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Industrial System for Chemical Inhibition of Vapor Cloud Explosions

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The oil industry operates installations and processes with important quantities of flammable substances within a wide range of pressures and temperatures. A particular hazard for this type of installations is an accidental release of a large quantity of flammable material resulting in the formation of a flammable cloud within the installation. Historical evidence has shown that the ignition of such a cloud can lead to an explosion producing shockwaves with enough energy to cause substantial physical damage to process plants and equipment and even lead to a total destruction of the installation. Such accidents are commonly named “Vapor Cloud Explosions” (VCE). According to Marsh (Marsh, 2016), Vapor Cloud Explosions account for the greatest frequency of losses in the energy sector. A new technology was developed for inhibition of Vapor Cloud Explosions, based on chemical inhibition using dry powders of carbonates or bicarbonates of sodium or potassium. The efficiency of the final design of the VCE mitigation system was tested on a very large scale in Vapor Cloud Explosion tests in California (US) in September 2016. A first implementation of the inhibition system is foreseen in the near future as part of a new cracker units in South-Korea and the United States.

1. Physical and Chemical Properties of the Inhibitor

1.1 Stability of the Inhibitor

When heated (above 80 to 100 °C), bicarbonates of sodium and potassium decompose to the corresponding carbonates with generation of water and CO_2. At ambient temperatures, this decomposition happens slowly. When heated further (above 850 to 900°C), the carbonates of sodium and potassium decompose to the corresponding oxides under generation of CO2

1.2 Toxicity

The high LD_{50} and LC_{50} values reported in literature to characterize the acute toxicity of sodium bicarbonate and potassium bicarbonate suggest that the risk of short term (< 1 minute) exposure of people to high concentrations of dusts of sodium bicarbonate or potassium bicarbonate is limited (Sax (1984), Kirk-Othmer Encyclopedia of Chemical Technology (1978), European Chemicals Bureau; IUCLID Dataset for Sodium Carbonate, p.62 (2000 CD-ROM edition), Organization for Economic Cooperation and Development (2002), The Merck Index (2006), European Chemicals Bureau; ESIS Database/IUCLID Dataset for Potassium Carbonate (584-08-7) p. 18 (2000 CD-ROM edition)).

1.3 Corrosive Properties

Carbonates (e.g. K_2CO_3 and Na_2CO_3) and bicarbonates of alkali metals are solid substances. However, since these products are well soluble in water, aqueous solutions of these substances can be formed when the inhibitor powder comes in contact with water from precipitation or from cleaning operations. For all concentrations, the pH of carbonate and bicarbonate solutions lie in the range of 8.3 to 12.2. These diluted solutions can come in contact with steel process equipment at high temperatures leading to evaporation of the water and resulting in (bi) carbonate solutions at high concentrations and temperatures. API 581 does not give corrosion rates for caustic/alkaline corrosion. In general, no significant corrosion problems are expected in case of activation of the VCE mitigation system because of the following reasons:

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- Significant corrosion of steel by (bi)carbonate solutions only occurs at high temperatures and high (bi)carbonate concentrations;
- The exposure time of steel equipment to aqueous solutions of carbonates and/or bicarbonates is limited;
- After activation of the mitigation system, there will be mechanical removal of the solid powder (using e.g. aspirators) followed by a cleaning of the exposed steel equipment with large amounts of water;
- An inspection will be performed each time mitigating system was activated;
- If necessary, insulation could be changed if during inspection, problems of corrosion are identified.

2. Minimum Required Airborne Inhibitor Powder Concentration

Several studies were conducted to establish the inhibitor efficiency as a function of inhibitor loading (Chelliah et al (2003), Ewing et al (1989, 1989b, 1992), Fleming et al. (1998), Hamins et al. (1994), Hoffman (1971), Hoorelbeke (2011), Linteris et al. (2001), Reed (1997), Rosser et al (1963), Trees et al. (1997), Wangsholm (2012), Wanigarathne et al. (2000)). Results obtained by Wangsholm (2012) indicate that for stoichiometric propane/air mixtures, the explosion overpressure can be reduced with 90% when K_2CO_3 particles with diameters between 20 and 50 µm are used with particle loadings of 15 to 55 g/m^3. Data for inhibition of stoichiometric mixtures of methane and propane (Rosser et al (1963), Hoffman (1971), Chelliah et al (2003), Reed et al (1997)) show that the explosion overpressure can be reduced with at least 75% when particles with diameters between 20 and 50 µm are used with particle loadings of 5 to 30 g/m^3 for $KHCO_3$ and 15 to 65 g/m³ for $NaHCO_3$. Results obtained by Hoorelbeke (2011) using commercially available fire extinguishing agents (Bi-Ex, based and $NaHCO_3$ and Purple K, based on $KHCO_3$) suggest that mass loadings of about 25 g/m³ and 10 g/m³ for respectively Bi-Ex and Purple-K are needed to reduce explosion overpressures with 75% for stoichiometric propane/air mixtures. To compensate for the presence of pockets with lower than average inhibitor concentration upon injection of flame inhibiting powders in industrial facilities, a design concentration higher than 20 g/m³ needs to be specified. A multiplication factor of 5 is arbitrarily applied, resulting in a target design inhibitor concentration of 100 g/m³.

