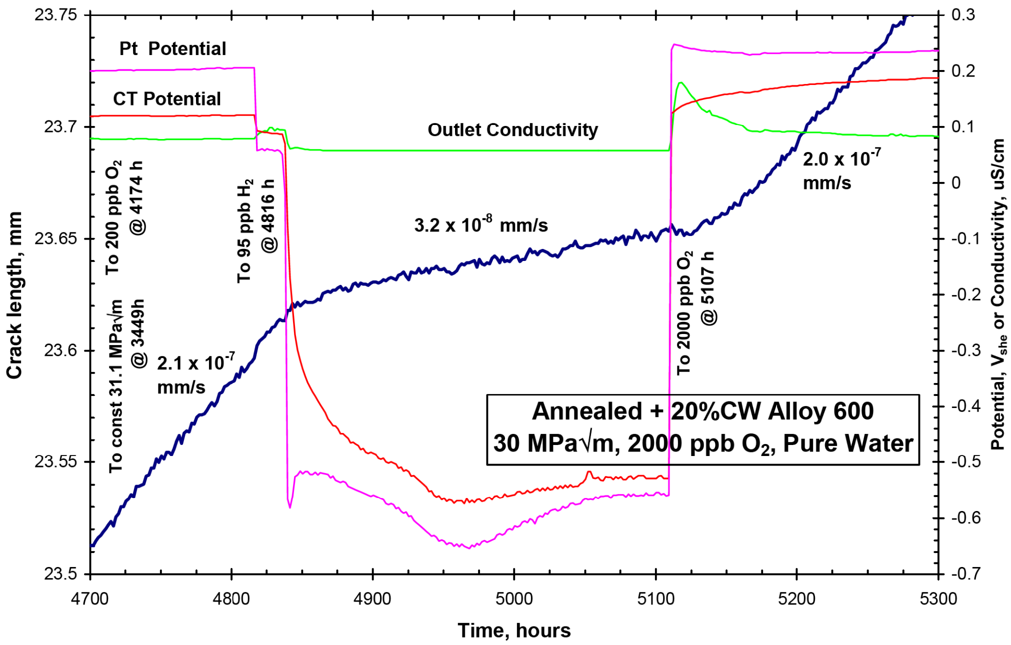

Figure 7. SCC response in 288 °C water for a 1TCT of unsensitized alloy 600 with 20% reduction in thickness at 25 °C.

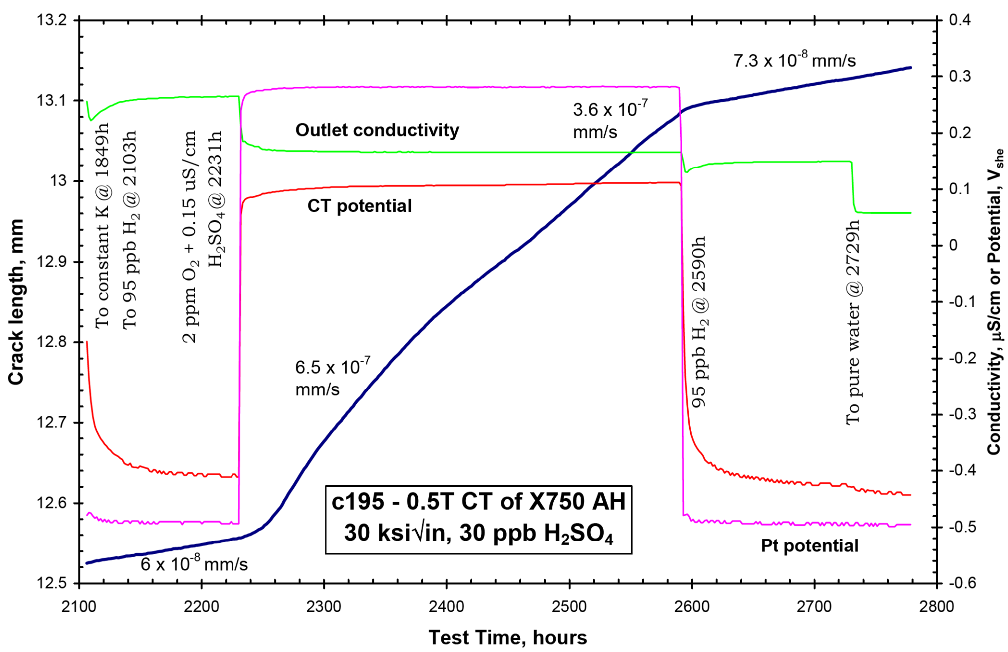

Figure 8. Crack length vs. time in 288 °C water for a 0.5TCT specimen of alloy X750.

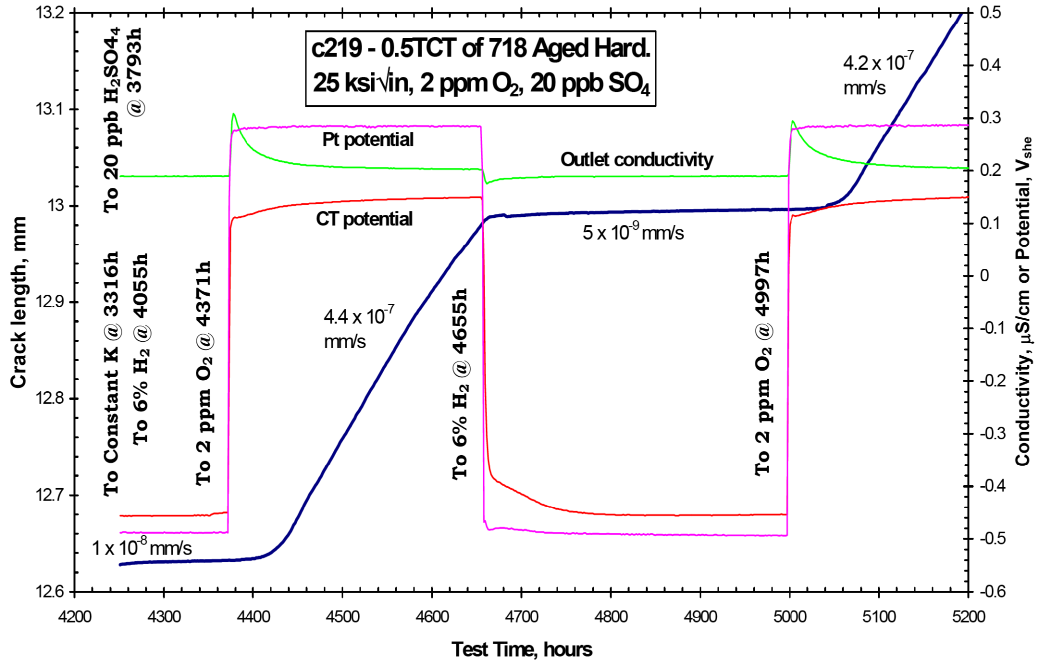

Figure 9. Crack length vs. time for 0.5TCT specimen of age hardened alloy 718 tested in 288 °C water.

