Prepared by WG-3

Safety Info 33/18

Incidents Involving Manually Actuated Isolation Valves in LOX Service

1 Introduction

In 2013 EIGA was advised of two very serious incidents involving large manually actuated isolation valves at air separation plants in liquid oxygen (LOX) service. In both incidents there were two fatalities. Wide ranging investigations were carried out and the preliminary results were detailed in the first edition of this Safety Information in 2013. The global industrial gases industry decided that due to the severity of the incidents a globally harmonized publication would be developed to cover the topic in more depth. This publication was published in 2015, EIGA Doc 200, *Design, Manufacture, Installation, Operation and Maintenance of Valves Used in Liquid Oxygen and Cold Gaseous Oxygen Systems.* Identical editions were published by the Asia Industrial Gases Association, (AIGA), Compressed Gas Association, (CGA) and the Japanese Industrial and Medical Gases Association, (JIMGA). In 2017 the publication was revised to take account of valves used in customer stations.
This Safety Information has been revised to reflect the publication of EIGA Doc 200 and to remind EIGA Members of the importance of following the recommendations in the publication.

2 Incident involving manually actuated butterfly valve

2.1 Incident overview

There was a violent metal fire (violent energy release) of a DN 150 (6 inch) manually actuated butterfly valve and the enclosed stainless steel and aluminium equipment in liquid oxygen service of an air separation plant. The valve was the discharge isolation valve of a standby oxygen pump.
The pump duct was partly destroyed. A significant quantity of perlite was blown out together with liquid oxygen from the plant.
The resulting fire combusted approximately 50 % of the valve as well as parts of the upstream check valve and parts of the surrounding pipe system. In total the fire consumed approximately 200 kg of stainless steel and aluminium.
There were two fatalities associated with this incident.

2.2 Incident summary

The normal process pressure for the relevant plant section was 31 bara. At the time of the incident the pressure upstream of the valve was between 1,0 and 2,6 bara. Downstream the pressure was 27 bara, due to the second oxygen pump that was running. The valve body and internal components were manufactured from stainless steel. The pump system had already been cooled down with LOX and it was in the process of being brought on-line by opening the downstream isolation valve. The incident happened during the initial opening of the valve. This pump had not been started at the time of the incident.
From the analysis of the residual parts found in the burned area it was assessed that the first ignition occurred in the small vertical and / or horizontal bearing parts of the butterfly valve. This then led to ignition of other larger parts such as the valve disc, valve body, part of the upstream check valve and piping sections. These were either partially or totally consumed by the fire.

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2.3 Incident investigation

2.3.1 The incident investigation team explored several possible immediate causes for the ignition. These included:

- adiabatic compression;
- particle impingement;
- hydrocarbon contamination; and
- metallic particles within the grease

2.3.2 After detailed analysis it was concluded that the most probable cause of ignition was the use of oxygen compatible grease that had been contaminated with hydrocarbon oil. The grease used in this case had been tested and approved by BAM[1] for use in gaseous oxygen service but had not been approved for liquid oxygen service.

2.3.3 The grease was possibly contaminated with mineral oil coming from the cryogenic stem extension that had not been fully cleaned for oxygen service. The hydrocarbon oil contamination was identified on other similar valves that were dismantled during the investigation. The grease was also potentially contaminated with aluminium particles which could have increased the frictional energy created during valve operation

2.3.4 The assumed kindling chain is that friction or mechanical impact during the opening of the butterfly valve ignited the contaminated grease which led to the ignition of the stainless steel bearing ring and other smaller stainless steel parts inside the valve then igniting the larger parts of the valve.

3 Incident involving manually actuated gate valve

3.1 Incident overview

A violent fire occurred in a DN200 (8 inch) manually actuated gate valve in a pressurized liquid oxygen line of an air separation plant. The valve was the downstream isolation valve of a double isolation configuration with a by-pass valve around the upstream isolation valve. The fire was confined to the downstream isolation valve with the ignition and combustion taking place in the upper part of the valve, breaching the pressure envelope. Part of the extended bonnet and the packing area was completely consumed by the fire. The lower part of the gearbox and the stem in this section was partly melted.
There were two fatalities associated with this incident.

