

# Implications of Feed Contamination on the Integrity of An Operating Plant - An Accident Case Study

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## SUMMARY

What appeared to be a simple tube failure in a hydrotreater heat exchanger turned out to be a system wide problem related to increased levels of chloride in refinery feedstock. An unexpected multiple tube failure in a high pressure heat exchanger caused significant overpressure in a cooling water header and resulted in considerable damage to a downstream cooling tower. Although no injuries were sustained, this accident had the potential for widespread injuries and destruction.

This incident was the result of a chronic buildup of chlorides in the feedstock being processed. Earlier failures had been experienced but these were not fully investigated and therefore, mitigating efforts were not fully effective. Had the feedstock contamination problem been fully understood and managed from a broader perspective, major losses could have been avoided. This paper demonstrates the importance of process monitoring to a level beyond that normally specified for the safe operation of a process unit. Process safety information / knowledge is a key element of effective Process Safety Management.

## INTRODUCTION

Syncrude Canada Ltd. operates a large oilsands recovery plant in northern Alberta. Using mining and extraction equipment and conventional refining processes, the plant produces approximately 250,000 barrels per stream day of light sweet blend crude (SSB) for pipeline shipment to markets in both the U.S. and Canada. The Upgrader, which resembles a large oil refinery, has two parallel production trains each consisting of a feed fractionation unit, a fluid coker and several hydrotreaters. The hydrotreater units are used to remove sulfur and nitrogen from the product streams to make them suitable for downstream refining. Hydrotreating is a hydrogenation process which takes place over catalyst at elevated temperature and pressure.

Unlike other typical oil refineries, Syncrude's feedstock is derived from oilsand. Several stages of water contact and mechanical separation are involved in the upstream processing. The heavy oil feedstock is highly susceptible to any materials it comes into contact with during processing. Process water and diluent naphtha are recycled extensively between the Extraction and Upgrading operating areas. In addition to this, the composition of the ore body varies widely across Syncrude's leases and introduces challenges to the day to day operation.

Syncrude's gas oil hydrotreaters were initially designed to process 50,000 BPD each but that capacity was increased to approximately 70,000 BPD in the latter part of the 80's. This was done by modifying several pumps and piping circuits and replacing some fired heaters. The hydrotreaters typically operate at a temperature of 380°C and a pressure of 1500 psig. The units consist of thick wall high pressure fixed bed reactors which contain pelletized catalyst over which the hydrogenation reaction takes place. Hot hydrogen is passed over the catalyst with the oil feedstock. Although the prime reaction process and associated equipment are simple, the hardware used to recover hydrogen, separate the by-products and cool the product are quite complex. A recycle gas centrifugal compressor, several banks of heat exchangers, separator drums, piping and control systems are required to support the downstream operation. Between each stage of separation is a knockout drum with associated effluent coolers. A bank of two alloy bundle exchangers cool the recycle gas prior to hydrogen sulfide removal and re-circulation. The effluent coolers utilize circulating cooling water as a coolant on the shellside with the high pressure process fluid on the tubeside. The tube bundles were constructed of Sandvik 3RE60 Duplex stainless steel. Nominal tube wall thickness was 0.0224" in consideration of the operating exposure.

