ALTA 2005
SX Fire Protection World Summit Proceedings

Following a spate of major fires in copper solvent extraction, the ALTA 2005 Copper Conference included a World Summit on SX Fire Protection. ALTA republished the proceedings in 2018 for the benefit of the industry, and especially for newcomers who have entered the industry since 2005.

Introduction

Following a spate of major fires in copper solvent extraction, ALTA 2005 Copper Conference included a World Summit on SX Fire Protection. The papers were presented by international experts and remain an important source of information for the cause, protection and prevention of fires in SX plants.

The topic was addressed in depth and covered the lessons learned from recent fires, designing and operating SX plants to alleviate the risk of fires, fire protection systems, the role of static electricity, utilisation of oil and gas industry experience and practice, and the likely impact of the recent fires on the requirements of insurers.

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ENGINEERING DESIGN FOR LOWERING FIRE RISK

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1. SUMMARY

The fire risk profile for solvent extraction plants (SX) has been raised recently due to two fire events at the Olympic Dam Operation (ODO) in South Australia and two other recent large fire events. Investigation of the first of the ODO events in 1999 did not result in any public domain information being made available. However the second event in 2001 has been made public via an edited internal report of the South Australian Metropolitan Fire Service

Many new and existing SX plants recognise that a fire risk identification and reduction activity needs to be undertaken to allow proper risk assessment of the alternate approaches available. This paper provides some historical perspective on SX fires; as well as interpretation of the SAMFS report as it relates to design aspects of SX plants.

The main SX fires have highlighted a number of failures of engineering and procedural controls. All these are well known in the hydrocarbon industries and need to be better appreciated in the mineral processing industries.

Fire prevention should be a paramount focus of SX plant design. This needs to include all the aspects of fuel supply, generation of flammable atmospheres, minimisation of static electricity and elimination of other ignition sources.

Many engineering companies have failed to ensure that all the available tools, standards and knowledge have been utilised in the design process. Some plants have been built without reference to even the most basic standards that should be in the toolkit of all designers.

Fire plume analysis and escalation scenario development are key tools in the understanding and minimisation of fire risk for SX plants. Both can provide significant benefits in eliminating risks (such as uncontrolled running pool fires) and involvement of other assets in a fire.

Business interruption planning needs to be made an integral part of the engineering control process. This ensures that the physical plant can be used after a fire event to maximise production and minimise the loss of cash flow.

Engineering controls are not enough for fire risk management. A strict system of risk management procedures and work descriptions needs to be in place and their use enforced and built into the site culture.

A significant number of SX plant fires can be traced to one or more failures of the operational management controls. Mostly this is related to a culture that is not focused on risk identification and removal but rather adherence to set protocols that become burdensome and observed more in the breach.

2. INTRODUCTION

The fire risk profile for solvent extraction plants (SX) has been raised recently due to two fire events at the Olympic Dam Operation (ODO) in South Australia and two other recent large fire events. Investigation of the first of the ODO events in 1999 did not result in any public domain information being made available. However the second event in 2001 has been made public via an edited internal report of the South Australian Metropolitan Fire Service (SAMFS) [1].

Many new and existing SX plants recognise that a fire risk identification and reduction activity needs to be undertaken to allow proper risk assessment of the alternate approaches available. This paper provides some historical perspective on SX fires; as well as interpretation of the SAMFS report as it relates to design aspects of SX plants. Further information on large hydrocarbon fires has been extracted from the literature along with significant input from the fire sciences. Particular attention is given to the aspects of:

- Minimisation of fire occurrences
- Minimisation of fire propagation
- Assessment of fire fighting effectiveness
- Recommendations for overall approach to the fire risk as well as detailed engineering aspects of implementation to ensure that the approach is properly implemented.

The author has been involved with the remediation of the ODO SX facility after the second fire event. No information that he has obtained under confidentiality with Western Mining has been divulged in this paper. Reliance is made only on the public domain information for the fire and on specific knowledge of general solvent extraction plant design and operation.

Much of the information in this paper is available in standard texts on the subjects of:

- Fires,
- Hydrocarbon storage and handling,
- Fire initiation risk minimisation,
- Fire escalation
- Fire fighting, and
- Management of hazardous areas.

