

Hydrogen Plant Explosion and Fire

Introduction

A certain hydrogen plant is designed to continuously produce hydrogen at a purity of 99.75% and at a rate of 510 m³ per day. Hydrogen is produced in two banks of cells filled with a strong solution of caustic soda. Current is passed through the cells to produce hydrogen and oxygen. The oxygen is vented directly to atmosphere while the hydrogen is piped to the gasholder.

The gasholder is a low pressure storage vessel capable of storing 28 m³ of gas. It is constructed in two parts. The bottom section is a large round tank. The upper section is an inverted tank or bell that is free to move within the main tank as pressure increases or decreases. The main tank is filled with water to form a water seal. Hydrogen from the cells enters the gasholder above the water line causing the bell to rise.

The purity of the hydrogen is monitored between the cells and the gasholder. If purity falls below 99.5% the hydrogen is vented to atmosphere.

The plant is installed with two compressors. Hydrogen is drawn from the gasholder by the duty compressor via the gas dryer and the filter. It is compressed to 12.4 MPa and delivered via high pressure (HP) dryers to the storage banks.

The plant is installed with four storage banks capable of storing 460 liters per bank. Each bank consists of 16 cylinders. Each cylinder is fitted with an overpressure protection device called a "bursting disc".

Details of Incident

One afternoon an assistant operator attended the hydrogen generation plant as part of a routine plant inspection. The plant was functioning correctly and no obvious problems were noted.

Approximately one hour later a large explosion was heard by a contractor in the contractor amenities area and the remaining staff in the administration building. Calls were received soon after by the duty shift manager advising him that there was a fire at the hydrogen generation plant.

The duty shift manager activated the site emergency plan. Calls were received by the local fire department and site fire fighting teams were on the scene within a few minutes.

The fire was attended by a number of local fire departments and was declared under control the following morning.

Gassing of the in service units was suspended for the entire period of the emergency, as the gas up stations were in the fire area.

Plant Configuration at Time of Explosion

At the time of the explosion "A" and "B" banks of cells were in service filling the gasholder. The low pressure (LP) dryer and LP filter were in service. "A" H₂

compressor was in service delivering high pressure hydrogen via the "B" HP dryer to "B" and "C" storage banks.

Results of Inspections

Visual inspections of the plant found the high pressure pipe work had ruptured or parted at the following locations:

- Between two valves adjacent to a compressor
- At the pressure regulating valve near the compressor room
- Above the B HP dryer
- At the inlet to the B bank manifold
- At various bottle fittings in B bank

In addition the following damage was noted:

- Pipe swelling at the compressor side of the HP regulating valve
- Pipe swelling at the HP NRV (dryer side)
- Damage to a compressor blow-down pneumatic valve
- Damage to a HP dryer blow-down pneumatic valve

Twelve of the sixteen B bank cylinders and six cylinders on C bank had been affected by the heat of the fire. Many of the copper vent pipes from the cylinders to atmosphere were discolored or melted indicating that many of the cylinder bursting discs had ruptured. The vacuum and purge pipe work around B and C banks had been destroyed by the fire.

The cladding at the eastern end of the building had been blown out above two storage banks. Debris from the site was distributed for 20 meters. Fire from a blown pipe at the rear of B bank impinged on the LP gasholder. Damage to the gasholder was superficial.

Initial Investigation

The damage to the HP pipe work suggested that the explosions occurred initially in the pipes between the compressor and the HP NRV. The swelling of the pipes indicated that a pressure wave had traveled along from the pipe from the direction of the compressors towards the storage bottles.

Such an explosion is possible if an explosive mixture of air and hydrogen existed in the pipes. Hydrogen will form an explosive mix with concentrations of hydrogen in air as low as 4% and as high as 76%. Where pure oxygen is the contaminant the explosive limit is less than 5% oxygen in hydrogen. Hydrogen in an explosive mix is well known to ignite inside pipes

The force of the explosions in the pipes had then caused consequential failures of fittings and joints at B and C storage banks. This released hydrogen into the storage shelter which subsequently ignited.

Plant Purging

Tests of gas in the LP gasholder indicated the presence of oxygen at a concentration of 4.7% and a small concentration of nitrogen. It was assumed that there was a possibility that the gas in the remaining A and D high pressure storage banks may have been contaminated. No attempt was made to sample the gas from the storage banks.

The LP gasholder was purged through the normal vent valves and filled with CO₂.

