INNOVATIONS IN THE DESIGN OF EMERGENCY SHUT-DOWN ACID INJECTION VALVES FOR HIGH PRESSURE ACID LEACHING OF NICKEL LATERITE ORE

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ABSTRACT

The extraction of nickel from laterite ore has progressed to the point where the use of autoclaves is now the cost effective alternate. This progression required the use of higher temperatures and pressures to support the complicated chemical process. Enhanced process equipment was also needed and some critical components had not yet been developed. A significant problem area was the method of injecting sulfuric acid into the autoclave to achieve accurate pH control. The isolation valves needed had previously never been made and a design did not exist. This paper will discuss the early stages of that design and the later innovations up to date, where the valve is now a proven piece of equipment that functions well in this severe service.

INTRODUCTION

During 1997, in Perth - Western Australia, the Bulong PAL Nickel Project (Bulong) was well under way and the design was progressing. The project process was based upon the extraction of nickel from laterite ore using the Kilborn Engineering Company flow sheet (see Figure 1). The project was being executed by a consortium of the Bateman Kinhill-Kilborn (BKK) companies. The process employed high pressure autoclave technology (HPAL), where a critical component of the process was the pH control of the fluid in each autoclave compartment.

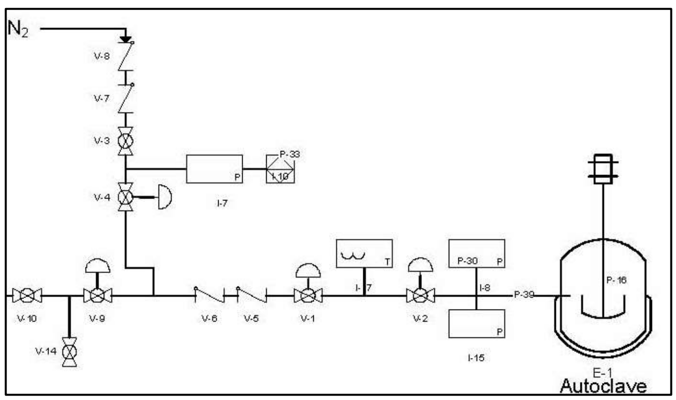


Figure 1. Kilborn Acid Injection System

To achieve this high level of control, concentrated sulfuric acid needed to be injected into the autoclave compartments, with a feed rate based upon pH measurement fed-back from within the vessel. Keeping the acid feed accurate was a major part of the exothermic reaction taking place within the autoclave. The typical requirement for metallurgy on a piping system handling 98% concentrated sulfuric acid at ambient temperature, is carbon steel or possibly low grade stainless steel. At the point where the acid injection system connected to the autoclave vessel a change to a more noble material could be needed. The acid was to be injected through a lance or dip tube delivering the fluid into the liquid phase of the vessel. These internal components were typically made from high grade titanium alloy with a lining of tantalum.

As the design progressed, the acid system evolved using commercially available stainless steel valves and fittings with a “spec break” adjacent to the vessel nozzle connection and down-stream of a block valve(s) and a swing check valve(s).

Hazard and Operability Analysis

Part of good practice in plant design is a procedure where the process and operations teams meet and discuss what-if scenarios. This procedure is called a Hazard and Operability Analysis or “HazOP”.

A HazOp study identifies hazards and operability problems associated with an operating scheme or plant. The concept involves investigating how the plant might deviate from the design intent. If, in the process of identifying problems during a HazOp study, a solution becomes apparent, it is recorded as part of the HazOp result. Although the HazOp study was developed to supplement experience-based practices when a new design or technology is involved, its use has expanded to almost all phases of a plant's life. HazOp is based on the principle that several experts with different backgrounds can interact and identify more problems when working together than when working separately and combining their results. It is now an accepted and standard function of good project execution.

The Bulong HazOp

During the HazOp for the Bulong Project a significant problem based around the acid injection system was discovered.

