64 ksi. It is interesting to note that the data points from two independent test sources match quite well---almost better than expected considering the inherent scatter in this test. CA6NM is a stainless type cast alloy. For this alloy made by the AOD process and heat treated to 75-77 ksi Y.S., a threshold stress of 85 percent or better is indicated by the data of Fig. 9. This corresponds to a stress of about 65 ksi. This is quite better than non-AOD values and substantially better than the type 410 alloy which exhibits a threshold stress of less than 20 percent when heat treated to 97 ksi Y.S. or a stress of less than 20 ksi (51,57,68 & 69). Interestingly enough, the 410 alloy has been widely employed at the well head of oil and gas wells. This appears to be quite consistent with the difference in break-points as determined by the tensile and the bend specimen where the tensile value was always substantially lower. It would appear that tensile test gives ultra conservative data.

The 450 stainless alloy showed a threshold stress near 45 percent of the 92 ksi Y.S., see Fig. 11. Of particular

interest, are the early results, as this is being written, of a determination of the threshold stress with the bent beam type specimen. At this time, the threshold stress has been bracketed between 60 and 70 percent of the 95 ksi Y.S. Again, a substantial difference is observed between the tensile and bent beam test results. Perhaps not surprisingly, the threshold stress behaves in the same manner as the break-point yield strength.

C-Ring Tests

The results of the C-Ring tests, in the standard NACE solution are given in Table 19. Since the grade numbers indicate a minimum yield strength, the rings were usually loaded to a stress approximately 5-10 ksi above the indicated minimum; the usual aim for commercial heat treatment. Reference to Table 3 indicates that a majority of the steels examined thus far are of the more economical grades depending upon higher than usual manganese for a measure of hardenability. These steels are not generally recommended for sour environment service except possibly at very low strength levels.

A cursory examination of this table clearly indicates the well-recognized sensitivity of steel to a sour environment above moderate strength levels. As an example, compare steels #1 or #2 with steel #6, all with essentially the same alloy composition, yet the P110 (RC29) failed and the K55 (RC19) did not fail. A comparison of steels #4 and #10 also illustrate the influence of strength level.

Although strength level is a vital factor, an evaluation on this basis alone would constitute a gross oversimplification. Hardenability and its relation to structure exerts a major influence on performance. Hardenability is primarily determined by the alloy content and for a given composition the full use of its potential for hardening will be sensitive to section size and quenching efficiency. The importance of hardenability resides in the fact that fine structures with uniform carbide distributions (i.e. tempered martensite) are more resistant to hydrogenous environments than the more coarse structures such as ferrite-pearlite mixtures i.e. normalized structures), all other things equal.

The influence of section size on the attainment of the fine structure (hardenability) is quite evident in a general comparison of the greater resistance to failure of the smaller, thinner, wall tubing compared to the heavier

casing.

Although the materials tested do not present a great variety of alloy steels, the influence of alloy on hardenability and thus structure can be seen, for example, in a comparison of steels #4 and #5 (See Tables 3 and 19) the compositions are essentially the same except that steel #4 has .30 percent molybdenum and did not fail while steel #5, without molybdenum, did fail. Molybdenum is a strong promoter of increased hardenability. Steels #13 and #14, essentially 4130 type analyses, also did not fail despite relatively thick wall sections. Examination of steels #12, #13 and #14 demonstrates the influence of the improved structure (martensite) obtainable by alloy and/or efficient fast quenching.

As indicated earlier in this report, temper embrittlement may be a factor in some cases. Not only tempering at inappropriate temperatures (i.e. $\sim 1150^{\circ}\text{F}$ or lower) but slow cooling through this temperature range can induce embrittlement. Only recently has consideration been given to fast cooling casing, tubing, etc., from the tempering temperature. General practice, however, is to slow air cool which in the larger diameters and/or wall thicknesses can lead to temper embrittlement. On the other hand, rapid water quenching from typical tempering temperatures could result in quite

high residual stresses both inside and out having been measured as high as 65 ksi circumferential and 25 ksi longitudinal (70). Fortunately, it usually is not necessary to drastically water quench to avoid temper embrittlement, particularly with the newer analyses being employed for casing and tubing in the quenched and tempered condition.