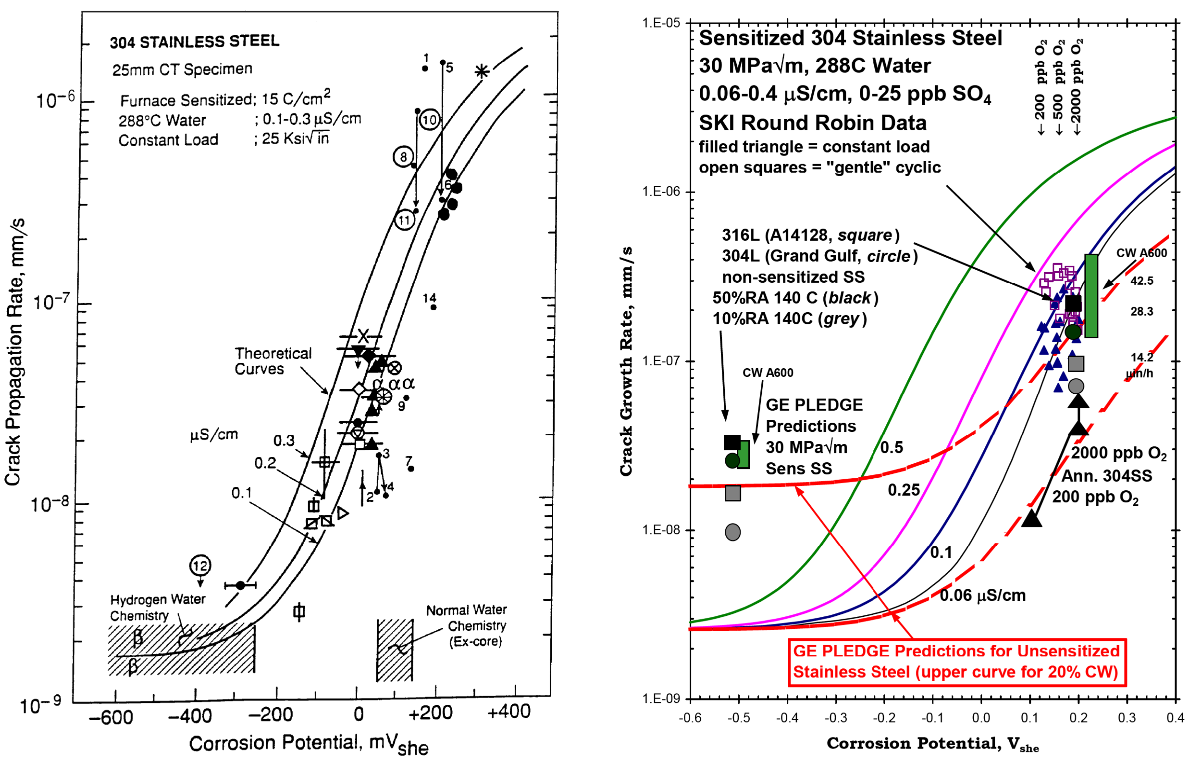

Figure 10. SCC growth rate vs. corrosion potential for stainless steels tested in 288 °C high purity water containing 2000 ppb O_2 and 95 – 3000 ppb H_2.

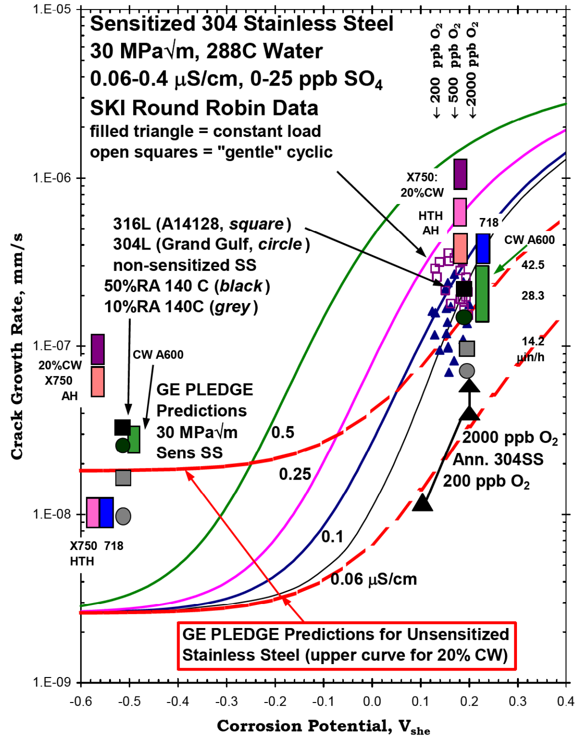

Figure 11. SCC growth rate vs. corrosion potential for stainless steels in various conditions, 20% cold worked alloy 600, and precipitation hardened alloy X750 tested in 288 °C high purity water.

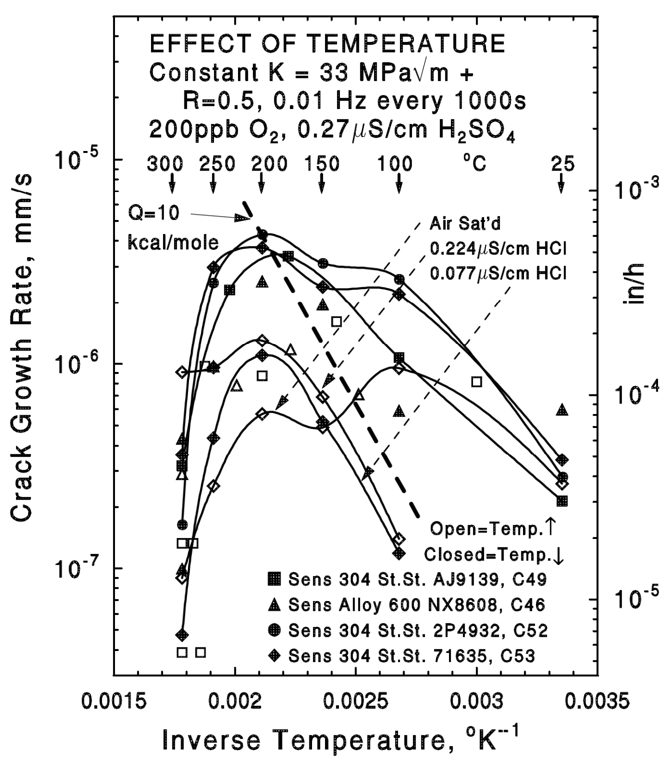

Figure 12. Effect of temperature on crack growth rate of sensitized 304 stainless steel and sensitized alloy 600 in water containing 200 ppb O_2 and 30 ppb SO_4 as H_2SO_4.

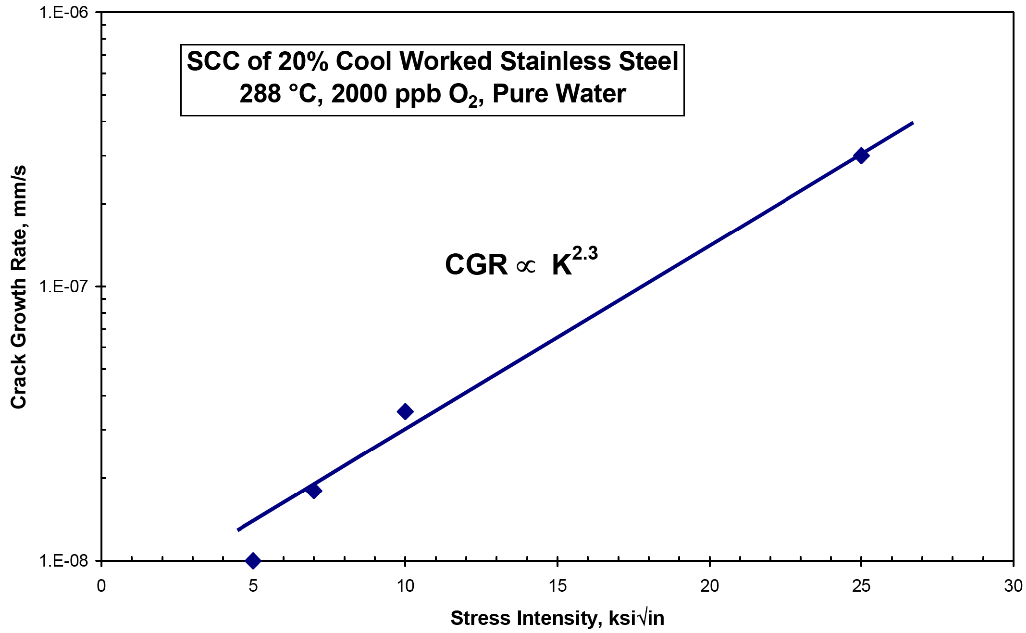

Figure 13. SCC response in 288 °C water for a 0.5TCT of unsensitized Type 316L stainless steel with 20% reduction in thickness at +140 °C.