Each autoclave vessel was protected against over pressure by two different devices. Primary protection was from American Society of Mechanical Engineers (ASME) Code certified safety relief valves (SRV). In the unusual event that the SRV did not function correctly, secondary protection was provided by a series of rupture discs. If both systems failed, then the process fluid could relieve from the autoclave vessel into the acid system piping, as this was the path of least resistance. The process fluid could migrate into the acid system through the dip tube and acid lance. The elevated pressure and temperature at the piping spec-break could easily put the entire system into jeopardy. With the fluid in the autoclave having an upset condition temperature of ~250°C and a pressure of ~4000 kPa, the block valves in the acid piping system would soon be compromised and fail, causing an uncontrolled leak of the autoclave process fluid. The result could also create a leak of H_2S (hydrogen sulfide) in concentrations that could be fatal.

It was obvious that the acid injection system was the weak-link in the entire process design associated with the autoclave.

Valve Development

At this time Valvtechnologies had been doing R&D into the use of their ball valves in the nickel-sulfide extraction process at Western Mining's Kwinana Refinery (Kwinana) in Western Australia. Some of the personnel from Kwinana were involved in the Bulong Project and contacted Valvtechnologies to request their input into the availability of a valve that could function under these severe process conditions. The valve would need to provide a zero leakage capability under the worse case scenarios of total plant upset.

Materials Research

Concurrently Valvtechnologies had been doing research in collaboration with the Mechanical Engineering Department at the University of Houston's Center for Reliability Ceramic's Research Unit, at the Cullen School of Engineering (Yu, Ortiz, Hunn and White 1999). The program was aimed at finding a monolithic ceramic material that could be cold pressed and manufactured economically, for use in severe service ball valves, as well as for other industrial uses. The research was not complete but a whisker-reinforced ceramic based upon silicon nitride had shown good strength characteristics when used as the ball and as also a sealing component for a valve.

Process Conditions and Materials Selection

Given the process conditions Valvtechnologies decided that their standard ball valve design would not be acceptable and a meeting was held between the project design group and the local Valvtechnologies agent, in Australia, to "brainstorm" the way forward. The project design group made available a hand written corrosion chart (for better quality this is redrawn for this paper) (see Figure 2) that identified the acceptable materials that could withstand the upset conditions, at the interface between the autoclave and the primary acid injection isolation valve.

The chart indicated that tantalum (Ta on the periodic table of elements) would be acceptable but a valve had never been manufactured from this metal.

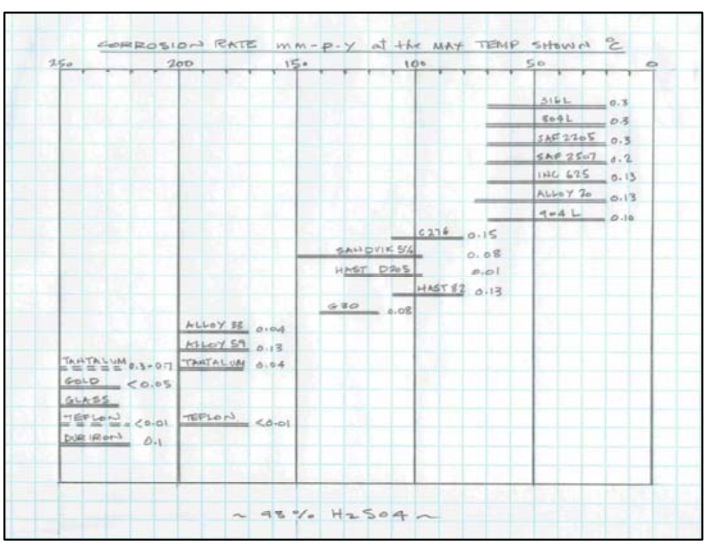


Figure 2. Corrosion rates for sulfuric acid

Tantalum is a very expensive metal and in its pure form it is ductile but has very low strength under bending. Current costs in 1997 were >US$500 per kilo and the theoretical weight tantalum for a 50 mm valve would be close to 80 kilos. Tantalum is very difficult to machine and due to limited resources; it is only available in fairly small diameters (in 1997 up to ~150 mm diameter).

The prototype valve was developed around an idea that incorporated a design where all wetted parts of the valve and ball would be made from solid tantalum, the seats would be ceramic and the seals and packing would be a synthetic and resilient material.

