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AT THE GEOTHERMAL NILAND TEST FACILITY

Alfred Goldberg

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ABSTRACT

We discuss the possibility of leakage in the geothermal-brine steam-separator drums made of carbon steel and clad with 316L stainless steel. Although the brine source is reducing, ingestion of some oxygen into the system is likely. Such ingestion must be carefully monitored, for in the presence of chlorides, even trace quantities of O_2 (<1 ppm) can cause stress corrosion cracking (SCC) of austenitic stainless steels. An example is given of intergranular corrosion in 304 stainless steel exposed to brine from Sinclair No. 4 well located in the Salton Sea area. Measures to prevent SCC are suggested. We describe the new grades of stainless steels that appear to be less susceptible to SCC in chlorides than are the more conventional austenitic grades.

INTRODUCTION

The flash separator drums at the San Diego Gas and Electric Company Geothermal Test Facility are made of carbon steel, ASTM A-53 Grade B. Two drums in the first and second stages are clad with 1.27-mm (0.05-in.) thick 316L austenitic stainless steel. Temperatures and pressures expected in those two drums are 188°C (370°F) and 153°C (308°F) and 1.03 MPa (150 psig) and 0.3 MPa (45 psig), respectively. The brine at the wellhead has a pH between 5 and 6, contains ~25 percent chloride salts, and is reducing. However, in the operation of the plant, especially during shutdown, oxygen ingestion into the system is possible. There is considerable evidence of stress corrosion cracking (SCC) of austenitic stainless steels in the presence of even trace quantities of Cl^- and O_2 , especially in acidic environments. Therefore, the possibility of leakage resulting from cracking of the stainless steel cladding must be carefully evaluated. The stainless steel is cathodic to the carbon steel, and therefore, rapid anodic corrosion as well as crevice corrosion will occur in the underlying carbon steel where the stainless steel

has cracked. Depending on the composition of the weld rod and the exact post weld heat treatment, stresses above the yield point may readily exist in the stainless steel cladding. Hoop stresses developed in the drum wall due to the brine fluids will be of the order of 110 MPa (10.6 ksi) which would add to the residual stresses.

STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS

The susceptibility of austenitic stainless steels to SCC in chloride-containing environments has been extensively documented both for industrial failures and laboratory tests.¹⁻⁷ Following 15 days exposure in simulated deaerated Niland brine (20 w/o dissolved solids) pressurized to 232°C, Type 316L stainless steel was one of the few alloys in which SCC was detected.⁷ Studies reported, however, have been largely for Type 304 stainless steel. They show that SCC is to be expected with only trace quantities of Cl^- and O_2 (1 or 2 ppm of each). For most austenitic grades, SCC has been observed for both the sensitized and solution-annealed conditions, with the sensitized condition being the more susceptible. The addition of Mo and reduction of C both decrease the susceptibility of austenitic stainless to most forms of corrosion, but the Mo additions may not always improve resistance to SCC, and in fact may at times lower it.⁴ This belies the generally held belief that Type 316 stainless steel always has superior SCC resistance to Type 304 (or 316L relative to either 316 or 304L). Although most information on SCC of austenitic stainless steels refers to Type 304, we can assume, without serious error, that such information also reflects the behavior to be expected for Type 316 (or 316L). In examining a large number of industrial failures, Truman reported that most austenitic stainless steels behave quite similarly in their susceptibility to SCC¹; among these were included Types 304, 304L, 316, and 316L. At temperatures above about 80°C, SCC occurs over a wide range of pH values; in highly acidic environments, SCC has been observed even at subzero temperatures.¹

In general, the susceptibility to SCC increases with increase in temperature, increase in pH (in highly acidic conditions, general corrosion or excessive pitting may predominate), increase in oxidation potential (O_2 , Fe^{+3} , NO_3^- , NO_2^- , $\text{Cr}_2\text{O}_7^{-2}$, etc.), and prestrain. The SCC is most aggressive in alternately wet and dry conditions and it is also more aggressive in the

vapor phase than in the liquid phase. However, the presence of oxidizing species is critical and if these are eliminated cracking should not occur.⁵

Examples of the influence of oxygen and chloride content on SCC for austenitic stainless steels are shown in Figs. 1 and 2⁽⁴⁾. Figure 1 is for an alternately wetting and drying situation which could reflect the conditions resulting from periodic shutdowns of the separators. The data show that, for SCC to occur in the presence of chloride (>1 ppm), very little oxygen (<1 ppm) is necessary. In turn, in the presence of oxygen (>1 ppm), very little chloride is necessary. These data were obtained for alkaline conditions; in acid solutions, the boundary separating the failure from the no-failure region should shift to lower chloride and oxygen contents. Figure 2 gives the time to cracking of Type 304 wires loaded in an aqueous chloride solution (probably near neutral pH). Although the data in Fig. 2 are limited to only two oxygen contents, one may infer from the trend in Fig. 1 that cracking would occur in less than 100 hours above some small maximum trace amount of oxygen content for a chloride content within the range of 10^3 to 10^4 ppm.

