Failure of High Pressure Gas Fittings and Valves in Refuge Alternatives

Summary of the hazard: “On Sunday, January 9, 2011, a catastrophic failure occurred in an oxygen cylinder fitting connected to the breathable air system in a refuge alternative located in an underground coal mine. The refuge alternative was an inflatable tent design manufactured by the A.L. Lee Corporation, model number 4042-35 manufactured on March 21, 2008. This refuge alternative is equipped with 12 high pressure oxygen cylinders, each pressurized at 4,500 psi with each connected to a main manifold. This catastrophic failure allowed a rapid release of oxygen, which pressurized the interior of the steel structure. The initial determination is that the pressure build-up inside the container forced open both the tent deployment door and the air-lock access door, ejecting a supply container and three 5-gallon water containers from the access door area onto a nearby rib.”¹ The subsequent investigation led to the discovery of cracks on multiple valves and fittings on other high pressure oxygen and air tanks used in similar refuge shelters. A significant number of fittings and valves on high pressure tanks have developed cracks after only three years of service. In one case, half of the valves and fittings in a refuge shelter had developed cracks. In a test report produced by the valve manufacturer (Sherwood) the cracks in three of six valves were classified as “moderate to severe”². The demonstrated short and unpredictable service life of the CGA brass valves and fittings is troublesome. The current situation left unchecked represents a safety hazard.

MSHA published two hazard alert documents—an Equipment Alert¹ and a subsequent Update Memo concerning the hazard.

Request for Assistance: The Salt Lake Technical Center (SLTC) was asked to perform a metallurgical analysis of the valves and fittings by the Mine Safety and Health Administration (MSHA). The samples sent to SLTC represent a small fraction of the brass fittings and valves that have developed cracks. Some cracked valves and fittings were sent to another lab³ for examination. In addition, Sherwood, the valve manufacturer, performed burst tests on some of the cracked valves.

The analysis performed at the SLTC revealed that the failures are a result of stress-corrosion cracking (SCC). The stress-corrosion cracks in the fittings and valves indicate that they are on the path to failure. It is well known that brass is susceptible to corrosion cracking in moist

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¹ http://www.msha.gov/equiphaz.HTM, accessed 4-21-2010
² Sherwood Valve LLC(2011), Tested Report LSN 1244 GV Mining Valve Safety Boss Tests forwarded to SLTC by MSHA
³ Sherry Laboratories, www.sherrylabs.com
atmospheres that contain certain chemical compounds. The presence of a corrosion product may be an indicator of stress-corrosion cracking. However, not every corrosion pit or corrosion product seen as surface corrosion will develop into a crack. Cracks preferentially develop at stress concentrations--this is evidenced in the samples SLTC received.

Three primary factors have been identified with the type of SCC failures in copper-based alloys seen here: a specific corrosive medium, a susceptible material, and tensile stress. Mitigating SCC involves eliminating one or more of the three primary factors. The evidence suggests that there is a chemical compound—not yet identified—in the humid mine environment that is responsible for the stress-corrosion cracks. Excluding the mine atmosphere by coating the valves or housing the air/oxygen storage systems within a sealed compartment may mitigate the SCC in the valves. Alternately, using a more corrosion resistant material than brass may mitigate the problem. Redesign to reduce stress may not be an option as one study suggests there is no threshold value below which SCC will not occur in 70-30 brass. While the study was conducted with a brass that contained 70% copper and 30% zinc alloy combination, the cracked brass fittings and valves are not very different at 62% and 60% copper and 36% and 39% zinc respectively.

This report is organized in the following manner. First, a background section is presented providing the reader with information on the terms and concepts used in this report. Second, is an inventory of the brass valves and fittings sent in for analysis. The section after that analyzes the brass valves and fittings and shows how they elicit evidence of SCC. Finally, there follows a discussion section and a short conclusion.

I. Characteristics of Stress-Corrosion Cracking (SCC)

Fracture Surface Analysis is the body of knowledge that allows for the examination and interpretation of features on the fracture surface of metals to understand the cause behind the fracture. There are only four principal modes of fracture, and each has distinct surface features that can be used to understand the process that created the fracture. These modes are: cleavage, fatigue, dimple rupture and, decohesive rupture.

Of these four only decohesive rupture and dimple rupture were observed in the samples. Metals and alloys are made of relatively small individual faceted grains. When a fracture path propagates along grain boundaries it is referred to as intergranular; when the fracture path runs through the grains it is referred to as transgranular.

Decohesive rupture is generally the result of a reactive environment or a unique microstructure and is almost exclusively associated with rupture along the grain boundaries. Decohesive rupture also exhibits little or no bulk plastic deformation. Dimple rupture refers to the dimples that are created on the fracture surface when metals are pulled apart.

4 The material presented in this section is taken from the ASM Handbooks listed below. In some cases it is quoted word for word. ASM International (1992). Vol. 12 Fractography and Vol. 13 Corrosion

A fracture surface covered by a corrosion product that evidences intergranular decohesive rupture is indicative of SCC. There may be more corrosion product covering the fracture surface at the origin than at the tip of the crack. Cracks that branch are yet another indicator of SCC.

