

# Industrial System for Mitigation of Vapour Cloud Explosions

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The oil & gas 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 “Vapour Cloud Explosions” (VCE).

Examples of major Vapour Cloud Explosions in refining and (petro)chemical industry include Flixborough (UK, 1974), Pasadena (US, 1989), La Mède (France, 1992), Milford Haven (UK, 1994), Longford (Australia, 1998), Texas City (US, 2005), Buncefield (UK, 2005) and many others. Major Vapour Cloud Explosions with devastating consequences also happened in offshore industry, as seen in Piper Alpha (1988), the P36 platform (2001) and Deepwater Horizon (2010). According to Marsh (Marsh, 2016) Vapour Cloud Explosions account for the greatest frequency of losses in the energy sector.

Extensive research has been conducted to assess the efficiency of chemicals - applied as solid powders - for inhibition of flames. Especially alkali metal compounds (especially carbonates and bicarbonates of sodium and potassium) have shown to be one of the more efficient flame inhibitor species. In this paper, the principles of flame inhibition by alkali metal compounds are briefly explained. Based on these principles, a practical implementation of an industrial system for chemical inhibition of Vapour Cloud Explosions is discussed. This implementation is based on the use of dry powders of carbonates and bicarbonates of sodium and potassium as flame inhibitor species. Several discussed aspects related to the development of a practical implementation of the Vapour Cloud Explosion mitigation technology involve the following:

- Physical and chemical properties of the inhibitor;
- Minimum required airborne inhibitor powder concentration;
- Particle size of the inhibitor;
- Process unit volume to be protected;
- Inhibitor injection technology selection;
- Dispersion of inhibitor powder in an industrial environment;
- Maximum delay for activation of the system;
- Detection & activation systems;
- Minimum duration of the mitigating action;
- Influence of meteorological conditions.

The efficiency of the final design of the VCE mitigation system was tested and confirmed on a very large scale in Vapour Cloud Explosion tests in California (US) in September 2016. A first industrial implementation of the mitigation system is foreseen in 2019-2020 as part of new cracker units in Daesan (South-Korea) and in Port Arthur (United States). The implementation of this technology allows to better protect against the occurrence of one of the most feared risks in oil & gas industry.

*Keywords: Vapour Cloud Explosion, explosion mitigation, alkali carbonate, inhibitor*

## 1. Introduction

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 “Vapour Cloud Explosions” (VCE). An example of the devastating effects of a Vapour Cloud Explosion is shown in Figure 1. According to Marsh (Marsh, 2016) explosions account for the greatest frequency of losses in the energy sector. These explosions are primarily Vapour Cloud Explosions.

A new technology was developed for mitigation of Vapour Cloud Explosions at an industrial scale. The technology is based on chemical inhibition using dry powders of carbonates or bicarbonates of sodium or potassium as flame inhibitor species. A description of the development of the technology and the final design of the system is given in this paper. Several aspects related to the use of the technology in an industrial environment are addressed. The efficiency of the final design of the mitigation system was tested on a very large scale in Vapour Cloud Explosion tests in California (US) in September 2016.

A first implementation of the mitigation system in TOTAL is foreseen in the near future as part of a new cracker units in South-Korea and the United States.

In the development of an industrial implementation of a system for chemical inhibition of Vapour Cloud Explosions, the following aspects need to be considered:

1. Physical and chemical properties of the inhibitor;
2. Minimum required airborne inhibitor powder concentration;
3. Particle size of the inhibitor;
4. Process unit volume to be protected;
5. Inhibitor injection technology selection;
6. Dispersion of inhibitor powder in an industrial environment;
7. Maximum delay for activation of the system;
8. Detection & activation systems;
9. Minimum duration of the mitigating action.
10. Influence of meteorological conditions.

Each of the above aspects is discussed in the following sections. The consideration of these aspects has led to a final design for the inhibitor injection system. This final design was tested on an industrial scale.

## 2. Properties of the Inhibitor

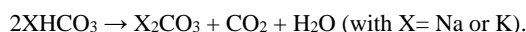
Carbonates and bicarbonates of sodium and potassium are odourless white crystalline powders with an alkaline taste. They are very well soluble in water (> 50 g/l, depending on temperature) and the density is in the range of 2.2 to 2.5 g/cm<sup>3</sup>.

Besides the chemical efficiency of the inhibitor, the following properties are important for an application of a VCE mitigating system on an industrial scale:

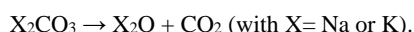
- Stability of the inhibitor over time;
- Toxicity of the inhibitor;
- Corrosive properties of the inhibitor.

### 2.1 Stability over Time

When heated above 80 to 100 °C, bicarbonates of sodium and potassium decompose according to the following reaction:



At ambient temperatures, this decomposition happens slowly. When heated further above 850 to 900°C, the carbonates of sodium and potassium decompose according to the following reaction:



NaHCO<sub>3</sub> decomposes to Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O and CO<sub>2</sub> starting at 50°C with total decomposition at 270°C. KHCO<sub>3</sub> decomposes to K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O and CO<sub>2</sub> starting at 100 – 120°C with total decomposition at 290°C. Na<sub>2</sub>CO<sub>3</sub> decomposes to Na<sub>2</sub>O and CO<sub>2</sub> at about 850°C (Linstrom et al., 2005) and K<sub>2</sub>CO<sub>3</sub> decomposes to K<sub>2</sub>O and CO<sub>2</sub> at 900°C (Linstrom et al., 2005).

### 2.2 Toxicity

The high LD<sub>50</sub> and LC<sub>50</sub> values reported in literature (see Table 1 for sodium carbonate and potassium carbonate with similar values for corresponding bicarbonates found in literature) suggest that the risk of short term exposure (< 1 minute) of people to high concentrations of dusts of sodium bicarbonate or potassium bicarbonate is limited. No serious adverse effects on human health are expected upon short term exposure of humans to (bi)carbonates of sodium or potassium upon activation of the inhibitor injection system.