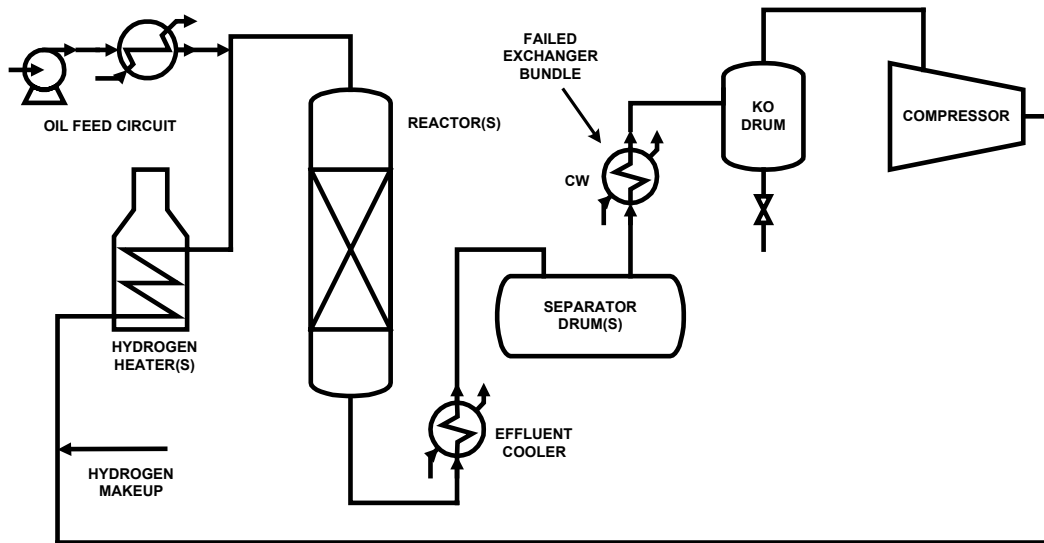


Figure 1. Simplified Flow Schematic

The initial plant design recognized the potential for tube failure within the exchanger bundles and provided a 3" rupture disc on the shell of the upper cooler. This was intended for overpressure protection of the exchanger shell and cooling water return header. It also ensured the quickest and simplest path for gas to escape without causing further damage. Given the complexity of the downstream equipment and the range of operating conditions encountered, the potential for incident is higher than for most units. Monitoring of changing process conditions is essential to achieving a two year run cycle.

## **THE INCIDENT**

In the early 90's, a unique type of failure occurred in one of two recycle gas coolers (heat exchangers) on a gasoil hydrotreater. These high pressure alloy exchangers operate with 1500 psig./330°C recycle gas on the tubeside and 75 psig./40°C cooling water on the shellside. While the design of most heat exchangers allows for a single tube failure, the incident experienced at Syncrude was well outside the norm. A multiple tube failure involving nine 1" adjacent tubes occurred within one bundle of a bank of two coolers and released 1500 psig. hydrogen and light hydrocarbon to the cooling water circuit. Both the heat exchanger and the 60" diameter cooling water return line sustained a mechanical shock. A large slug of hydrogen and hydrocarbon was released at the cooling tower. Blue flames were observed from the top of several cells of an eleven cell cooling tower for a brief time accompanied by an explosion. The incident occurred at 3 A.M. making these observations possible. Extensive mechanical damage was sustained by two cells in the tower and four vertical pipe distributors were knocked to the ground. The cooling tower was disabled for a period of three days till temporary repairs could be made. There were no injuries sustained and the hydrotreater was removed from service for approximately ten days pending the replacement of the heat exchanger bundle.

The cited incident is noteworthy for several reasons. The multiple tube failure represents an extreme scenario not considered during the design of a unit. Understanding that failure mechanism is key to preventing a recurrence. The sudden release of high pressure hydrogen and light hydrocarbons into a low pressure circuit produced a mechanical shock and had the potential to rupture or weaken other parts of the system. The damage to the cooling tower threatened the operation of the entire plant. Finally, any high pressure external release of energy (hydrogen to atmosphere) presents a significant hazard to workers who might have been in close proximity. Had this incident occurred when operations and maintenance staff were on the structure, serious injuries or fatalities would have been a likely consequence.

Ironically, a similar failure had occurred four months earlier on an adjacent and similar hydrotreater unit. The investigation of that incident had not reached closure since there were some outstanding technical issues. Notably, experts could not agree on the magnitude of the failure or its precise cause. Failure to act on this earlier incident set the stage for a repeat incident to follow. Normally, when a high level system failure occurs, it is a sign that something is fundamentally wrong. Unless corrective measures are applied in a timely manner, another similar incident can be expected.

## **INVESTIGATION FINDINGS**

A formal investigation was conducted with the input and assistance of a multi-disciplined team of engineers, process operators, metallurgists and equipment specialists. Interviews with process operators, supervisors and other eyewitnesses were conducted within 24 hours of the incident. The event was believed to have spanned a period of approximately 30 minutes. Within the process unit (the hydrotreater), the operation was normal until seven minutes prior to the principal

explosion. At that time, the control panel operator observed a step change in the hydrogen makeup requirements which are needed to keep the unit at full pressure. This was verified using on-line computer data. Further analysis of process conditions revealed a continual drop of system pressure until the major event. This suggested that the incident was made up of at least two separate but related failures. By means of hydrotesting and equipment inspection the initiating failure was finally located. It occurred within the first bundle of a 2-series bank of exchangers in the recycle gas cooling circuit. The operating pressure within the entire unit decayed rapidly and light gas was expelled through the rupture.