**Stress-Corrosion Cracking** is a term used to describe service failure in engineering materials that occur by slow, environmentally-induced crack propagation. The cracks are a result of the combined and synergistic interaction of mechanical stress and corrosion reactions. In other words, the combined simultaneous interaction of mechanical and chemical forces results in crack propagation; neither factor acting independently or alternately would result in the same effect. It should be clearly understood that SCC is not a result of stress concentration at corrosion-generated surface flaws. That is not to say that surface finish does not have an influence on where cracks initiate: frequently cracks do initiate at surface flaws that either preexist or are formed during service by corrosion. SCC will not occur without local applied or residual stress. The stresses required to cause SCC are small, usually below the macroscopic yield stress, and are tensile in nature. Compressive residual stress can be used to prevent the phenomenon. Three conditions are required for sustained SCC in copper-based alloys: a susceptible material, a corrosive environment specific to the material, and adequate stress.

**Susceptible Material** The phenomenon of SCC in brass was first observed 100 years ago. SCC was initially called seasonal cracking because it coincided with the high humidity of the rainy season in India and the concentration of ammonia in the atmosphere. Removing the brass components from the ammonia atmosphere and annealing to remove residual stress solved the problem.

**Corrosive Environments** Ammonia and ammonia compounds are the corrosive substances most often associated with SCC of copper alloys but sulfates, nitrates, and chlorides have also been shown to attack brass. Interestingly, even distilled water and water with only 0.005% sulfur dioxide have been shown to attack brass. In the case of ammonia both oxygen and moisture must be present to be corrosive to copper alloys. Moisture films on a surface provide the medium whereby a variety of different electrolytes can attack brass. According to MSHA not all mines are humid, some are extremely dry. Mine humidity in general varies with season and mine location. Ground water release during mining operations would tend to elevate the humidity in some cases.

**Adequate Stress** Fittings and valves experience stresses when they are put into service. The tightened nut holds the nipple against the valve. The valve threads see pressure from tightening the PRD (Pressure Relief Device).

**A Closer Look at Corrosion Product and Process** Dezincification was suggested by MSHA as a possible corrosion process. Dezincification is the process in which zinc is selectively leached from zinc-containing alloys leaving a relatively weak layer of copper and copper oxide. Dezincification is most commonly found in copper-zinc alloys containing less than 85% copper.

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6 The material presented in this section is taken from the ASM book listed below. In some cases it is quoted word for word. ASM International (1993). Russell H. Jones (Ed.), Stress-Corrosion Cracking Material Performance and Evaluation
7 Yield Stress is the stress level in a ductile material in which large strains—or changes in the size or shape of the body—take place without an increase in load.
after extended service in water containing dissolved oxygen, especially under stagnant conditions. Dezincification has alternatively been referred to as “dealloying”, “parting”, or “selective leaching.” Specifically, this is corrosion in which zinc is preferentially removed from an alloy, leaving an often porous residue of the elements that are more resistant to the particular environment. It has been reported that dezincification appears to be one of the principal contributing factors in the SCC of copper-zinc alloys. The preferential dissolution or loss of zinc at the fracture surface interface during SCC results in the corrosion products having a higher concentration of zinc than the adjacent alloy. This dynamic loss of zinc near the crack aids in propagating the stress-corrosion fracture.

On a microscopic level it might be explained in the following way: zinc preferentially reacts with a chemical species in the moist environment producing a chemical compound referred to as a corrosion product at the surface. The corrosion continues beneath the primary corrosion layer. With the zinc atoms removed from the lattice of the alloy, the result is a gradual replacement of sound brass with a weak porous lattice of copper or copper oxide. This porous layer, having lost its strength, hardness, and ductility, is more susceptible to local residual or applied stress, allowing for the formation of microscopic tears or cracks. The tears produce or expose a fresh reactive surface for the process to repeat. By this means the cracks propagate when there is sufficient local stress to advance the crack front.

The leaded brass alloy compositions were reported by MSHA to be CuZn38Pb2 (C37700) and CuZn36Pb3 (C36000) respectively for the valve and the nut. That means that within the copper matrix, zinc is 38% and 33-37.5%, and lead is 1.5-2.50% and 2.50-3.70%, respectively. The metal content of the corrosion product, however, on both the valves and nuts is zinc-rich (approximately 80%) with minor amounts of copper and lead. These compositions suggest dezincification of the alloy.

II. Samples Received for Analysis

SLTC received two shipments of samples. The first shipment contained fittings divided into 5 groups. The second shipment contained two valves which have been designated by SLTC as Group 6. In total, 14 samples were sent to SLTC. The initial sample identifiers supplied by MSHA are used in this report. Table 1 lists the valves, fittings and associated information received from MSHA: sample identifier, manufacturer, refuge serial number, name of the mine from which the samples were taken and associated comments. Comments in red indicate MSHA saw cracks on the body of the nut or valve. Photographs of the samples have been inserted between rows of the table. This report addresses the examination of high pressure oxygen valve and fittings (CGA 701) first, followed by the high pressure air valve and fittings (CGA 347).