Figure 1 Consequences of VCE in Pasadena (1989)



Table 1 Toxicity data for alkali metal compounds

Substance	LD <sub>50</sub>	Reference
Na <sub>2</sub> CO <sub>3</sub>	LD50 Rat oral 2800 mg/kg	Kirk-Othmer Encyclopedia of Chemical Technology (1978)
	LD50 Rat oral >5000 mg/kg (post exposure observation period 8 days)	European Chemicals Bureau; IUCLID Dataset for Sodium Carbonate, p.62 (2000 CD-ROM edition).
	LD50 Rat oral 4090 mg/kg	Sax (2004)
	LC50 Rat inhalation 2300 mg/m <sup>3</sup> /2 hr	Sax (2004)
	LD50 Rat (Wistar) oral (gavage) 2800 mg/kg bw /Sodium carbonate monohydrate/	Organization for Economic Cooperation and Development (2002)
	LC50 Mouse inhalation 1200 mg/m <sup>3</sup> /2 hr	Sax (2004)
	LD50 Mouse intraperitoneal 116.6 mg/kg (post exposure observation period 30 days)	The Merck Index (2006)
	LD50 Mouse subcutaneous 2210 mg/kg	Sax (2004)
	LC50 Guinea pig inhalation 800 mg/m <sup>3</sup> /2 hr	Sax (2004)
	LD50 New Zealand rabbit dermal >2000 mg/kg bw /Sodium carbonate monohydrate/	Organization for Economic Cooperation and Development (2002)
K <sub>2</sub> CO <sub>3</sub>	LD50 Rat oral >2000 mg/kg	European Chemicals Bureau; ESIS Database/IUCLID Dataset for Potassium Carbonate (584-08-7) p. 18 (2000 CD-ROM edition)
	LD50 Rat oral 1870 mg/kg	Sax (2004b)
	LD50 Mouse oral 2570 mg/kg	Sax (2004b)

## 2.4 Corrosive Properties

Information of corrosion by (solutions of) carbonates and bicarbonates of alkali metal compounds can be found amongst others in API581, NACE Publication 34108 (2008), Nikitina et al (1982) and Nikitina and Khvatkova (1985). Carbonates 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. Furthermore, 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. The following information related to the corrosive properties of carbonates and bicarbonates of sodium and potassium could be extracted from Craig (1995):

- No data are given on the corrosion of carbon steel by potassium carbonate solutions or sodium bicarbonate solutions.
- Stainless steels are resistant or show good corrosion properties against the effects of potassium carbonate solutions at temperatures up to boiling point.
- Most metals and alloys are resistant or show good corrosion properties against the effect of sodium bicarbonate solutions.
- Carbon steels show good resistance to sodium carbonate and are used extensively in sodium carbonate solutions up to boiling temperatures.
- Stainless steels perform very effectively in sodium carbonate service. Rates of stress corrosion cracking are similar to those in caustic solutions, but at considerably elevated temperatures.
- In laboratory tests conducted at 100% relative humidity and ambient temperature, solid sodium carbonate was very corrosive to aluminium alloy 3003. Other tests showed that aqueous solutions of sodium carbonate (1 to 10%) were corrosive to aluminium

alloy 1100. However, this corrosive action was effectively inhibited by the addition of silicates (sodium carbonate has been transported in aluminium hopper cars).

- Zinc and zinc brasses are attacked by sodium carbonate, but exhibit beneficial results from various inhibitors.

In general, no significant corrosion problems are expected in case of activation of the VCE mitigation system because of the following reasons:

- The carbonate solutions are not saturated with CO<sub>2</sub>;
- 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 has been activated;
- If necessary, hot insulation could be changed if during inspection, problem of corrosion is identified.

### 3. 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)).

A study by Wangsholm (2012) shows that the effectiveness of K<sub>2</sub>CO<sub>3</sub> drops significantly if the inhibitor concentration in the flammable mixture drops below 20 to 50 g/m<sup>3</sup>. This means that the inhibitor concentration in the area to be protected against the effects of a Vapour Cloud Explosion needs to be at least 20 g/m<sup>3</sup>. The results obtained by Wangsholm were further analysed and indicate that for stoichiometric propane/air mixtures, the explosion overpressure can be reduced with 90% when K<sub>2</sub>CO<sub>3</sub> particles with diameters between 20 and 50 µm are used with particle loadings of 15 to 55 g/m<sup>3</sup>. For rich propane/air mixtures, the inhibitor efficiency is lower and the overpressure reduction is about 75% when particles with diameters between 20 and 50 µm are used with particle loadings of 60 to 80 g/m<sup>3</sup>.

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<sup>3</sup> for KHCO<sub>3</sub> and 15 to 65 g/m<sup>3</sup> for NaHCO<sub>3</sub>.

Experiments with commercially available fire extinguishing powders (Bi-Ex, based on NaHCO<sub>3</sub> and Purple K, based on KHCO<sub>3</sub>) were conducted by Hoorelbeke (2011). The efficiency of Bi-Ex and Purple K as inhibitors was tested for lean (3.5 vol.%), stoichiometric (4 vol.%) and rich (5 vol.%) propane/air mixtures in a 20 l sphere. The results indicate that mass loadings of about 25 g/m<sup>3</sup> and 10 g/m<sup>3</sup> for respectively Bi-Ex and Purple-K are needed to reduce explosion overpressures with 75% for stoichiometric propane/air mixtures. For rich propane/air mixtures, about 50 g/m<sup>3</sup> is needed for both Bi-Ex and Purple-K to reduce explosion overpressures with 75%.

A practical application for mitigation of VCEs on an industrial scale is based on the injection of flame inhibitors in the area that needs to be protected. The inhibitor concentration will not be perfectly homogeneous in this area, independently of the technology used for injection of the inhibitor particles. The presence of areas or pockets with higher and lower than average inhibitor concentration is expected. To compensate for the presence of pockets with lower than average inhibitor concentration, a design inhibitor concentration higher than 20 g/m<sup>3</sup> needs to be specified. A multiplication factor of 5 is arbitrarily applied, resulting in a target design inhibitor concentration of 100 g/m<sup>3</sup>.