Conventional methods of analysis employed in incident investigation typically examine process, mechanical and human (testimonial) evidence and compare the results. Ideally, this helps to map out a precise sequence of events which led to the failure. In the case of a “high energy” process release, this is not always possible. The energy release is so intense that extensive damage is widespread and the process material involved are either removed or contaminated with firewater. In the case of this incident there was evidence of an internal explosion accompanied by a bang and external flame approximately 1 kilometer from the initiating failure.

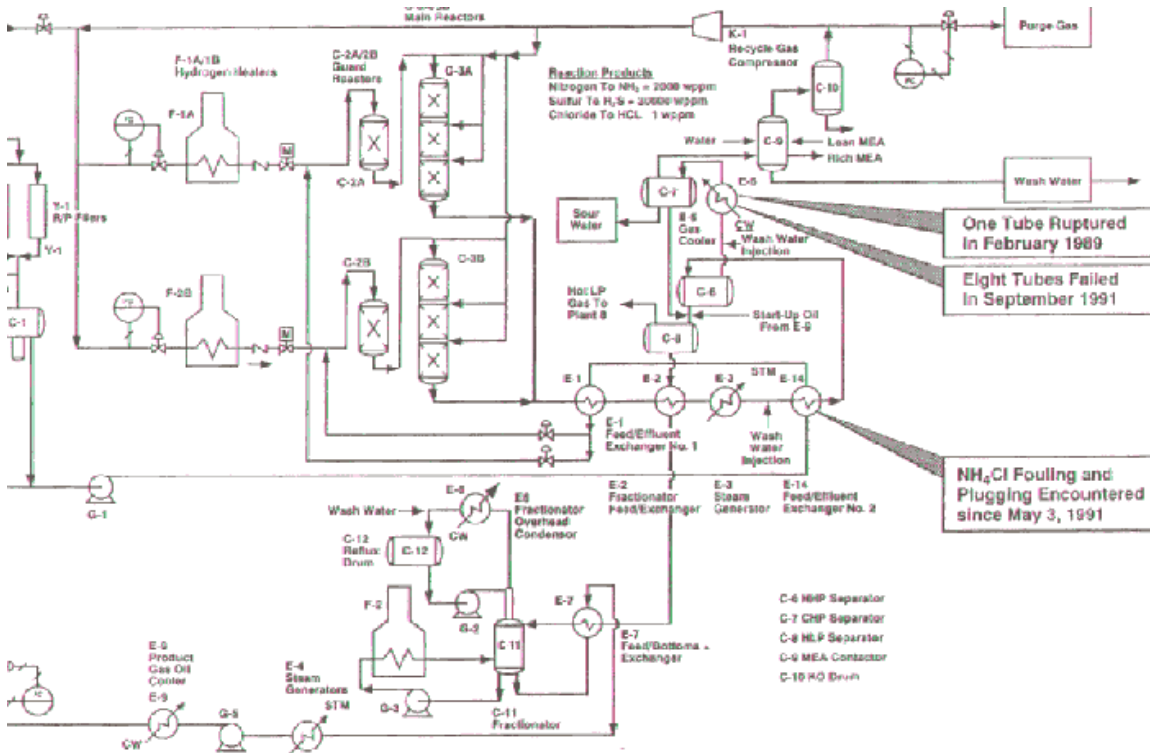


Figure 2. Process Sketch Identifying Failure

From this point, the investigation focused its efforts almost entirely on the physical damage associated with the initiating failure in the exchanger. In addition to a severely distorted alloy bundle, nine one inch tubes appeared to have failed simultaneously. The failures were all in close proximity to one another. Such a failure mode is highly inconceivable. Mechanical equipment always fails at a single point as

a result of one precise mechanism. This weakest link theory has been well established. Secondary failures are quite common and may be related to the same cause as the initiating failure or some other mechanism altogether.

