Chemically Speaking LLC

Can Cooling a Cylinder with Dry Ice Embrittle It?

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Cylinders in the US are required to be capable of being cooled down to -30ºF (-34ºC) in the US. Gas suppliers routinely cool cylinders using a dry ice cold bath, can these carbon steel cylinders become embrittled at -109ºF (-79ºC) creating a potential risk of a cylinder failing when physically impacted. They are regularly lifted 5-6 ft off the ground to take them in and out of dewars with an ice bath temperature of -109ºF (-79ºC). If they were to fall the impact forces would be significant, would this crack the cylinder open? Since the DOT requires cylinders to be designed to withstand a cold temperature of -30ºF (-34ºC) without impact embrittlement, there was concern that we exceeded this temperature.

Background:

Ordinary carbon steels can exhibit reduced fracture resistance at low temperatures and can be at risk of brittle fracture when subjected to stress. Plain carbon steels at temperatures below about -50°F (-46ºC) has been known to fracture in a brittle manner. This can be due to thermal stresses or when subjected to impact loads. This raises a concern with carbon steel cylinders being cooled to temperatures below -50ºF (-46ºC). Many low pressure (<500 psig) carbon steel cylinders are made of low grade carbon steel that could embrittle at these temperatures, some are welded. These are thin wall welded cylinders used for consumer gases such a propane, butane, ammonia.

At the Solkatronic Morrisville facility, a variety of carbon steel cylinders were used as process cylinders that were routinely immersed in dry ice/d-limonene baths to cool them to temperatures of -109ºF (-79ºC). These chilled cylinders were used to collect light impurities, intermediate process or were the final product cylinders. These systems were operated from 1987-2009 without incident. The only incident that occurred was with a final hydrogen selenide product cylinder in Jan 2001 when an operator filled the cylinder twice, liquid filling it. This ruptured a few minutes after it was removed from the cooling bath. This is a practice that is done by many gas suppliers without incident.

After Solkatronic was acquired in 1998, there was a similar concern by the parent company that these cylinders could crack open when physically impacted such as it being dropped when being lifted by hoist out of the cooling bath.

Testing:

To determine if this was a safe practice, a third party testing laboratory was contracted to perform testing. Initially, Charpy V-notch impact testing was performed on sections from six cylinders typically chilled to these temperatures. The Charpy V-notch impact testing is a test to determine metal toughness or nil ductility temperature. CGA in Pamphlet G6.7 defines the Nil Ductility Transition Temperature (NDTT) as the temperature below in which metals are brittle enough to fracture. For the test, nil ductility was defined as any lateral expansion measurement below 15 mils as per the ASME pressure vessel code. Testing was performed over a range of temperatures from 150°F (-101^{o}C) down to cryogenic temperatures.

All cylinders that were tested had been previously used in the processes

1. lecture bottle, DOT3E-1800 (carbon steel) indicated nil ductility close to -100°F (-73^{o}C).
2. 16 liter, DOT 3AA-2015 (4130 steel) retained sufficient toughness at temperatures down to at least -150°F (-101^{o}C).
3. 49 liter, DOT 3AA-2400 (4130 steel) retained sufficient toughness at temperatures down to at least -150°F (-101^{o}C).
4. 110 liter, DOT 4AA-480 (welded carbon steel) Ammonia process. Since there are 2 halves welded together, a sample from each half was tested. The top half of indicated nil ductility between -100°F (-73^{o}C) and -150°F (-101^{o}C) the bottom half of indicated nil ductility between 0°F (-18^{o}C) and -100°F(-73^{o}C) .
5. 110 liter, DOT 3A-480X (seamless carbon steel) Ammonia. indicated nil ductility between -150°F (-101^{o}C) and -320°F.
6. 50 liter, DOT 3A-480 (seamless carbon steel) Chlorine. Indicated nil ductility between 0°F (-18^{o}C) and -100°F (-73^{o}C).