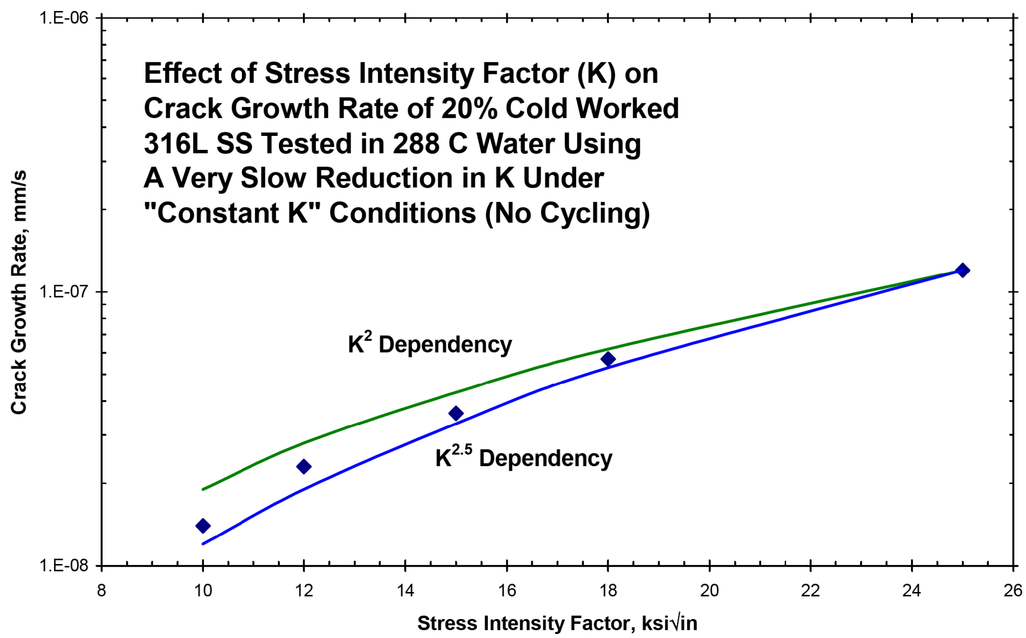

Figure 14. SCC response in 288 °C water for a 0.5TCT of unsensitized Type 316L stainless steel with 20% reduction in thickness at +140 °C.

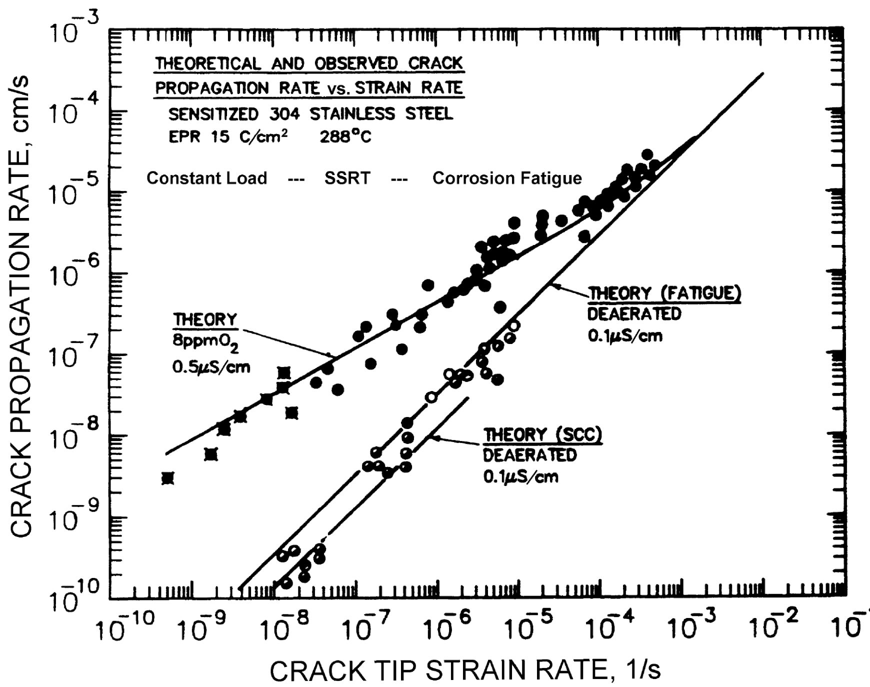

Figure 15. Crack growth rate vs. crack tip strain rate, showing the effect of material and water chemistry on the growth rate of stainless steel in 288 °C water. The crack tip strain rate captures in a more fundamental fashion the effect of stress intensity factor (K), and is proportional to K^4.

2.0 Crack Initiation Measurements

2.1 Background

A second task was undertaken in January 2000 to evaluate crack initiation in concentrated ground water environments. Time-to-failure experiments were performed in multispecimen Keno autoclaves to allow simultaneous testing of multiple materials, heat treatments, and stress levels in a reasonably short time. The effects of material, applied stress, welding, surface finish, shot peening, cold work, crevicing, and aging treatment were investigated for Alloy 22, Titanium Grade 7, and 316NG stainless steel. Sensitized 304 stainless steel specimens were included to provide benchmark data. Testing of multiple specimens was used to allow determination of statistical differences among material conditions. Microstructural effects on time-to-failure were studied for Alloy 22, where heat treatments designed to produce topologically close-packed phases (TCP) and long-range ordering (LRO) were investigated. This research complements high-resolution crack-growth-rate data presented in Section 1.0.

2.2 Experimental Procedure

Time-to-failure experiments are being performed on smooth tensile specimens, where each specimen is individually loaded by the internal pressure of a large "Keno" autoclave. Figure 2-1 schematically shows a cross section of a Keno autoclave, which is constructed from 347 stainless steel and has a volume of 55 liters. The autoclave has the capability of simultaneously loading up to three 304 stainless steel manifolds, where each manifold can support fifty 304 stainless steel specimen module assemblies, for a total of 150 specimens in the autoclave. A schematic of a module assembly is shown in Figure 2-2. The load on each specimen is created by the pressure differential across a sliding seal on a piston connected to the specimen, where internal pressure of the autoclave is on one side and atmospheric pressure is on the other side of the manifold. On failure, the piston and specimen cause a numbered indicator ball (i.e., "Keno") to be ejected into the manifold. The indicator ball runs down the manifold into a track, past a sensor (which records the time of failure), and into a tube where it is stored so the failure sequence is known. Failure events, temperature, and pressure are acquired and stored via data acquisition software.

Since the outer shell of the waste package will encounter the Yucca Mountain environment, this study focuses on Alloy 22 (the current selected material for this application). In the present study, mill annealed Alloy 22 (mill heat 2277-9-3192) with composition 21.53Cr, 13.34Mo, 3.93Fe, 2.92W, 0.27Mn, 0.96Co, 0.006P, 0.001S, 0.27Si, 0.17V (wt%) is used.

The composition of the aqueous mixed-salt solution was determined in a parallel study designed to closely simulate saturated Yucca Mountain ground water [1]. Because of system limitations associated with the Keno test system, the saturated test solution (BSW) used for performing the crack growth tests was diluted to 15% of the initial BSW composition. The concentration of the more dilute Keno solution is provided in Table 2-1. With respect to two of the key anions that contribute to the corrosion processes (chloride and nitrate), their effective concentration in the resulting solution was ~25%. Therefore, this solution will be referred to as "~25% BSW" (based on Cl^- and NO_3^- concentrations). By contrast, other ions like K are at 15% concentration. There are several possible sources for the lack of exact ion proportionality between the CT and Keno tests. In the saturated CT solution, undissolved solids / precipitates remain after mixing at 105 °C, while there is little evidence of this in the 15% Keno solution. There may also be some influence of the methods used to maintain solution level in the autoclaves. In the CT systems, the liquid loss should be entirely evaporative, so small amounts of pure water are added perhaps once a month to maintain solution level. In the Keno system, both leakage (by the individual seals) and evaporative loss can occur, so a 7.5% solution (half concentration) is used to maintain level by periodic "topping off" the autoclave during the Keno tests. Small amounts of solution (~ 100 ml) were periodically removed from the Keno autoclave and characterized using ion chromatography. These results are included in Table 2-1.