All rings were also tested in the notched condition and all failed. This is not surprising considering the deleterious influence of cold work developed at the notch root on loading and the stress concentration imposed by the notch (71-74)

The data of Table 20 give the results of a brief study to determine if commercially treated casing, tubing, etc., may indeed be subject to temper embrittlement. Note that steel #5 as received did fail, but after being retempered and quenched from the tempering temperature it did not fail. On the other hand, steel #9 which did not fail in the as received condition, exhibited failure after given a temper embrittling treatment. Steel #10 failed in the as received condition; however, after quite rapid air cooling from 1200°F one of two duplicate tests did not fail, indicating some improvement with respect to temper embrittlement. Steel #11 (P110) failed as received; this could be partly the result

of the rather high strength and partly due to temper embrittlement. However, when retempered at 1200°F to substantially reduce the strength, the quench specimen did not fail and the slow cooled one did fail from temper embrittlement. This rather cursory examination clearly indicates that temper embrittlement in many instances can and will actually limit the performance of casing and other components of a geothermal power system. It should be appreciated that although temper embrittlement may aggravate the situation in a sour environment, its deleterious influence on performance is by no means restricted to sour environments.

Fracture Mechanics Tests

Double Canterlever Beam Specimen (DCB)

The DCB test technique has been extensively employed for a study of a variety of steels particularly at Climax Molybdenum Corp. An examination of a series of air melted Mn-Mo-C90 casing steels indicated that SSC resistance was favored by lower Mn, lower austenitizing temperature and

fast cooling from the tempering temperature (75,76). Several analyses of potential well head steels clearly revealed the improved resistance caused by the difference in microstructure (martensite) resulting from increase in hardenability (77). Other studies involved a series of .30C steels with varying Cr, Mn, S, and additions of Cb and/or V. Here, a modified 4130 (.75Mo, .035Cb) exhibited increased resistance to SSC at the higher tempering temperature (78,79) quite consistent with observations obtained by all the various test techniques such as bent beam, tensile, rings, etc. Also, a general correlation between the $K_{I_{SSC}}$ and the Shell bent beam specimen was observed in terms of rank ordering of several pertinent alloys (80).

The DCB results are summarized in Table 21. The three laboratory air melted steels (3Cr-1Mo-.10, .20, .30C) were examined on the basis of a literature indication that environmental cracking resistance was superior in martensitic steels with an untwinned structure (low carbon) compared with twinned structures (81). Our $K_{I_{SSC}}$ values were all relatively low and somewhat disappointing, so our fracture mechanics studies were redirected to more promising alloys.

The two laboratory vacuum melted steels (V1312, V1313) test values are plotted on Fig. 12 for comparison with the scatter band for a number of heats of commercial 4130 (53). It is apparent that both steels exhibit a higher K value scatter band than 4130. Steel V1312 is essentially a Mo-Cb modified 4130 and V1313 is the same except V has been substituted for Mo.

The K values for the high purity laboratory heats (1550, 1551) are plotted on Fig. 13 for comparison with the 4130 scatter band. Table 1 indicates that these two steels contain .75 Cr and 1.5 Mo with and without 1 Cu. It is apparent that these steels possess a higher K value scatter band than 4130 over the strength range of primary interest. The Cu addition does not seem to have any influence.

Test Results Scatter

This report should not be concluded without a brief discussion of the scatter in test results. Our experience indicated that all test methods exhibited some scatter in the data but that the NACE tensile showed substantially the greatest amount followed by the two point bend test.

Some of this scatter must be inherent in the test method but other factors are involved.

It is unfortunate that the range of strength levels suitable for use in sour environments require tempering on the steep part of the Y.S. or RC vs tempering temperature curve. Fig. 14 illustrates this point. Here, the strength is plotted against the tempering temperature. Although the plot is labeled schematic, the data correspond approximately to those for the modified 4130. On this curve we have shown a band corresponding to plus or minus approximately 10°F, reasonable laboratory control and better than normal industrial control. It is evident that this spread in temperature corresponds to approximately a spread of 3RC or 10-12 ksi in the Y.S. This is a significant difference even for laboratory tests in view of the limited useful strength range in sour environments.