Based on the test results, the 4130 high alloy carbon steel cylinders (DOT3AA) were approved for dry ice/ d-limonene service since they had a nil ductility point well below -100°F. A surprising result was the 3A-480X which is a lower alloy carbon steel had a nil ductility down to a temperature of -320^{o}F (-196^{o}C), LIN temperature.

As a note, the European Industrial Gas Association (EIGA) in the late 1980's did extensive testing of 3A cylinders manufactured in Europe between 1904 and 1930 for CO_2 service. Many had been in service 60 years. One test was impact from a height of 13.2 ft (4 m). Several cylinders were filled to maximum fill with CO_2 and chilled to -13^{o}F (-25^{o}C). (CGA TR-2 High Pressure Cylinders In Service Performance). As a liquefied gas CO_2 if withdrawn rapidly from the cylinder as a gas, can auto refrigerate to its boiling point of -109^{o}F (-78^{o}C) subjecting the cylinder to severe thermal stress.

Additional testing

The results also indicated that further testing must be done with the low pressure cylinders to insure that they were safe to use. Solkatronic Morrisville, routinely used low pressure welded carbon steel cylinders for ammonia and chlorine purification. Since the nil ductility for some of these were above -100°F (-73°C) further testing was required. Conventional engineering practice is to select materials with transition temperatures below the minimum operating temperature -109°F (-78°C). It became a concern as to whether the steel that the cylinders are formed from may not be suitable for this low temperature and could be breached if severely impacted at this low temperature.

For instance, if the hoist failed during lifting or lowering and the chilled cylinder impacted the floor.

The test program was designed to simulate actual conditions when embrittlement failure could occur. Other situations of concern were:

1. A chilled cylinder accidentally bumped and falls over on its side impacting an object such as a nearby hand truck
2. A chilled cylinder accidentally topples off a loading dock

The six test cylinders were filled with d-limonene to a net weight of 150 lbs to simulate a full ammonia cylinder. These cylinders were cooled to the nominal temperature of -109°F (-78°C) in a bath of dry ice and d-limonene. Cylinders were allowed to remain in the dewar until the vigorous boiling of the bath calmed down to a neutral state, indicating the cylinder has reached temperature equilibrium with the coolant, this required about 30 minutes. Manufacturing dates of the cylinders ranged from Jan 1945 to September 1998.

A plug was installed in each cylinder where the cylinder valve would normally be inserted. The 6 cylinders included 3 DOT-4AA welded and 3 DOT-3A seamless. Each test included one of each type.

The cooled cylinders were pulled from the bath with a hoist attached to a forklift. Tip over or drop testing proceeded immediately thereafter. All tests dropped directly onto a concrete floor or onto a item placed on the concrete floor. Testing was recorded via photographs and video.

Test Results

A description of each test and resulting damage are as follows:

1. Test #1 – A welded cylinder was dropped from a height of 6 inches (15 cm) while canted 30 degrees off vertical. No deformation was noted on the foot ring at the point of impact with the concrete floor.
2. Test #2 – A non-welded cylinder was dropped from a height of 6 inches (15 cm) while canted 30 degrees off vertical. No deformation was found at the point of impact with the floor.
3. Test #3 – A non-welded cylinder was placed in an aluminum cylinder cage and dropped in a vertical position from a height of 6 feet (1.8 m). Although the cage was damaged, no damage was found on the cylinder.
4. Test#4 – A welded cylinder was placed in an aluminum cylinder cage and dropped in a vertical position from a height of 6 feet (1.8 m). Although the cage was damaged, no damage was found on the cylinder.
5. Test #5 – A non-welded cylinder was allowed to fall over while resting in a cylinder cage that was at floor level onto a piece of 2-inch (5 cm) angle iron (open side down). A slight indent was found on the cylinder side wall at the point to impact with the angle iron.
6. Test #6 – A welded cylinder was allowed to fall over while resting on a 2" x 6" (5 cm x 15 cm) piece of wood that was at floor level onto a piece of 2-inch (5 cm) angle iron (open side down). A slight indent was found on the cylinder side wall (adjacent to the weld) at the point of impact with the angle iron. There was also evidence of additional damage (a dent in the cylinder shoulder and a slight indent in the side wall) that occurred when the cylinder bounced after initial impact.
7. Test #7 – Test #6 was repeated, but with the cylinder falling on the side 180° away from the side impacted in Test #6. A dent was found on the cylinder sidewall midway between the shoulder and the weld. As in Test #6, there was evidence of additional damage (two slight dents adjacent to the primary dent) that occurred when the cylinder bounced after initial impact.
8. Test #8 – A welded cylinder was dropped in a horizontal position from a height of 6 feet onto a piece of 2-inch (5 cm) angle iron (open side down). A deep dent was found on the cylinder sidewall about two inches above the weld.
9. Test #9 – Test #8 was repeated, but the cylinder was dropped on the side 180° away from the side impacted in Test #8. A deep dent (Figure 9) was found on the cylinder sidewall about 3 inches (7.5 cm) above the weld. There was also some minor secondary denting that occurred when the cylinder bounced after initial impact.

