THE CURLY CASE OF THE CORRODING CHLORINE PIGTAILS

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79th Annual WIOA Victorian Water Industry Operations Conference and Exhibition
Bendigo Exhibition Centre
31 August to 1 September, 2016

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ABSTRACT

Chlorine gas is an agent used for primary disinfection of drinking water and disinfection of treated effluent. Melbourne Water has 920kg chlorine gas drums installed at five sites, and 70kg chlorine cylinders at two sites, which connect to a common manifold via an auxiliary valve, pigtail and manifold valve. In February 2016 discolouration was found on the nuts of pigtails at two sites which indicated possible corrosion and the potential for a chlorine leak. An organisation-wide incident was declared and all pigtail/valve connections were systematically inspected for evidence of corrosion. Symptoms of corrosion included discolouration or removal of plating, deposits of corrosion products, moisture leaking out of connections, and valve threads that were brittle or missing in parts. The last symptom was of critical concern as loss of thread integrity could lead to a loss of containment of chlorine gas. A detailed incident analysis was completed and examined many potential root causes including moisture ingress, leaking gaskets and dezincification of the brass. Actions from the incident included modifications to standard operating procedures, maintenance regimes, procurement procedures, equipment specifications, and asset information recording. While the exact root causes were not established, the understanding gained through the investigation process allowed the incident team to develop control measures to resolve the issue.

1.0 INTRODUCTION

Chlorine gas is used for disinfection of drinking water and treated effluent. A common chlorine gas setup is to have banks of 920kg drums connected to common manifolds. The drums are connected to the manifolds via an auxiliary valve, pigtail connection, and manifold valve. Melbourne Water has chlorine gas drums installed at a number of sites.

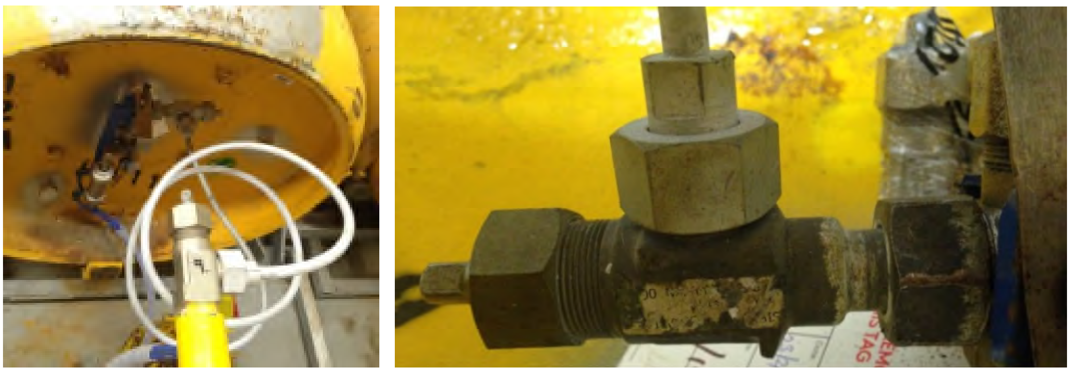

Figure 1: ***Drum setup (left), pigtail/auxiliary valve connection (right)***

In August and September 2015 a number of valves seized at Western Treatment Plant (WTP – sewage treatment plant) and were replaced in October 2015. By February 2016, some of the new pigtails had discoloured so were replaced and put on nitrogen pressure test. Two weeks later the pigtails discoloured again. Two of these valves had brittle threads that could be snapped off. An incident was declared due to concerns for a potential chlorine leak. Independently of the WTP incident, a Water Supply Operator emailed Asset Management in February regarding a pigtail nut at Greenvale treatment plant with liquid in the nut. The fact that similar issues had been discovered at two separate sites, in two separate product streams, suggested the potential for widespread corrosion at chlorine gas sites, and an organisation-wide incident was declared.

An incident response team was formed with the objectives to maintain safety of all Melbourne Water staff, contractors and the general public, to maintain supply of safe drinking water and recycled water, and to identify the root cause. An inspection at Greenvale found some valves with threads partly eaten away but external plating was intact. Missing or brittle threads presented a risk of loss of containment of chlorine. The incident response team arranged for an urgent inspection of valves at all chlorine drum sites.