During the design work Valvtechnologies calculated that the tantalum parts of the valve needed to be stronger than elemental tantalum and using HC Stark Inc. (www.hcstark.com) as a resource; it was decided to use an alloy of tantalum and tungsten in percentages of 97.5% Ta and 2.5% W. This provided the strength needed to utilize the tantalum as a manufactured component. Valves are typically designed using a code of practice that designates the parameters for the use of certain materials that have American Society for Testing and Materials (ASTM), Unified Numbering System (UNS) and other designations. Valvtechnologies based their design upon the ASME B16.34 Code - Valves, Flanged, Threaded and Welding End. As Tantalum was not a material normally used for valve manufacture there was no pressure/temperature table available that could be utilized in the design work. Using good engineering practice Valvtechnologies developed their own pressure/temperature rating for these materials (see Figure 3).

PRESSURE/TEMPERATURE RATING FOR UNSR05252

Maximum working Pressure for Ta-2.5% / B365 UNSR05252 for Standard Class Calculated by extending B16.34 Annex F to this material

	Working pressure (psi) per ANSI Class			
Temp (F)	150	300	600	900
-20 to 100	276	720	1440	2160
150	252	658	1317	1975
200	237	617	1234	1851
250	231	603	1205	1808
300	226	588	1177	1765
350	220	574	1148	1722
400	214	560	1119	1679
450	207	540	1080	1620
500	200	520	1041	1561
550	191	498	996	1493
600	181	473	946	1419

Equation used : Pst = SI / 8750 * Pr (B16.34 Annex F)
where Pst = rated working pressure (psi)
Pr = pressure rating class index as per B16.34
SI = 60% of yield strength (psi) at temp T (Yield strength from H.C Stark)

Figure 3. Pressure/Temperature rating of Ta

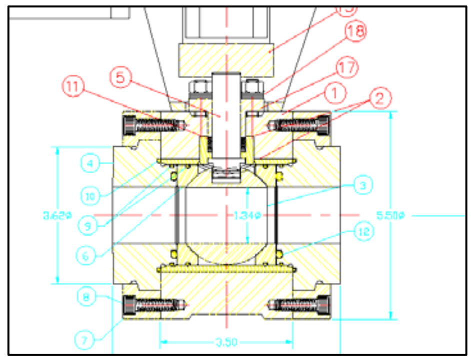


Figure 4. Original valve design

Experience from the work done through the University of Houston allowed faith in the use of silicon nitride and after some searching, Ceradyne Inc. (www.ceradyne.com), a ceramics manufacturer, was found that could produce the complex shape and machined accuracy needed for the seats of the valve.

Previous experience gained from the seals used for the autoclave mixers provided good data that Kalrez® as manufactured by E. I. du Pont de Nemours and Company (Dupont) (www.dupont.com) would be acceptable. Through discussion with DuPont and their applications engineering group, the selection for these components was fine-tuned.

Original Valve Design

The original design concept was a valve with the configuration as shown in Figure 4. The body of the valve would be “wafered” between the piping flanges. This avoided the need to use the tantalum material as a flange, as under tightening and subsequent bending load the flange could break. The pressure/temperature rating and project piping specification dictated the use of ASME Class 600 flanges for this service. As the flange bolting needed to straddle the valve body, the bolt pattern dimensions on Class 600 did not allow sufficient clearance, thus the bolting pattern was increased to match ASME Class 900. This in-turn caused the mating flanges for the valve to be ASME Class 900.

Many months of development from this stage provided enough faith in the design and product that the Bulong Project ordered valves in size 50 mm and 80 mm for installation at the job site, located near to Kalgoorlie in Western Australia.

Features of the original design

- Body – 316 stainless steel lined with 6 mm thick tantalum
- End Caps – Tantalum with a serrated face for pipe flange mating
- Retainers – 316 stainless steel
- Ball – Tantalum coated with chrome oxide (Cr_3O_4)
- Seats – Silicon nitride
- Seals – Kalrez®
- Load springs – Kalrez® with inner core of synthetic rubber
- Stem – Tantalum coated with chrome oxide

The acid injection valves continued to function well, up the time the plant was closed down in 2003, due to the shortage in a reliable supply of sulfuric acid.

The Murrin Murrin Project

At the same time the Bulong project was under construction in Western Australia, the giant Anaconda Nickel – Murrin Murrin Project (Murrin Murrin) was also progressing. Murrin Murrin was being designed and constructed by Fluor Corporation and the acid system design differed from that of Bulong, whereby the acid was injected vertically into the autoclave through the vapor space, rather than into the liquid space as with Bulong.