### 4. 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:

- The effectiveness of solid inhibitors depends on the size of the particles.
- 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 (i.e. lower extinguishment concentration, lower inhibitor concentration for the same decrease of burning velocity and extinction strain rate).
- 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 with typical temperature profiles and typical residence times in the flame reaction zone (burning velocity in the range of 30 to 50 cm/s). 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 application of dry powders in real fires shows that larger size particles penetrate the fire plume more easily. This means that for practical application and effective agent delivery to the burning surface, there exists the need to increase the particle size. For instance, it was found that for practical applications a water droplet size of 100 to 200 µm is more effective than 20 µm droplets which were found effective in laboratory configurations. However, for the use of inhibitors as mitigating agents for Vapour Cloud Explosions, the latter statement is not relevant as the inhibiting powder is injected into the flammable vapour cloud prior to its ignition.

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) as explained in Table 2 that includes some reported optimum particle diameters for alkali metal compounds.

Table 2 Optimum particle size for flame inhibition

Substance	Flame Type	Optimum Particle diameter ( $\mu\text{m}$ )	Reference
$\text{NaHCO}_3$	Laminar propane/air counter flow non-premixed flame	< 38	Fleming et al (1998)
	Heptane pool fire	< 16	Ewing et al (1989b)
	Laminar non-premixed counter flow methane/air-flame	0-10	Chelliah et al (2002)
	Counter flow diffusion methane flame	< 20	Linteris et al (2001) Wanigarathne et al (2000)
	Counter flow diffusion flame, liquid heptane	0 – 10 (non monotonic behaviour)	Hamins et al (1994) Trees et al (1997)
	Simulations	< 17 (for flame velocity of 50 cm/s) < 3 (for flame velocity of 300 cm/s)	Mitani (1983)
	Methane/air premixed flame ( $\phi=1$ ) Acetylene/air premixed flame ( $\phi=1$ ) Hydrogen/air premixed flame ( $\phi=1$ )	16 9 3	Dounia et al. (2017)
	Premixed methane/air flame ( $\phi=1.2$ )	12 - 28 $\mu\text{m}$	Iya et al. (1975)
	Turbulent flame	< 20	Hoorelbeke (2011)
	$\text{KHCO}_3$	Laminar propane/air counter flow non-premixed flame	< 38
Heptane pool fire		< 22	Ewing et al (1989b)
Turbulent flame		< 20	Hoorelbeke (2011)
$\text{Na}_2\text{CO}_3$ $\text{K}_2\text{CO}_3$	Turbulent flame	< 20	Hoorelbeke (2011)

## 5. Process Unit Volume to be protected

A number of Quantitative Risk Assessment studies for refineries and petrochemical sites were performed by Roosendans (2018). In these QRA studies, the risk of Vapour Cloud Explosions in congested process units was analysed. The median of the surface area of the 430 studied congested process areas is about 1.800  $\text{m}^2$  and the average surface area is about 2.900  $\text{m}^2$ . 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 Vapour Cloud Explosions (Roosendans, 2018). Considering a congested surface of 1.800  $\text{m}^2$  and a flammable cloud height of 3 m, a volume of about 5.000  $\text{m}^3$  needs to be protected. For propane as flammable substance, a flammable propane/air with a size of 5.000  $\text{m}^3$  corresponds to 200 to 870 kg of propane (depending on the concentration of propane in the flammable cloud).

## 6. Inhibitor Injection Technology Selection

A feasibility study was subcontracted (Technip, 2011) to identify available technologies suitable for mitigation of Vapour Cloud Explosions by injection of solid inhibitor particles. The selection of the technology is based on the following requirements:

- Possibility to use the technology in a highly congested area;
- Compatibility of the selected technology with existing flammable gas detection systems;
- The footprint and size of the system components must be compatible with available space in process units (also for retrofitting purposes);
- The throw length (maximum horizontal distance reached) must be large enough to overcome a long range and wide area;
- Possibility to support a continuous or multi shot discharge;
- High speed of activation of the system (the activation time must be compatible with the speed of development of a Vapour Cloud Explosion);
- Limited number of skids;
- Easy maintenance and testing;
- Limited use of external utility systems;
- Reliable technology.

The technology 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 in more detail:

- 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 (injection of water in the exhaust of jet turbines);

A study was performed on the strengths and weaknesses of each of the technologies described above upon use for mitigation of Vapour Cloud Explosions by injection of solid inhibitor particles. Finally, the technology that was retained is based on a large capacity dry chemical powder injection skid. In this technology, the dry powder is stored at atmospheric pressure in a drum. Upon activation of the system, the drum is pressurized at 10 to 12 barg (depending on the supplier) by nitrogen stored in cylinders at 200 barg. The actuation of the valve on the nitrogen cylinder to pressurize the powder drum is pneumatic. The nitrogen is also used for fluidization of the powder. When the pressure in the drum reaches the required level, a valve is opened to discharge the powder at about 10 barg at the discharge nozzle. This technology was preferred over the other available technologies, primarily because of the following reasons:

- High speed of activation;
- Possibility for multi shot or continuous discharge of the powder;
- Ease of installation inside a congested process unit;
- Limited footprint occupied by the skid;
- Optimum volume covered by nozzle and per skid.

The selected technology allows easy maintenance. The skid is made of a single piece equipment mounted on an iron cage that allows easy transport to a workshop for necessary maintenance activities. A periodic inspection of the powder drum (every 40 months) and hydraulic testing after 10 years of service is proposed following feedback from suppliers. The quality of the powder is warranted for a duration of 5 years. However, the powder could be replaced every 40 months during inspection of the powder drum.

## 7. Dispersion of Inhibitor Powder in an Industrial Environment

A number of large scale dispersion tests were performed to study the dispersion behaviour of inhibitor powder clouds. The inhibitor powder injection system used during the tests is described in the previous section. 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 measurements of the inhibitor powder concentration were performed using optical probes. The main components of the probe are a LED and a photodiode. These two diodes are placed on opposing sides on a fork facing each other. When the path between them is obstructed or partially covered, the light received by the photodiode decreases, and the magnitude of obstruction can be recorded. In this way the powder concentration can be measured. By calibrating the probes with known concentrations of the same powder as used in the experiments, a correlation between the magnitude of obstruction and powder concentration is obtained.