It is apparent from the above that a run of commercial casing, tubing, etc., may easily show variations in Y.S. of 25-35 ksi. Another potential source of scatter from a practical point of view involves the possibility of varying degrees of temper embrittlement. Since the appropriate tempering temperatures are near the top or above the embrittling range, varying cooling rates from the tempering

temperature can result in different degrees of embrittlement. Of course, controlled moderately fast cooling from the tempering temperature and avoidance of compositions that require tempering at the lower temperatures should minimize this problem.

SUMMARY

1. Four different types of tests have been employed. Where comparisons were possible the different types of tests qualitatively ranked the alloys in the same order.
2. A fine grained version of 4130, modified with higher Mo and Cb additions appeared to be the best commercially available steel that we examined for down hole service.
3. High purity versions of several of the commercial alloys of interest, particularly the modified 4130, exhibited somewhat higher yield strength break-points.
4. The lower carbon varieties of the 41xx type steels do not seem to be as resistant to SSC as their higher carbon (.30-.35C) counterparts.
5. The SSC resistance is improved the higher the tempering temperature necessary to achieve a given yield strength.
6. The resistance to SSC of the constructional type steels is essentially independent of the chloride concentration.
7. For the constructional steels, the yield strength

break-point is 15-20 percent higher at service temperatures near 300-450°F. However, a definite critical yield strength does exist which can not safely be exceeded. Elevated temperature service does not provide complete immunity.

8. The influence of pH is quite analogous to that of temperature. Increasing values of pH up to 7 raise the useable yield strength. Again, there is no immunity only a higher yield strength break-point.
9. Overaging of A286 stainless steel appeared to be beneficial at a still respectable strength level. Underaging to the same approximate strength was not effective. Increased chloride concentration increased sensitivity to failure.
10. No evidence of SSC or embrittlement was observed in K Monel 500 treated to both 140 and 170 ksi. This included modified NACE solution with 5 and 20 NaCl and also coupled with iron.
11. MP35N did not exhibit SSC over a range of temperatures from ambient to 425°F in both standard and 20 percent modified NACE solution including 75 ksi pressurized H₂S. When coupled to iron failure was observed

at ambient but not at elevated temperatures.

12. No failure was observed in 304 in the annealed condition at ambient temperature; but when cold worked, chloride concentrations above 1% increased sensitivity. At elevated temperatures, failure was encountered at all chloride concentrations. In the cold worked condition, 310 displayed the usual sensitivity to chloride concentration and to elevated temperatures.
13. A comparison of break-point yield strength values obtained by the tensile and bent beam specimens for the same material gave break-point numbers 20-30 percent higher for the bent beam tests. This was well outside the range of scatter or corrosion effects even considering the relatively high degree of scatter observed with the tensile tests.
14. Several versions of well head equipment constructional steels with adequate hardenability have demonstrated good SSC threshold values at adequate yield strengths. In particular, are included, the 2 1/4Cr-1Mo and a lower Ni version of 86xx steels.
15. Two corrosion resistant steels, CA6NM and 450 have shown a substantially higher threshold stress in

relation to their yield strength than their counterpart (410) currently in common use.

16. C-ring tests of commercially heat treated casing and tubing indicated the influence of strength and the superior properties of quenched and tempered structures based on martensite.
17. Several selected C-rings of commercially heat treated casing or tubing clearly gave indications of temper embrittlement. Unless carefully controlled this can constitute a major limitation on down hole steels.
18. The $K_{I_{SSC}}$ values for several modified 4130 type steels fell in a scatter band well above that for a series of 4130 commercial steels over the strength range of primary interest.

