

## EXPLOSION HAZARDS IN LARGE SCALE SOLUTION PURIFICATION BY METAL DUST

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Gas and dust explosions hazards associated with purification of solutions by continuous large-scale (400m<sup>3</sup>) processing in mildly acidic environments are discussed. A case study, in which two explosions occurred in a new multimillion dollar plant, is used to illustrate the key factors for safe design.

Gas generation, flammability, potential sources of ignition, options for explosion protection and the consequences of the explosions are described with emphasis on the major problems encountered during the assessment.

Explosion, Hydrogen, Metal, Acid, Zinc, Gas evolution, Static electricity, Nitrogen purging

### INTRODUCTION

Solution purification is often a large scale continuous operation involved in the production of metals by electrochemical methods.

In the production of zinc, purification of process liquor is performed in two stages. Firstly, copper, which is an impurity present in large quantities, is precipitated at elevated temperature by the addition of a zinc slurry. The precipitated copper is then filtered and washed. The second stage of the process involves the removal of any residual copper and other impurities such as cobalt, cadmium and nickel by the addition of an antimony or arsenic reagent and zinc dust containing 1% (approx.) lead, again at an elevated temperature. The resulting primary purification (PP) and secondary purification (SP) cementates are then leached, separately, in dilute sulphuric acid to produce copper sulphate and zinc/cadmium sulphate, respectively.

It is worth pausing at this stage, to take in the scale of this form of chemical processing, with respect to the case study:-

Purification area covering approximately 10,000 m<sup>2</sup>

30 vessels ranging in size from 1 to 400 m<sup>3</sup>

Large liquid inflow/outflow, up to 550 m<sup>3</sup>.hr<sup>-1</sup>

Many vessels interconnected with no isolation

Tanks permanently open to atmosphere via overflow.

On Saturday 10th March 1990, the case in question, which had been in operation just 3 months, suffered an explosion in one of the large 400m<sup>3</sup> leach tanks. Fortunately, there were no serious injuries.

The incident occurred in a tank fitted with explosion relief. Although the tank itself did not sustain any damage, nearby windows in a series of contractor's cabins were blown in by the blast. There was no evidence of flame propagation through the vent header system.

The design 'basis of safety' for the Zn leach tanks in question, was aimed at minimising the period over which flammable hydrogen-air mixtures could be present, allied to explosion relief. High rates of extraction were provided whilst the tanks were on stand-by (ie. an air purge) and on commencement of leaching (with the vent closed) to rapidly increase the hydrogen concentration. Once above the UEL and when the gas evolution rate had decreased, the fan speed dropped to maintain the concentration outside the explosive range. At the end of the leaching period, the dual speed fans were used to 'extract at high rate' with the vent open, to allow air to flush the gas in the tanks from above the UEL to a concentration below the LEL.

It was considered, even from an initial review, that the explosion prevention/protection methods which had been employed were not sufficiently robust and, in addition to the questionable design philosophy, the size of the explosion vents had been vastly underestimated - processing in the 'old' plant had taken place without incident over many years. There was some good fortune in that the tank was still standing and nobody had been injured, but the future for the new plant did not look healthy without a change in safety strategy.

It is interesting to note that similar preventative measures (ie. avoidance of flammable atmospheres) had also been used in the Copper Sulphate area, for the upset condition of zinc being added to an acidic solution when no dissolved copper was present. Sparge pipes (used in normal operation for oxidation) provided air to dilute the evolved hydrogen below the lel.

At this point (19th March), a report was issued to the Company, which outlined the various shortfalls and presented a series of interim corrective measures, based on minimising ignition risks, whilst work began on the design of a new safety system. Investigation of the actual cause of the incident was not considered to be worthwhile, as the potential sources of ignition were numerous.

Eight days later and less than three weeks after the first explosion, a second and more violent explosion occurred blowing

the roof off one of the tanks inside the process building. A journalist reported

"...the blast caused quite a bit of damage in the immediate area and a contractor was admitted to hospital for observation while his hearing was checked.."