The influence of chloride content, pH, and temperature for Type 304 stainless steel is shown in Fig. 3.¹ The chloride content was obtained by adding NaCl to distilled water under air. Even in high purity water, SCC can occur with as little as 0.2 ppm O_2 , and Truman proposes that all austenitic stainless steels (including 316L) will fail in pure water containing oxygen if loaded to above the at-temperature yield strength.¹ Steigerwald observed SCC for solution-annealed Type 316 in high purity water with <0.1 ppm O_2 .⁶

Residual welding stresses or fabrication stresses are frequently sufficient to cause failure by SCC.^{4,5} Furthermore, corrosion products themselves can create sufficient internal stresses to propagate a crack³ once conditions (initial pitting, rupture of oxide film at slip offsets, etc.) have been established to initiate a crack. For example, an initially stress-free Type 304L stainless steel ultimately developed SCC following a 3-month exposure in a $MgCl_2$ environment.³

The examples of SCC described above illustrate the importance of maintaining an awareness of the possibility of this mode of fracture. Relatively high localized residual stresses may well be present in the welded cladding of the separator drums. Action should be taken to avoid possible failure of these drums.

Fig. 1. Proposed relationship between chloride and oxygen content of alkaline phosphate treated boiler water and susceptibility to stress corrosion cracking of austenitic stainless steel exposed to the steam phase with intermittent wetting. (Based on Williams from Ref. 4)

Fig. 2. Effect of chloride and oxygen on time to cracking Type 304 stainless steel wire held at constant load in single phase aqueous environment. (Based on Staehle from Ref. 4)

Fig. 3. Effect of pH, chloride content, and temperature on the stress corrosion cracking of Type 304 stainless steel under residual weld stresses. As-welded tube specimens; NaCl dissolved in H₂O under air; exposure time up to 8000 hours. (Based on data taken from Ref. 1.)

CORROSION OF SENSITIZED 304 SS IN GEOTHERMAL BRINE

Recently, we examined several Type 304 SS converging-diverging nozzles that had been exposed to the Salton Sea geothermal brines (Niland area) for scaling studies. Metallographic observations made on two of these nozzles are described here. One nozzle, which suffered considerable grain boundary corrosion, had been exposed for five hours and 45 minutes to brine from Sinclair No. 4 Well. This nozzle had experienced a temperature drop from 224.7 to 110°C from throat to exit along the diverging portion. A second nozzle had been exposed for three hours to brine from Magmamax No. 3 Well; the corresponding temperature drop was from 174 to 82°C. The diverging nozzle tubes were approximately 655 mm long.

Figure 4 (a) shows a view of a polished transverse section taken from Sinclair No. 4 nozzle about 70-mm from the exit end (approx 120°C). Intergranular corrosive attack is clearly indicated, although exposure in the brine was under six hours. A view of an etched transverse section near the throat of the same nozzle (182°C) is shown in Fig. 4 (b). The scaling rate at the higher temperature was about 1/16 of that measured for the lower temperature. Penetration by intergranular corrosion was considerably greater at the higher temperature, where less scale had been deposited. Figure 4 (b) clearly shows that the steel is in a sensitized condition and if it had been exposed under any significant load it would surely have failed catastrophically in that period of time. Residual welding stresses and the internal brine pressure may have, in fact, contributed to the observed corrosive attack.

Figures 5 and 6 show several views of a transverse section of the diverging portion of the nozzle where it was welded to the throat (174°C). The nozzle was exposed to Magmamax No. 4 Well. The weld joint is shown in Fig. 5 (a). Circumferential variations in the weld are illustrated by comparing Figs. 5 (b) and 5 (c) which are two views about 180 degrees apart. In one case the weld had penetrated through the inner surface of the nozzle; in the other case, it had not. Evidence of sensitization due to welding can be seen in the heat-affected zone in Fig. 5(c). Its influence on corrosion could not be assessed since no significant corrosion (as distinct from scaling) was observed in this nozzle. Both nozzles had been exposed to reducing brines.

(a) 500X, as-polished

(b) 500X, electroetched
in oxalic acid.