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TABLE 1 - ANALYSES
CONSTRUCTIONAL STEELS

<u>STEEL</u>	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Cr</u>	<u>Mo</u>	<u>Cb</u>	<u>V</u>	<u>Ni</u>
4118	.20	.80	.008	.012	.27	.51	.11	---	---	---
4123	.23	.84	.036	.016	.36	.93	.20	---	---	---
4130	.33	.53	.015	.029	.27	.91	.21	---	---	---
4135 Mod.	.34	.86	.013	.010	.28	1.08	.83	.054	---	---
4340	.35	.76	.007	.011	.25	.82	.25	---	---	1.79
V1312	.26	.50	<.005	.005	.21	1.01	.78	.04	---	---
V1313	.26	.52	<.005	.004	.22	1.01	.78	---	.06	---
3Cr-1Mo	.31	.57	.006	.019	.25	3.12	1.06	---	.18	---
3Cr-1Mo	.20	.53	.007	.020	.23	3.10	1.03	---	.20	---
3Cr-1Mo	.10	.58	.006	.015	.21	3.14	1.04	---	.18	---
2 1/4Cr-1Mo	.19	.55	.013	.008	.22	2.20	1.00	---	---	---
2 1/4Cr-1Mo Cast	.15	.75	.015	.007	.23	2.73	.92	---	---	---
8620 Cast	.14	.60	.023	.010	.53	.70	.45	---	---	.48
8630 Cast	.32	.86	.021	.002	.74	.57	.34	---	---	.63
4135 Mod.*	.34	<.003	.006	.003	.03	.98	.94	.036	---	---
V1397*	.35	.003	.006	.003	.011	1.40	.20	<.02	<.006	<.02
1550*	.28	.009	<.005	.005	.012	.72	1.59	.052	.05;	Cu <.02
1551*	.28	.007	<.005	.003	.01	.73	1.57	.048	.05;	Cu .98

*High Purity

TABLE 3
ANALYSES - C-RINGS

<u>STEEL</u>	<u>C</u>	<u>MN</u>	<u>P</u>	<u>S</u>	<u>SI</u>	<u>CR</u>	<u>MO</u>	<u>V</u>
1	.26	1.47	.013	.015	.20	--	--	--
2	.25	1.53	.011	.018	.19	--	--	--
3	.35	1.58	.009	.015	.18	--	--	--
4	.24	1.62	.011	.012	.22	--	.30	--
5	.25	1.40	.010	.014	.19	--	--	--
6	.43	1.24	.013	.017	.19	--	--	--
7	.43	1.16	.015	.016	.21	--	--	--
8	.37	1.58	.017	.014	.20	--	.14	.06
9	.26	1.42	.008	.017	.08	--	--	--
10	.23	1.61	.015	.011	.14	--	.33	.06
11	.26	1.54	.013	.019	.18	--	--	--
12	.13	.45	.010	.007	.51	9.0	.95	--
13	.32	.54	.008	.014	.29	.97	.22	--
14	.32	.53	.008	.023	.27	1.1	.29	--

TABLE 4

SULPHIDE STRESS CRACKING OF MODIFIED 4135 STEEL

AMBIENT TEMPERATURE

<u>RC</u>	<u>Y.S. MPA (KSI)</u>	<u>No./FAILED</u> <u>No./TESTED</u>
5% NaCl pH 3.5-4.0		
30	883 (128)	2/2
29	869 (126)	3/3
28	848 (123)	2/5
27	827 (120)	0/1
26	800 (116)	0/3
24	759 (110)	0/4

20% NaCl pH 2.5-3.5

33	952 (138)	4/4
31	903 (131)	4/4
30	883 (128)	2/5
29	869 (126)	1/2
28	848 (123)	0/3
27	827 (120)	0/2
26	807 (117)	0/2
24	759 (110)	0/1

TABLE 5

YIELD STRENGTH BREAK-POINTS FOR DIFFERENT STEELS
EXAMINED IN THE STANDARD NACE SOLUTION

<u>MATERIAL</u>	<u>Y.S. (MPa)</u>	<u>KSI</u>
STANDARD 4130	759	(110)
4135 MODIFIED	841	(122)
V1312	814	(118)
V1313	814	(118)
4123 (COMMERCIAL PIPE)	772	(112)
4118 (COMMERCIAL CARBURIZING GRADE)	<759	(110)
4340	<744	(108)
2 1/4Cr-1Mo-.31C	827	(120)
2 1/4Cr-1Mo-.19C	820	(119)
V1397 (4130 HIGH PURITY)	841	(122)
4135 MOD. HIGH PURITY	869	(126)