All of the recommendations made are consistent with 'good engineering practice'; particularly with regard to elimination of static electricity and protection of other assets in a fire event scenario.

3. SX FIRE EXPERIENCES

Introduction

The experiences with SX fires have been sporadic over the last thirty to forty years. However in the recent past a number of large fires have occurred, that has focused the industry on fire safety and fire prevention. This section will quickly cover some of the more significant fires. Due to the limited space the treatment will be high level with the key points brought out. A more detailed analysis has been prepared for presentation to groups undertaking risk assessments of SX facilities (Miller [2]).

Only the more significant fires involving large proportions of the SX organic have been addressed here. Other smaller fires have been reported that have involved only limited volumes of organic (Bateman [3]).

In many cases there has been a knee-jerk reaction to implement almost anything that could be construed as appearing to the decrease the risk of an SX fire. Many of the decisions have been made on the basis of limited technical knowledge. There is however a great deal of information that can be gained from the integrated knowledge base that exists outside of the mining and minerals processing industries.

Kristiansand (1970's)

Not a lot of information is available regarding this event other than that it used a tertiary ammine extractant in a diluent similar to Rossing (McKenzie [4]). The fire was in the cobalt refinery and was reported to have been initiated from welding operations taking place during maintenance.

Rossing (early 1980's)

The Rossing fire is the first that has been widely reported and has some significant anecdotal evidence still available (McKenzie [5], Sylvester [6], Kessler [7]). The plant used a tertiary ammine in a high flash point diluent to reconcentrate uranium after a primary ion exchange (IX) extraction. The plant had two trains of SX separated by a common tank farm, spillage handling and services area. The SX was supported off the ground by columns and beams, as was the case with most SX plants built during that period.

The fire started in a spillage sump in the central area and initiated the automatic fire sprinkler system. Being a hydrocarbon fire the sprinklers did not extinguish the fire. The sump filled with fire-water and the fire spread on the surface of the water until it was under the SX mixer-settlers. The vessels eventually failed from the fire underneath and contributed to the fuel load and the spread of the fire.

The initiation of the fire is subject to some differences in recollection. However the consensus is that a leaking temporary hose delivered organic on to the drive of a sump pump, which subsequently ignited. The exact initiation scenario has not been recollected.

Eventually one entire train of the SX was consumed by the fire incident. Production interruption was minimised since a second SX train was available. This decision to split the trains into two was a conscious one by the client and engineering company at the time (Bert Viljoen and Western Knapp).

Gulf Chemicals (1980's)

There is little independent evidence for this fire other than some anecdotal recollections (at least once removed from the operation (Goodman [8])). It appears that the general industry approach of referring to diluent as kerosene was taken one step further when kerosene was actually purchased for use in the plant. The plant was not designed or operated to cope with such a low flash point carrier; and a fire ensued that destroyed the SX facility.

Olympic Dam 1999

No cause for this fire was published outside of Western Mining Corp. However some idea of the extent of the damage can be gauged from the SAMFS report [1] on the second fire. The fire involved the tank farm of the copper SX plant. The diluent was the industry standard with a high flash point.

The fire began somewhere near the loaded organic tank and involved this tank and other nearby tanks storing organic. Fire fighting apparently managed to limit the damage to the loaded organic tank and local environs. There was no damage to the uranium circuit, nor to the copper mixer-settlers.

Olympic Dam 2001

The 2001 Olympic Dam fire has been subject to significant reporting that has been made available through the SAMFS [1]. Not only has the level of damage been well documented but a likely ignition scenario proposed and tested. From this outcome it can be inferred that the ignition of the first fire is likely to be the same (or very similar) as the second fire.

The fire started in the copper SX tank farm and was of very significant size by the time that fire fighting appliances were able to reach the site. A significant quantity of water and foam was used in the extinguishment attempts that followed. The fire burnt for at least 36 hours in total; suffering many flare ups and re-escalation during this period.

With the accumulation of fire-water in the below-ground tank farm, the fire spread to the uranium SX when the intermediate bund overflowed. This prolonged the fire and increased the number of assets involved. The fire was eventually extinguished when the fuel was consumed.