Figure 2: ***Brittle threads on valve (left), moisture in pigtail nut at Greenvale (right)***

2.0 DISCUSSION

Inspection of disconnected valves and pigtails at WTP, Greenvale, Cardinia, Silvan and Tarago treatment plants found a range of internal and external corrosion symptoms including plating discolouration or removal, coloured corrosion products, moisture, brittle or removed threads and pink colouring indicating dezincification of valve surfaces and even internal threads and brass packing components in some cases.

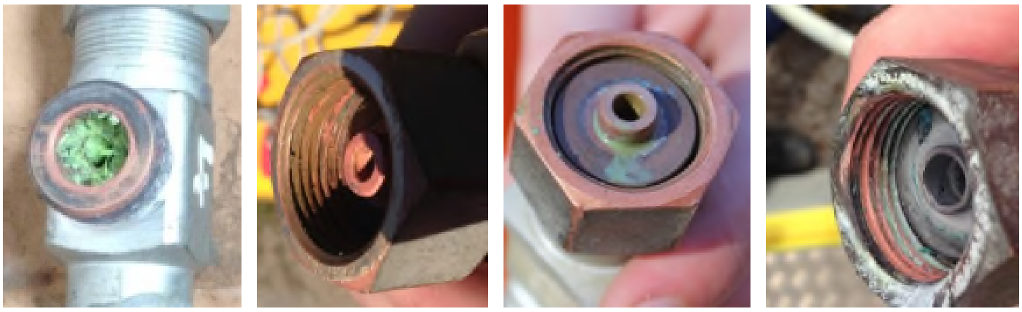

Figure 3: ***Observed corrosion symptoms (L to R): 1 green precipitate, 2 pink dezincified surfaces, 3 green moisture, 4 white/brown corrosion/plating removal***

The incident team analysed the incident data using the MORT analysis techniques: events and causal factors charts, fault tree analysis, hazard-barrier-target analysis, and change analysis. The incident team engaged ALS to complete laboratory analysis on corroded valves and pigtails and a corrosion expert from AECOM to assist with data interpretation. Using these techniques, in combination with interviews with field staff, and analysis of lab data and photos, the incident team developed a series of potential root causes.

2.1 Challenges with the Incident Analysis

The incident events were unknown and there was no fixed time period so it was difficult to define the incident scope. To inspect all 74 valves, the incident team had to work around operational constraints such as drum changeovers and maintenance to minimise disruption.

In addition, the team needed to replace corroded valves and pigtails at the time of investigation, which added further delays due to the long lead time on equipment delivery. Another challenge was the difficulty of preserving information. Each inspection included up to twelve valves and pigtails. Labelling valves was critical so that photos did not get mixed up. It was also important to photograph valves quickly before the surfaces changed from being exposed to atmosphere. Because the inspections occurred concurrently with the incident analysis, the team learnt over time what information to look for on valves, so some important data such as gasket condition was not recorded early on. There was also limited data recorded about valve changeovers.

2.2 Incident Analysis Findings

The investigation found that the valves were dezincifying (selective leaching of zinc). That is, valve material was susceptible to dezincification and, in the presence of chlorine and moisture, hydrochloric acid formed and selectively leached zinc out of the brass leaving behind a porous and mechanically weakened copper structure on valve internals. In some cases, chlorine was escaping past the sealing gasket leading to external corrosion (including dezincification) of the pigtail nut and valve threads. The incident analysis team investigated further to identify root causes. Due to the challenges experienced in this incident analysis, it was not possible to pinpoint definitive root causes, however a list of possible root causes was developed and used to recommend mitigation actions.

2.3 Valve Material

Dezincification can occur in copper-zinc alloys like with have a zinc concentration of 15% or more (Selvaraj 2003, P49). Positive Material Identification (PMI) testing was completed on four valves to determine the metal composition and showed that the brass contained approximately 38% zinc and therefore was susceptible to dezincification. Spectroscopy was completed on the valves which is more accurate and found 39-40% zinc.