TABLE 6

**YIELD STRENGTH BREAK-POINTS FOR SEVERAL STEELS
EXAMINED AT VARIOUS CHLORIDE CONCENTRATIONS**

CHLORIDE CONCENTRATION Y.S. MPa (KSI)

STANDARD 4130

0%	780 (113)
1%	759 (110)
5%	759 (110)
20%	814 (118)

4135 MODIFIED

0%	827 (120)
1%	855 (124)
5%	841 (122)
20%	855 (124)

V1397 (4130 HIGH PURITY)

0%	855 (124)
1%	848 (123)
5%	841 (122)
20%	855 (124)

TABLE 7

THE INFLUENCE OF TEMPERATURE ON THE YIELD
STRENGTH BREAK-POINTS IN THE STANDARD
NACE SOLUTION.

<u>MATERIAL</u>	<u>TEMPERATURE</u> <u>°C (°F)</u>	<u>Y.S. BREAK-POINT</u> <u>MPa (KSI)</u>
STANDARD 4130	AMBIENT	759 (110)
	102 (215)	965 (140)
	218 (425)	965 (140)
MODIFIED 4135	AMBIENT	841 (122)
	102 (215)	952 (138)
	218 (425)	952 (138)
V1397	AMBIENT	841 (122)
	102 (215)	986 (143)
V1312	AMBIENT	814 (118)
	102 (215)	915 (140)
V1313	AMBIENT	814 (118)
	102 (215)	952 (138)
2 1/4Cr-1Mo-.31C	AMBIENT	827 (120)
	102 (215)	965 (140)

TABLE 8

THE INFLUENCE OF PH 6-7 ON THE YIELD STRENGTH
BREAK-POINTS AT AMBIENT TEMPERATURE AND 5% NaCl

<u>STEEL</u>	<u>Y.S. MPA (KSI)</u>
4130 STANDARD	965 (140)
4135 MODIFIED	965 (140)
V1397 HIGH PURITY	979 (142)
V1312	965 (140)
V1313	979 (142)

TABLE 9
SULPHIDE CRACKING OF A286 STAINLESS STEEL
IN STANDARD NACE SOLUTION

<u>TEST TEMPERATURE</u> <u>°C (°F)</u>	<u>AGEING TREATMENT</u> <u>TEMPERATURES °C (°F)</u>	<u>Y.S. MPa (KSI)</u>	<u>No./FAILED</u> <u>No./TESTED</u>
5% NaCl			
AMBIENT	649 (1200) - 4 HRS.	1241 (180)	0/2
102 (215)	649 (1200) - 16 HRS.	1310 (190)	0/1
163 (325)	649 (1200) - 16 HRS.	1310 (190)	1/1
163 (325)	704 (1300) - 16 HRS.	1062 (155)	0/1
20% NaCl			
218 (425)	621 (1150) - 1 HR.	1138 (165)	1/1
218 (425)	649 (1200) - 1 HR.	1165 (170)	1/1
218 (425)	649 (1200) - 4 HRS.	1199 (175)	1/1
218 (425)	649 (1200) - 16 HRS.	1310 (190)	3/3
218 (425)	704 (1300) - 16 HRS.	1062 (155)	1/3

TABLE 10

SULPHIDE STRESS CRACKING OF K MONEL

<u>TEST TEMPERATURE</u>	<u>HEAT TREATMENT</u>	<u>Y.S. MPA (KSI)</u>	<u>No. FAILED</u> <u>No. TESTED</u>
5% NaCl			
AMBIENT	8 HRS. 538°C (1000°F) F.C. TO 482°C (900°F) W.Q.	1165 (170)	0/1
163°C (325°F)	16 HRS. 593°C (1100°F) F.C. TO 482°C (900°F) A.C.	965 (140)	0/1
218°C (425°F)	SAME AS ABOVE.	965 (140)	0/2
20% NaCl			
218°C (425°F)	8 HRS. 538°C (1000°F) F.C. TO 482°C (900°F) W.Q.	1165 (170)	0/1
218°C (425°F)	16 HRS. 593°C (1100°F) F.C. TO 482°C (900°F) A.C.	965 (140)	0/2