A pressuring gas was used to create the internal pressure in the autoclave due to the lack of substantial vapor pressure at 105-125°C. The gas mixture was altered to avoid producing an unrealistically high fugacity of oxygen. A mass flow controller was used to mix air with nitrogen to produce ~1 atmosphere "partial pressure" of air. The pressure of the gas mixture was increased to about 2600 psi using a gas booster and was stored in a gas cylinder. The pressure regulator controlled the inlet pressure to the autoclave, and a needle valve was used to maintain a stable flow rate through the autoclave of about 50 – 100 sccm. Temperature was controlled using a three-zone, independent, multiple band heater system on the autoclave, with temperature monitored at multiple locations within the autoclave to ensure temperature uniformity.

It is not unusual to have some leakage of solution around some of the piston seals, particularly during specimen failure. In concentrated environments there is some concern for even slight leakage around the piston seals that would produce salt encrustation and restriction of seal movement. Thus, it was decided to use the more dilute solution than used in the crack growth rate tests. It was also considered important to maintain a moderately high pH (e.g., ≈ 10), and discussions with Greg Gdowski of LLNL produced agreement to use the solution in Table 2-1. This also made it easier to mix the ≈ 55 liters of autoclave solution.

Two runs of Keno testing were performed (the second run is still in test). A smaller initial matrix of 50 specimens was tested first at 125°C. The results from this small matrix were used to determine the stress levels and material conditions to be used in the following larger scale run (150 specimens) performed at 105°C. The matrix of specimens for the initial matrix is shown in Table 2-2. In addition to the as-received Alloy 22 and as-received Titanium Grade 7, 20% cold worked specimens and as-machined + shot peened specimens of both materials were also included in the test matrix. Type 316NG stainless steel in the as-received and shot peened conditions was tested. Finally, sensitized type 304 stainless steel was included as a baseline and was tested in the as-received and shot peened conditions. Shot peening was performed on the machined and cleaned specimens using GP60 glass pellets to an intensity of 6 – 8 N (several thousands of an inch depth). Shot peening services were provided by Metal Improvement, Carlstadt, NJ.

The full matrix (Run 2) allowed investigation of the effect of material, applied stress, welded regions, crevice geometry, surface finish, cold work, and aging treatments designed to produce topologically close-packed phases (TCP) and long range ordering (LRO) in Alloy 22. The matrix of specimens for the full matrix is shown in Table 2-3. Welded specimens were centered on the fusion line so that the specimen gage included both the weld and the heat-affected zone (HAZ). The TCP (HT1) and LRO (HT2) aging heat treatments were suggested by previous studies performed at Lawrence Livermore National Laboratory (LLNL) [2,3]. The TCP heat treatment applied was 700°C for 175 hrs. The LRO heat treatment used was 1000 hrs at 520°C. Due to the time required for LRO heat treatment, these specimens were added to the autoclave several weeks after the Keno testing initiated. (This difference in testing time for the LRO specimens is evident in the time-to-failure plots to be presented).

The microstructure of mill annealed Alloy 22 consists of an FCC solid solution with occasional M_6C carbides distributed throughout the matrix [2], as shown in Figure 2-3a. (Note that carbides were not observed in this investigation). Optical metallography for the heat treated and welded conditions is also shown in Figure 2-3a. TCP phases and long range ordering (LRO) were not observed by optical microscopy.

Higher magnification TEM was used to investigate the possible presence of small precipitates not visible by optical microscopy. As-received C22 contained a low density of dislocations (Figure 2-3b), but no precipitates were observed. For as-received + HT1 (700^{o}C/ 175 hr) material, the grain boundaries are covered with Mo-rich precipitates (Figure 2-3b). No precipitates were observed in the matrix. The as-received + HT2 (520^{o}C/ 1000hr) material contained a high density of fine, coherent Ni_2(Cr,Mo) phase, as did the as-received + cold worked + HT2 material, also shown in Figure 2-3b. Additional TEM analyses using dark field imaging were unable to discern the effect of cold work on the relative amount or size of the ordered Ni_2(Cr,Mo) phase.
Surface roughness measurements were performed on several specimens to determine the intrinsic defect size associated with machining. Results in Figure 2-4 show surface maps for an as-received Alloy 22 Keno specimen surface machined to 150 RMS compared to a prestrained Alloy 22 Keno specimen also machined to 150 RMS. Straining increased the surface roughness to 278 RMS. Since peak-to-valley height (i.e., “defect depth”) is roughly 3 times the RMS measurement, the as-received specimen peak-to-valley height was ~ 420 microinches compared to ~ 830 microinches for the strained specimen. Note that all specimens are exposed in the strained condition in the Keno test.

In an effort to produce a tight crevice geometry for creviced specimens in Full Run 2, creviced specimens were plastically pre-strained to 93% of the intended SCC experiment stress. After pre-straining, crevices were produced using 0.75 inch diameter Teflon bar stock that had the center drilled out to the diameter specified by its respective prestrained specimen. The Teflon cylinders were then cut in half lengthwise and the two halves were clamped onto the specimens using stiff titanium wire. Diffusion of oxygen through bulk Teflon at 105^{o}C was assumed negligible.

Time-to-failure results are plotted as a function of the ratio of applied stress to yield stress in an attempt to normalize the large differences in yield strength between materials used in the study. Tensile tests were performed in 125^{o}C or 105^{o}C air to determine applicable yield strength values. Yield strength results (used in ensuing time-to-failure plots) are presented in Table 2-4.

2.3 Results and Discussion for Run 1

The first run was started on June 7, 2000 at 4 pm after the specimens had been at temperature in the solution for several days. The pressure was slowly increased from 200 to 900 psi over a period of about five minutes. During the first day and a half, 13 specimens failed. Table 2-2 identifies the times and sequences of these failures. As expected, the first failures were sensitized 304 stainless steel (this was expected to be the most susceptible material) and as-received Titanium Grade 7 (which was tested at the highest fraction of its ultimate tensile strength, ~ 0.93). The failure stresses are plotted as a function of test time in Figure 2-5.

Some loss of autoclave solution was observed. The solution level was tracked by sliding a stainless steel bar through a Conax seal and monitoring resistivity, which changed dramatically when the bar reached the liquid level in the autoclave. When the level dropped by several inches, solution was added to the autoclave using a high pressure pump (the liquid level was always kept above the top specimen and module). Because it appears equally likely that liquid loss can occur both by humidification of the mixed gas (which flows at about 50 – 100 sccm; a condenser is used to minimize this loss) and by leakage past the module threads or the piston seal, solution diluted by 50% compared to the starting solution was added to the autoclave to replenish the lost solution.

Periodic sampling and analysis of the liquid is performed to ensure that the composition changes as little as possible. The amount of liquid added to the system was in the vicinity of 2% per week, so shifts in concentration vs. time were limited. The composition of the initial solution and the refilled autoclave solution was analyzed to provide guidance for the make-up water occasionally added. Approximately 100 ml of solution was collected from the autoclave on June 19th and submitted to the Materials Characterization Laboratory at the GE Global Research Center for ion analysis. Results indicate that the composition of the solution was 88 - 100% of the initial composition for all ions analyzed, as shown in Table 2-1, indicating that solution additions of 50% of original Keno autoclave solution is adequate for maintaining the autoclave solution composition.

System pressure was increased from 900 psi to 1000 psi on June 19th, 2000 (282.5 hrs cumulative test time, as shown in Table 2-5, which produced failures in the remaining sensitized 304 stainless steel specimens within a few hours of the pressure increase. The applied specimen stress for the sensitized 304 stainless steel specimens at system pressure equal to 1000 psi was 60-61 ksi, or $1.4\sigma_{YS}$. These failures are included in the time-to-failure plot in Figure 2-5.