3. Particle Size of the Inhibitor

A review of literature on the influence of inhibitor particle size on combustion inhibition effectiveness was conducted by Babushok (2016). Based on the literature review, Babushok comes to the following conclusions:

- In most cases, in the particle size range of 1 to 300 µm, a decrease of the size of the inhibitor leads to an increase of the flame inhibition effectiveness;
- Most experimental and theoretical research indicates that particles in the range of 10 to 30 µm evaporate to a great extent in the flame zone of typical hydrocarbon flames and are very effective for inhibition of flames. However, the use of particles with sizes below 10 to 20 µm does not result in higher inhibition effectiveness.
- The optimum particle size depends on flame velocity and residence time of the particle in the flame reaction zone. For most hydrocarbon flames, particle sizes in the range of 10 to 30 µm seem to be the most effective for flame inhibition.

The above conclusions by Babushok are also valid for carbonates and bicarbonates of sodium and potassium. The latter compounds are very effective flame inhibitors when the solid inhibitor particles are small enough (order of 10 to 30 microns).

4. Process Volume to be Protected

A number of QRA studies for refineries and petrochemical sites were performed by Gallot, Robillard and Roosendans (Roosendans, 2018). In these QRA studies, the risk of Vapor Cloud Explosions in congested process units was analyzed. The median of the surface area of the 430 studied congested process areas is about 1.800 m. The median of the calculated height of the 42.798 studied flammable clouds is about 3.5 m and the average calculated flammable cloud height is about 6.6 m. This value for flammable cloud height is consistent with the recommendations by Alderman et al. (2014) who stated that the congested volume should be defined based on a geometry with a maximum height of 7.6 meters. The results based on the QRA studies are consistent with the size and height of flammable clouds involved in some historical Vapor Cloud Explosions. Considering a congested surface of 1.800 m² and a flammable cloud height of 3 m, a volume of about 5.000 m3 needs to be protected. The protection of such a volume requires 4 inhibitor injection modules, as discussed later in this paper.

5. Inhibitor Injection Technology Selection

A feasibility study was subcontracted to identify available technologies for mitigating of Vapor Cloud Explosions by injection of solid inhibitor particles (Technip, 2012). The selection of the technology is based on a number of requirements such as the possibility to use the technology in a highly congested area, the compatibility of the selected technology with existing flammable gas detection systems, the footprint and size of the skid (must be compatible with available space in process units), the throw length (maximum horizontal distance reached that must be large enough to overcome a long range and wide area), a high speed of activation of the system, a limited number of skids; easy maintenance and testing, limited use of external utility systems and reliability of the technology. The technology proposed for mitigation of VCEs by chemical inhibition was selected based on a review and analysis of the existing technologies for injection of solid particles, including technologies already used for firefighting and explosion mitigation in confined areas. The following technologies have been identified and were investigated:

- Explosion suppression systems;
- Powder fire extinguishing modules;
- Large dry chemical powder systems (Fixed piped dry powder system & Fixed dry powder monitor);
- Impulse Storm;
- Water gun at aero dynamic lift;

A study was performed on the strengths and weaknesses of these technologies. Finally, the technology that was selected is based on a large capacity dry chemical powder injection skid. This technology was preferred over the other available technologies, primarily because of its speed of activation, the ease of installation inside a congested process unit, the limited footprint occupied by the skid and the optimum volume covered by per nozzle and per skid.

6. Dispersion of Inhibitor Powder in an Industrial Environment

A number of large scale dispersion tests were performed to study the dispersion behavior of inhibitor powder clouds. The dispersion tests were performed in a closed down steam cracker installation at the TOTAL site of Carling in France. In total 3 test campaigns were organized in 2012. In the 3 campaigns, the inhibitor powder concentration was measured at various locations and heights in the unit. The following general conclusions can be drawn from the dispersion test campaigns:

- A continuous release of powder is the easiest solution for sustaining a cloud meeting the requirements of the design basis (tests were also conducted with a pulsating injection of inhibitor powder but these tests were not successful);
- The following design characteristics of the inhibitor injection skids were confirmed during the dispersion test campaigns:
  - Continuous and constant powder flow rate of 2 to 2.5 kg/s per skid during 300 s;
  - One nozzle per skid;
  - Bore diameter of the nozzle: 10-11 mm;
  - Quantity of powder per skid to protect a congested volume of 1.250 m³: 600 to 750 kg of powder.