Other near-by assets were preserved by the use of enclosure and cooling sprays. The copper SX mixer-settlers used a combination of metal sheeting and cooling sprays to prevent their involvement. Similar cooling sprays prevented the involvement of the large FRP pulsed columns at the edge of the fire area.

Metcalf 2003

There has been very little public domain information made available on this incident by the owner. It is hoped that this situation will improve in the near future.

Mariquita 2003

The Mariquita fire was witnessed from off the site. Further anecdotal information has been circulated in the industry that suggests the fire was started by welding or grinding activities near the SX vessels. The subsequent fire consumed the whole SX plant. No fire fighting activities were undertaken. No other assets were involved and there was no escalation of the fire outside of the SX area. The fire burnt all the available fuel and reduced the HDPE lined vessels to the aqueous water line.

The physical separation of the SX plant from the other assets was the prime reason for the lack of involvement of the other assets. The lack of any fire fighting did not introduce any excess fluids into the SX bunded area. As a result there were no running pool fires and the fire was contained within the SX bund.

Asset separation and prevention of running pool fires were the prime factors behind the lack of escalation to other assets.

Confidential Pilot Plant 2004

An SX pilot plant suffered a fire in an organic storage tank [9]. The fire appears to have started with the direct electric heating element in the tank. Escalation was prevented by the ability of the plant operators to extinguish the fire with local fire extinguishers.

Lessons from the SX fires.

It is evident that there are a number of common threads running through the initiation, escalation, and extinguishment activities that need to be considered when assessing the fire risk reduction protocols.

In all cases there was some form of breakdown in procedural controls. These are not only the operational procedures but include a wide range of control failures:

- Site procedures for control of fuel escape
- Site procedures for elimination of ignition
- Site procurement procedures
- Corporate procedures for risk reduction (escalation scenario development etc)
- Engineering procedures for risk reduction (inclusion of expertise in hydrocarbon handling)
- Detailed engineering procedures for compliance with Codes and Standards

It is not just the site operating procedures that need to be audited but also all the procedures used in the project development, implementation, operation and modification of the project. In all cases appropriate review of the procedures available and the actual practices adopted should have identified the increased risk profiles.

Another common thread is the realisation of the poor outcomes from positive fire fighting activities. Many of the fires were actively spread by the attempt to extinguish them. This is one of the corporate procedural failures in not considering the effects of actions in fire events. Scenario analysis is now a key aspect of more recent risk assessment tools.

A key observation from all the fires is the speed with which they spread. The development from a small fire (that could be approached with a hand held extinguisher) to a very large fire was very rapid. A number of anecdotal reports indicate that many SX plants have small fires that are extinguished with appropriate hand held units. These do not normally involve the organic but the other combustibles in such plants – electrical cables, greases and oil accumulations, waste and trash accumulations.

4. THE FIRE PROCESS

The fire process itself is an interesting area of very intense and extensive study by a large number of organisations. When one delves into the process a little deeper it is easy to see that the fire process can be modelled theoretically for only small constrained volumes. Outside of this the fire tends to a combination of so many site and material specific factors that modelling usefulness is limited.

However the fire can be considered on a larger scale where (like hydrodynamics) the effects of turbulence and macro scale factors can be modelled without the need for more fundamental process models to be available. There is a large body of knowledge on fire processes with the most accessible being Drysdale [10], NFPA [11] and NFPA [12]. These are weighty volumes and form the basis of much of the discussion in this section.

The usual three factor triangular cause analysis for fires is relevant requiring:

- A source of fuel (the SX organic)
- Presence and access to air (oxygen)
- A source of ignition for a sufficient period of time to generate a self perpetuating flame

The liquid fuel to be ignited needs to have a flammable atmosphere for the ignition source to be effective. In some cases the energy content of the ignitions source is sufficient to create this local flammable atmosphere.

Some of the engineering characteristics of liquid pool fires are discussed in this section.

4.1. LIQUID CHARACTERISTICS

Flash Point

The flash point (that determines the susceptibly to ignition) has minimal influence on the liquid burning characteristics once it has burned for a short period of time. [11 ch 6, p8-87]. However the flash point is a good indicator of the ability of the liquid to withstand low energy initiation processes for short periods of time.