The Keno system was depressurized and cooled on July 14th, 2000 after 885.5 hrs of total testing to investigate the degree of salt encrustation and possible negative effects on ball drop. The autoclave was drained and the manifold removed on July 18th. The autoclave solution was stored in sealed plastic jugs. Photos showing the manifold, modules, and an example of a failed specimen are presented in Figure 2-6. Inspection of the manifold and modules revealed some isolated areas of severe corrosion and encrustation (Figure 2-7). A total of twenty specimen failures were observed in the manifold, but salt deposits had prevented ball drop in 5 instances (and thus prevented recording of the failure time). Examples of the salt deposits in the manifold and in the modules are presented in Figure 2-8. The 5 unrecorded failures are noted in Table 2-2 as "time-to-failure at t < 885.5 hrs". The twenty failures included all the as-received and as-received + shot peened Titanium Grade 7 and sensitized 304 stainless steel specimens. Each of the twenty fractured specimens was removed from its respective module and examined by scanning electron microscopy.

Because of the severity of the corrosion in a few areas of the stainless steel manifold and specimen modules, the pH of the autoclave solution was evaluated as a function of temperature. The solution pH changed from 12.4 at room temperature to 10.9 at 94°C. Boiling occurred at 104.5 - 106.5°C. A parabolic curve fit to the measured pH data suggests that the solution pH inside the Keno autoclave is 10.3 at 105°C and 9.2 at 125°C. These pH levels were not unexpected and do not explain the severity of the corrosion of the manifold and modules. Details of the pH measurements and the results are provided in Appendix 2-1.

The thirty unfractured specimens were removed from their modules, inspected for salt encrustation and macroscopic corrosion, rinsed with demineralized water, dried with compressed air, and placed back in the manifold in their original locations. The autoclave was reassembled and filled with the previously drained solution. Roughly 1.5 liters of new solution (diluted to 50% of the original Keno composition) was added to fill the autoclave to 0.5" from the head. Temperature settings were lowered from the initial 125°C to 105°C to eliminate boiling of solution as it escaped past the seals on specimen failure, thus reducing the formation of the salt deposit. The Totalizer was checked and confirmed to be working correctly. Pressure was increased to 1000 psi with no problems. Cumulative experiment time was re-started at 885.5 hrs in parallel with the pressure increase to 1000 psi at 10:30 am August 3rd, 2000 (shown in Table 2-5).

No additional failures occurred at 1000 psi. Pressure was increased to 1100 psi on August 8th (1003.5 hrs total test time). No failures occurred at 1100 psi. Problems with the conductivity rod used to measure the autoclave fluid level were encountered on August 18th, at which point the specimens were unloaded and the temperature was reduced to 98°C for ~ 6 hrs. The conductivity fixture was rebuilt, although the capability to measure the exact fluid level was not restored. The system was reloaded to 1100 psi at 105°C.

On August 21st, pressure was increased to 1200 psi (1321 hrs total test time). Several cold worked Titanium Grade 7 and 316 NG stainless steel (both the as-received and shot peened conditions) failed over several days at this pressure. On August 23rd, the pressure regulator was noted to be unusually sensitive to small adjustments. This sensitivity and instability worsened with time, and a new pressure regulator was ordered from Tescom. Additionally, pressure drift increased vs. time, and was especially pronounced after the addition of new solution, presumably because of the reduced gas space. On September 15th, 2000, the system pressure drifted up to 1600 psi (cumulative test time = 1922 hrs). At the time that the overload was discovered, the system pressure and temperature were immediately reduced to 200 psi and 80°C. However, thirteen specimens failed during the overload, including the as-received Alloy 22 (6 specimens), as-received + shot peened Alloy 22 (4), the remaining cold worked Titanium Grade 7 specimens (2) and the last 316 NG stainless steel specimen (1). Only the 20% cold worked Alloy 22 specimens (6 total) remained unfractured.

Because of the unacceptable instability of the system pressure, the system was allowed to cool, was unloaded, drained, and disassembled on September 18th, 2000. The manifold was removed from the autoclave. Due to the lower system temperature (105°C vs. 125°C), salt deposits were not observed on the manifold, specimens, or modules, although corrosion on a few of the stainless steel end caps was noted. Because of the lack of salt deposit, ball drop successfully occurred for all fractured specimens. Examples of the modules and manifold are presented in Figure 2-9, where it is clearly observed that the lower system temperature (105°C vs. 125°C) prevented salt deposit formation. Fractured specimens were removed and submitted to the Materials Characterization Laboratory at the GE Global Research Center for scanning electron microscopy.

The SCC resistance of Alloy 22 is evident in the plot of failure stress vs. time-to-failure in Figure 2-5. Alloy 22 specimens exhibited the highest failure stress and longest time-to-failure. As-received Alloy 22 failures occurred at 1922 hrs by ductile overload, confirmed by ductile failure observed on Alloy 22 fracture surfaces. At 1922 hrs, the system pressure reached 1600 psi due to problems with the regulator, translating to an applied stress of 111 - 117 ksi (depending on the exact gage diameter) for the Alloy 22 specimens (all conditions). The 125°C air ultimate tensile strength for the as-received Alloy 22 was 104 ksi (also measured in this program and using the same specimen geometry). Fracture surfaces of four Alloy 22 specimens were observed by SEM, including specimens #21, #43 (as-received) and #7, #17 (as-received + shot peened). No indications of SCC were observed. Microvoid coalescence typical of ductile overload failure is the dominant fracture feature; typical examples are presented in Figure 2-10. The tensile strength (133 ksi at 125°C) for the cold worked Alloy 22 specimens was not exceeded during the overload; these 6 specimens are the only ones that did not fail during the pressure overload.

The 316 NG stainless steel specimens also failed by ductile overload. Although the tensile strength was not measured in this program, an average value for three heats of 316 NG stainless steel used in separate research studies suggests an ultimate tensile strength of ~75 ksi at ~100°C. Failure times occurred between 1412 and 1524 hrs (one failure occurred at 1922 hours). The system pressure during this time period was ~ 1200 to 1300 ksi, translating to applied specimen stresses between 68 to 75 ksi. Three specimens were observed by SEM, including two as-received (#3, #23) and one shot peened specimen (#9). Only dimpled ductile fracture was observed, confirming the likelihood of overload failure. Typical images representative of the failure surfaces for the 316 NG stainless steel specimens are presented in Figure 2-11.

As expected, the sensitized 304 stainless steel specimens failed at the lowest applied stresses (54-60 ksi) and lowest failure times (0.5 to 285.9 hrs), as indicated in Figure 2-5. SCC fracture surfaces for these specimens exhibited an intergranular morphology, as shown in Figure 2-12. The Titanium Grade 7 specimens (as-received and as-received + shot peened conditions) also failed early in testing (0.7 to 49.8 hrs) and at relatively low applied stress (49-56 ksi), although at higher applied %UTS than the sensitized 304 stainless steel specimens (92% vs. 72-80%, respectively). The transgranular fracture mode for the Titanium Grade 7 Keno specimens (Figure 2-13) was similar to that observed for the air tensile test. X-ray micro diffraction analysis was performed on the Titanium Grade 7 Keno specimen fracture surfaces to determine the presence of titanium hydrides; none were found.

Shot peening had no effect on time-to-failure for either the sensitized 304 stainless steel specimens or the Titanium Grade 7 specimens.

2.4 Results and Discussion for Run 2 (Full Matrix)

The full matrix design was shown in Table 2-3. The matrix design allowed investigation of the effect of material, applied stress, welded regions, crevice geometry, surface finish, cold work, and aging treatment. The applied stress was lowered from Run 1 to Full Matrix Run 2 for sensitized 304 stainless steel and Titanium Grade 7 in an effort to reduce the early (i.e., infant mortality) failures observed in Run 1. New solution was mixed for Run 2 with composition identical to that used in Run 1 (previously presented in Table 2-1).

Based on the experience gained in Run 1, several modifications were made to improve the Keno systems prior to the Full Run 2. A new pressure regulator was installed to provide better control of the system pressure. The system temperature was lowered to 105°C, which is slightly less than the solution boiling point. This change in temperature prevented salt deposit formation on the manifold, allowing the balls to freely fall and to be correctly recorded by the data acquisition system. An improved system for monitoring autoclave solution level was installed. Additionally, a pressure transducer was installed, allowing computer acquisition and close monitoring of pressure data. Installation of a back pressure regulator was added as a safety measure.