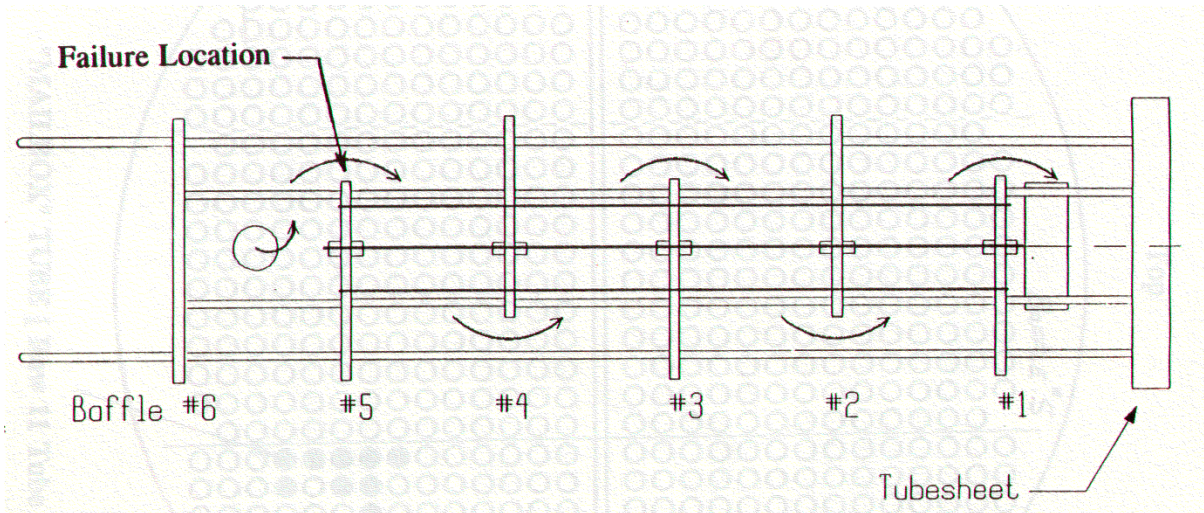


Figure 3. Bundle Flow Configuration

While the prime effort continued on the exchanger, some technical resources were assigned to examine the cooling tower and the cooling water return line. Hazard modeling (fire and explosion) was used to reconcile the physical damage to the total energy released in the incident. It was soon evident that a large volume release had occurred, well in excess of that which could pass through a break in a one inch pipe. Light vapor in the large water lines caused severe cavitation and water hammer and destroyed the return bend on the inlet headers of the cooling tower. The electric fans on the cooling tower were a probable source of ignition and likely caused the vapor to explode. The explosions damaged the wooden slats on two of the cells.

The heat exchanger bundle that failed had been in service for five years. Close examination of all tubes in the bundle revealed acute localized thinning at the top of the tubes near the tubesheet. Finally, it was determined that one tube had a unique type of fracture. It had split longitudinally for approximately 3 inches and the metal had bent outwards resembling a mailbox. It was speculated that because of the high pressure of release the cutting action of hydrogen and associated vibration simply caused the remaining tubes to fail. Ultimately, this process would continue till some form of equilibrium was reached. The multiple tube failure was in reality a two event failure separated by perhaps as much as seven minutes. Although the rupture disc did release to atmosphere, most of the discharge traveled down the cooling water circuit and was released into the cooling tower.