Fire Point

The hydrocarbon liquid, if at its flash point, will flash with an ignition source but then self extinguish. The Fire Point is the temperature at which the flame will not merely flash but also self sustain and continue to burn at the liquid surface. The fire point consistently exceeds the flash point by between 20^0C and 40^0C.

Auto-ignition Temperature

The auto-ignition temperature is that point at which the total energy input via the heating process is such that the flammable atmosphere will spontaneously combust. The auto-ignition temperature for most hydrocarbon liquids with a carbon chain length of above eight is approximately 210 ^{0}C. [11 ch 6, p8-91]. Auto-ignition is important when considering the permitted surface temperature of internally heated apparatus such as electric motors, shorted electrical and instrument equipment and heaters and heat exchangers.

Effect of Temperature

The Figure 4.1 illustrates that the higher the temperature the wider is the range of the flammable mixtures

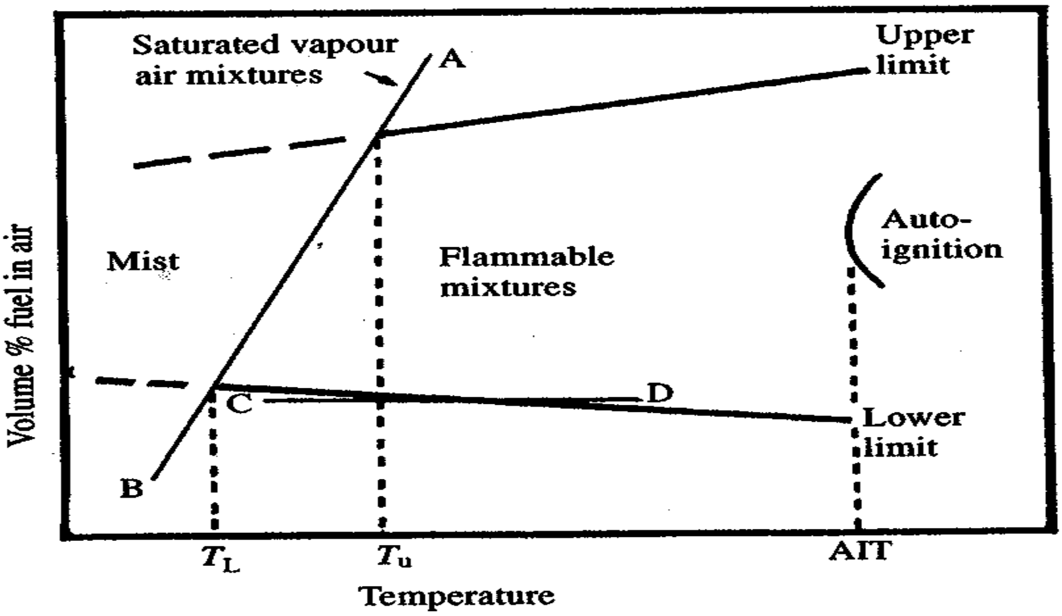

Figure 4.1: Temperature relationship with Vapour and Mist Flammability Properties

Also indicated on Figure 5.1 are the smaller ranges for the aerosol flammable mixtures and the area where auto ignition can be expected.

Most fire prevention systems tend to focus on the ignition source and do not consider deeply enough the creating and sustaining of the flammable atmosphere. Many of the following sections cover these topics in more detail to allow the engineering designer to properly evaluate the fire prevention measures to be included in the project.

4.2. FLAMMABLE GAS ATMOSPHERE

In order to ignite a pool of (the usual high flash point) diluent, a flammable gas atmosphere needs to be created *and sustained* for a period of time. This time is required for the local energy release from the fire to sustain the local high temperature to prolong the flammable atmosphere. Once this auto thermal process has established it will spread quickly to involve the total surface of the organic. The rate of spread is extremely fast once established.

Assuming that the plant is using a high flash point (>70^{0}C), narrow cut diluent; and that the temperature is close to ambient, (<40^{0}C) there is *no flammable gas atmosphere* formed by the vapour above any free surface of the organic. Theoretically then there is no hazardous atmosphere, requiring specific procedures or electrical apparatus. However there are a significant number of other factors that need to be taken into account in consideration of the fire initiation process.