3.2 Incident investigation

3.2.1. The process pressure for the relevant plant section was 59,3 bara. The incident happened during a restart of the internal compression (IC) LOX system whereby the upstream pressure of the double isolation was already at the normal operating pressure of 59,3 bara. The actual operating pressure at the downstream valve at the time of the incident could not be ascertained as there was no local pressure indication and the evidence indicates that the subject valve and downstream drain valves were passing. The valve and its inner parts were manufactured from stainless steel.

3.2.2 The evidence suggests that ignition first occurred in the stem area where there was a Polychlorotrifluoroethylene (PCTFE) guide ring.

3.2.3 The investigation identified that other valves in the same service had been visibly wetted with silicone oil with traces of mineral oil in the spindle and packing area, as well as in this guiding ring area. Some of these valves also experienced ignition of the PCTFE guide ring with it being either totally or partially consumed, though without breach of the pressure envelope.

3.2.4 The failure analysis indicated that the start of the ignition was at this PCTFE guide ring, wetted with silicone oil, most probably by mechanical excitation (single or repetitive impacts). The mechanical excitation could have arisen from the subject valve being partially open (with a pressure drop across the valve), or from vibration induced from operation of the upstream 'by-pass' valve. The evidence suggests that the fire could have progressed in stages, firstly with ignition by mechanical excitation at the guide ring which was subsequently expelled followed by free passage of LOX into the extended valve bonnet thereby igniting the stem, stem packing and extension bonnet tube.

[1] Bundesanstalt für Materialforschung und -prüfung

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3.2.5 Whilst there remains uncertainty on the source of mechanical excitation, it was concluded that the main reason for the incident was the silicone oil and/or traces of mineral oil found to be present on the valve internals, which can be ignited in gaseous oxygen (GOX) or LOX if energy is present.

3.2 Key technical issues

It could not be definitively concluded where the silicone oil or mineral oil came from, however it is most probable these were introduced during assembling of the valve in the original equipment manufacturers' (OEM) workshop. For this particular incident, the manufacturing process of the valve packing was found to use silicone oil as an additive. Based on analysis of an unused packing, solvent extraction confirmed the presence of silicone oil in the packing. Despite the fact that compression failed to expel visible amounts of silicone oil, it cannot be excluded that either in the initial assembly of the valves or under certain process circumstances the silicone oil may have been expelled from the packing and migrated to the valve internals.

4 Recommendations

Following detailed investigations, a number of primary recommendations were made that apply to both incidents and these are detailed below. EIGA Doc 200 has considered the recommendations made in the original SI 33, and these remain unchanged.

4.1 Awareness at valve manufacturers and their sub suppliers regarding cleanliness requirements for oxygen service should be reinforced. An inspection test plan with sign off on critical stages should be maintained for each individual valve or traceable batch.

4.2 The manufacturing process for valve packing should be without any oil or grease. During assembly or re-assembly of the valves after cleaning, use of oil shall be avoided and grease should be avoided.

4.3 If the use of grease is unavoidable during the re-assembly of components wetted by the oxygen, only oxygen compatible grease shall be used, with the amount used being kept to a minimum. This grease needs to be oxygen compatible for the foreseen design conditions (i.e. pressure, temperature, phase). The oxygen compatibility of the grease shall be tested and certified by experts in this field.

4.4 If any compositional changes are made to any non-metallic components including greases, then the oxygen compatibility shall be tested or retested as necessary and certified.

4.5 For cleaning for oxygen service, valves shall be fully disassembled. Any cleaning agent that is used shall be removed completely, in particular from cavities and recesses.

4.6 The use of non-metallic materials inside valves, should be minimized as much as is possible.

4.7 If non-metallic products are used, these shall be tested and certified for oxygen compatibility for the related operational conditions.

4.8 Quality assurance and quality control measures at sub suppliers should be verified and witnessed by the purchaser for oxygen related valves and equipment.

4.9 It should be considered during plant operation, design and selection of materials that LOX valves could also be in GOX service for certain operating times or cases. Additional safety layers for the operating personnel should be considered for such LOX valves, these include:

- remote operation;
- specific operating procedures, such as equalising GOX/LOX pressure prior to operating isolation valves;
- safety distance for personnel when actuating valve remotely; and
- exempt materials for valves in throttling services.

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