A detailed procedure involving nitrogen purging and remote operation of vent valves was developed for purging of the HP storage banks. The banks were successfully purged allowing repairs to the plant to begin.

Detailed Investigation

All possible points of air ingress were identified and checked as the possible cause of the explosive mixture. The main sources are dealt with in detail below:

1. **LP Filter** - The LP filter is fitted with a U bend water seal that is open to atmosphere. If the water seal is lost the air could be drawn into the line through the U tube. The seal is fitted with a clear plastic sight tube. The seal is checked regularly and topped up with colored water if the level is low. The seal was found to be dry after the incident. It is possible that the water had been blown from the tube during the explosion. The seal was dismantled and the elements were found dirty but not blocked. During the inspection it was confirmed that under blocked filter condition the compressor could not draw the seal water into the line.
2. **LP Dryer** - The LP dryer is also fitted with a U bend water seal that is open to atmosphere. This water seal is a steel tube and can only be checked by dipping the open end. Because it is fed from the dryer it is generally spilling water when in operation. The bend was found full of water after the incident.
3. **LP Pipe low point drain at LP gasholder** - There are two pot style water sealed drains at the low point in the inlet and outlet pipes from the LP gasholder. These drains cannot be checked for water level visually or by dipping. The drains were opened and found full of water. The drain lines from the hydrogen pipes were found to be partially blocked.
4. **LP Gasholder** –Mal-operation or sticking of the bell may allow air to enter the gasholder. Samples of gas were taken from the top of the gasholder and tested for oxygen and nitrogen. The results were 2.4% oxygen 4.6% nitrogen. As the proportions are not consistent with air a second test sample was taken from the inlet of the gasholder. The results of the second test showed 4.7% oxygen. Nitrogen was not identified in the sample. The operation of the gasholder was checked with nitrogen. The gasholder bell was found to operate smoothly with no stiction points. It also maintained pressure when filled with nitrogen. An internal inspection of the gasholder found that the inlet and outlet pipes extended only 12 to 15 mm above the normal water level. Drawings indicated that this should have been at least 50 mm above the water.

5. Oxygen Ingress from Cells - During operation the cells are designed to separate the oxygen from the hydrogen. Under abnormal conditions oxygen can enter the hydrogen system and cause contamination. The LP purity analyzer monitors the purity of the hydrogen and if it falls below 99.5% the analyzer opens a vent valve to prevent the contaminated hydrogen from reaching the gasholder. The LP purity monitor was checked. The 240 volt to 220 volt isolation transformer that powers the analyzer was found open circuit on the secondary winding. The operation of the LP Purity analyzer was confirmed as "non fail safe". On loss of power or sample the analyzer output remains at the last recorded value. The indicated purity as found after the explosion was 99.8% with no power to the analyzer. The trip signal to operate the vent valve is driven by the indicator and would not have activated under these conditions. Supply supervision alarming was not connected to this part of the circuit. The hydrogen inlet pipe work and filter were found choked with water preventing hydrogen from passing to the monitor. These filters are regularly checked by office staff and no abnormalities were noted earlier on the day of the explosion. It is considered that the build up of water occurred after the event due to residual water in the line. Once sufficient repairs had been carried out the cells were returned to service. On initial operation the cells attained a purity of 99.5% which then fell away to less than 92%. Investigations found that a number of cells had low electrolyte levels. Once they were topped up to normal working level the purity returned to 99.5%. This operation was repeated a number of times with the same result. The cause of low electrolyte level was determined to be blocked water inlet pipes at the affected cells. Blockages were occurring at the inlets due to a build up of magnetite and other contaminants. The low purity associated with low electrolyte levels may indicate that the dividing diaphragms between the oxygen and hydrogen generation cells has deteriorated allowing crossover of gases as the level drops. This will be further investigated. In addition 6 cells (3 on each bank) were found to produce gas at a purity below 99.5% with one on each bank below 97%. This again is thought to be a result of deterioration of diaphragms and will be further investigated.

Conclusions

Explosions in the hydrogen HP feed pipes caused the failure of welds and connections at the storage banks allowing hydrogen gas to be released in large quantities from B and C storage banks. The escaping hydrogen self ignited resulting in an explosion and fire.

The cause of the initial explosions was due to the spontaneous ignition inside the HP feed pipes of an explosive mix of hydrogen and oxygen.