The factors that can sustain the flammable atmosphere for sufficient time to reach the auto-thermal stage include:

- Presence of a wick that allows a very local auto-thermal reaction to be sustained until the larger surface becomes involved
- Creation of a flammable atmosphere from the presence of aerosols caused by turbulence or other energy inputs. This is the path that is used in designing oil burners and diesel engines
- Presence of a local source of energy that raises the organic above its flash point, which is then ignited. This is the typical scenario with welding and grinding sparks and

sustained electrical sparks in and around a small pool of organic. A lightning strike would also fall into this category if it struck onto an organic vessel.

- Raising the organic above its auto-ignition temperature. Once at this temperature the flammable atmosphere auto-ignites due to the excess energy levels present.

The presence of wicks can lower the effective fire point considerably. The large surface area of the wick provides the local conditions to sustain a flame even if the fuel source is not in itself flammable. This is the reason that candles burn. The local flame radiant energy melts the wax and this in turn is transported to the flame by capillary movement in the wick. It is for these reasons that all wick type materials need to be eliminated from the SX plant area.

The presence of aerosols in the plant atmosphere can also create a flammable atmosphere. This fire scenario is very close to those involving dusts. The lower flammability limit for gaseous hydrocarbons is typically 48 g/m^3. [11, chap 5, p2-89]. This is also illustrated in Figure 4.2.

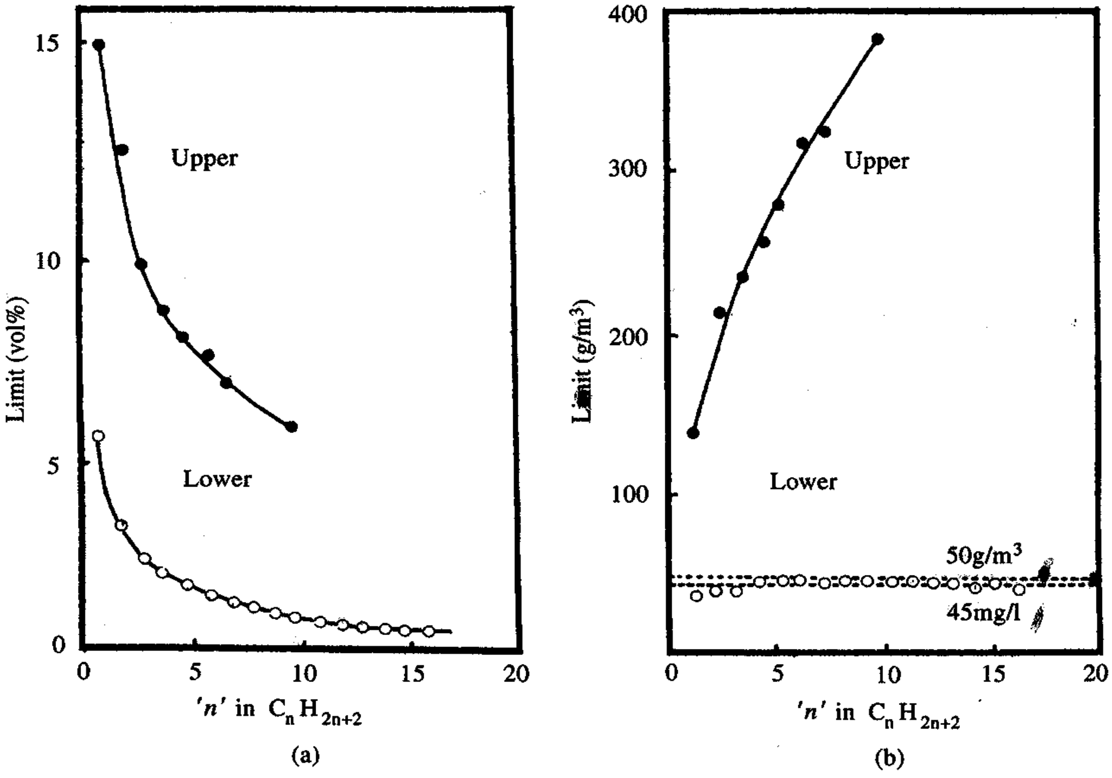

Figure 4.2: Upper and Lower Flammability Limits for Hydrocarbons

The concentration flammability limits for aerosols can be calculated by subtracting the vapour concentration from the 45 mg/L lower flammability limit. If the total hydrocarbon load was just aerosol (like a dust) then it would be sufficiently dense that it would be nearly opaque. In any plant where a *visible* aerosol is present it likely that a high risk exists that a flammable atmosphere is present.