The original design of Murrin Murrin utilized an acid system with valves and piping made from 904L stainless steel. The HazOp at Murrin Murrin did not suggest anything of a higher grade than this material. During commissioning there was an uncontrolled discharge from an autoclave and the acid system was destroyed by hot acidic slurry. Anaconda Nickel contacted Valvtechnologies in the early part of 1999 to discuss the use of the acid system valve developed originally for Bulong.

The system design was reviewed and a recommendation to use 2 isolation valves in series, with a purge system between was selected. Due to project budget restraints and to better understand the selection of the correct materials for each valve in series, Valvtechnologies again enlisted the help of the University of Houston's Cullen School of Engineering and their super-computer. Rather than make the assumption that the application needed the expensive Tantalum materials for each valve a finite element analysis (FEA) was performed to simulate the heat loss during an upset situation. The closed valve acid system was modeled by a graduate student at the University of Houston and the temperature at various points in the piping configuration (see Figure 5) was calculated using the following data:

- The distance from the autoclave to the first valve and then to the second valve would be the minimum allowable, based upon the type of piping system used.
- Each valve had a seat upstream and down stream and each would seal on both seats during an upset condition.
- The temperature at the closed valve, adjacent to the autoclave nozzle, would be no greater than 260°C during an upset condition.
- There would be a continuous purge of ambient temperature nitrogen between the 2 isolation valves, when they were closed.
- The piping system would be uninsulated and the subject to maximum ambient temperature of 40°C.

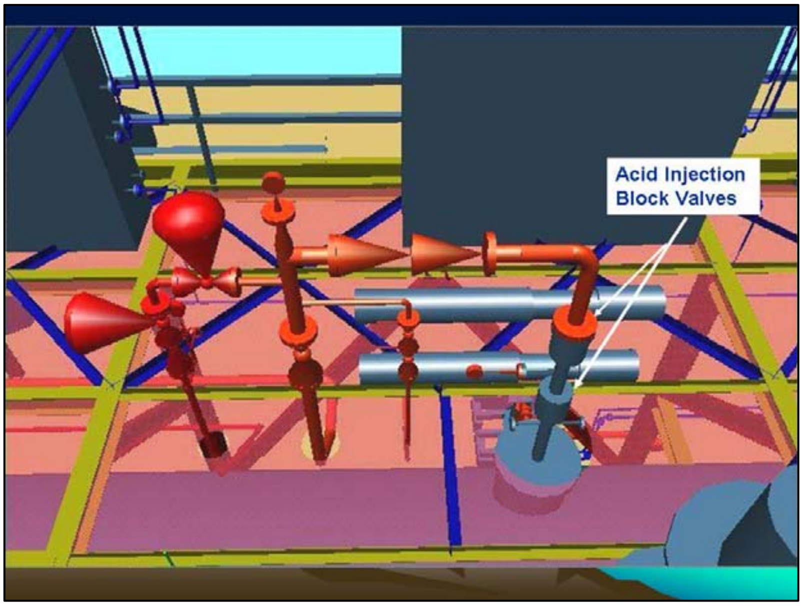


Figure 5. Acid injection system piping configuration

The results suggested from the FEA indicated that tantalum valves may not be needed for the second isolation valve. The heat loss could allow an alternate material at the second isolation valve, as the corrosion rate was less when the temperature subsided. After more consultation with the project engineers the primary valve was specified as tantalum and the second isolation valve was specified with metallic wetted parts to be made from Hastelloy® C2000® material which is a (Ni-Cr-Mo) C-type alloy, as manufactured by Haynes International (www.haynesintl.com). This material is far less expensive than tantalum, thus providing the project with the cost savings required and level of security needed.

Valves in sizes 50 mm and 80 mm, in both tantalum and C2000®, were ordered and installed during late 1999 and early 2000.

Operating Results at Murrin Murrin

After plant start-up the valves were put under duress, during an upset condition and the results showed that although the valves performed correctly and sealed, there were some areas that could be improved.

A series of pictures taken after removal of a primary isolation valve, in tantalum material, illustrated these results.

- Figure 6 shows the valve after removal.
- Figure 7 shows the autoclave side of the ball where the chrome oxide coating had failed, but still had maintained an acceptable seal.
- Figure 8 shows the opposite side of the ball and indicates the process fluid had not leaked across the valve.
- Figure 9 shows the ceramic seat on the autoclave side of the valve and indicates the slight leak path.
- Figure 10 shows the ceramic seat on the opposite side of the valve and appears undamaged.