The following day (28th March), the Statutory authority (Department of Mines) issued the Company with a plant closure order, suspending use of the purification section, resulting in the loss of 600 tonnes per day zinc production.

### ASSESSMENT

It is fair to say that the activity at this stage of the project was frantic and certainly not helped by the Company's aim (albeit optimistic but understandable, and made publicly) to start up again by the end of the week.

#### Flammability

It is widely recognised that three components are needed before combustion can occur - a fuel, an oxidant and a source of ignition.

In this process, the fuel is present by virtue of the chemistry ie. evolution of hydrogen, resulting from the action of dilute acids on metal powders. Also, parts of the plant handles finely divided (dry) zinc, a Group A material (ie. capable of forming flammable dust clouds with air at ambient temperatures). The oxidant arises purely from residual air within the processing plant.

It is worthy of note that ignition sensitivity is very much dependent upon the concentration of the fuel-air mixture. Ignition sensitivity increases to a maximum close to stoichiometry. It is important to note also, the wide limits of flammability for hydrogen (Table 1), compared to many common solvent vapours.

Table 1. Flammability Characteristics of Hydrogen

Flammable range (in air)	: 4 - 75 % v/v <sup>1</sup>
Detonable region (in air)	: 18 - 59 % v/v <sup>1</sup>
Auto-ignition temperature	: 585 °C <sup>1</sup>
Minimum oxygen for combustion (using N <sub>2</sub> )	: 5 % v/v <sup>1</sup>
Maximum explosion pressure	: 7.4 bar.g <sup>2</sup>
Kg value	: 659 bar.m.s <sup>-1</sup> <sup>2</sup>
Minimum ignition energy	: 0.017 mJ <sup>1</sup>

Potential Ignition Sources

Potential sources of ignition are evident in all processing plant. The more general types such as naked flames, welding, lightning, smoking etc. which are (or should be) controlled in any hazardous area, are not considered here. However, the more easily recognisable inherent sources (including some which are less obvious), which are specific to the operation of the plant and the process chemicals, are listed below.

Electrical equipment should be selected on the basis of an area classification exercise. In this instance, there were agitator motors, pH probes, screw feeders, fans etc. all of which needed to be considered. In addition to the above, the possibility of hydrogen seepage to other sections of the plant via cable trays, conduit, etc. had to be taken into account when specifying suitable apparatus.

Mechanical friction can occur, leading to overheating, from malfunction of agitator blades or shafts, or from failure of an agitator bearing, for example. Also, ingress of tramp metal is a source of risk with powered devices such as mills, screw feeders etc. Ignition probability depends on the auto-ignition temperature (AIT) of the mixture and the degree and extent of overheating. In this case study, the level of frictional heating to produce 'hot spots' above 580°C would be considerable but this doesn't detract from the need to take precautionary measures against binding friction.

Mechanical impact sparks can take the form of 'low energy' types (eg. steel on steel, steel on stone etc.) or the more energetic form involving flint type materials or the Thermite reaction. The latter can arise from glancing impacts involving metals such as aluminium, titanium, magnesium and zirconium (or their alloys) in the presence of 'oxygen donors' like rust. Unlike steel/concrete sparks which are low in temperature, thermite sparks are 'white hot' and are attributed to the highly exothermic reaction



It is considered that both types of spark are capable of igniting hydrogen-air mixtures and may have arisen in this situation, simply from insecurely fastened fittings, or during sampling operations - a number of the tanks were fabricated from concrete, although normally internally lined with an elastomer coating.

The incendivity of a spark is dependent upon its ability to transfer heat to the surrounding flammable atmosphere and therefore depends on temperature, size, residence time etc. Also, the physical as well as chemical make-up of the

atmosphere is important. For example, the turbulence may be such that heat transfer from impact sparks is insufficient to cause ignition. However if the airflow, say through a mill, is interrupted, perhaps momentarily, and the level of turbulence decreases, it may then be possible for sufficient energy to be transferred from the hot particle to the flammable atmosphere and initiate an explosion. Tests to evaluate the incendivity of friction sparks are, therefore, normally conducted at near quiescent conditions.