However the coarser droplets will tend to fall into an upward propagating flame and thus increase the local concentration. As a result the lower flammability limit *decreases* as the droplet diameter increases as indicated in Figure 4.3.

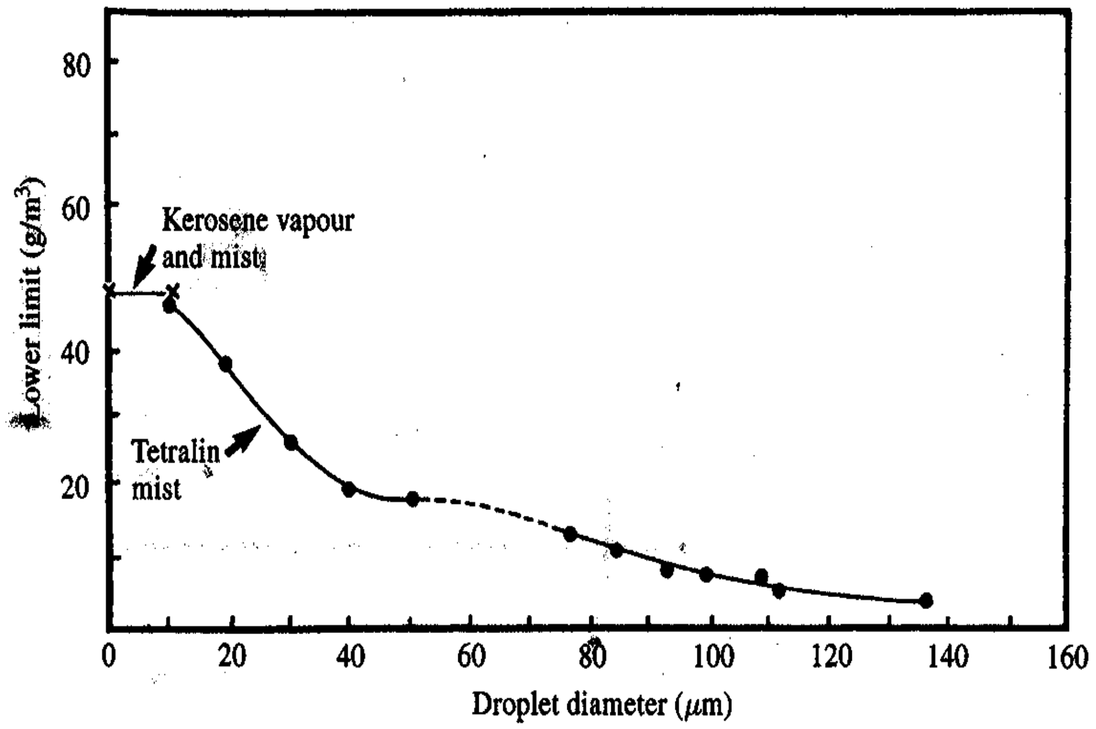

Figure 4.3: Reduction in Lower Flammability Limit of Aerosols with Droplet Diameter

Thus it is important to eliminate all sources of mists and aerosols particularly those that do not have a well defined size distribution. These can be created in spindle sump pumps, free falling streams (such as settler organic weirs and tank entries) and above poorly baffled mixer boxes.

Other high risks are associated with froths and foams. These also create situations where ignition could be initiated at temperatures below the flash point. Particular risk areas are the tops of mixers and settlers and the organic collection launder and entry to tanks. In fact almost anywhere that energy is being dissipated into the organic.

4.3. BURNING RATE OF LIQUIDS

The burning rate of hydrocarbon liquids (regression rate) tends to a constant as the pool fire diameter increases and as the boiling point increases. The rate is proportional to the ratio of the net heat of combustion to the sensible heat of vaporisation. [11 ch 6, p 8-96]. This is illustrated in the Figure 4.4, which indicates a regression rate of four mm per minute for pool fires the size of typical settlers.