Figure 6. Valve after removal.

Figure 7. Autoclave side of ball.

Figure 8. Opposite side of ball.

Figure 9. Seat on autoclave side. **Figure 10. Seat on opposite side**

Corrective action was taken to upgrade the coating to titanium dioxide (Ti_2O_3) as this coating had been seen to perform well on other equipment at the plant with a higher bond strength and better corrosion resistance.

Additionally the valve packing had leaked and the stem showed signs of corrosion from the fuming sulfuric acid, due to the vertical injection configuration. It was ascertained that the coating failure had allowed the packing to leak and in-turn had allowed more acid vapor to attack the substrate of the stem coating. Here, the corrective action was to provide uncoated stems and thus avoid the same problem. To avoid the risk of the tantalum stem galling against the valve body, a thrust washer was installed in this location. The stem also appeared to have "twisted" slightly under actuator load. Works was done to consider a redesign of the valve body to allow a larger diameter stem and also to upgrade the stem to a new, stronger material could be made available (from H C Stark) which is an alloy of tantalum with 10% W (UNS 205256).

The Goro Project – Lessons Learned and Applied

In 2001, when work commenced on Inco's Goro Nickel Project (Goro), the project benefited from the lessons learned by Valvtechnologies in designing, supplying and servicing acid injection valves in two existing projects. Detailed design work continued but was stalled when; in December, 2002 the owner put the project on hold due to cost overruns.

When work proceeded in 2004 Goro's design raised the bar for Valvtechnologies with the requirement for some tantalum valves in 100 mm size. The project design team also increased the safety factors for all equipment and this affected the design of valves. Typical safety factors for the sizing of automatic actuators were based upon 1.0 or 1.5 times the calculated torques, assuming slurry as the process fluid. On Goro this was dictated as 2.0 minimum and this created a new set of problems for the designers at Valvtechnologies. The pneumatic actuators became larger and heavier than previously provided. Support of the actuators became a problem due to their size, weight and center of gravity.

The valve maintenance work at Murrin Murrin had been executed by a company (Score-Pacific) in Western Australia that specialized in the on-site plant maintenance of all types of valves. This company had worked closely with Valvtechnologies in upgrading the acid injection system valves and was certified as the Valvtechnologies service agency. Goro engaged this company as consultants for their valve selection process and as a result many upgrades were incorporated into the design specifications and valves manufactured (see Figures 11, 12 & 13)

Major Changes and Upgrades for Goro

- Body designed to have external alignment guides for easier installation between flanges.
- Stem increased in diameter by 10% and material changed to tantalum with 10% W (UNS R205256).
- Ball coating changed to titanium dioxide (Ti_2O_3).
- Body material and flange retainers changed to Alloy 20.
- Actuator mounting changed from carbon steel to stainless steel.
- Actuator and all accessories changed to stainless steel.
- Top-works of the valve equipped with a bearing to better support the actuator (see figure 13).