Fig. 4. Type 304 SS nozzle with 4:1 expansion ratio exposed 5h-45 min to brine from Sinclair No. 4 well. View (a): near exit end of nozzle, $T = \text{approx. } 120^{\circ}\text{C}$, average scaling rate = $325 \mu\text{m}\cdot\text{h}^{-1}$. View (b): near throat, $T = 182^{\circ}\text{C}$, average scaling rate = $20 \mu\text{m}\cdot\text{h}^{-1}$. Note preferential attack along sensitized grain boundary areas.

Fig. 5. Type 304 SS nozzle with 8:1 expansion ratio exposed 3h to brine from Magmamax No. 3 Well. View (a) shows weld joint between diverging nozzle and throat. View (b) and (c) show microstructures of weld and base metal. Note that weld penetrated in (b) and not in (c). Note some sensitization in heat-affected zone in view (c). Near throat, $T = 174^{\circ}\text{C}$; average scaling rate = $2.8 \mu\text{m}\cdot\text{h}^{-1}$ at section shown. Electro-etched in oxalic acid.

(a) 450X - as polished

(b) 450X - as polished

(c) 500X - electro-etched
in oxalic acid

Fig. 6. Same sample as in Fig. 6. View (a): Entrapment of scale along rough surface of penetrated weld. View (b): Downstream next to weld. View (c): area traversing weld/base metal boundary. Note that irregular scale surface stops at boundary.

An interesting facet of this study was the effect of surface roughness on scaling. A view of a polished section where the weld had penetrated the inner surface is shown in Fig. 6(a). Scale can be seen trapped at weld surface irregularities. The surface just downstream from the weld in the same cross section sample shows uniform scale deposit as seen in Fig. 6(b). Figure 6(c) shows a view traversing the weld/base metal boundary. One can see that the uneven scale deposits at the weld surface stops at this boundary. Some evidence of sensitization can be seen in the heat-affected zone. The effect of entrapped scale deposits on corrosion is uncertain; it may induce crevice-type corrosion due to local differences in the concentration and migration of chemical species to and from the metal surface as a result of local thickness variations in scale deposits. Thus, welding may accelerate corrosive attack and failure due to sensitization, due to residual welding stresses, and possibly due to its effect on scaling.

POSSIBLE SOLUTIONS TO THE SCC PROBLEM

We will now consider what actions should be taken to minimize the possibility of SCC of the 316L stainless steel clad and resulting drum failure.

Unless the fabrication history can be clarified, we should consider the worst situation: the flash drums are in the as-welded, fabricated condition, and therefore the cladding has residual weld stresses of the order of its yield strength. (The residual weld stresses will be intensified since stainless steel has a much higher coefficient of expansion than plain carbon steel.) Sensitization is also likely, although this is not a prerequisite for SCC.

If no oxygen ingestion occurs, then the brine should remain reducing, and SCC is unlikely to take place. However, nearly 400 ppm O_2 was found in the noncondensable gases of the steam from the first separation stage, according to the 1974 Report on the Geothermal Field Test at the Niland Reservoir. The apparent anomaly is probably due to oxygen contamination from the holding tank. Some infusion of O_2 may occur in the pilot plant system (e.g., valves, joints, etc.); only a trace amount is necessary at some local point of entry for SCC to occur. Therefore, if the cladding is to be retained, O_2 content must be watched closely. By conventional techniques, 1 ppm O_2 can be detected. By using concentration techniques the resolution probably can be

increased to perhaps 50 ppb. We do not currently know whether, for example, 1, 0.1, or 0.01 ppm O_2 is a safe upper limit to avoid SCC in hot chlorides.

What are the alternatives? The safest alternative would be to remove the cladding in these two vessels. If the cladding is kept, then close surveillance of the redox potential and oxygen content should be maintained, with provisions for isolating these drums from the system if danger of failure is indicated. Reducing additives might be considered. Cathodic protection could be used, but here we have the danger of introducing cathodic charging of hydrogen with possible hydrogen embrittlement. Finally, one might consider the use of a nitrogen purge and blanket, at least during shutdown. In any event the interior of the vessel should be inspected for cracks during shutdowns.

SOME NEW DEVELOPMENTS IN STAINLESS STEELS

New stainless alloys, both ferritic and duplex (ferritic-austenitic) types have recently been developed⁸⁻¹⁰ which have better resistance to SCC (in $MgCl_2$, $FeCl_3$, $6H_2O$ and/or $NaCl$ solutions) than do conventional austenitic types. Ferritic stainless steels (such as Ni-free Types 430 or 446) are known to be more resistant than the austenitic types to chloride/oxygen SCC; however, their use was restricted because of welding problems (poor weld ductility and loss of corrosion resistance after welding), lower toughness, and inferior pitting resistance. With control of C and N contents through vacuum melting, the low ductility problem was eliminated; the lower carbon content as well as the use of Ti- or Nb-stabilizers also reduced the intergranular corrosion of weldments. The ferritic stainless steels that have recently been developed are largely Ni-free and contain between 18 and 28% Cr and between 1 and 5% Mo. In the development of these steels, it was shown that small quantities of Ni (>1%) or Cu (>0.5%) increased their susceptibility to SCC in chlorides. Furthermore, small Mo additions to Fe-Cr stainless alloys containing a minor amount of Ni did not improve their resistance to SCC, and may even lower it.