The experimental set-up in the 3 test campaigns included of 2 inhibitor injection skids located at opposite sides of the monitored area. During the tests, the wind direction and wind speed were recorded. Video recordings are also available. Some pictures taken during the 2<sup>nd</sup> test campaign are given in Figure 2. 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;

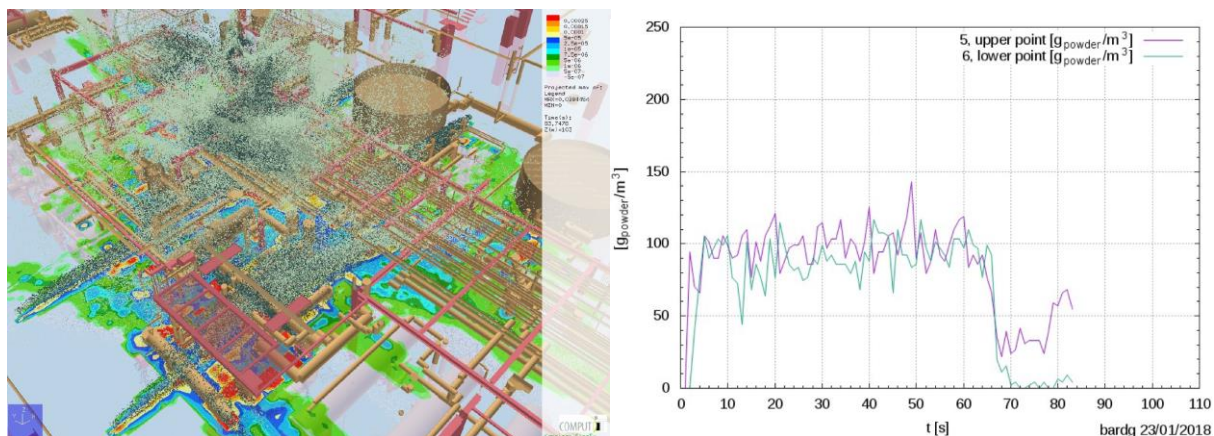
- The following design characteristics of the inhibitor injection skids were confirmed during the dispersion test campaigns:
  - ✓ Continuous and constant powder flow rate of 2 to 2.5 kg/s per skid during 300 s;
  - ✓ One nozzle per skid;
  - ✓ Bore diameter of the nozzle: 10-11 mm;
  - ✓ Quantity of powder per skid to protect a congested volume of 1.250 m<sup>3</sup>: 600 to 750 kg of powder.
- The pressure and nitrogen flow rate should be kept constant to guarantee a constant flow rate of powder along the injection period;
- The multi shot sequence for injection of inhibitor powder is no longer investigated and is no longer considered for the final design of the injection technology (because of failure to guarantee a constant concentration in the monitored area using this approach).

Figure 2 Pictures taken during 2<sup>nd</sup> test campaign



The dispersion experiments of the 3<sup>rd</sup> 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. An illustration of the results is shown in Figure 3, showing the volume fraction of powder with visualization of the particle spray (left figure) and the predicted evolution in time of the powder concentration (g/m<sup>3</sup>) in powder measurement probe 5 and 6 (figure on right).

Figure 3 Illustration of powder dispersion simulations using a 3D code (left) and predicted powder concentrations (right)



The experimental data show a lot of noise and average values are not easy to extract. 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.

## 8. Maximum Delay for Activation of the System

Studies in literature suggest that in most cases the build-up of a flammable vapour cloud with VCE potential takes some time (Wiekema (1984), Strehlow (1973), Lenoir and Davenport (1992)). If ignition of the flammable vapour cloud occurs instantaneously or a very short time after the start of the leak, then the resulting phenomenon will likely be a jet fire or a fireball. On the other hand, upon long duration releases of flammable gases/vapours, 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, even if there is an appreciable delay before ignition. The design of the proposed industrial system of chemical inhibition of Vapour Cloud Explosions is such that the time required to have the required airborne concentration of inhibitor in place is about 30 to 60 seconds (see Figure 4). This time delay for deployment of the system is fully compatible with the time required for build-up of most flammable vapour clouds with VCE potential.

## 9. Detection & 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;
- 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 Vapour Cloud Explosion. Therefore, only the pre-ignition strategy is feasible. The latter was confirmed in a detailed study by the company GexCon (GexCon, 2012d).

## 10. 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 activation of Emergency Shutdown Valves (ESD), activation of water curtains and water deluge systems, evacuation of the site and mobilization of emergency response team. 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.

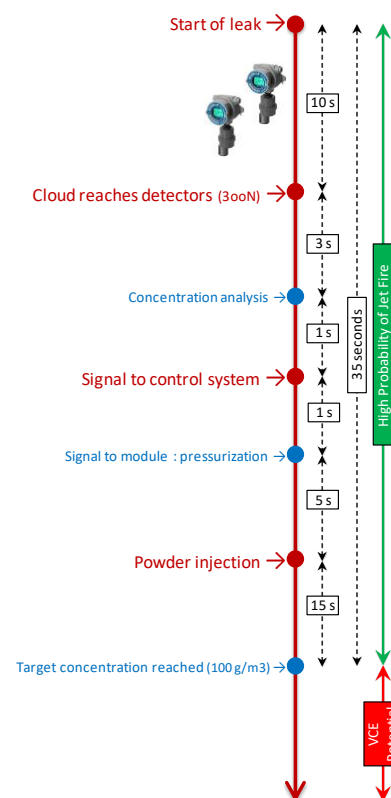
## 11. Influence of Meteorological Conditions