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9 C37700 and C36000 refer to the unified numbering system (UNS) for alloys managed jointly by ASTM International and SAE International. A UNS number alone does not constitute a full material specification because it establishes no requirement for material properties, heat treatment, form or quality.
10 Alloy composition obtained from the UNS alloy lookup on the following web site http://matweb.com/search/SearchUNS.aspx accessed 4-13-201.
Table 1: List of Valves & Fittings Sent to OSHA Lab for Failure Analysis

<table>
<thead>
<tr>
<th>#</th>
<th>MSHA Sample Number</th>
<th>Suspected Fitting Manufacturer</th>
<th>Refuge Serial Number</th>
<th>Mine Name</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Group 1</td>
</tr>
<tr>
<td>1</td>
<td>Unused Exemplar CGA 701 Nut</td>
<td>Superior</td>
<td>N/A</td>
<td>N/A</td>
<td>Dimensionally¹ Correct Nut: Unused Condition</td>
</tr>
<tr>
<td>2</td>
<td>Unused Exemplar CGA 701 Nipple</td>
<td>Superior</td>
<td>N/A</td>
<td>N/A</td>
<td>Unused Condition</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Group 2</td>
</tr>
<tr>
<td>3</td>
<td>CGA 701 Assembly A2</td>
<td>Superior</td>
<td>LS9044</td>
<td>Sentinel</td>
<td>Dimensionally Incorrect Nut: Fully Separated Nut: Caused oxygen release at Sentinel</td>
</tr>
<tr>
<td>4</td>
<td>CGA 701 Assembly B1</td>
<td>Superior</td>
<td>LS9044</td>
<td>Sentinel</td>
<td>Dimensionally Incorrect Nut: Nut partially separated through flange</td>
</tr>
<tr>
<td>5</td>
<td>CGA 347 Assembly D2</td>
<td>Superior</td>
<td>LS9044</td>
<td>Sentinel</td>
<td>Compressed Air Fitting; Shows signs of corrosion</td>
</tr>
</tbody>
</table>

¹ Dimensionally correct according to CGA(Compressed Gas Association) V-1 2005, Standard for the Compressed Gas Cylinder Valve Outlet and Inlet Connections
<table>
<thead>
<tr>
<th>#</th>
<th>MSHA Sample Number</th>
<th>Suspected Fitting Manufacturer</th>
<th>Refuge Serial Number</th>
<th>Mine Name</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>CGA 701 Assembly B3</td>
<td>Superior</td>
<td>LS9028</td>
<td>Flint Ridge</td>
<td>Dimensionally Correct Nut; Cracks through nut threads</td>
</tr>
<tr>
<td>7</td>
<td>CGA 701 Assembly C3</td>
<td>Superior</td>
<td>LS9028</td>
<td>Flint Ridge</td>
<td>Dimensionally Correct Nut; Cracks starting through nut threads</td>
</tr>
<tr>
<td>8</td>
<td>CGA 347 Assembly F1</td>
<td>Superior</td>
<td>LS9028</td>
<td>Flint Ridge</td>
<td>Compressed Air Fitting; Shows signs of corrosion; Connection was leaking; threads on cylinder valve to which it was attached were cracked.</td>
</tr>
<tr>
<td>9</td>
<td>CGA 701 Assembly from Refuge at #45 Block</td>
<td>Superior</td>
<td>LS9045</td>
<td>Sentinel</td>
<td>Dimensionally Incorrect Nut; Nut partially separated through flange</td>
</tr>
<tr>
<td>10</td>
<td>CGA 701 Assembly from Refuge at #2 Block</td>
<td>Superior</td>
<td>LS9046</td>
<td>Sentinel</td>
<td>Dimensionally Incorrect Nut; Nut partially separated through flange</td>
</tr>
<tr>
<td>11</td>
<td>CGA 701 Assembly from Refuge at #3 Block</td>
<td>Superior</td>
<td>LS9043</td>
<td>Sentinel</td>
<td>Dimensionally Incorrect Nut; Nut shows signs of corrosion; No apparent fracturing</td>
</tr>
<tr>
<td>#</td>
<td>MSHA Sample Number</td>
<td>Suspected Fitting Manufacturer</td>
<td>Refuge Serial Number</td>
<td>Mine Name</td>
<td>Comments</td>
</tr>
<tr>
<td>----</td>
<td>--------------------</td>
<td>-------------------------------</td>
<td>----------------------</td>
<td>-----------</td>
<td>----------</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>CGA 701 Assembly Western</td>
<td>LS9039 or LS9040 (A.L.Lee is unsure)</td>
<td>Imperial</td>
<td>Dimensionally Correct Nut; Shows signs of corrosion; No apparent fracturing; Provided as a comparison to fittings suspected to be made by Superior</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>CGA 347 valve mounted in a stainless steel block with a Swagelok fitting elbow (left photo)</td>
<td>Sherwood unknown unknown</td>
<td>Three visible cracks on safety boss</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>CGA 701 valve mounted in a stainless steel block with a Swagelok fitting elbow (right photo)</td>
<td>Sherwood unknown unknown</td>
<td>Visible cracks on the safety boss</td>
<td></td>
</tr>
</tbody>
</table>
III. Examination of the CGA 701 High Pressure Oxygen Samples