Static electricity ignition hazards arise from an accumulation of electrostatic charge on

- metal plant, items and fittings
- plant personnel
- insulating plastics
- liquids and powders
- particulates in air (mist/spray, dust).

If plant items are electrically conducting AND securely bonded to earth, hazardous potentials will not arise. The earthing of isolated metal is the first and most important step in eliminating electrostatic hazards.

In this case study, electrostatic charging could arise from the flow of particulates in vent pipework, or externally due to steam leak impingement or by some other form of frictional contact such as rubbing a plastic dip-can with a cloth during cleaning. There was also the possibility of zinc powder accumulating in non-conducting polymeric ducting, thereby forming an isolated conductor - this can be a serious problem in pneumatic transfer operations involving fine metal powders.

It is sufficient to say that there are numerous sources of electrostatic charge generation and hydrogen is highly sensitive to this form of ignition.

Chemical reactions in certain cases, can generate sufficient heat to ignite flammable atmospheres. In the Purification Plant, a number of substances were known to be capable of exothermic activity when damp (with water or more especially dilute acid). This pyrophoric behaviour is characteristic of many fine metal powders and is enhanced by

- a decrease in particle size
- an increase in temperature
- availability of occluded air (oxygen)

- a reduced pH level
- an increase in thickness (of residue).

Although normally, the process metals were in the form of a slurry, the possibility of residues becoming lodged on vessel walls, agitator shafts, dip-pipes, sampling elements etc., and drying out, and the subsequent risk of ignition was not insignificant.

Despite the high AIT of hydrogen-air, this was a serious and inherent source of ignition.

Radio frequency sparks are not always recognised as a potential source of ignition, but electromagnetic waves produced by radio frequency transmitters can induce electric currents in any metal structure on which they impinge. The efficiency of the structure, which adventitiously acts as an aerial, and hence the magnitude of the induced current, depends on the shape, orientation and size relative to the wavelength of the transmitted signal and the strength of the electromagnetic field. A spark can occur when parts of the structure, which are normally in contact, break or separate momentarily, if the induced voltage and current at the break point are sufficiently large.

#### Explosion Prevention Methods

Operating below the LEL is impractical at hydrogen evolution rates of  $2500 \text{ m}^3 \cdot \text{hr}^{-1}$ . Taking 25% lel as the maximum allowable concentration, this would require a volumetric flow rate for dilution air in the region of  $70 \text{ m}^3 \cdot \text{s}^{-1}$  between two tanks.

Operating above the UEL is rarely acceptable unless combined with an inert gas purge to ensure that the gas composition does not enter the flammable region. Figure 1 shows a flammability diagram for hydrogen-oxygen-nitrogen, indicating the boundaries of the flammable envelope.

Elimination of potential ignition sources can be, and indeed is, used in many processes handling flammable solvents, following a detailed (and expert) assessment. However, in the case of sensitive gas mixtures such as this, it is not good practice.

Reduction of oxygen is the only remaining preventative measure that can be employed with sufficient integrity to ensure safety under such rigorous conditions.

### Explosion Protection Methods

Containment in the example of the case study, was not feasible due to the lack of pressure strength of the vessels. Added to this there was the risk of pressure piling and detonation between interconnected vessels.

In essence, this method would require the replacement of all vessels, as a minimum, which of course was inconceivable at this stage.

Venting was employed on two of the tanks, but as stated, was insufficient in size. With many vessels being interconnected however, there was still the problem of flame transmission, leading to pressure piling or even detonation.

After ignition of a hydrogen-air mixture, run up to detonation can occur within 2 metres in 0.3 metre diameter pipework. (Detonation pressures can be 20 to 30 times greater than the measured maximum explosion pressure).

Explosion suppression was not practical in this size of plant because of the rapid rate of combustion (and pressure rise) and the required 'throw' (4-5 m) of the suppressing chemicals to extinguish the fire-ball.