The relationship between weather conditions, source term and development of a flammable vapour cloud was studied by Atkinson et al. (2017). In 50 percent of the 24 studied cases, the vapour cloud developed in documented nil/low wind conditions. In another 21% of the studied cases (5/24) the dispersion pattern suggested a nil/low wind condition but no records are available to prove this. In the remaining cases (7/24) the vapour cloud dispersed in light or moderate winds and correspond to large releases that were almost ignited immediately. In a “nil/low wind” condition, the wind is so weak close to the ground that it only strips away a small proportion of the vapour accumulating around the source. Rather than being picked up and moved downwind, the vapour flow in these case is gravity driven spreading out in all directions and/or following any downward slopes around the source. The flammable zone reached more than 500 m from the source in several cases. Rather than being catastrophic failures of large pipes or vessels that produce a significant vapour cloud in any weather condition, many of the most serious Vapour Cloud Explosions were relatively small but sustained leaks, where vapour accumulated near the source and built up a substantial cloud over tens of minutes. The study by Atkinson et al. (2017) also revealed that no precipitation was recorded in any of the 24 studied cases, possibly because most precipitation is accompanied with presence of wind. However, no specific research could be found on the impact of precipitation on the occurrence of Vapour Cloud Explosions and this remains a topic for further investigation.

## 12. Final Design for Inhibitor Injection System

Based on the results of the different test campaigns to study the dispersion behaviour of inhibitor powder, a final design of an inhibitor injection system was developed. A schematic drawing of the system is given in Figure 5. The design allows a manual activation as well as an automated activation of the system (based on a confirmed gas detection). The final design has the following characteristics:

Figure 4 Delay for deployment VCE mitigation system





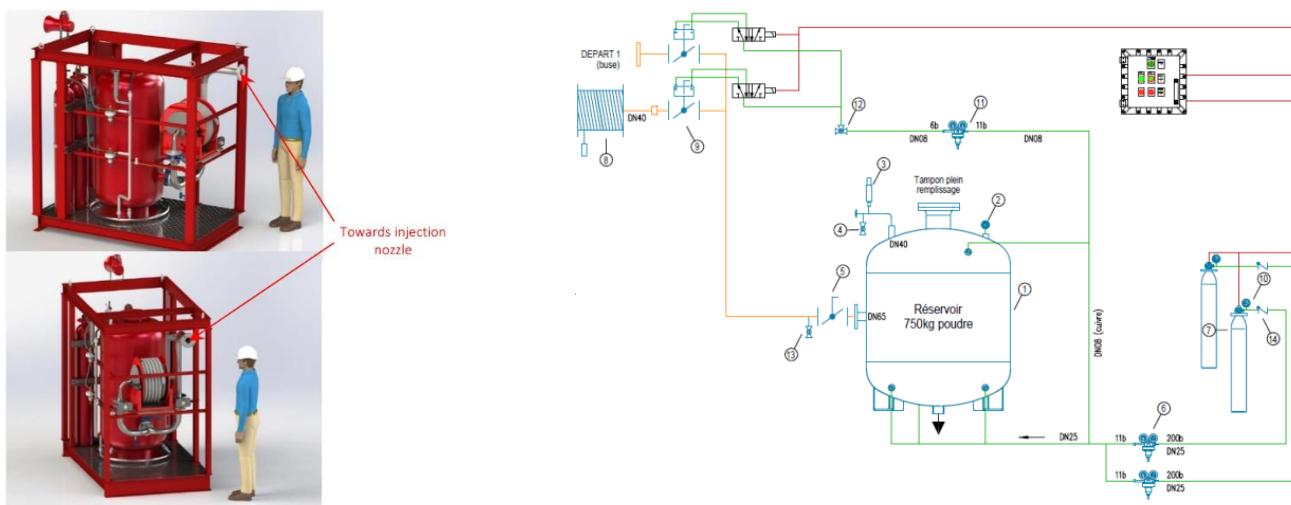
- A volume of 5.000 m<sup>3</sup> (1250 m<sup>2</sup> x 4 m) can be protected by 4 modules;
- The modules are autonomous and powered by nitrogen pressure. The nitrogen bottles are connected via a pressure control valve to the powder drum of the module. The operating pressure of the powder drum is 16 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<sup>3</sup> 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<sup>3</sup>. 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 (no external utilities needed for activation and operation of the skids, except the triggering signal) allow easy retrofitting of existing sites. The modular design of the system and the limited footprint of the individual autonomous injection skids (no external utilities needed for activation and operation of the skids, except the triggering signal) allow easy retrofitting of existing sites.

### 13. Inspection, Testing & Maintenance

A general inspection of the inhibitor injection modules every 40 months is recommended by the suppliers. Hydraulic testing is recommended after 10 years of service. For reliable and adequate operation, the inhibitor injection modules need to be subjected to periodic testing. A detailed test protocol needs to be developed with the supplier of the modules. The test protocol needs to include detailed instructions for execution of the protocol, specification of the test frequency, specification of specific hardware needed to perform the test etc. Testing of the inhibitor injection modules may be performed without pressurization of the powder drum using a modified test protocol. The inhibitor injection modules were designed for easy maintenance and mobility. The modules are composed of a single pressure vessel (powder drum) installed in a steel frame allowing easy transport to a dedicated workshop for maintenance activities. Maintenance activities include amongst others the flushing of hoses, pipes and nozzles with nitrogen or air to avoid accumulation of powder and clogging. The quality of the inhibitor powder is generally guaranteed by the supplier for a duration of 5 years. However, preventive replacement of the inhibitor powder can be envisaged every 40 months during the general inspection of the modules.

Figure 5 Drawing of final design of inhibitor injection skid



Nr	Description	Nr	Description	Nr	Description
1	Powder drum with capacity of 750 kg	6	Pressure regulator 200 – 11 bar	10	Pressure gauge (0-250 bar)
2	Pressure gauge (0 – 16 bar)	7	Nitrogen bottle (50 l, 200 bar)	11	Pressure regulator 11 – 6 bar
3	Safety valve	8	Hose rail	12	3 way valve
4	Purge valve	9	Pneumatic butterfly valve	13	Flush valve
5	Butterfly valve				

## 14. Utilities

Each inhibitor injection module is pressurized using at least two 50 l bottles of nitrogen at 300 barg. The use of multiple nitrogen bottles is needed to assure a constant pressure in the powder drum during the entire powder discharge time. Nitrogen is preferred over carbon dioxide because of its reduced sensitivity to temperature variations. The control system of the inhibitor injection modules and gas detection system are powered by a set of 2 existing feeders from 2 independent 230 VAC distribution panels in an instrument technical room (ITR). These 2 distribution panels are powered by separate feeders: one UPS feeder and one non UPS feeder.