A. General Microscope Examination of the Samples

First, the CGA 701 brass nuts, nipples and a valve from 8 assemblies were examined to verify the information supplied with the samples with respect to cracks and crack location. Multiple photographs were taken of the cracks and the one complete fracture. Some of those photographs are included in this report in the section specific to the valve or fitting. Second, the nuts were measured to verify the size specifications required by the Compressed Gas Association Standard (CGA). Next, a subset of the nuts the one valve were sectioned to view the fracture surfaces. Finally, the alloy chemistry was determined.

Brass Nipples: The nipples had no visible cracks. The nipples from the two manufacturers are different (See Photos 8 and Photo 9).

![Photo 8: Noses of different nipples: Western nipple Group 5 (left) and Superior nipple B1 Group 2 (right).](image)

![Photo 9: Western nipple Group 5 (left) and Superior nipple B1 Group 2 (right). Both these nipples meet CGA 701 dimensional requirements.](image)

The Western nipple has an inline filter; the Superior nipple does not. The Superior nipple has a smaller drill diameter. The Western nipple is stamped: CAUTION HIGH PRESSURE ONLY OVER 3000 PSIG. The Superior nipple has no markings. The Superior nipple B1 and the Western nipple were measured against the criteria listed on the CGA (Compressed Gas Association) V-1 October 1994 mechanical drawing specification sheet for CGA 701 fittings. Both nipples meet the criteria.

Brass Nut Cracks: The cracks on the undersized nuts developed in different locations than cracks on the dimensionally correct nuts. The cracks on the dimensionally correct nuts originate on the outside surface and propagate through the thread wall towards the flange. The cracks on the dimensionally incorrect nuts originate on the sharp interior corner of the nut and propagate upwards through the flange. It is not surprising that cracks have preferentially formed in an area
on a nut that did not meet the design specifications i.e., the stress would be higher in the undersized flange.

**Brass Valve Cracks:** The cracks on the valve developed on the exterior outside surface of the safety boss and propagate through the thread wall towards the body of the valve (see Photo 23 below).

**B. Measurement of Dimensionally Correct vs. Dimensional Incorrect Nuts**

MSHA indicated that some of the nuts do not meet CGA 701 dimensional requirements, even though all of the nuts have a CGA stamp. According to the CGA drawing supplied by MSHA, the nuts should have a minimum length of 1.125 inches and a flange minimum thickness of 0.250 inches. Table 2 is a comparison of the measurements of four CGA 701 nuts. The first two nuts in the table are dimensionally incorrect and were manufactured by Superior. The third and fourth nuts in the table are dimensionally correct but represent the two different manufacturers: Superior and Western. Multiple measurements were taken. The average is reported in the table. The flange thickness was calculated by subtracting the bore depth (0.875 inches) from the minimum length (1.125 inches) See Figure 1 on the next page. On the dimensionally incorrect nuts, the flange thickness was found to be undersized by approximately 40% and the length undersized by 9%. According to MSHA, the company was informed that they produced a product that did not meet CGA 701 specifications.

<table>
<thead>
<tr>
<th>Nut ID</th>
<th>Specification</th>
<th>A2</th>
<th>B1</th>
<th>B3</th>
<th>Western</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flange thickness = 0.250 minimum</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flange Width</td>
<td>0.1532</td>
<td>0.1505</td>
<td>0.2533</td>
<td>0.2592</td>
<td></td>
</tr>
<tr>
<td>% Undersized</td>
<td>39%</td>
<td>40%</td>
<td>meets spec</td>
<td>meets spec</td>
<td></td>
</tr>
<tr>
<td>Specification</td>
<td>Hexagon nut length = 1.125 minimum</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nut Length</td>
<td>1.0225</td>
<td>1.0205</td>
<td>1.1306</td>
<td>1.1351</td>
<td></td>
</tr>
<tr>
<td>% Undersized</td>
<td>9%</td>
<td>9%</td>
<td>meets spec</td>
<td>meets spec</td>
<td></td>
</tr>
</tbody>
</table>

Measurements are in inches.
A2, B1 and B3 were manufactured by Superior.
C. Fracture Surface and Corrosion Product Analysis

SLTC selected four CGA 701 samples for a more in-depth examination. The samples selected represent the different manufacturers and fracture locations. The selections were:

- The dimensionally incorrect Superior nut B1 (Group 2) partially fractured through the flange.
- The dimensionally correct Superior nut B3 (Group 3) with fractures perpendicular to the threads.
- The Western nut (Group 5) listed as having no fractures.
- The Sherwood valve (Group 6) having fractures perpendicular to the safety boss threads.
The samples were sectioned to more easily view the interior and fracture surfaces. One section was mounted and polished to view a crack in a cross sectional manner. The sections were examined using a Keyence microscope and a Hitachi S3500N Scanning Electron Microscope (SEM) equipped with a PGT energy dispersive X-ray spectroscopy (EDS) unit. The Keyence digital microscope system has a depth of field 20 times larger than an optical microscope. It is a hybrid of conventional microscope which utilizes a fixed base, and videoscope. It produces a high depth of field 2D image of a 3D object by taking a series of pictures that are stitched together. The SEM was used to look at the fracture surface details. The EDS unit was used to analyze the corrosion product. The EDS is a microanalysis technique used for elemental analysis. The X-ray energy emitted corresponds to the presence of a specific element, and the amplitude corresponds to the quantity of the element.