10. Test #10 – A non-welded cylinder was dropped in a horizontal position from a height of 6 feet onto a piece of 2-inch (5 cm) angle iron (open side down). A deep dent was found on the cylinder sidewall approximately midway between the shoulder and the foot ring. There was also some minor secondary denting that occurred when the cylinder bounced after initial impact.

Post Testing Examination

No evidence of cylinder sidewall cracking was found when external surface of each cylinder was examined visually with up to 2X magnification. Therefore, the cylinders with the most severe sidewall denting were sectioned for internal examination and subsequent liquid penetrant and metallographic examination. The most severe sidewall dents occurred in horizontal drop tests from 6 ft (1.8 m). As found on the external surface, visual examination of interior surface of all the sections removed revealed no evidence of cracking. Only slight bulges were evident on the ID at the areas of OD dents. The most severe dents (those formed during initial impact) from Tests #8, #9, and #10 were examined on the interior side using liquid penetrant. No cracks were detected. Metallographic examination was performed on cross sections removed from the apex of the most severe dents in the cylinders used in Tests #8, #9, and #10. Additionally, cross sections were removed from the welds near the severe dents on the welded cylinder used in Tests #8 and #9. All samples revealed a typical ferritic microstructure as expected for carbon steel cylinders. No evidence of cracking was detected.

Charpy V-notch Impact Testing

After the drop testing, samples were removed from the cylinders used in Tests #8, #9, and #10 to determine the nil ductility temperature of the steel used in each cylinder. The cylinders were: (Tests #8 and #9) and Charpy V-notch impact test results on both halves of welded cylinder indicated nil ductility between -50°F (-45°C) and -100°F (-73°C). Conversely, Charpy V-notch impact test results on non-welded cylinder indicated the nil ductility temperature was below -150°F (-101°C). Both confirmed the earlier testing results.

In the case of the DOT 3A cylinder, the impact test results indicated the cylinder was in a ductile condition during the drop testing and would not have been expected to crack or catastrophically fracture upon impact. On the other hand, the test results on the DOT 4AA cylinders indicated the cylinder would be below the nil ductility temperature during drop testing and theoretically had the potential to crack or fracture catastrophically upon impact. The test results showed no visual indication of cracking.

Conclusion:

In conclusion, all cylinders tested, even the plain welded carbon steel cylinders proved to be ductile even upon impact at dry ice/d-limonene temperatures of -109°F (-78°C). Other companies such as Scientific Gas Products have cooled cylinders with dry ice for many years without incident.

The 3A cylinders were even capable of LIN temperatures. Of all the cylinders the seamless DOT 3AA 4130 alloy was the best at these temperatures. It would be prudent however for the user to test a few cylinders used in this type of service from each cylinder manufacturer to confirm that the alloy and fabrication method used are comparable.

Eugene Ngai