The design basis which now emerged (with hydrogen there rarely is more than one option) was to utilise the main nitrogen supply from an EXISTING air separation plant, via a common inlet and vent header system - this to be supplied to ALL tanks in which hydrogen could be present.

In addition to the two SP and four copper sulphate tanks in which a risk of explosion was originally perceived, MORE THAN 25 vessels were identified as having propensity for hydrogen generation.

By this time, problems were beginning to mount simply due to the scale and the urgency of the operation.

Large scale filtration was essential to the purification process but this resulted in large quantities of water (some containing Zn residue) being washed to a sealed drainage system - the possibility of hydrogen generation and pyrophoric residues had to be dealt with. Also, quite severe stresses were now being exerted on GRP tank nozzles by the additional pipework, giving rise to the possibility of cracks and poor sealing of tanks. Similarly, agitator shafts now had to be sealed, since they too were a source of hydrogen egress and were situated directly beneath the gear-boxes.

Much of the pipework had to be rearranged in order to ensure that the vessels were fully purged of air. This required locating the inlet and outlet header pipework, on the

top of each tank, as far away as possible, to ensure an efficient 'sweep' of the tank space (see figure 2). Procedures also needed to be established for taking tanks on and off stream, giving the problem of the need to purge with pure nitrogen, since most of the time hydrogen, generated from the purification process, was contaminating the main nitrogen supply.

### DESIGN BASIS

All vessels, twenty-six tanks in all, were to operate under 1 - 20 mbar.g pressure, with restriction orifices (to balance the tank pressures and rated on the individual pump-flows) being used to provide 5 mbar.g nitrogen under zero inflow/outflow conditions. (A schematic showing one tank is shown in figure 3).

The aim of the nitrogen header was to provide a high integrity supply of inert gas (more correctly oxygen-free gas) to maintain the tank pressures, whilst allowing for inter-breathing between the vessels. In addition, the nitrogen supply had to maintain a purge of the vent stack to prevent back diffusion of air into the system, in the event of a low pressure condition. Figure 4 shows the effect of increasing the concentration of air (oxygen) from various levels outside the flammable region - increasing air at constant pressure would result in sensitive and explosive atmospheres.

Examples of the instrumentation associated with the operation of the mainstream nitrogen supply header are as follows:

- Low pressure detection of nitrogen supply
- Continuous monitoring of oxygen in the supply
- Pressure control of mainstream nitrogen
- Pressure differential to detect reverse flow
- Lute seal alarms on tanks and vent stack, etc. etc.

In the event of a malfunction with the mainstream inert gas supply, the basis behind the instrumentation was to stop tank inflow and outflow, isolate the supply and maintain tank pressures with secondary nitrogen.

The secondary (high pressure) nitrogen supply from an independently supplied liquid N<sub>2</sub> supply, also provided back-up to the vent header, again activated by hard-wire trips under a variety of fault conditions. Overpressure protection was afforded by lute seals.

Pressure equalisation was achieved by restriction orifices since they were considered to be more reliable than control



valves, plus, there was the advantage that they could be fabricated on site without the worry of lengthy delays in procurement.

It must be said that the speed at which the design took shape (literally) was quite astonishing, with engineers and tradesmen of all disciplines working a 24 hour shift.

Modifications to the Copper Sulphate section of the plant were taking place in parallel to improvements in the Zn leach area, which posed new and additional problems, basically because some of the plant was open to atmosphere.

Unfortunately, the relatively simple task of adding these vessels to the new inerting system was not going to be possible here, without major alterations to the plant (eg. enclosing the large screw feeders which carried slurry from the repulp tanks).

It is rare that avoidance of flammable atmospheres by ventilation is chosen as a basis of safety inside vessels but in this processing area, this was the best option. Since air sparging was a necessary part of the process, the design centred around maintaining hydrogen concentrations at less than 25% l<sub>el</sub> in enclosed vessels and by providing extraction over open-topped plant (eg. screw conveyors).