**Examination of the B1 nut:** This dimensionally incorrect CGA 701 nut was sectioned to open up a crack that had propagated completely through the flange on one side but had not broken through on the other side. This revealed the fracture surface and a cross-sectional view of an incomplete through-fracture. Photo 10 shows how the nut was sectioned. Photo 11 is a close-up of the crack in the mounted section. The crack’s origin is at the sharp interior corner of the nut with the crack propagating toward the exterior surface of the flange. Photo 12 is an SEM photomicrograph of the same crack seen in Photo 11. Photo 12 shows the beginning of porosity caused by dezincification.

*Photo 10: How the B1 nut was sectioned. The mount is the inside corner of the nut. To the right of the mount is a portion of the inside corner that had completely fractured through the flange.*

*Photo 11: A close up of the mounted cross section of the inside corner of B1. The crack originates on the inside corner and propagates up through the flange. Keyence Z50-500X.*
Photo 13 is an SEM fractograph of the fracture surface that was opened up by sectioning the nut. The surface is predominantly *intergranular decohesive rupture*. There appears to be a small component of dimple rupture present. Pitting is visible on the fracture surface. Pitting indicates corrosion. The fracture surface features seen in Photo 13 show stress-corrosion cracking (SCC). There is evidence of over tightening at the sharp 90 degree interior corner of the nut.
Photo 14 shows a portion of the crack around the circumference of the flange on the exterior top surface of the nut. The bluish white corrosion product is composed of an oxidized zinc compound. A microanalysis of the residue by SEM EDS shows it to be zinc-rich with minor amounts of copper and lead. The Handbook of Chemistry and Physics, 69th Edition indicates the color of ZnO is white and zinc sulfates are colorless.

Photo 15 shows a white bluish corrosion product along the crack that initiated from the interior and traveled through the flange to the exterior surface. The presence of corrosion product on the inside of the flange—not on a surface that would normally see leak detection fluid—suggests that the humid mine atmosphere contains a corrosive species. The threads on the nut are not sealing threads. When tightened they serve to hold the nose of the nipple against the curved surface on the valve to create a seal between the nipple and the valve (see Figure 1). They do not seal out the humid atmosphere. Corrosion product generally covers the interior threads as well.
Examination of B3: This dimensionally correct CGA 701 nut was sectioned as shown in photos 16 and 17. There are two visible cracks that can be seen in those photos. The cracks begin at the exterior surface and propagate through the nut wall perpendicular to the threads toward the flange, branching at the end (see Photo 18). The branching is indicative of SCC. Because the cracks in the dimensionally incorrect nut B1 originated from the interior inside corner—a stress concentration position—this area was examined on the dimensionally correct nuts as well. Photo 19 shows corrosion product at this location on the wedge section that was cut for examination. Localized concentration of corrosion product on an interior high stress area—a surface not subject to mechanical abuse or liquid leak detection fluid—is likely a precursor to crack formation. Whether or not a crack propagates depends on the specimen geometry and how the magnitude of the stress field at the crack tip changes as the crack develops. A thin layer of corrosion product was also found on the threads. While it appears the stress is sufficient in this area to produce a corrosion product possibly initiating SCC, there is no evidence of significant crack propagation. Photo 20 shows the outside surface where the crack shown in photo 16 initiated; bluish white corrosion product is visible in the crack and on the surface.

Photo 15: Bluish-white corrosion product at the inside corner where the crack through the flange originates. Keyence 50-500X lens composite photo.
Photo 16: Section cut from the nut showing one of two visible cracks in nut B3.

Photo 17: Second visible crack at the 12 o’clock position in photograph.
Photo 18: Shows the branching at the end of the crack seen in Photo 16. Branching is characteristic of SCC. Keyence 50-500X lens composite photo.

Photo 19: Showing the inside corner of the wedge section that was cut from the nut. Note the corrosion residue present at the inside corner were the stress would be higher. Keyence 50-500X lens composite photo.
Examination of Western Nut: This nut was sectioned in the same manner as the Superior nut B3 (see Photo 21). The wedge section cut from the nut allowed for close examination.

The nut was unremarkable except for the corrosion product visible at the sharp inside corner similar to the other dimensionally correct nut. Again, localized concentration of corrosion product on an interior high stress area—a surface not subject to mechanical abuse or liquid leak detection fluid—is likely a precursor to crack formation. However, while there is no significant cracking at this location it is suggestive that the stress is higher in this locality.