TABLE 11

**SULPHIDE STRESS CRACKING OF MP35N^o
NOT COUPLED TO IRON**

<u>HEAT TREATMENT</u>	<u>TEST TEMPERATURE</u>	<u>NO. FAILED</u> <u>NO. TESTED</u>
593°C (1100°F)-4 HRS.	AMBIENT	0/5
704°C (1300°F)-4 HRS.	AMBIENT	0/1
538°C (1000°F)-1 HR.	102°C (215°F)	0/1
593°C (1100°F)-4 HRS.	163°C (325°F)	0/1
593°C (1100°F)-4 HRS.	218°C (425°F)	0/5

COUPLED TO IRON

593°C (1100°F)-4 HRS. 288°C (550°F)-20 DAYS	AMBIENT	2/2
593°C (1100°F) + 354°C (670°F)- 16 HRS.	AMBIENT	1/2
354°C (670°F)- 16 HRS.	AMBIENT	2/2
538°C (1000°F)- 1.5 HRS.	AMBIENT	2/2
593°C (1100°F) - 4 HRS. 288°C (550°F) - 20 DAYS	102°C (215°F)	0/2

- THESE DATA INCLUDE BOTH 5 AND 20% CHLORIDE SOLUTIONS WITH NO SIGNIFICANT DIFFERENCE.

**ACID HYDROGENATION
COUPLED TO IRON IN 50% HCL**

1000°F-1 HR.	AMBIENT	2/2
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TABLE 12

PRESSURIZED AUTOCLAVE TESTS MP35N

H₂S CHARGED AT AMBIENT TEMPERATURE TO 75 KSI PRESSURE;
OTHERWISE CHARGED WITH ARGON. HEAT TREATMENT, 1400°F-
4 HRS. - AIR. STRESSED TO 100 PERCENT OF Y.S; 190 KSI

* TESTED AT 425°F - 30-32 DAYS.

CONDITION

1	25% NaCl
2	25% NaCl + SATURATED H ₂ S
3	25% NaCl + 0.5 ACETIC ACID
4	25% NaCl + 0.5 ACETIC ACID +
SATURATED H ₂ S + 1 GRM/L SULPHUR.

NO FAILURE IN ANY CONDITION. THE TEST SPECIMENS IN
NaCl + ACETIC ACID WERE AS BRIGHT AFTER AS BEFORE.
THE OTHERS EXHIBITED A SLIGHT TAN DISCOLORATION WHICH
WAS MOST PRONOUNCED IN THE TEST ENVIRONMENT CONTAINING
ELEMENTAL SULPHUR.

* TESTED IN QUADRUPLICATE

TABLE 13

**SULPHIDE STRESS CRACKING OF 30% COLD WORKED
304 STAINLESS STEEL AT 1379 MPa (200 KSI).**

<u>CHLORIDE PERCENT</u>	<u>pH</u>	<u>TEST TEMPERATURE C (°F)</u>	<u>No. FAILED No. TESTED</u>
0	3.5	AMBIENT	1/5
1	3.5	"	0/2
5	3.5	"	5/5
5	6.5	"	2/2
20	2.5	"	3/3
1	3.5	102 (215)	1/1
20	2.5	102 (215)	1/1
1	3.5	163 (325)	1/1
20	2.5	218 (425)	1/1

**IN THE ANNEALED CONDITION, NO FAILURES WERE ENCOUNTERED
IN 4 TESTS IN 0 PERCENT CHLORIDE.**

TABLE 14

SULPHIDE STRESS CRACKING OF 310
AUSTENITIC STAINLESS STEEL COLD WORKED
30 PERCENT FOR 1241 MPa (180 KSI)