Table 1: ***Results of valve substrate spectroscopy***

Sample	Location	Fe	Ni	Cu	Zn	Sn	Pb
A Body	Greenvale	0.20	0.07	~57	**39.7**	0.19	3.06
B Body	WTP	0.27	0.06	~58	**39.0**	0.27	2.79
F Body	Cardinia	0.23	0.06	~57	**39.9**	0.26	2.80
Yan Yean	Yan Yean	0.25	0.06	~57	**39.4**	0.26	2.80

Brass can be a single phase structure (alpha phase) or two phase/duplex structure (alpha-beta phase). Dezincification is more likely in the latter. Laboratory analysis showed that the brass had an alpha-beta microstructure and hence was susceptible to dezincification.

Through discussions with operators, there was a general consensus that the valves had changed over time with regard to how quickly they corroded and how they looked and operated. Anecdotally the new valves were softer, the spindles moved more easily and when the plating was scratched off by spanners the valves turned pink underneath which previously had not happened.

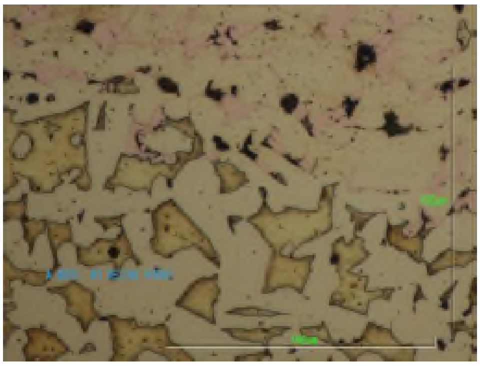

Figure 4: ***Microstructure analysis of a Greenvale valve showing alpha-beta structure: beta phase (darker patches) in alpha phase (lighter coloured background)***

Discussions with the manufacturer revealed that the factory location had changed five years ago and that the bass brass alloy had changed slightly in 2014 to a more machinable alloy with a slightly higher lead content.

Table 2: ***Comparison of old and new brass content from manufacturer***

Brass	Copper	Lead	Iron	Zinc
Old brass	56-58%	1.5-2.5%	0-0.3%	40.2-43.5%
New brass	57-59%	2.5-3.5%	0%	37.5-40.5%

A literature review of corrosion mechanisms for dezincification found that lead provides dezincification resistance in alpha brass but can accelerate dezincification in alpha-beta brasses (Davies 1993, P4). However, the research is not conclusive. A five year old valve from Yan Yean was analysed for comparison to see if there was a difference in the microstructure or lead content. Analysis (Table 1) showed an alpha-beta microstructure and no significant difference in lead content. Therefore, while it was clear that there had been changes in the composition and manufacture of newer valves, it was not conclusive whether these changes had caused the accelerated corrosion of valves and pigtails.

2.4 Moisture in Valves

Dezincification needs an electrolyte for the corrosion mechanism to work. Moisture was observed dripping externally from or inside a number of pigtail/valve connections. The incident analysis team identified a number of potential sources of moisture. Moisture was found in valves stored in the manufacturer's stores which either entered the valves through pressure testing in a water bath, or while in storage due to humidity and valve packaging not being airtight. Review of the moisture content in the chlorine gas used showed increasing moisture content over the last five years, though still below the wet chlorine limit of 150ppm. Laboratory analysis of the corrosion products found cadmium- nickel- and zinc- chlorides which are all hygroscopic, ie. they readily absorb moisture. Therefore after a small amount of corrosion, the corrosion products absorb moisture and the valve corrodes further. The grease applied to the valve internals may also be hygroscopic or act as an electrolyte. Another potential electrolyte was atmospheric exposure during drum changeovers; at some sites disconnected valves were capped, at others valves were not capped as they were reconnected soon after being disconnected. Investigation found that the caps used are not airtight so would keep moisture out. Also, while valves may have been disconnected for as little as twenty minutes, only a few minutes are needed to allow moisture from the air to enter the valve and initiate corrosion.

2.5 Gasket Sealing Problems

Discussions with the valve supplier suggested that discolouration of pigtail nuts indicated a very low level chlorine leak below detection limits indicating that these connections had poor seals. Gaskets are used to seal the pigtail/auxiliary connection and the auxiliary/drum valve connection. Gaskets used were 1.5mm thick Tesnit (aramide fibre). Operators reported that the gaskets currently used had a larger inner diameter than older gaskets from years ago and the new ones were more prone to slip when installed. Inspection of valves found that some gaskets were worn, torn, unevenly compressed or in some cases broken into pieces when the pigtail nut was disconnected which suggested overtightening. The gaskets commonly stuck to the sealing surfaces and had to be removed with scrapers or wire brushes to clean the valve sealing face before applying a new gasket. Optical assessment of valve sealing faces showed track marks from wire brushing which may have allowed chlorine to pass around the gasket in older valves. There was no common tightening method or understanding of how tight a connection was needed to achieve the correct compression of the gasket to create a seal. Torque wrenches had been trialled unsuccessfully in the past and were not used for connections.