## 15. HSE Aspects related to the Use of the Inhibitor Injection System

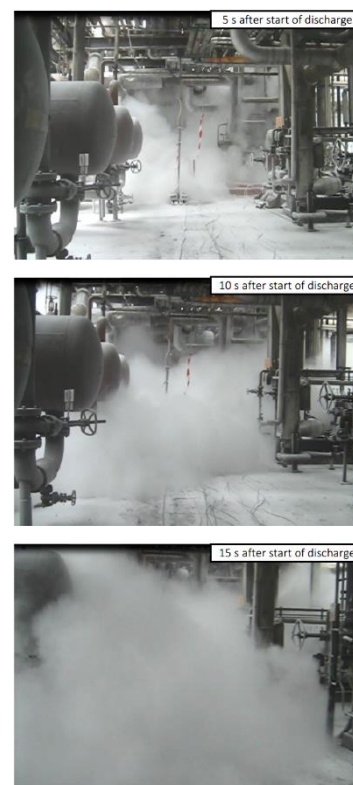
### 15.1 Risks to People

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.

The latter was observed during the powder dispersion tests at the Carling site. Visibility in or near the inhibitor powder cloud was limited, as shown in the sequence of pictures in Figure 6 showing the evolution and visibility in the inhibitor powder cloud. The pictures are taken with a 5 second time interval from the start of the discharge of the inhibiting powder. People present during the powder dispersion test felt mild irritation of skin, eyes and airways.

As a result of these risks, the timely evacuation of the process unit in which the inhibiting powder is to be injected is mandatory. The preferred evacuation strategy is to enable and facilitate evacuation of the unit before the start of the powder discharge. Depending on the location of the operator, a minimum time of 15 seconds is required to escape to a safe location. An alarm system (visual and audible) is required to warn operators before discharging the powder. To avoid spurious activation of the inhibitor injection modules, the alarm of an imminent powder discharge can be based on a voting logic (e.g. 20% of LFL reached by at least 2 gas detectors, 2ooN).

Figure 6 Visibility in powder cloud



### 15.2 Risks to Environment

Upon activation of the inhibitor injection modules, inhibitor powder will be dispersed in the process unit. The following situations are possible:

- Intentional activation of the inhibitor injection modules upon confirmed flammable gas detection without ignition of the flammable gas;
- Intentional activation of the inhibitor injection modules upon confirmed flammable gas detection with ignition of the flammable gas (and mitigation of the VCE by the inhibiting powder);
- Spurious activation of the inhibitor injection modules.

In all the above cases, 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 (since an ignited flammable cloud is in many cases followed by secondary fires). After activation of the inhibitor injection modules, the majority of the released inhibiting powder must be mechanically removed (by scooping or by using aspirators) before flushing the residual powder with large amounts of water. 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. To limit the impact of this effluent with high pH on the waste water treatment, the following precautions must be taken:

- Remove all solid inhibiting powder as much as possible using mechanical devices (scooping, using aspirators etc.);
- Isolate the water drain system of the process unit in which the inhibiting powder is released and pump the effluent from this system in a dedicated tank;
- Send the remaining effluent to the emergency retention pit of the waste water treatment plant (if necessary after neutralization with acid to lower the pH) for specific treatment.

### 15.3 Risks to Assets and Process

The inhibitor is a very fine powder (particles with diameters in the order of 5 to 100 micron). In case of discharge into a process unit, this fine powder could enter sensitive equipment and instrumentation and cause damage. Experts of TOTAL were consulted to assess the impact of fine carbonate and/or bicarbonate particles entering sensitive equipment and instrumentation. Aspects such as the impact on rotating machines, the impact on electrical installations, corrosion by carbonates and bicarbonates, the influence on instrumentation and the impact on equipment working or powered with air were discussed and assessed.

The discussion with the experts did not reveal fundamental problems related to the use of fine inhibitor powder in an industrial environment. However, some points of attention were raised:

- For rotating equipment, there is a possible ingress of fine powder particles inside the equipment so that inspection is required each time that the inhibitor injection modules are activated. The availability of spare equipment for critical items needs to be verified.
- If heated, bicarbonates decompose in the corresponding carbonate. When dissolved in water, an alkaline solution with a pH of about 12 is formed. At these high pH levels, there is a risk of carbonate cracking (form of stress corrosion cracking) on hot equipment (temperature > 40°C). To avoid carbonate cracking, the process equipment need to be rigorously cleaned and flushed after activation of the inhibitor injection modules.
- For instrumentation working with air, the air intakes need to be inspected for fouling or clogging after activation of the inhibitor injection modules. The reliability of catalytic or infrared detectors may be affected by the inhibiting powder.
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## 16. Large Scale Explosion Tests

Large scale explosion tests were conducted in September 2016 to verify the behaviour of the inhibitor injection system on an industrial scale. The tests were conducted on 15/09/2016 and on 22/09/2016 at the CHES test site of SRI International in Livermore, California. The tests were conducted as part of a sub-project in the framework of a research program (called REPSEA: “REsearch Partnership to Secure Energy for America”) initiated by the US Department of Energy following the Macondo disaster. 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. A picture of the test rig is given in Figure 7.

Figure 7 Large scale test site at the CHES test site

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. The total volume occupied by the rig is about 1.500 m<sup>3</sup>. The structure of the modules is made of rectangular steel profiles. In this structure, horizontal 2 inch pipes are added, uniformly divided over the whole height of the module. On top of this, vertical 8 inch pipes were added over the whole length of the module with variable spacing between the 8 inch pipes. The degree of congestion in the rig is very high and significantly higher than can be expected in real industrial process units.

For the explosion test, methane gas is injected via 5 injection points at different locations of the 59 m long rig until a concentration slightly above the stoichiometric concentration is reached (about 10 vol.%).