CHLORIDE PERCENT	PH	TEST TEMPERATURE C (°F)	No. FAILED No. TESTED
1	3.5	AMBIENT	0/1
5	3.5	"	0/2
5	6.5	"	0/2
20	2.5	"	2/2
1	3.5	102 (215)	1/1
20	2.5	102 (215)	1/1
1	3.5	163 (325)	1/1
1	3.5	218 (425)	1/1

TABLE 15

NACE TENSILE TEST BREAKPOINT Y.S.
4135 MODIFIED - HIGH PURITY

Y.S. MPa (KSI)	FAIL-No FAIL	TIME-DAYS
717 (104)	FAIL	7
676 (98)	FAIL	29 DAYS
648 (94)	No FAIL	26 DAYS
565 (82)	No FAIL	31 DAYS
544 (79)	No FAIL	30 DAYS

TABLE 16

NACE TENSILE TEST BREAKPOINT Y.S.
2 1/4Cr-1Mo - .19C

Y.S. MPa (KSI)	FAIL-No FAIL	TIME-DAYS
(669) (97)	FAIL	7
(662) (96)	FAIL	9
(600) (87)	FAIL	7
(600) (87)	FAIL	25
(572) (83)	N.F.	30
(565) (82)	N.F.	31
(551) (80)	N.F.	33

TABLE 17

NACE TENSILE TEST BREAKPOINT Y.S.
2 1/4Cr-1Mo - .15C AOD CAST

Y.S. MPa (ksi)	FAIL-No FAIL	TIME-DAYS
(669)(97)	3 FAIL	~1
(600)(87)	2 FAIL	1
(586)(85)	1 FAIL	14
(551)(80)	1 FAIL	20
(551)(80)	No FAIL	30

TABLE 18

NACE TENSILE TEST
DUPLEX STAINLESS STEEL
APPROX. 25 PERCENT FERRITE
STRESSED AT THE YIELD STRENGTH, 55 KSI

AMBIENT, STD. SOLUTION, NO FAIL 30 DAYS
228°F SATURATED NaCl, No H₂S, NO FAIL 30 DAYS

TABLE 19
C-RING TESTS

STEEL	SIZE	*GRADE	**HEAT TREATMENT	RC	WALL, IN.	FAIL- No FAIL
1	7" CASING	P110	QUENCH + TEMPER	29	.46 INCHES	2 FAILED
2	7" CASING	P110	QUENCH + TEMPER	29	.34 INCHES	2 FAILED
3	7" CASING	N80	NORMALIZED	19	.36 INCHES	1 No FAIL
4	7" CASING	L80	QUENCH + TEMPER	21	.28 INCHES	2 No FAIL
5	7" CASING	N80	QUENCH + TEMPER	23	.27 INCHES	2 FAILED
6	7" CASING	K55	HOT ROLLED	19	.26 INCHES	2 No FAIL
7	2-7/8" TUBING	J55	NORMALIZED	19	.19 INCHES	2 No FAIL
8	2-7/8" TUBING	N80	NORMALIZED	20	.17 INCHES	4 No FAIL
9	2-7/8" TUBING	N80	QUENCH + TEMPER	25	.18 INCHES	2 No FAIL
10	2-7/8" TUBING	P105	QUENCH + TEMPER	32	.16 INCHES	2 FAILED
11	7" CASING	P110	QUENCH + TEMPER	30	.50 INCHES	2 FAILED
12	2-3/4" TUBING	N80	NORMALIZE + TEMPER	21	.48 INCHES	2 No FAIL
13	3-3/4" TUBING	C80	QUENCH + TEMPER	21	.40 INCHES	2 No FAIL
14	5-1/2" TUBING	C90	BORE QUENCH + TEMPER	20	.42 INCHES	2 No FAIL