The effect of Ni additions to an Fe-18Cr alloy base on the SCC in boiling 42% $MgCl_2$ is shown in Fig. 7. These results, together with those obtained in the development of the new ferritic grades of stainless steels, strongly suggest that, for resistance to SCC in non-reducing chloride environments, steels must not contain between about 1 and 45% Ni. However, by keeping the impurity content low (<1 ppm metallic impurities and <10 ppm C) no evidence

Fig. 7. Effect of increasing the nickel content on the susceptibility of Fe-18Cr base wires in boiling 42% MgCl_2 . (Based on Copson from Ref. 4)

for SCC was found in high-purity 18Cr-14Ni austenitic stainless steel bend specimens exposed for 1000 hours in boiling (154°C) MgCl_2 solution.¹¹ By contrast, addition of 0.1% P or 1% Pt caused cracking in 10 hours.¹¹ The addition of P promoted the entry of atomic hydrogen (poison, $\text{H}^\circ + \text{H}^\circ \rightarrow \text{H}_2$), and the Pt increased the hydrogen exchange currents.¹¹ Thus, the role of alloying (or impurity) elements is far from clear, for it appears that the presence of Ni may not be inherently detrimental, but that it may cause a secondary effect by its presence with some impurity. Further work must be done to clarify this question. Interestingly, ferritic stainless steels (as well as austenitic) can become quite sensitive to SCC when thiourea $\{\text{CS}(\text{NH}_2)_2\}$ is added to heated LiCl solution;¹¹ the S evidently acts to aid H° entry by poisoning H° recombination to H_2 . Another example of an exception to the relatively poor resistance of austenitic stainless steels to chloride SCC is the high resistance of the 18Cr-18Ni-2Si alloy to SCC in boiling (154°C) MgCl_2 solution.¹¹

Recent developments in the duplex ferritic-austenitic and the completely austenitic stainless steels are reviewed by Steigerwald.¹⁰ The duplex steels have better resistance to SCC than do the austenitic steels, and they have higher yield strengths -- 440-586 MPa (64-85 ksi) -- than the ferritic steels or the conventional austenitic steels such as Types 304 or 316. They differ primarily from the new ferritic steels in that they contain almost 4 to 5% Ni. That this Ni does not detract from their corrosion resistance again points out that the real effect of Ni is not clear. The results shown in Fig. 4 suggest that alloys with this range of Ni should show relatively low resistance to SCC in chlorides.

The advantages of the new austenitic stainless steels appear to be primarily in their relatively high yield strengths, approximately double that of the value of 240 MPa (35 ksi) for Type 316. They also show improved resistance to pitting and crevice corrosion, as well as to SCC, in chlorides, when compared with the conventional austenitic stainless steels. These new austenitic steels typically contain 19 to 22% Cr, 0 to 3% Mo with variable amounts of Ni and Mn, e.g., ARMCO 22-13-5 (22Cr-13Ni-5Mn-2.25Mo-0.2Nb-0.2V-0.3N).

The nature and distribution of impurities (such as P and S) seem to be important factors contributing to the large differences observed in the resistance to SCC of austenitic stainless steels (i.e., conventional types versus high-purity heats and some of the new grades).¹² Supporting this is the

observation that the sulfide composition (MnS or FeS) and distribution affect the resistance of carbon steels to (pitting) corrosion. In carbon steels, the sulfide inclusions are usually more noble than the ferrite and therefore the ferrite is preferentially attacked; by contrast, these inclusions in stainless steels are generally less noble than the passive surface of the matrix, and are usually preferentially attacked.

Although studies on the effect of alloying elements, such as Mo, Cr, Ni, Co, Si, etc., on corrosion resistance are continuously being done, these observations clearly indicate the need for more extensive studies on the effects of impurities present both in the alloy and in the environment. Many of the new stainless steels are still only available in limited quantities and sizes, and service experience is probably very limited. The screening tests being planned or already in progress for the current geothermal brine endeavors offer excellent opportunities for close interaction with those industrial organizations active in developing chloride-tolerant alloys. We hope that such interaction will lead to the early development of long-life alloys for the hostile geothermal brine environments.

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