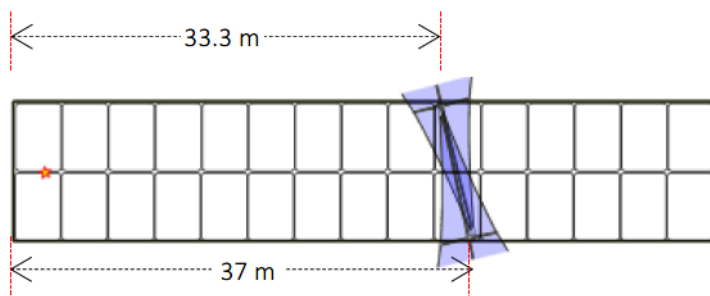


The methane gas is contained in the rig by covering the entire rig with thin sheets of plastic film. The mixing of the injected methane gas in the rig with ambient air is performed with electric fans installed inside the rig. When a homogeneous methane/air mixture is obtained in the rig, the mixture is ignited using 2 different technologies (for reasons of redundancy): using a spark and using a heated filament. The gas concentration in the rig is sampled at different locations of the rig and measured with analysers. Pressure transducers and ionization probes installed in the centre of the rig allow measuring respectively overpressures and location of the flame front. Two inhibitor injection skids were used during the test. The 2 skids are positioned upfront the rig at the side of the ignition location, at a distance of about 5 m for module 1 and at a distance of about 10 m for module 2. A scheme with the layout of the rig, injection skids and injection nozzles used in the test is given in .

### 16.1 Test 16

In Test 16, the released quantity of powder per skid was near the targeted flow rate of 1.5 kg/s per skid. The total amount of injected powder during the injection time of about 10 seconds was about 30 kg. The location of inhibitor powder injection nozzles is shown in Figure 8.

Figure 8 Location of inhibitor injection nozzles in Test 16



Most of the injected powder was dispersed in module row 10. With the volume of a module row being about  $100 \text{ m}^3$ , the average powder concentration in this module row can be estimated to be about  $300 \text{ g/m}^3$ . The ignition of the flammable methane/air mixture was followed by a strong explosion that was perceived to be a detonation. A preliminary review of the video footage confirmed the transition to a detonation near module rows 5 – 6, with a flame speed going from about  $500 \text{ m/s}$  to about  $800 \text{ m/s}$  and accompanied by a coupling of the flame front with the shock wave. This flame speed of  $800 \text{ m/s}$  is about 45% of the theoretical detonation flame speed (being  $1800 \text{ m/s}$  according to Chapman-Jouget) and this regime is qualified as a quasi-detonation. 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  $800 \text{ m/s}$  to about  $400 \text{ m/s}$ ) and this despite a relatively short injection time (about 10 seconds) and rather narrow powder cloud.
- The strong deceleration of the flame results in a decoupling of the flame front and the shock wave.

The flame speed profile recorded in Test 16 is shown in Figure 11. The damage to the rig confirms the occurrence of two quasi-detonations. The two lines of modules in the rig are separated upstream and downstream of the inhibitor powder injection area. The modules at row 15 have slid over a couple of meters. 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 relation to the first quasi-detonation: it is clear that - to get optimum performance of the inhibition technology - the inhibitor powder injection needs to be installed at the module row 5 (and not module row 10) knowing the area in which the start of the DDT was observed in Test 16 (module row 5 to 6). The latter information was included in the design of Test 17.

## 16.2 Test 17

Knowing the extent of damage to the rig in explosion Test 16 and in order to speed up the preparation of the test, the rig used to conduct explosion Test 17 was shortened to 7 module rows instead of 15 module rows in Test 16.

This smaller setup allows capturing the initial acceleration of the flame, to inject the inhibiting powder in an area before the location of DDT (in Test 16 DDT was observed at module rows 5 to 6) and to leave sufficient space downstream the powder injection zone to assess the behaviour of the flame when it exits the inhibitor loaded flammable methane/air mixture. The location of inhibitor powder injection nozzles is shown in Figure 10. The methane gas is introduced in the rig via 3 injection points. The location of the 2 inhibitor injection skids was the same as in Test 16. However, the injection nozzles were repositioned: one injection nozzle 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 shorter distance between the injection nozzles and the inhibitor injection skids allowed the use of a single flexible hose. The 2 inhibitor injection skids were activated simultaneously in Test 17. As can be seen in Figure 12, the powder cloud dispersed in about  $\frac{3}{4}$  of the rig, with high powder concentration levels in module rows 4 and 5 over the entire module height and a progressive dispersion of the powder cloud in lower parts of neighbouring modules, up to module row 2. The injected powder flow rate was close the target flow rate of  $1.5 \text{ kg/s/skid}$ . The total released amount of powder during the injection time of 33 seconds is about  $100 \text{ kg}$ . 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.

Figure 9 Location of injection skids/nozzles

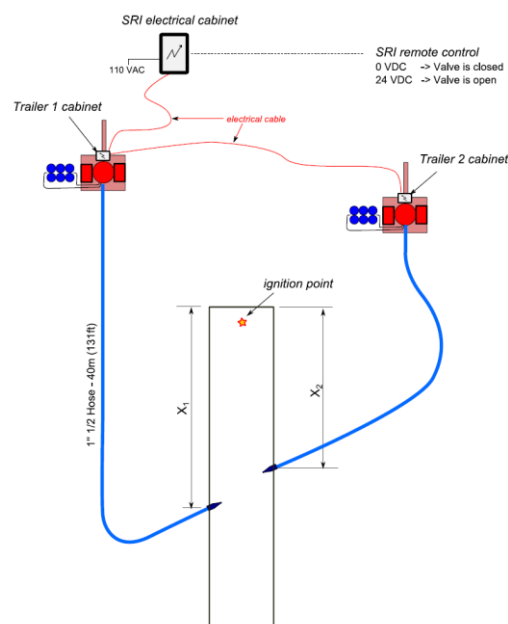
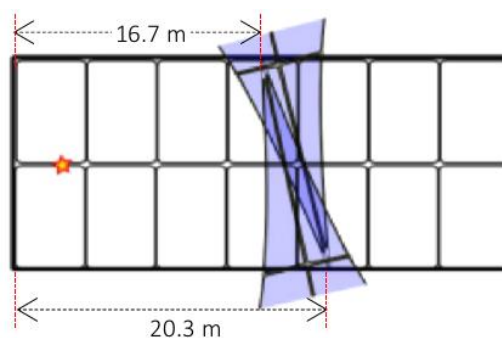


Figure 10 Location of injection nozzles in Test 17



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.