Keno autoclave Run #2 was started in December 2000 and has been exposed for 9644.6 hours to date. The sequence of pressure loading is shown in Table 2-6. The system was taken off line in July 2001 due to unacceptably high leakage rate of solution from the autoclave. The system was dismantled and the manifolds removed, where it was learned that several modules had severely corroded threads at the module/manifold interface. These modules broke at the threads so that it was impossible to remove the threaded end of the modules from the manifolds. Examples are shown in Figure 2-14. It was not possible to put the manifolds back into operation in this condition. Fifty new 316L module assemblies and three 316L manifolds were ordered and manufactured as replacements. The replacement modules were received in August 2001 and the manifolds were received in November 2001.

Keno Run #2 has produced 40 specimen failures during the 9644.6 hrs of exposure to date, as shown in Figure 2-15. Note that time zero begins at 1000 psi in Figure 2-15, soon after the pressure increase to 1500 psi (the target value) at 168.5 hrs. Several sensitized 304 stainless steel and Titanium Grade 7 failures occurred soon after the increase to 168.5 hrs, suggesting that 168.5 hrs may be a more accurate "time zero". However, time zero was not adjusted since sensitized 304 stainless steel failures occurred at $t < 168.5$ hrs, and there was not a obvious method for how to normalize this data. Increased applied stress decreased time-to-failure for the as-received Titanium Grade 7 specimens, as shown in Figure 2-15. Note that one as-received Titanium Grade 7 specimen remains unfailed after > 6140 hr. The composition of this specimen was confirmed by semiquantitive X-ray analysis in August 2001.

Due to unacceptably high leakage rates, the autoclave was cooled and emptied at 2462 hrs (March 25, 2001) to investigate the root cause of the leakage. Several module assemblies had severely corroded, causing a high system leak rate. A total of 12 modules were replaced with new assemblies. Additionally, a replacement manifold was installed due to severe corrosion of the pipe threads on one of the original manifolds.

During this downtime, the opportunity was taken to remove several unfailed specimens for closer observation. Unfailed 316NG stainless steel and Alloy 22 specimens were removed from the manifolds, including as-received 316NG stainless steel, as-received Alloy 22, LRO Alloy 22, TCP Alloy 22, and welded Alloy 22 specimens in the highest stress conditions (31 specimens total). No SCC cracks or large pits were observed on the surfaces of these specimens using dye penetrant analysis. All removed specimens were shiny with no evidence of corrosion or cracking, examples of which are shown in Figures 2-16 to 2-18. Limited small regions of damage (finer than the surface finish) were observed on some of the specimens (both 316NG and Alloy 22), but it is not known if the damage was produced during machining or during the environmental cracking experiment. All specimens (except for the three used for macros in Figs 2-16 to 2-18) were returned to their original positions in the autoclave manifolds. The autoclave system was returned to pressure on May 3, 2001.

In July 2001, the customer requested a notched specimen design that would allow investigation of the effect of large defects on time-to-failure for several Alloy 22 material conditions. Several specimen geometries were designed and proposed. It was decided that a multiple notch design would provide more information than a single notch design, in that more material surface per specimen would experience the stress concentration provided by the notch root. The chosen specimen design contains three circumferential U-shape grooves (notches), one in the gage center and one located either side the gage at a distance of 0.20 inch from the center notch, as shown in Figure 2-19. Finite Element Analyses (FEA) were performed by Mishko Mastilovic at BSC to ensure that the stress fields of the multiple notched specimens were independent of each other and did not overlap. (Overlapping stress fields could reduce the stress concentration factor of the middle notch). Since the specimens were prestrained, an elastic analysis was used. It was determined that a notch inter-distance of 0.2 inches would produce independent notch stress fields; this distance was used in the selected specimen design. FEA results are shown in Figure 2-20, where it is observed that the stress concentrated region is local to the notch tip. FEA results corresponded well with elastic stress concentration calculations performed at GE GRC, where the calculated stress concentration factors were 3.55 (FEA) and 3.38 (from elastic stress calculation at GE GRC).

Eight specimens each of as-received Alloy 22, as-received Alloy 22 + HT1 (700^{o}C/175 h), and welded Alloy 22 were machined in the notched geometry shown in Figure 2-19, for a total of 24 notched specimens. Specimens were machined in steps; smooth Keno specimens were first machined and shipped to GE GRC. The weld specimens were etched with an oxalic acid solution to ensure weld fusion line location near the center of the specimen (Figure 2-21). Prestraining in RT air at 100% of the intended Keno stress was performed on all specimens to minimize plastic deformation at the notch root during the ensuing Keno loading. The prestrained specimens were then shipped back to the machining vendor where the gages were turned smooth and notches were machined. An example of a specimen machined by the three-notch design is shown in Figure 2-22. The notched specimens were added to the autoclave in March 2002 and have been exposed for 14,5760 hours with no failures to-date (Figure 2-15).

The autoclave system was down for extended periods during July 2001 through March 2002 due to substantial corrosion of the system components (Table 2-6). During this time period, all modules were removed and checked for corrosion. Manifolds had corroded at the pipe threads. Replacement modules and manifolds made of 316L stainless were ordered and delivered. The autoclave was reassembled with the new components and returned to service in March 2002. The test was again interrupted in June 2002 and restarted in July 2002, after which it ran continuously until November 2003. Only one failure (the final titanium Gr.7 specimen) occurred in this time period, and unfortunately the indicator ball was never found (some do disintegrate from corrosion), so there is a large uncertainty band shown for this specimen on Figure 2-15. When the system was disassembled in late November 2003, one module was severely corroded, and several others showed significant corrosion (i.e., more than several square cm), but in no instance did it collapse the module.

Due to the lack of SCC failures to-date for the Alloy 22 and 316NG materials (uncreviced and creviced), meaningful statistical analysis is not possible at this time. The lack of SCC failures in Alloy 22 at high applied stress in high temperature, concentrated mixed salt solution strengthens the high environmental cracking resistance (but not immunity) reported for this material using precracked compact tension specimens under constant load in similar environments, as shown in Section 1 and other studies [4].

There is some concern for galvanic coupling between the alloy 22 specimens and the stainless steel modules/holders, manifold and autoclave in the Keno tests. The most extreme condition may be the areas where there is active crevice corrosion of the stainless steel, as documented in this report. However, a review of the data on sensitized 304 stainless steel, titanium grade 7, and alloy 22 specimens showed that there was no correlation between specimens that failed (or didn't fail) and their proximity to areas of localized corrosion of the stainless steel system parts. There is still some possibility that the lower corrosion potential of stainless steel will galvanically couple and cathodically polarize the titanium grade 7 or alloy 22 specimens. This certainly had no obviously beneficial effect on the titanium grade 7 specimens, which failed relatively early in life. To evaluate the differences in corrosion potential, coupons of stainless steel and alloy 22 were measured against a Pt coupon ("reference electrode") in autoclaves used for recent the CT tests which are being performed at 150 °C. Early in test, the corrosion potentials were similar, but after several hundred hours the potential of alloy 22 rose somewhat and the potential of stainless steel dropped somewhat (Figure 2-23), producing a difference in corrosion potential of about 100 mV. So some effect of galvanic coupling can't be excluded, although it should be noted that elevated levels of dissolved O_2 are being used in the Keno tests, which will elevate the corrosion potential of alloy 22. Additionally, the corrosion potential measurements in the CT systems were performed at a higher temperature (150 °C), where the difference in corrosion potential is expected to be higher because of the elevated corrosion rate vs. temperature.