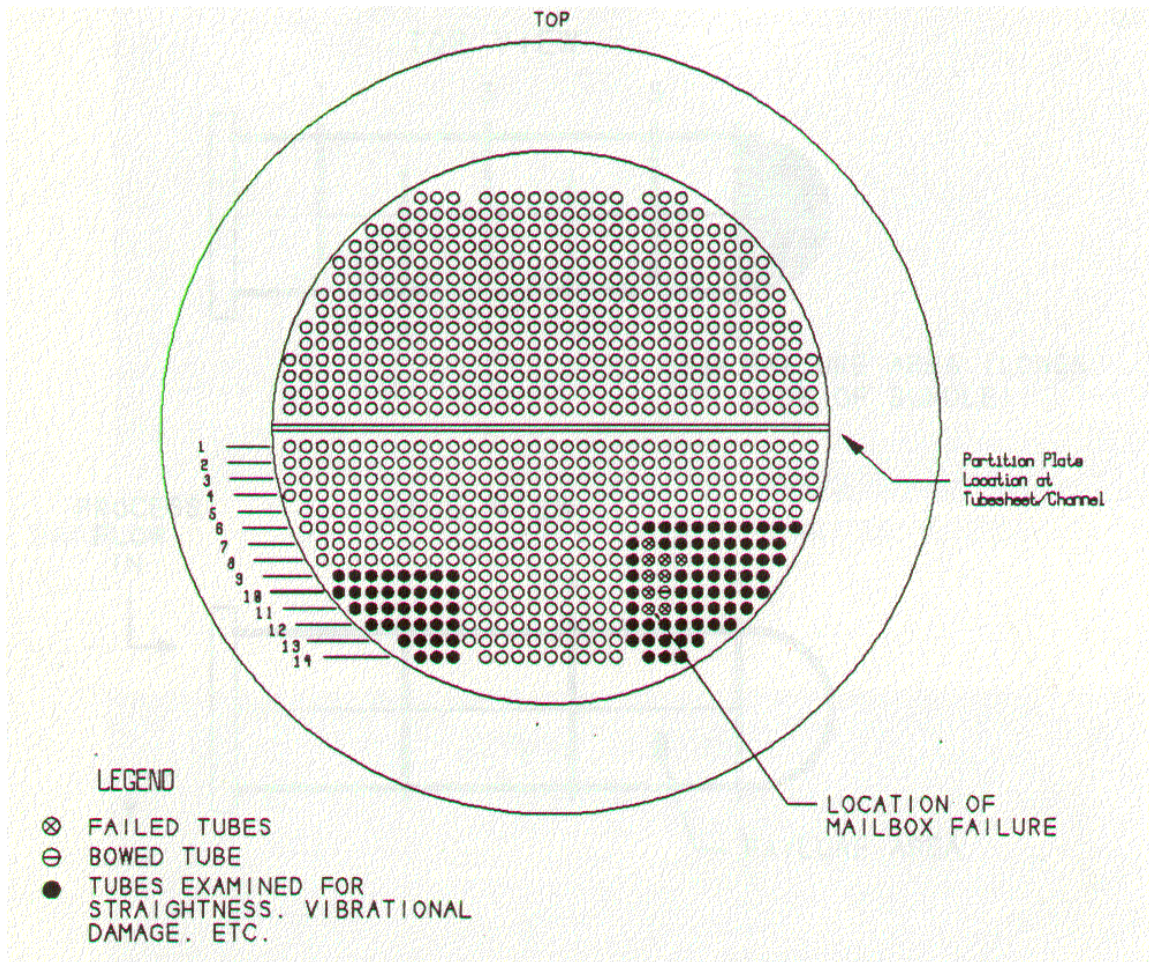


Figure 4. Pattern of Tube Damage in Failed Bundle

A detailed metallurgical examination was conducted of all the tubes in the ruptured bundle. Tube ID measurements taken randomly 6" from the tubesheet and compared with readings from a previous inspection suggested potential metal loss of 40 thousandths of an inch in one calendar year. At this rate of loss, it was not considered safe to simply repair the damaged exchanger and return it to service. The mystery partly solved, the question became "how and why did the exchanger bundle suddenly experience dramatic metal loss along the top inside diameter?". What had changed? The principal operating parameters had remained constant since 1985. A modified shutdown procedure involving less steam allowed collection of solids at the far end of the exchanger bank. These solids contained 28% chloride and 11.8% ammonia. While ammonia is a normal byproduct of hydrotreating, chloride is not. In fact, chloride is a foreign species in any oil refining operation and is responsible for the destruction of costly alloy metals via a mechanism known as chloride stress corrosion cracking.

The metallurgical analysis revealed the failure to be the result of ammonium chloride corrosion to the inner surface of the tubes. The chloride acted both as a poison in the liquid phase to debond the iron sulfide scale, and as a corrosive medium in areas beneath the hydrolysed ammonium chloride deposit. The exchanger tubes had been

embrittled as evidenced by a 33% drop in ductility from the specified minimum for the Sandvik alloy. The initiating mailbox failure originated from a small corrosion defect at the highest stress location (thinnest wall) portion of the tube. There was no evidence of stress corrosion cracking.

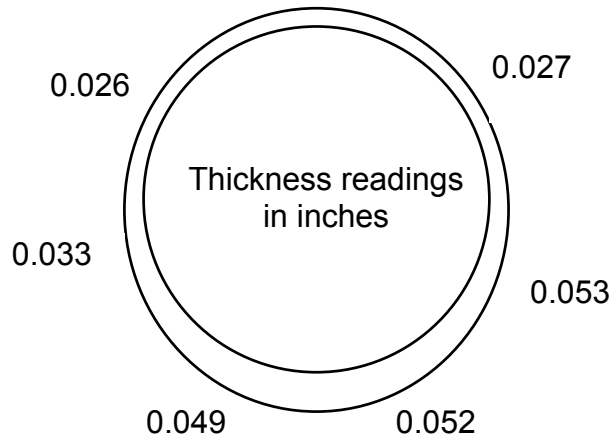


Figure 5. Cross Section of Corroded Tubes

Corrosion fatigue is a result of simultaneous action of cyclic stresses and chemical attack. Cyclic stresses also include the effects of vibrational loading. Hydrolysed ammonium chloride produces hydrochloric acid underneath the deposit which produces pitting of metal surfaces. The pits act as notches which reduce the fatigue strength of the material. When corrosion attack occurs simultaneously with fatigue loading, a pronounced reduction in fatigue properties results which is greater than that produced by prior corrosion of the surface. As a result, when corrosion and fatigue occur simultaneously, the chemical attack greatly accelerates the rate at which the crack propagates.