The integrity of this method relies on knowing the MAXIMUM gas generation rate under all conceivable operations.

Initial data, which was used for calculation of the original design ventilation requirements of 1000 m<sup>3</sup>.hr<sup>-1</sup> air, (between four tanks) suggested a maximum hydrogen evolution rate of 4 m<sup>3</sup>.hr<sup>-1</sup> per tank.

In chemical processing, there is always a range of operating variables. Temperatures, pressures, concentrations, addition times, feed rates etc. all vary from one batch to the next and to different extents. This is inevitable and is the reason for considering such effects as part of the hazard assessment - this provides for a safe envelope of operating conditions. From an extensive HAZOP exercise and based on previous experience, it became apparent that the quoted values may be higher, but by how much?

A series of experiments was performed to quantify the extent of gas evolution, taking into account

- a) a wide variety of different samples
- b) multiple experiments for reliability
- c) worst case solids loading (and any recycling)
- d) worst case acidity

- e) process abnormalities (eg. spillage of zinc solution into bunded areas, which were emptied back into repulp tanks ie. high Zn content).

The final design of the ventilation system was based on a maximum gas generation rate value (which included a safety factor of two) of  $45 \text{ m}^3 \cdot \text{hr}^{-1}$  per tank.

It is now clear why there was a second explosion in a part of the plant which was unprotected.

Throughout this period of intense activity, there were also 'rumblings' occurring which were extraneous to the 'engineering' work, from the general public, the Department of Mines, the workforce and senior management.

Emotions were running high over this difficult period as one might expect. The Company was (and still is) the biggest single industrial enterprise and longest established major employer in the area. Hence, the threat of losing their livelihood for many people was very real. On the other hand, there were workers who were not sure whether it was safe to return to work at all and literally feared for their lives. This, of course, is a fairly common reaction to a major incident, but at the time added to the pressures on those attempting to build a system which would guarantee the safety required.]

On 20th April, 23 days after the Department of Mines had issued the closure order, process liquor was re-introduced into the new plant.

Attention was then turned to dry zinc (dust) handling. Again this was an area which had been overlooked in terms of explosion hazards. Up to the slurring stage, the explosion hazard in this section of plant, which incorporated IBC's, hoppers, bucket elevators etc. resulted from ignition of airborne dust.

Zinc is an St1 powder and carries a UN 4.3 classification for transport purposes, which identifies the material as dangerous when wet. Hence the opportunity for pyrophoric activity existed here also. In fact, many of the potential ignition sources mentioned previously were evident but the ignition risk (probability) was much lower. However, zinc fires were known to occur with regularity.

Safety at this stage was to be based on explosion relief. In addition, isolation measures were introduced (eg. removal of a flight from a screw conveyor to provide a material choke) to prevent flame propagation in the event of an explosion. Externally, precautions centred around dealing with both dust accumulations, by good housekeeping, and damp /moist residues.

### CONCLUSIONS

It is clear that there was a severe underestimation of the extent of hydrogen formation, in the original (3 months old) design.

There was lack of recognition of the fact that hydrogen is extremely sensitive to ignition. The minimum spark ignition energy of stoichiometric hydrogen-air is an order of magnitude lower than most common solvent vapours and more than two orders of magnitude lower than a spark which is detectable by touch.

There were considerable problems throughout the project:

- Plant personnel and contractors were under severe pressure to start-up.
- Initially, unrealistic start-up schedules were given by senior management.
- Production losses were running high and had the old Purification Plant not been operational and therefore able to support production over this period, the incident may well have been fatal to the business.
- Certification of the safety system and indeed permission to start up, was needed but from whom - the safety engineering contractor, the Department of Mines or senior management ?

Not least of the problems was rationalising proven engineering design concepts and practices versus giving the customer satisfaction.

Here was a situation, which if not for good fortune, could have had disastrous consequences not only for the Company, in terms of loss of a major part of it's business, but also for the local community which depended on the success of the enterprise.