Photo 20: Right inset picture is the origin of crack on outside surface of the nut. Corrosion product with in the crack and on the surface.

Photo 21: Showing how the Western nut was sectioned. There are no visible cracks.
Examination of Sherwood 701 Valve. There are three cracks that originate on the exterior surface of the safety boss and propagate through the thread wall toward the valve body. The cracks are seen in Photo 23 below at the 1, 6 and 9 o’clock positions. Sections were cut from the safety boss to view the fracture surfaces of two of the cracks and a cross sectional mount of the third crack.

Photo 23: Sherwood high pressure oxygen valve, cracks have formed at the 1, 6 and 9 o’clock positions on the PDR port. Wall thickness approx. 0.1 inches.

Photo 22: Corrosion deposits on inside corner of nut. Keyence composite photo.
Photo 24 shows a side view of the valve; the larger oxygen port on the left has an approximate wall thickness of 0.25 inches and the safety boss on the right has an approximate wall thickness of 0.1 inches. Measurements were taken from the root of the thread. It was reported but not confirmed that there are torque specifications for the Pressure Relief Device (PRD), and that the PRDs are installed by the manufacturer. There were no visible cracks on the oxygen outlet. The safety boss sees continual pressure exerted by gas inside the tank. Photo 25 shows the outlet port on the valve.

Photo 26 and 27 show the cracks at the 9 and 6 o’clock positions in Photo 23. The branching at the end of the crack is typical of SCC seen in Photo 26 and corrosion product is visible in the crack. Photo 27 shows the corrosion product within the crack at the 9 o’clock position in Photo 23.
The PRD was removed. It had visible corrosion product on the threads. Using a carbon sticky tab the corrosion product was lifted from the PDR thread surface for SEM EDX analysis. The residue is zinc rich with minor amounts of copper and lead. Photo 28 is an SEM fractograph of the corrosion product removed from the threads for analysis. Photo 29 is the PRD with corrosion product visible on the surface.

Photo 28: Corrosion product removed from PRD threads for EDS analysis. Zinc is the major metal element.

Photo 29: Pressure relief devise (PRD) removed from the oxygen valve. Corrosion product is visible on the surface and within the threads.

The small section cut from the valve was viewed using an SEM; corrosion product covered the fracture surface making it difficult to view the actual fractured metal. The small section was sonicated in isopropyl alcohol (IPA) for 20 minutes to try and remove the corrosion from the fracture surface. IPA was chosen because it does not react with the brass. The corrosion product proved difficult to remove by sonication. Fractographs 30 and 31 shows the corrosion product remaining on the fracture surface after sonication. Even though the corrosion product covers the surface, the surface features suggest intergranular attack in photo 31. Photo 32 is a photo of the fracture surface without the corrosion product. This surface is similar to the fracture surface of the nut, showing decohesive rupture at the grain boundaries and corrosion pitting on the grains. Photo 33 is a higher magnification view of the fracture surface; the rectangular particles on the fracture surface are broken fragments of the corrosion product. The particles appear to be crystalline.

Photo 30: Corrosion product still remains on the fracture surface even after 20 minute sonication to remove it.

Photo 31: Surface features suggest intergranular attack beneath the corrosion product on the fracture surface.
D. Alloy Composition

A chemical analysis of the Western nut, Superior nut (B1) and the CGA 701 valve was performed using optical emission spectrometry to confirm that the alloys meet the ASTM specification reported by the manufacturers. Both nuts meet ASTM designation for C36000. The lead in the valve alloy was low when compared against the ASTM C37700 criteria.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Pb</th>
<th>%Sn</th>
<th>%Zn</th>
<th>%Fe</th>
<th>%Ni</th>
<th>%Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Western Nut</td>
<td>2.20</td>
<td>0.11</td>
<td>35.4</td>
<td>0.18</td>
<td>0.038</td>
<td>62.0</td>
</tr>
<tr>
<td>Superior Nut B1</td>
<td>2.21</td>
<td>0.12</td>
<td>35.7</td>
<td>0.20</td>
<td>0.039</td>
<td>61.8</td>
</tr>
<tr>
<td>Alloy C 36000 criteria</td>
<td>2.50-3.70</td>
<td>--</td>
<td>33.0-37.5</td>
<td>≤0.35</td>
<td>--</td>
<td>60.0-63.0</td>
</tr>
<tr>
<td>CGA 701 Valve</td>
<td>1.14</td>
<td>0.14</td>
<td>38.8</td>
<td>0.25</td>
<td>0.045</td>
<td>matrix</td>
</tr>
<tr>
<td>Alloy C 37700 criteria</td>
<td>1.50-2.50</td>
<td>--</td>
<td>39.0</td>
<td>≤0.30</td>
<td>--</td>
<td>58.0-62.0</td>
</tr>
</tbody>
</table>

---Denotes other at ≤ 0.50

IV. Examination of the CGA 347 samples

A. General Microscope Examination of the Samples
The CGA 347 brass nuts, nipples and a valve from 3 assemblies were examined to verify the information supplied with the samples with respect to cracks and crack location. Multiple photographs were taken of the cracks and the one complete fracture. Some of those photographs are included in this report in the section specific to the valve or fitting.