• MINIMUM YIELD STRENGTH, KSI

** OUTSIDE ONLY WATER QUENCH UNLESS OTHERWISE NOTED.

TABLE 20
C-RING TESTS
TEMPER EMBRITTLEMENT STUDY

STEEL	HEAT TREATMENT	HARDNESS	FAIL/NO FAIL
STEEL #5 7 INCH CASING N80 Q + T	AS RECEIVED.	RC 23	2 FAILED
	1200°F- 1 HR. WATER QUENCH.	RC 22	2 No FAIL
STEEL #9 2-7/8" TUBING N80 Q + T	AS RECEIVED.	RC 25	2 No FAIL
	STEP-COOLED, 1125°F TO 950°F IN 25° - 1/2 HR. INCREMENTS	RC 25	2 FAIL
STEEL #10 2-7/8" TUBING P105	AS RECEIVED	RC 32	2 FAIL
	1200°F AIR COOLED	RC 30	1 FAIL 1 No FAIL
STEEL #11 7" CASING P 110 REHEAT TREATED	1200°F - 1 HR. WATER QUENCH	RC 23	1 No FAIL
	1200°F - 1 HR. SLOW COOLED	RC 23	1 FAIL

Table 21

DCB Data

<u>Material (Heat No.)</u>	<u>HRC</u>	<u>K_ISSC (ksi√in.)</u>	<u>HRC</u>	<u>K_ISSC (ksi√in.)</u>
6906	28	18	25	23
3Cr-1Mo-.10C	28	17	24	20
	25	26	25	23
	25	22		
6869	22	25	26	26
3Cr-1Mo-.20C	22	27	26	18
	24	20	28	17
	25	24	28	19
6868	24	22	29	12
3Cr-1Mo-.30C	24	18	31	12
	24	22		
V1312	27	32	28	30
	28	33	28	32
	28	28	28	27
	29	29	29	30
	28	28	29	29
	26	35	28	28
	26	32	28	31
V1313	28	19	30	24
	30	22	31	23
	30	28	30	19
	30	20		
V1550	28	24	27	27
	28	30	28	25
	29	31	28	19
	28	24	27	23
	28	28		
V1551	26	32	29	27
	26	24	27	23
	29	30	27	21
	27	30	27	26
	27	31

Fig. 1a: Bent Beam type specimen showing example of no-fail vs. fail.

Fig. 1b: Test unit for standard NACE tensile test evaluation in sour environment.

FIG. 2

C - RING EQUATION FOR STRESS

$$\delta = 2000 \sigma \left[\frac{\pi R \gamma_2}{4E} \right] \left[\frac{12 R^2}{6 t R^2 + R t^2 - \gamma_2 t^2} \right]$$

WHERE

δ = diametrical deflection, inches

E = young's modulus

σ = stress, ksi

t = ring thickness, inches

OD = ring outer diameter, inches

$\gamma_2 = OD/2$; $D = (OD - t)$; $R = D/2$

FIG. 4: NACE TENSILE SSC HIGH PURITY 4135 MODIFIED, QUENCHED AND TEMPERED.

FIG. 5: NACE TENSILE SSC 2 1/4 Cr - 1 Mo - .19C. QUENCHED AND TEMPERED.

FIG. 6: NACE TENSILE SSC 2 1/4 Cr - 1 Mo - .15C CAST STEEL. QUENCHED AND TEMPERED.

FIG. 7: NACE TENSILE SSC 8620 Y.S. = 80 KSI. CAST STEEL. QUENCHED AND TEMPERED.

FIG. 8: NACE TENSILE SSC 8620 Y.S. = 90 ksi. CAST STEEL. QUENCHED AND TEMPERED.

FIG. 9: NACE TENSILE SSC 8630 Y.S. = 85 KSI, AOD CAST STEEL, QUENCHED AND TEMPERED.

PERCENT YIELD STRENGTH

THRESHOLD STRESS

CA 6 NM 77 ksi Y.S.

○ Si = .53

△ Si = .03

TIME TO FAIL (hrs.)

FIG. 10: NACE TENSILE SSC CA6NM Y.S. = 77 ksi, AOD CAST STEEL. NORMALIZED, DOUBLE TEMPER.

FIG. 11: NACE TENSILE 450 STAINLESS STEEL, Y.S. = 92 KSI, QUENCHED AND TEMPERED.

FIG. 12 : $K_{I_{SSC}}$ VS. HARDNESS

FIG. 13 : $K_{I_{Ssc}}$ VS HARDNESS

FIG. 14: TEMPERING TEMPERATURE VS. STRENGTH WITH BAND PLUS OR MINUS 10°F.