In the two year period leading up to the incidents on the hydrotreaters, inorganic chloride levels in bitumen feedstock from the Syncrude mine had increased significantly to approximately 40 wppm. These higher levels of contamination had been analyzed by Syncrude laboratory staff but the results did not trigger any reaction or response. Consequently, the trend was not communicated to those responsible for operating the units. Had spot data been communicated to Operations, it might not have been acted on since chloride is not recognized as a key variable in any refinery processes, especially at low concentrations.

Another change had contributed to the exchanger failure. The wash water injection rate was reduced through a procedural modification. Wash water is generally introduced to ensure that water soluble contaminants are flushed out of dead zones. Salt plugging is a common nuisance phenomenon in hydrotreaters and this can be avoided by injecting a continuous stream of water.

It was ultimately determined that two changes highlighted above acted together to produce a relatively high concentration of inorganic chloride within the exchanger tubes. The wash water along the bottom of the tubes was sufficient in quantity to dilute the chloride and remove it from the tubes. This was not the case in the upper portion of the tubes. Corrosion cracking progressed until a single point failure occurred. This failure was assisted by vibration in the vicinity of the tubesheet.

Syncrude had the knowledge and technical capabilities in-house to solve the problems which contributed to this incident. That knowledge may not have been applied in the day to day operation due to other priorities or distractions. Many organizations are able to demonstrate excellence in an emergency situation but routine operations are seldom challenged if they don't pose problems. All hazardous processes must be thoroughly analyzed from time to time and the results should be discussed at the management level. In this way, long term plant operating decisions can be made with confidence.

## **RECOMMENDATIONS**

Several significant recommendations were derived from the investigation:

1. The bundles of the recycle gas coolers were replaced with new bundles fabricated from Inconel. This alloy is highly resistant to attack from chlorides at a wide range of concentrations. Plans were made to shutdown the other hydrotreaters and install similar metallurgy in critical exchangers.
2. A chloride coping strategy was developed which included short term monitoring of chloride levels in process streams and evaluated adjustments in operating strategies in upstream units.
3. Discussions were initiated with other oil companies to determine what similar experience existed with chlorides and what had been done to remedy the problem. This incident benchmarking is an important vehicle for learning about hazards and improving safety performance.
4. Modifications to the cooling tower piping manifold were evaluated to improve the resistance to mechanical shock. A hydraulic simulation of the system under upset conditions was contracted out to a local university.
5. A long term capital program aimed at reducing or eliminating chlorides from hydrocarbon feedstock was initiated. Some of the projects evaluated for future installation included electric desalting and an extra stage of water decanting and centrifuging in upstream oil recovery processes.

## **LESSONS LEARNED**

The lessons learned from this incident were far reaching and ultimately affect many aspects of how a company designs, builds, operates and maintains its process equipment. Some of the key lessons included:



1. Changes and trends in secondary variables, trace impurities etc. challenge the basic assumptions used to design the unit. Unless these are monitored from the onset to establish a baseline, subtle changes or trends which occur over time will not be noticed. Ultimately, a major incident or series of incidents can bring an organization to its knees.
2. A comprehensive test run should be conducted for each operating process on a plantsite early in its initial run. The rationale for performance of each piece of equipment should be established. The test run results should be used as a benchmark against future changes and operational trends.
3. Operating practices including monitoring, sampling, data collection and analysis should be formally established for each process. It is important that primary and secondary operating variables be routinely tracked and that an acceptable operating window be defined.
4. A process hazards analysis should be conducted to identify potential threats or hazard scenarios that could affect the integrity of the process or the equipment. The analysis should include trace contaminants or changes in stream properties.
5. Unit test runs should be repeated at least every five years and any changes in operating variables, stream properties etc. reconciled to the initial test run.
6. Formal incident investigations should establish the precise cause of equipment failures and trigger immediate changes to either design, metallurgy or operating procedures to prevent a recurrence. The concept of extraordinary failures should be discounted early and not used as an excuse for practices that may not be best of industry.
7. Effective communication within a large organization is paramount to achieving a safe and reliable operation in the long term.

The sharing of major accident case studies across industry provides an opportunity for other organizations to learn. Ultimately, the host organization benefits as technology improves and addresses real operating problems.