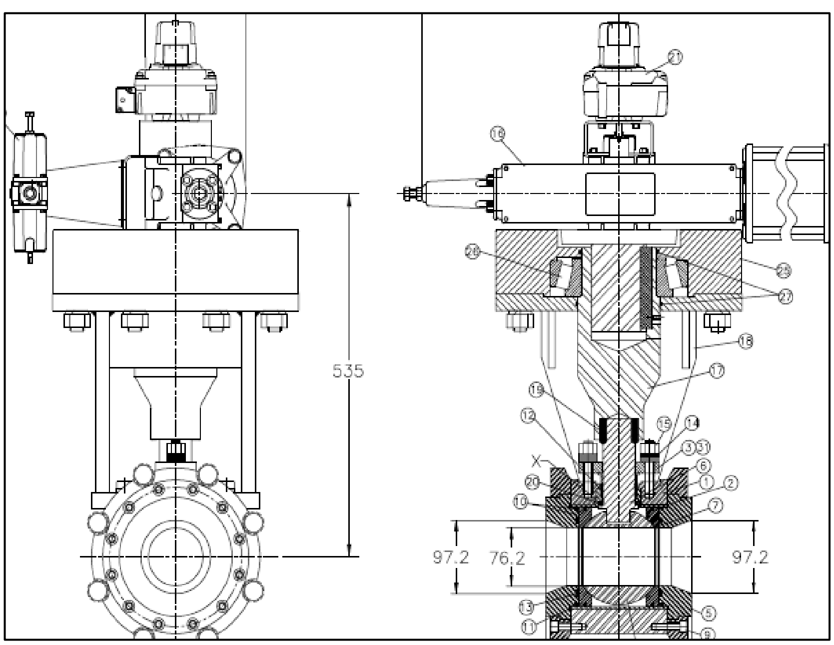
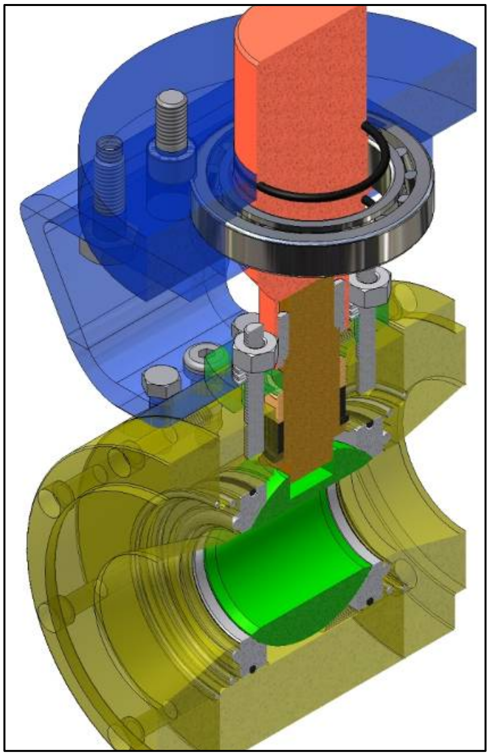


Figure 11. Goro valve design



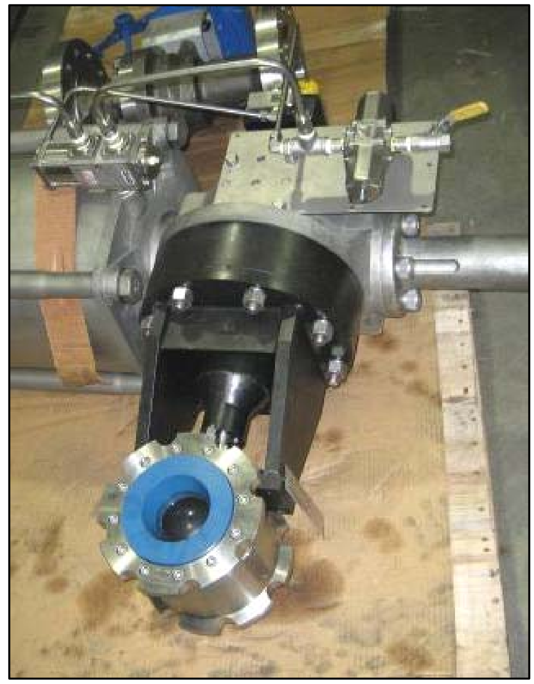


Figure 12. Goro valve section **Figure 13. Goro valve**

Other PAL Nickel Projects

During the Goro work valves were supplied to the Coral Bay HPAL Nickel Plant (Rio Tuba) in the Philippines. The design used tantalum valves in a double valve arrangement with a nitrogen purge connected to a center spool (see Figure 14). These valves did not have the benefit of all the upgrades applied for Goro but have still functioned well and have operated in shut-down mode with reliable results. For the current upgrade at Rio Tuba, latest generation valves are now being provided. In late 2007, Valvtechnologies was awarded the supply of all acid injection system valves for the Ambatovy HPAL Nickel Plant in Madagascar and have recently provided a proposal to the Ramu HPAL Nickel Project in Papua New Guinea.

Figure 14. Rio Tuba acid isolation valves

Conclusion

From a need and a concept in 1997, Valvtechnologies created a unique valve that performs in the most arduous of process conditions. The close cooperation between process and design engineers for operating and consulting companies provided the knowledge and resources for this to happen. With the world shortage of nickel and other minerals, such engineering innovations can only reassure mining companies that solutions can be found.

Currently other upgrades to the design are being considered to extend valve life and improve reliability up to the next level.

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