2.5 Conclusions

Alloy 22 and 316NG exhibit excellent SCC resistance after 4500 – 9600 hrs exposure in hot concentrated salt solution (pH=10.3 at 105°C) designed to simulate the chemistry of concentrated Yucca Mountain ground water, as shown by constant load tests on smooth, creviced, and notched tensile specimens in several microstructural conditions. Sensitized 304 stainless steel is highly susceptible to SCC in this environment. Titanium Grade 7 is susceptible to SCC in this environment, particularly at a very high percentage of the ultimate tensile strength. Shot peening did not affect time-to-failure for sensitized 304 stainless steel or Titanium Grade 7. To date, an effect of surface roughness on time-to-failure has not been observed.

The stainless steel Keno autoclave system is attacked by the concentrated Yucca Mountain ground water simulation. Many components, particularly manifolds and modules, have corroded beyond repair. Much of the 2001/2002 effort was spent searching for leaking modules and replacing corroded parts. It is highly recommended that a higher alloyed system be built to continue these experiments. Such a system ***is required*** to study any chemistry more aggressive in nature than the current salt solution.

2.6 References

1. P.L. Andresen, P.W. Emigh, L.M. Young, "Stress Corrosion Cracking of Annealed and Cold Worked Titanium Grade 7 and Alloy 22 in 110°C Concentrated Salt Environments", Corrosion 2001, Paper No. 1130, (Houston, TX: National Association of Corrosion Engineers, 2001).
2. T.S.E. Summers, M.A. Wall, M. Kumar, S.J. Matthews, and R.B. Rebak, "Phase Stability and Mechanical Properties of ALLOY 22 Alloy Aged in the Temperature Range 590 to 760°C for 16,000 hours", Lawrence Livermore National Laboratory Report #UCRL-JC-130816, in Scientific Basis for Nuclear Waste Management XXII, ed. by David J. Wronkiewicz and Joon H. Lee, Materials Research Society (1999), 919-926.
3. T.S.E. Summers, personal communication, December 2000.
4. J.C. Estill, K.J. King, D.V. Fix, D.G. Spurlock, G.A. Must, S.R. Gordon, R.D. McCright, R. Rebak, and G.M. Gordon, "Susceptibility of Alloy 22 to Environmentally Assisted Cracking in Yucca Mountain Relevant Environments", Paper No. 02535, Corrosion/2002, (Houston, TX: National Association of Corrosion Engineers, 2001).

Table 2-1. Keno Autoclave Solution Composition Tables

Calculated Molar Composition of Keno Solution (M)

Na_2CO_3	KCl	NaCl	NaF	$NaNO_3$	Na_2SO_4	$Na_2SiO_3.9H_2O$
0.27	0.35	0.41	0.013	0.43	0.03	0.04

Preliminary Run 1: Effect of Leakage and Refilling on Solution Composition

Measured by Ion Chromatography

Ion	Initial composition 6/7/00 wppm (calculated)	% of Initial composition 6/19/00	% of Initial Composition 8/3/00
Potassium	12182	88	81%
Nitrate	23779	100	84%
Sulfate	2271	102	76%
Chloride	25169	98.7	99%
Fluoride	216	?	?

Full Run 2: Effect of Leakage and Refilling on Solution Composition

Measured by Ion Chromatography

Ion	Initial composition 12/4/00 wppm (calculated)	2/12/01 % of Initial Composition	2/26/01 % of Initial Composition	7/2/02 (after shutting down autoclave)	8/1/02 (new solution on 7-11-02)
Potassium	12182	98%	97%	94%	90%
Nitrate	23779	104%	101%	94%	97%
Sulfate	2271	104%	101%	93%	95%
Chloride	25169	102%	98%	90%	92%
Fluoride (ppm)	216	$64 < x < 275$	$64 < x < 275$	$81 < x < 394$	$140 < x < 560$

*Note confidence intervals on measurements range from +/- 0.4% (nitrate) to +/- 14% (potassium).

Table 2-2. Specimen Details for Keno Preliminary Run (Run 1)

	Material	Sample No.	Diam piston end	Diam spec center	Diam cap end	Sample OAL	Cyl. No.	Piston No.	Ball No.	Failure Time & Date	Time-to-Failure (hrs)+	Comments
1	**C-22 as rec** YS = 47 ksi* UTS = 104	1	0.118	0.118	0.118	2.253	S560	436/439	11	3:00 pm 9/15/00	1922	overload
2		11	0.119	0.118	0.118	2.252	S558	343/382	32	3:00 pm 9/15/00	1922	overload
3		21	0.12	0.119	0.119	2.249	S551	22/497	53	3:00 pm 9/15/00	1922	overload
4		31	0.121	0.119	0.12	2.252	S626	79/21	72	3:00 pm 9/15/00	1922	overload
5		41	0.119	0.118	0.118	2.251	S566	174/161	84	3:00 pm 9/15/00	1922	overload
6		43	0.119	0.119	0.118	2.252	S625	506/293	87	3:00 pm 9/15/00	1922	overload
7	**C-22 20% CW** YS = 125 ksi* UTS = 133	5	0.119	0.118	0.118	2.274	S554	545/511	24			unfailed
8		15	0.119	0.118	0.119	2.275	S614	514/229	40			unfailed
9		25	0.119	0.118	0.118	2.270	S52	371/417	60			unfailed
10		35	0.119	0.118	0.119	2.279	S617	493/215	77			unfailed
11		45	0.119	0.117	0.119	2.268	S526	272/548	89			unfailed
12		48	0.118	0.117	0.119	2.264	S527	258/59	94			unfailed
13	**C-22 as rec shot peened**	7	0.119	0.119	0.121	2.251	S531	172/190	26	3:00 pm 9/15/00	1922	overload
14		17	0.119	0.117	0.119	2.252	S535	105/90	43	3:00 pm 9/15/00	1922	overload
15		27	0.121	0.120	0.119	2.253	S533	28/279	67	3:00 pm 9/15/00	1922	overload
16		37	0.119	0.117	0.118	2.253	S539	499/154	79	3:00 pm 9/15/00	1922	overload
17	**Ti-G 7 as rec** YS = 36 ksi* UTS = 53	2	0.136	0.135	0.135	2.157	S553	547/413	17	time unknown	<885.5	failed
18		12	0.135	0.135	0.136	2.301	S561	341/264	33	5:48 pm 6/9/00	49.8	13th failure
19		22	0.136	0.135	0.135	2.173	S624	93/160	56	2:05 am 6/8/00	10.1	11th failure
20		32	0.136	0.135	0.136	2.292	S621	380/288	74	4:42 pm 6/7/00	0.7	2nd failure
21		42	0.136	0.134	0.135	2.163	S559	439/432	85	4:42 pm 6/7/00	0.7	3rd failure
22		47	0.136	0.134	0.135	2.173	S563	133/289	93	5:48 pm 6/7/00	1.8	9th failure
23	**Ti-G 7 20% CW** YS = 72.5 ksi* UTS = 75.5	6	0.135	0.134	0.135	2.269	S552	376/113	25	5:51 am 8/22/00	1336.9	21st failure
24		16	0.136	0.135	0.135	2.275	S522	431/236	42	11:05 am 8/24/00	1390.1	24th failure
25		26	0.134	0.134	0.135	2.258	S538	333/---	62	5:11 pm 8/23/00	1372.2	22ndfailure
26		36	0.135	0.134	0.135	2.263	S524	375/505	78	7:40 am 8/24/00	1386.7	23rd failure
27		46	0.135	0.135	0.135	2.252	S528	338/148	92	3:00 pm 9/15/00	1922	overload
28		49	0.135	0.135	0.135	2.292	S530	264/83	95	3:00 pm 9/15/00	1922	overload
29	**Ti-G 7 as rec shot peened**	8	0.135	0.134	0.134	2.150	S549	410/493	27	time unknown	<885.5	failed
30		18	0.135	0.134	0.136	2.169	S536	467/539	45	time unknown	<885.5	failed
31		28	0.135	0.134	0.135	2.174	S537	482/145	69	2:12 pm 6/9/00	46.2	12th failure
32		38	0.134	0.134	0.135	2.300	S547	---/197	80	time unknown	<885.5	failed
33	**316 NG SS** YS = 28.7 ksi*	3	0.134	0.133	0.134	2.245	S555	11/484	20	3:00 pm 9/15/00	1922	overload
34		13	0.133	0.132	0.133	2.258	S622	158/105	34	10:40am 8-29-00	1509.7	failed
35		23	0.132	0.132	0.134	2.254	S623	385/391	57	9:11 am 8/25/00	1412.2	failed
36		33	0.134	0.132	0.133	2.256	S620	508/298	75	11:41 am 8/25/00	1414.7	failed
37	**316 NG SS shot peened**	9	0.133	0.132	0.134	2.241	S546	121/119	28	11:55pm 8-29-00	1522.9	failed
38		19	0.133	0.133	0.133	2.242	S534	90/228	46	12:39am 8-30-00	1523.6	failed
39		29	0.135	0.133	0.133	2.245	S541	558/121	70	6:02 am 8-30-00	1529.0	failed
40		39	0.133	0.132	0.135	2.26	S550	399/350	98	3:54pm 8-29-00	1514.9	failed
41	**Sens 304 SS** YS = 42.5 ksi* UTS = 75	4	0.129	0.129	0.132	2.266	S556	555/317	23	6:20 pm 6/7/00	2.3	10th failure
42		14	0.129	0.129	0.129	2.263	S619	382/547	35	4:55 pm 6/7/00	0.9	4th failure
43		24	0.129	0.128	0.130	2.262	S529	113/405	58	5:26 pm 6/7/00	1.4	7th failure
44		34	0.129	0.129	0.129	2.262	S557	298/498	76	5:13 pm 6/7/00	1.2	6th failure
45		44	0.129	0.129	0.13	2.269	S523	548/352	88	1:56 pm 6/19/00	285.9	15th failure
46		50	0.129	0.129	0.129	2.266	S525	300/433	96	time unknown	<885.5	failed
47	**Sens 304 SS shot peened**	10	0.130	0.129	0.130	2.274	S540	24/35	30	5:04 pm 6/7/00	1.1	5th failure
48		20	0.128	0.128	0.129	2.262	S615	238/345	47	4:32 pm 6/7/00	0.5	1st failure
49		30	0.128	0.128	0.128	2.262	S618	553/22	71	5:26 pm 6/7/00	1.4	8th failure
50		40	0.129	0.128	0.128	2.265	S628	197/222	83	12:04 pm 6/19/00	284.1	14th failure