The dispersion experiments of the 3rd test campaign in September 2012 were simulated using a CFD code (KFX). For this purpose, a 3D model was developed of the environment in which the powder was dispersed. A comparison between experimentally observed powder concentrations and the concentrations obtained in the powder dispersion simulations show the same trends with values within a factor of 2 to 2.5.

7. Maximum Delay for Activation of the Inhibitor Injection System

Studies in literature suggest that in most cases the buildup of a flammable vapor cloud with VCE potential takes some time (Wiekema (1984), Lenoir and Davenport (1992)). If ignition of the flammable vapor cloud occurs instantaneously or a very short time after the start of the leak, than the resulting phenomenon will likely be a jet fire or a fireball. On the other hand, upon long duration releases of flammable gases/vapors, the flammable cloud will reach a steady state some time after the start of the release. Once such a steady state has been reached, the mass of material available in the cloud for combustion does not increase. The design of the proposed industrial system of chemical inhibition of Vapor Cloud Explosions is such that the time required to have the required airborne concentration of inhibitor in place is about 30 to 60 seconds. This time delay for deployment of the system is fully compatible with the time required for buildup of most flammable vapor clouds with VCE potential.

8. Detection and Activation Systems

Two strategies for activation of the system have been investigated: pre-ignition (injection of the inhibitor inside and around the flammable cloud before ignition) and post-ignition (injection of the powder after the flame is detected). In a pre-ignition strategy, the activation of the inhibitor injection system is based on gas detection. For activation of the modules, 2 possibilities can be defined: manual activation (the activation sequence is launched directly by an operator in a control room, irrespective of the gas detection status) or automatic activation (the activation sequence is launched automatically upon confirmed gas detection). In case of a post-ignition strategy, the implementation is based on detection of flames and/or explosion. However, the post-ignition strategy was rejected since both the speed of flame detection allowing a fast activation of the mitigation system and the responses time of the inhibitor injection skid upon activation by a detection system are not compatible with the time-scale of a Vapor Cloud Explosion. The latter was confirmed in a detailed study by GexCon (GexCon, 2012).

9. Minimum Duration of the Mitigating Action

The design of the inhibitor injection skid as discussed in the previous sections allows a minimum duration of the mitigating action of about 5 minutes. This time should be sufficient for other mitigating barriers to become active. These other mitigating barriers may include Emergency Shutdown Valves (ESD), water curtains and/or water deluge systems, evacuation of the site and mobilization of emergency response teams. If longer times than 5 minutes for the duration of the mitigating action are needed, then this can be achieved by installing injection skids with larger powder capacities.

10. Final Design for Inhibitor Injection System

Based on the results of the different test campaigns to study the dispersion behavior of inhibitor powder, a final design of an inhibitor injection system was developed. The final design has the following characteristics:

- A volume of 5.000 m^3 (1250 m^2 x 4 m) can be protected by 4 inhibitor injection modules;
- The modules are autonomous and powered by nitrogen pressure. The nitrogen bottles are connected via a pressure control valve to the powder drum of the module. The operating pressure of the powder drum is 16 barg.
- The quantity of powder in the drum of each module is 600 to 750 kg;
- Upon activation, every module delivers a continuous powder flowrate of 2 to 2.5 kg/s, assuring an airborne powder concentration of about 100 g/m^3 during about 5 minutes;
- Every module has one nozzle located at a height of about 4 meters and with an internal diameter of 10 to 11 mm;
- The modules are positioned in groups of 4, protecting a volume of about 5.000 m^3. The modules are located at the side of the congested volume to be protected and the powder is injected towards the unit.

The modular design of the system and the limited footprint of the individual autonomous injection skids allow easy retrofitting of existing sites.

11. HSE Aspects related to the Use of the Inhibitor Injection System

The proposed flame inhibitors are carbonates and bicarbonates of sodium and potassium. None of these products are toxic for people, but irritation effects are possible, especially since these inhibitors are applied as a finely divided powder. The discharge of large amounts of powder may create hazards to personnel such as reduced visibility and temporary breathing difficulty. As a result of these risks, the timely evacuation of the process unit in which the inhibiting powder is to be injected is mandatory.