The nuts and nipples were not reported to contain cracks. That was confirmed by microscopic examination. Additionally, the CGA 347 nuts were not reported to be dimensionally incorrect and were not measured to verify the CGA size specifications.

The Sherwood CGA 347 valve (see Photo 34) did contain two cracks on the safety boss. These cracks formed on the parting surface of the forging at the 12 and 6 o’clock positions. The cracks at the 12 and 6 o’clock position are seen in Photo 35 and Photo 36 below.

![Photo 34: CGA 347 valve. Two cracks had formed on the safety boss.](image)

**Photo 34:** CGA 347 valve. Two cracks had formed on the safety boss.

**Photo 35:** Crack that formed at the 12 o’clock position on the parting surface of the safety boss.

**Photo 36:** Crack that formed at the 6 o’clock position on the parting surface of the safety boss.
V. Discussion

Analysis of the fittings and valves evoked numerous peripheral issues that need discussion. First, the corrosive compound has not yet been confirmed. Next, the apparent high rate of oxygen valve and nut components that have developed cracks compared to the air valve and nut components. And the apparent lack—to date—of failures in low pressure valves and nuts (less than 3000 psi). Finally, the burst tests performed by the valve manufacturer, mitigation of SCC and two proposed solutions to SCC found on the valves.

**Identification of the corrosive compound** responsible for the SCC of the brass fittings and valves requires additional testing beyond the scope of this investigation. Identification of the corrosion products may help to understand the incident and prevent future failures. The corrosive compounds may only assist in the reaction and not be a reaction product. It is possible that there is more than one corrosive species responsible for the corrosion. The leak detection fluid used by one manufacturer (Sherlock Leak Detector Type CG) was reported to contain a sulfur compound that may have a corrosive effect on brass. However, the manufacturer denies that the fluid contains sulfur. The MSDS sheet did not specifically identify the minor components however the manufacturer’s representative said the fluid was mostly water with minor amounts of a surfactant and ethylene glycol (0.9%). Ethylene glycol is used as a desiccant because of its affinity for water. It is therefore possible that use of the leak detection fluid might enhance the collection of moisture on the surface of brass and retard the moisture from leaving or evaporating from the surface.

Mines are known to be sulfur-rich. The corrosion product found on the sharp interior corner of the nut—a surface that would not normally be exposed to leak detection fluid—suggests the humid mine atmosphere carries a corrosive species, but it may not be the only source of a corrosive species. While a sulfur compound is suspect, it was not positively identified in the EDS microanalysis.

**Nut Design Consideration:** Based on the information available to SLTC it appears that the oxygen nuts develop cracks at a faster rate than air nuts, suggesting that the service life is greater for a CGA 347 air nut than a CGA 701 oxygen nut. This prompted a comparison of the specification sheets for both types of nuts. It is possible that the slight difference in the geometry could account for this. The 347 nuts have a counter sink that extends down the interior surface 0.125 inches (no threads at this position). Whereas the 701 nuts do not have a counter sink, the threads extend to the outside surface. It is possible that the difference in design reduces the stress enough at the outer surface on the 347 nuts to delay SCC. Additionally, the length of the two nuts are different, the air nut is longer by ¼ inch, although the thread length is the same for both nuts. The rate of stress-corrosion crack-propagation is influenced by the stress-intensity factor or the applied load. Mechanical design differences may account for a longer service life for the air nuts but may not prevent SCC from ultimately causing a failure.

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12 Personal conversation with Gale at Winton Products Co. Inc. on 5-17-2011. Phone number 704-399-5151
13 EDS; Energy Dispersive X-ray spectroscopy is a qualitative analytic technique used for the elemental analysis of a sample.
Failures in low pressure tanks (3000psi): It has been reported that some refuge manufacturers have chosen to use low pressure tanks. SLTC is unaware of cracks forming in a similar fashion on lower pressure tank nuts and valves. In similar mine environments it is possible that cracks may eventually develop in low pressure oxygen and air fittings made of the same brass alloy, one study\textsuperscript{14} suggests there is no stress threshold below which SCC will not occur in 70-30 brass.

Sherwood Tests: Sherwood attributed the safety boss crack formation in the valves to SCC. The valve manufacturer conducted burst tests to look for ejection of the safety plug. They used six valves with cracks having “small to very severe safety boss cracks” they increased the pressure on the cracked valves to see if they would leak, crack further, or eject the safety plug prior to the pressure disc bursting. From the tests Sherwood concluded that “a catastrophic ejection of the safety plug is not likely to occur when some cracking is evident on the safety boss of the forging resulting from exposure to the aggressive mining environment.”