Table 2-3. Specimen Matrix for Keno Full Run (Run 2)

Material	Heat	Condition	Finish	Specimens per Condition			Total Specimens
				System Pressure = 1500 psi			
Alloy-22			RMS	85 ksi	93 ksi	100 ksi	
	2277-9-3192	As-received	150	6	6	6	18
	2277-9-3192	As-received	72		6		6
	2277-9-3192	AR + HT1 (700°C/175 h)	150	6	6		12
	2277-9-3192	AR + HT2 (520°C/1000 h)	150	6	6		12
	2277-9-3192	AR + 20%CW + HT2			6		6
	2277-9-3192	20% Cold worked			6		6
	2277-9-3192	AR + Creviced	150	6	6		12
	2277-9-3192	AR + HT1 + Creviced	150	6	6		12
	2277-9-3263 B-575	Weld and HAZ	150	6	6		12
Ti-Grade 7				40 ksi	45 ksi	50 ksi	
	CN0171	As-received	150	6	6	5	17
	CN0171	Creviced	150		6		6
NG 316 SS				65 ksi	70 ksi		
	29861	As-received	150	6	6		12
	29861	As-received	72		6		6
	29861	Creviced	150		6		6
304 SS				45 ksi	50 ksi		
	AJ9139	Sensitized (621°C/24h)	150	6	6		12
	AJ9139	Sensitized + creviced	150		6		6
Total							161
					Effective stress 85 ksi		
Alloy 22 notched*	2277-9-3192	As-received	150		8		8
Alloy 22 notched*	2277-9-3192	As-received + 700°C/175 h	150		8		8
Alloy 22 notched*	2277-9-3263 B-575	Weld and HAZ	150		8		8
Grand Total Full Matrix							**185**

*Notched specimens added to the Keno autoclave 3-4-02

Table 2-4. Tensile Properties in 125°C Air

Material/Condition	Yield Strength (ksi)	Ultimate Tensile Strength (ksi)
Alloy-22 As-received	47	104
Alloy-22 As-received + 20% CW	125	133
Alloy-22 As-received + HT1 (700°C/175 h)	49*	107*
Alloy-22 As-received + HT2 (520°C/1000 h)	70*	149*
Alloy-22 20% CW + HT2 (520°C/1000 h)	133*	179*
316 NG As-received	28.7**	-
Titanium Gr 7 As-received	36	53
Titanium Gr 7 20% CW	72.5	75.5
304SS Sensitized (621°C/24 h)	42.5	75

* Determined at 105°C
** Interpolated using RT and 288°C data

Table 2-5. Sequence of Pressure Changes during Keno Preliminary Test (Run 1)

Date/time	**Cumulative Test Time (hrs)**	**System Pressure (psi) (after change)**	**Temperature (°C)**
6-7-00 4:00 pm	0	900	125
6-19-00 10:30 am	282.5	1000	125
7-14-00 1:30 pm	885.5	0	RT
8-3-00 10:30 am	885.5	1000	105
8-8-00 8:30 am	1003.5	1100	105
8-21-00 to 8-30-00	1321-1520	1180 - 1240*	105
8-30-00 to 9-15-00	1520-1922	1200 - 1350*	105
9-15-00 3:00 pm	1922	1600	105
9-15-00 4:30 pm	1923.5	200	RT
9-18-00 8:00 am	1987	0	RT

*Problem with pressure regulator becoming increasingly incapable of maintaining constant pressure. New Tescom regulator was installed on 9-28-00. Additionally, system modifications were made to accommodate pressure changes during solution addition.

Table 2-6. Sequence of Pressure Changes during Keno Full Run 2 (105^{o}C)

Date/time	Cumulative Test Time (hrs)	System Pressure (psi)	Comments
12-4-00 1:30 pm	0	To 1000	Test start
12-11-00 2:00 pm	168.5	To 1500	Target pressure
12-12-00 7:00 am	185.5	To 0	Leak rate high; 25 failures to-date
12-20-00 3:11 pm	185.5	To 1249	18 specimens added to autoclave (12 C22+LRO, 6 C22+LRO)
12-21-00 7:00 am	201.3	To 1400	Increasing pressure to target
12-21-00 3:20 pm	209.65	To 1500	Target pressure
3-25-01 11:30 am	2461.8	To 0	Leak rate high; modules with corroded threads identified; dye penetrant 31 specimens and return to test; 3 unfailed specimens (#100, 87, 45) removed for photos
5-03-01 10:50 am	2461.8	To 1500	Replacement manifold installed; at target pressure
5-23-01 6:15 pm	2949.3	1500	316NG failure (uncreviced) due to pressure overload from adjacent Keno autoclave seal failure
7-12-01 3:30 pm	4146.5	To 0	High leak rate; 8 modules corroded at threads; replacement 316L manifolds ordered; remove unfailed#98 for mat'l verification (Ti G7)
1-16-02 thru 2-14-02	4146.5	0	Removed modules, cleaned, inspected for corrosion, replaced as needed
3-4-02 11:00 am	4146.5	To 100	Replacement manifolds installed; notched specimens included
3-6-02 1:40 pm	4146.5	To 1487	System at pressure
5-15-02 12:50 pm to 5-17-02 11:15 am	5825.7	Pressure decrease from 1498 to 417	Valve not re-opened after filling; slow loss of pressure; open valve and increase pressure
5-17-02 11:35 am	5872.5	To 1496	System at pressure
6-20-02 3:50 pm	6692.75	To zero	Leak rate too fast; heaters off; shut down test
6-20-02 to 7-11-02	6692.75	0	Replace corroded module, cleaned and checked all modules, made new solution
7-11-02 10:30 am	6692.75	To 1500	Re-start test
11-11-02 10:30 am	9644.6	Time-to-date	Test running