__Figure 3:__ ***1. Unevenly compressed gasket, 2. Torn gasket, 3. Gasket stuck to sealing face, 4. Broken gasket, 5. Scratches on valve sealing face***

2.6 Quality Assurance of Valves

During the incident many new valves leaked through the spindles when installed as the gland nuts were not tight enough. Operators tightened the gland nuts on leaking valves and resolved the issue. The incident analysis traced this to a quality assurance process implemented by the valve supplier after they investigated the valve seizing event in 2015 and found that the grease used on the valve internals was inappropriate for use with chlorine and caused the seizing. Subsequently the incident analysis team reviewed the supplier's laboratory analysis and found that the "grease" seen on seized valve internals was actually corrosion products. The supplier also found moisture inside valves in their stores. From October 2015 the supplier stripped all valves to check for moisture. They dried and reassembled them with a new grease suitable for chlorine. The supplier tightened the gland nut, to seal the internal PTFE packing, until it felt tight and until the valve passed a 3000kPa nitrogen leak test. The incident team found that PTFE is subject to cold flow creep: when compressed by the gland nut, the packing shrinks and the gland nut needs to be retightened. Also, when the auxiliary valve is exposed to liquid chlorine, the valve cools very quickly. The PTFE cools faster than the brass and breaks the seal allowing chlorine to pass the spindle. Melbourne Water worked with the supplier during the course of the incident to improve the valve stripping process and pressure testing, ultimately deciding to abandon this process as it added more risk than it prevented.

2.7 Restorative Actions

Affected equipment will be engineered out or substituted. Valves will be replaced with bronze valves, airtight caps and different flexible connections where feasible. PTFE gaskets with a smaller inner diameter are currently being trialled. The following administrative controls will also be implemented or updated to mitigate the likelihood of future corrosion. A single standard operating procedure will be developed which incorporates drum changeovers, nitrogen purging, pressure testing and leak testing, and tightening of connections to achieve a seal. Guidance for valve condition assessments in maintenance instructions and improved asset information records will also assist with data collection to monitor corrosion trends. These actions were adopted based on the incident analysis report from July 2016 and will be implemented throughout the remainder of 2016. While the corrosion issues have not been resolved at the time of writing, it is anticipated that the implementation of these actions will remove the incidence of valve and pigtail corrosion.

3.0 CONCLUSION

Throughout this incident Melbourne Water has learned many things. Firstly, valves are dezincifying and we now have a better understanding of the corrosion mechanisms involved. Also, discolouration of pigtail nuts can now be linked to low level chlorine leaks. It is now understood that nitrogen pressure tests on liquid riser systems will still contain chlorine at the valve and hence a valve can corrode during a nitrogen pressure test. The incident analysis team also established that exposure to atmospheric moisture is enough to initiate corrosion in a susceptible valve. Changes that will be made include improvements to standard operating procedures and maintenance instructions, asset information as well as procurement of new equipment. This incident has improved the understanding of operational staff and provided an opportunity to share learnings from the incident with the wider industry which could prove important for other organisations using similar equipment.

4.0 ACKNOWLEDGEMENTS

Thanks must go to the incident response team: Colin Hughes, Michael Dunne, Darsh Dalal, Trevor Gulovsen, Igor Posenjak, Rachel Smith, Tim Chambers and Martin Bowles. In addition to the incident response team, a number of others assisted with the incident analysis including: Steve McMeakin, Stuart Richardson, Stuart Smith, Claire May, Thomas Richardson (Woods Group PSN), Niranjan Panchal (Woods Group PSN), Angus MacKintosh (Woods Group PSN), Sarah Furman (AECOM), Steven Finger (ALS), John Everton (ALS), and Bernard Hedger (Spectrometer Services).

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