The synchronized images in Figure 13 show clearly the significant difference of combustion regime observed in Test 16 and Test 17. 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. However, the flame needs about 1 second to cross the inhibitor injection zone with an estimated speed lower than 10 m/s

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.

Figure 11 Development of flame speeds in the rig

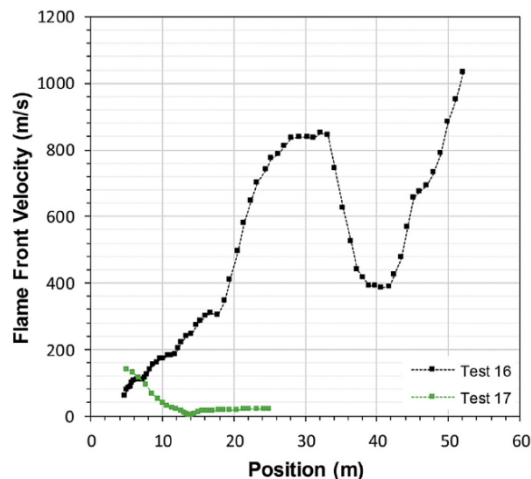


Figure 12 Dispersion of powder cloud in Test 17

The latter was confirmed by physical inspection of the rig and inhibitor injection skids. No damage to the rig and injection skids was observed, nor by thermal effects nor by overpressure effects. Inside the rig, all mixing fans are still in place and most of them intact. Some of the fans are showing superficial burning damage as a result of the passing flame front. No damage was observed to the structural elements of the rig and none of the rig modules have moved. The plastic sheeting used to cover the rig burned and melted but was not shattered as in Test 16.

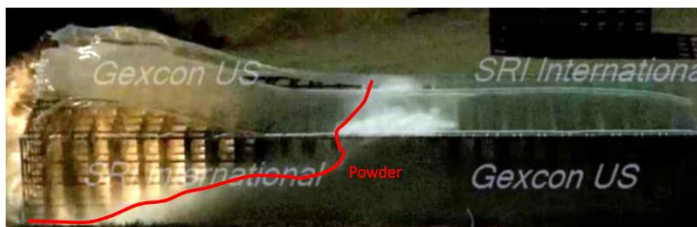
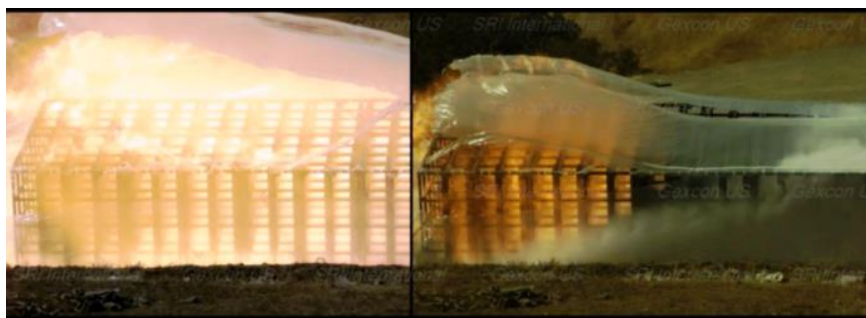


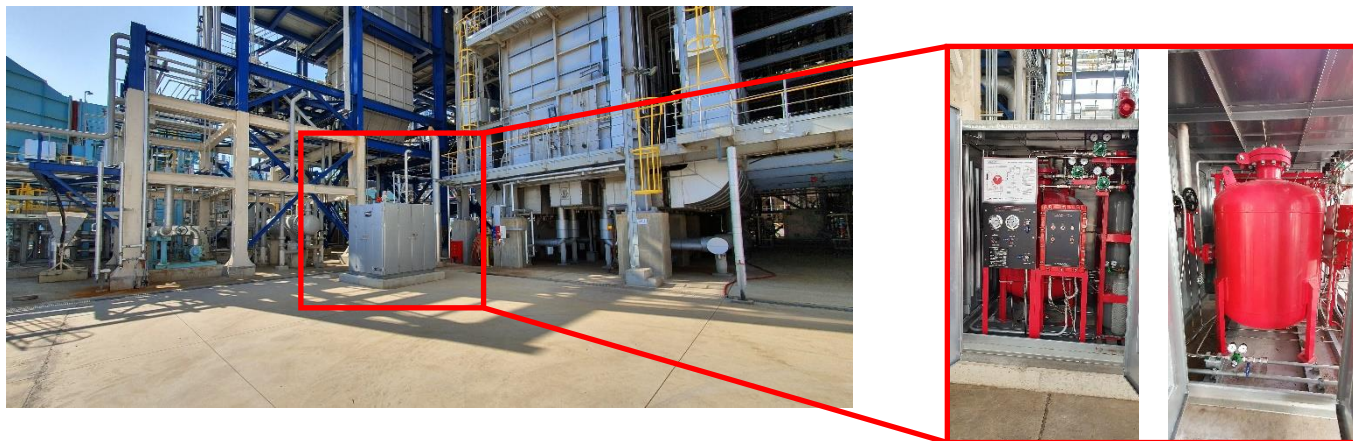
Figure 13 Comparison of Test 16 and Test 17



### 17. Industrial Implementation of the Vapour Cloud Explosion Mitigation Technology

Some projects in TOTAL have been identified in which a full implementation of the VCE mitigation technology is realized (Side cracker project in South-Korea, Side cracker project in the United States). Some pictures of the implementation in South Korea are given below.

Figure 14 Picture of one of the installed inhibitor powder injection module in a petrochemical site (South-Korea)



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