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Figure 1. Flammability Diagram for Hydrogen (1.0 bar.a & 273K) <sup>1</sup>

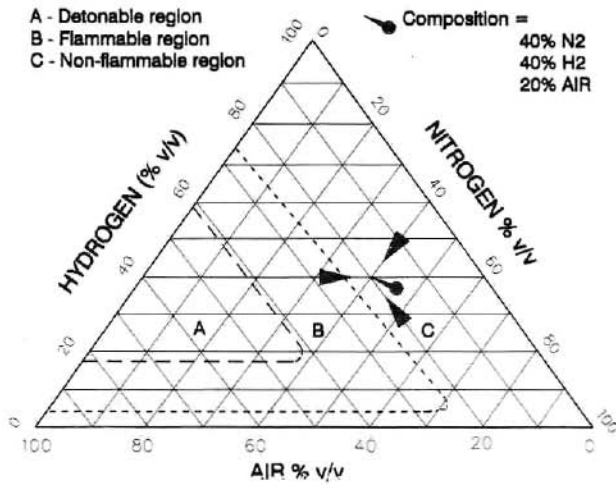


Figure 2. Tank Ullage Purging - Arrangement of Nozzles

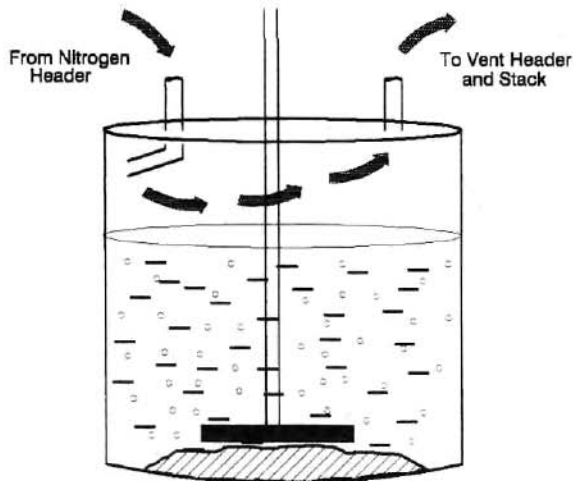


Figure 3. Schematic of Nitrogen and Vent Headers

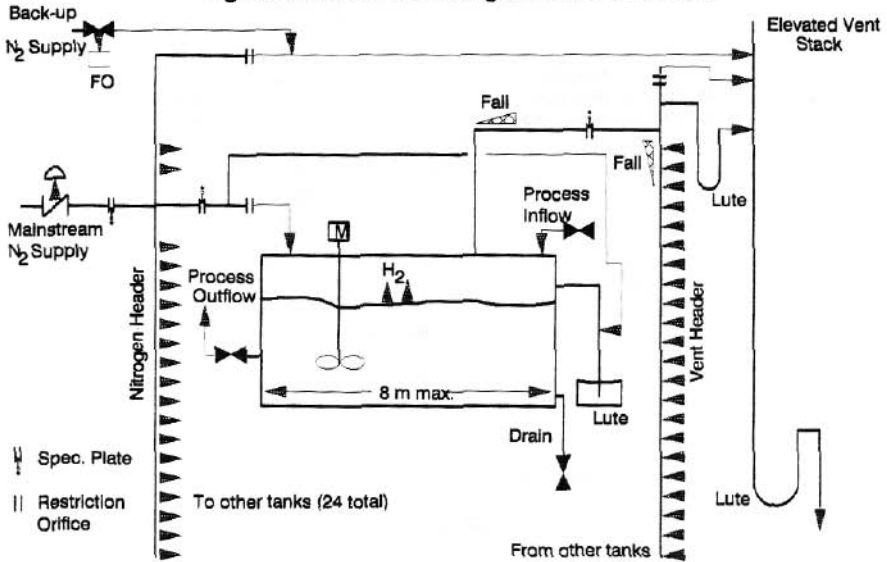


Figure 4. Flammability Diagram showing Air Ingress Scenarios from Outside the Flammable Envelope