It is concluded that the ingress of the oxygen to the system was from the hydrogen cells. The prime cause of the contamination was blockages in the water makeup lines to some cells allowing high levels of oxygen to mix with the hydrogen as electrolyte levels fell.

The low purity hydrogen was not detected by the low pressure purity analyzer

due to the failed isolation transformer.

There are a number of other potential air ingress points on the LP system that could have allowed contamination. These points are however considered unlikely to have been the cause of the contamination resulting in the explosion.

Recommendations

A number of improvement options have been identified.

1. Cells

Six cells are producing hydrogen at a purity below 99.5%. The inter chamber diaphragms are suspected as the source of cross contamination of hydrogen and oxygen. Five cells were overhauled in 1998 due to low hydrogen purity. In all cases the diaphragms were found to be in poor condition and replaced. Cells that were overhauled in 1998 were found to be producing at 99.8% during the post explosion testing.

Recommendation 1.1 - Overhaul and replace the diaphragms on all cells showing low purity results. Check on a routine basis the individual cell purity levels to monitor the deterioration of performance of individual cells.

Certain contaminants are produced as a result of the process that settle to the bottom of the cells. These contaminants particularly magnetite can block the water makeup ports and the drain valves. This was found to be the case on 6 makeup ports and on most drain valves. The blocked drain valves made it very difficult to clean the cells and to unblock the makeup ports.

Recommendation 1.2-Replace the drain valves with open port ball valves to improve the drain operation and to allow effective cleaning of the cells. Instigate a routine for the yearly draining and cleaning of all cells.

2. Purity Analysis

Recommendation 2.1- Replace the existing LP purity analyzer with a fail safe model that ensures the vent valve is opened under the conditions described above. Carry out a risk assessment of the current LP purity analyzers to determine the level of risk associated with a loss of sample flow.

The plant is not fitted with HP purity analyzers to confirm the purity after the compressor. Given the number of possible air ingress points in the pipes under vacuum and the higher probability of explosion of impure hydrogen in the HP system it is essential to be able to detect low purity after the compressors.

Recommendation 2.2 - Fit hydrogen purity analyzers that fail safe either between the stages of the compressor or immediately after the compressor. Carry out a risk assessment of the current IP and HP purity analyzers to determine the level of risk associated with a loss of sample flow failure.

3. Drain Piping

The drain piping installed at the hydrogen generation plant is of two types. The first is a simple U tube arrangement which is installed at the LP filter, LP dryer and before and after the LP vent pipes. The second type is a low volume closed pot style that can hold 2 to 3 liters of water. These are installed before and after the LP gasholder. In all cases the seal liquid level is maintained by the process. There is no external top up facility. With the exception of the LP filter U tube there is no visible means of checking the water level.

Recommendation 3.1- Fit pot type water seals with open trough water makeup as a replacement for the existing U tube and pot type seals. The original design drawings for the gasholder show the inlet and outlet pipes extend 50 mm above the water line. The actual measured extension was less than 20 mm. Small variations in the level control could allow water to enter the lines.

Recommendation 4.1 - Increase the pipe length to extend them to 50 mm above the water level.

5. Building

The building is fitted with partially closed in ends that can trap the gas under the roof. The current construction standard for this type of facility is to have the storage banks in an open area rather than inside a building of any kind. Any leakage will then quickly disperse into the atmosphere and not form an explosive mixture. This is not practicable at the current plant but improvements are possible.

Recommendation 5.1 - Remove the end sheeting from the building to increase ventilation.

6.0 Compressor Suction Pressure

The investigative committee recommends investigating the installation of suction pressure trip devices to each compressor. The suction line of the compressors will operate under vacuum for at least part of the system. An indication of a leak from atmosphere in these lines will be a decay in the vacuum at the suction of the first stage compressor.

This type of protection has proven unreliable in this application at this plant, causing spurious trips of compressors. The installation of HP purity analyzers under recommendation 2.2 and improved drain pots under recommendation 3.1 is considered to provide positive protection against the ingress of air on the suction pipe work.

6. Gassing Facilities for Generators

The gassing stations for the generators are located behind the HP storage banks and were inaccessible during the incident. The operating generator hydrogen pressures steadily decayed during this period but remained in-service. If

however access into the plant had been delayed further all operational units may have been forced offline.

Recommendation 7.1 - An investigation be carried out into the feasibility of establishing a gas up station away from the hydrogen generation plant possibly near the CO₂ plant to allow the units to be gassed from transportable pallets in an emergency.