Upon activation of the inhibitor injection modules, inhibitor powder will be dispersed in the process unit. As a result of this, large amounts of inhibiting powder will remain in the process facilities. This inhibiting powder may be mixed with firewater in case of ignition of the flammable gas and extinguishment of the fire by the fire brigade. Because of the nature of the inhibiting powder (carbonates and bicarbonates of sodium or potassium, which are well soluble in water) the pH of aqueous solutions is quite high. Adequate precautions need to be taken to limit the impact of effluent with high pH on the waste water treatment.

The inhibitor is a very fine powder (particles with diameters in the order of 5 to 100 micron). Another point of attention related to this is the inspection of rotating machines and air intakes of equipment (such as furnaces) after discharge of inhibiting powder.

12. Large Scale Explosion Tests

Large scale explosion tests were conducted in September 2016 to verify the behavior of the inhibitor injection system on an industrial scale. The tests were conducted on at the CHES test site of SRI International in Livermore (California, US) as part of a sub-project in the framework of a research program initiated by the US Department of Energy (REPSEA). The test rig is composed of 15 rows of 2 identical nearly cubic steel modules of 3.7 m long x 3.7 m wide x 4 m high, made of rectangular steel profiles. In total 17 large scale explosion experiments were conducted. In two of the 17 experiments (Test 16 and Test 17), the inhibitor injection system described in previous sections was tested. In these tests, methane gas was used at stoichiometric concentration. Two inhibitor injection skids were used during the test. The 2 skids are positioned upfront the rig at the side of the ignition location.

In Test 16, the amount of powder injected was 1.5 kg/s per skid during 10 seconds. Most of the injected powder was dispersed in module row 10. The ignition of the flammable methane/air mixture was followed by a strong explosion that was perceived to be a detonation flame speeds going from about 500 m/s to about 800 m/s and accompanied by a coupling of the flame front with the shock wave. The following observations were made based on videos and flame speed measurements:

- The flame experiences a strong deceleration when it travels through the area with inhibiting powder (from about 800 ms/s to about 400 m/s) and this despite a relatively short injection time and rather narrow powder cloud.
- The strong deceleration of the flame results in a decoupling of the flame front and the shock wave.

Inside the rig, the damage is extensive: fans completely destroyed, failure of welded connections between rig and pipes, deformation of braces holding pipes in place etc. The results of Test 16 are encouraging in a way that a larger quantity of inhibitor powder would probably have avoided the second quasi-detonation.

In Test 17 the rig was shortened to 7 module rows instead of 15 module rows in Test 16. One injection nozzles was located between module rows 4 and 5 and the other injection nozzle at the other side of the rig between module rows 5 and 6. The injected amount of powder was 1.5 kg/s/skid during about 33. After ignition of the flammable methane/air cloud, it became clear that the test was a success because of the absence of the characteristic bang associated with a detonation. Also the video footage confirmed the absence of a detonation. Further analysis of data confirmed the absence of a quasi-detonation such as observed in Test 16. In Test 17, the initial phase of flame expansion in module row 1 is comparable to the initial flame expansion in Test 16. However, the acceleration of the flame is slowed down as of module row 2 because of the presence of inhibitor powder at ground level. At this stage, the flame continues to propagate through the modules but at a speed of approximately 75 m/s, which is the same as the steady state flame speed observed in the reference test with methane without additional congestion in the rig structure. High speed video footage of Test 17 reveals that the flame is almost stopped when it enters the area with high inhibitor powder concentration (module rows 4 and 5) but manages to cross this area at the top of the inhibitor injection zone. These flame speeds are compatible with a phenomenon called “flash fire” in which the combustion of the flammable mixture takes place without generation of significant overpressure. No damage to the rig and injection skids was observed, nor by thermal effects nor by overpressure effects.

13. Conclusions

The oil industry operates installations and processes with important quantities of flammable substances within a wide range of pressures and temperatures. A particular hazard for this type of installations is an accidental release of a large quantity of flammable material resulting in a devastating Vapor Cloud Explosion. An industrial system for chemical inhibition of Vapor Cloud Explosions was developed, based on the use of dry carbonates and bicarbonates of sodium and potassium as flame inhibitor species. Several aspects of the proposed technology were analyzed and verified to ensure its compatibility with the requirements posed by an industrial environment. A final design for an industrial inhibitor injection system was developed. The efficiency of the final design was tested in large scale experiments and found to be adequate, opening the way for a full scale application of the chemical inhibition technology. The positive effect of the system for Vapor Cloud Explosion mitigation by chemical inhibition has also been demonstrated in simulations using empirical models and CFD codes applied on real industrial facilities. Some projects in TOTAL were identified in which a full implementation of the VCE inhibition technology as described in this paper is foreseen.

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