The test does not address the event under investigation. A short-term over-pressurization event is not equivalent to a long term constant stress-corrosion cracking event. Over-pressurization of the valves can be eliminated with a functional pressure gauge in place to ensure the tanks are not over filled. Cracks induced by over-pressurization are different than those created by stress-corrosion cracking. Stress-corrosion cracks branch in unpredictable ways as seen in Photos 11 and 12.

According to MSHA when the nut failed in the Sentinel mine, it was held in place by manifold piping. But, the sudden release of 5676 cubic feet\textsuperscript{15} of oxygen caused the access door to be forced open and the ejection of supplies and oxygen from the refuge shelter. The oxygen did not just slowly leak out but was released in a violent episode. Among the ejected supplies were 3 five-gallon water jugs weighing 42 lbs. each. Fortunately no one was present or injured.

The release of pure oxygen sudden or not creates an oxygen enriched atmosphere (OEA). OEAs are recognized as a safety hazard. In oxygen enriched atmospheres, the reactivity of oxygen significantly increases the risk of ignition and fire. Materials that may not burn in normal air may burn vigorously in an oxygen-rich environment. Sparks normally regarded as harmless may cause fires. Materials that burn in normal air may burn with a much hotter flame and propagate at a much greater speed in an oxygen-enriched atmosphere. In an oxygen-enriched atmosphere the combustible material that most directly affects the safety of the personnel is clothing.

SCC mitigation in copper-based alloys generally involves modifying one or more of the three primary factors associated with SCC: susceptible material, specific corrosive environment, and tensile stress. It is possible that better sealing against the mine atmosphere and moisture could reduce or even negate the effects of SCC and/or dezincification. Using a leak detection fluid that does not attract moisture could also help. MSHA reported that there are different types of refuge shelters. For example, there are both soft sided inflatable tents and hard sided units. MSHA has noted that some refuge shelters appear to seal better than others. The percentage of nuts and


\textsuperscript{15} Based on 4500psi, K size cylinder and 12 tanks in the manifold.
valves that have developed cracks is noticeably different between the refuge types. This suggests that corrosive exposure varies according to refuge type and mine atmosphere. To date, there are no tests that have positively identified the corrosive species in the humid mine environment. If a cause cannot be identified it is difficult to craft a solution. Mechanical redesign to lower stress may not remedy the problem. Corrosion tests performed by Pugh, et al. suggest that there is no threshold stress below which SCC will not occur for 70-30 brass\(^2\). Therefore, reducing the stress on a component by redesign may prolong the service life but may not prevent SCC from ultimately causing a failure.

**Proposed Solutions:** Sherwood suggests two possible remedies;\(^1^6\) make the valves of Monel or chrome plate the brass valves. Monel is a nickel-copper alloy that has been used successfully in highly corrosive conditions. Chrome plated brass valves may also prove successful.

### VI. Conclusion

Specifically, SLTC was asked to respond to the following questions:

1. To what extent did the surface corrosion that can be seen on the brass fittings contribute to the failure? Is what we see just surface corrosion that is not impacting the material or does the presence of this corrosion indicate that the fittings are in danger of failing?

   **Answer:** The stress-corrosion cracks in the fittings and valves indicate that they are on the path to failure. It is well known that brass is susceptible to corrosion cracking in moist atmospheres that contain corrosive compounds. In this scenario, corrosion product is a precursor of a corrosion crack. However, not every corrosion pit or corrosion product seen as surface corrosion will develop into a crack. Cracks preferentially develop at stress concentrations--this is evidenced in the samples SLTC received.

2. What is the approximate life expectancy of the brass nuts? In other words, how long do you think dimensionally correct, unfinished brass nuts would last in the mine environment based on the condition of the fittings that we sent to you?

   **Answer:** The best estimate for the service life would be obtained from in-service observations. The valves and nuts sent to SLTC for analysis are known in the industry as CGA 701 and CGA 347\(^1^7\) nuts and valves. These nuts and valves have developed stress-corrosion cracks within three years of being put into service. Service records are the most reliable guidelines to predict life expectancy as long as they contain all pertinent information and the data is accurately interpreted.

3. Can you recommend any method of inspecting these nuts for cracks other than removing them from the refuge chambers and performing a thorough visual examination?

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\(^{1^6}\) Personel conversation with Mia Daniels an engineer at Sherwood, the valve manufacturer.

\(^{1^7}\) CGA is the Compressed Gas Association. They publish standards for compressed gas fittings and valves. The identifier 701 indicates that these fittings and valves are to carry oxygen exclusively, and 347 indicates compressed air usage only.
Answer: We would refer this to a specialist in non-destructive testing (NDT). However, it could be expected that inspections of the valves and fittings maybe difficult in a coal mine environment due to diminished lighting or a non-existent power source.

The analysis performed at the SLTC revealed that the cracks are a result of stress-corrosion cracking (SCC) and the evidence suggests that dezincification is a contributing factor. The stress-corrosion cracks that have formed in the fittings and valves indicate that they are on the path to failure. The demonstrated short and unpredictable service life of the CGA brass valves and fittings is troublesome. The current situation left unchecked represents a safety hazard.

Fern Stones

Metallurgist