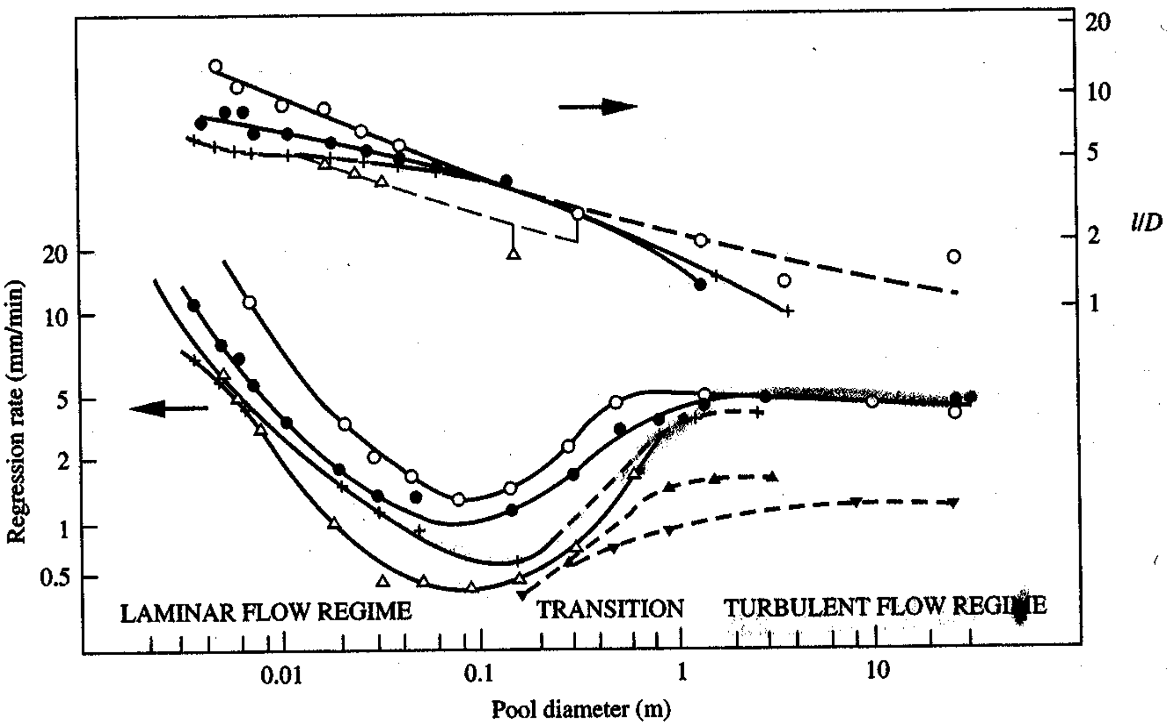

Figure 4.4: Regression Rate of Pool Fires

The right hand axis also indicates the flame height / pool diameter (l/D). For typical settler sizes (of 10m or more) the l/D tends towards a value of between 1.0 and 2.0. This is consistent with the flame heights that were inferred from the photographs of the ODO, Morenci and Mariquita fires.

This information would indicate that a settler fire should last about one hour for a depth of 300 mm. The Mariquita fire would appear to have burnt for approximately this length of time before consuming all the fuel.

4.4. FLAME TEMPERATURES

The theoretical minimum flame temperature is in the order of 1500 to 1600 K(1300 C), although flame temperatures of over 1500 C can exist for most gaseous and liquid fuels [11, p82]. These temperatures are well above the melting point of steel. As a result a large flame (from a settler pool fire) with little immediate radiant cooling will have sufficient temperature to melt the steel container in which it is contained. The time to failure in these circumstances is of the order of five to ten minutes.

4.5. ESCALATION

Over the surface of the settler

Once initiated flame spreads over the surface of the settler by a continuous process with a number of steps [11, p 235]:

- Behind the flame front steady pool burning will develop
- Under steady conditions a flow of air will be set up against the direction of the flame advance as air is entrained into the base of the flame plume.
- The flame spreads by raising the local temperature to a level that creates a flammable atmosphere. The flame flashes over the flammable atmosphere just created and spreads to begin the process anew

As the bulk liquid temperature is raised so the rate of flame spread increases

As the size of the pool increases, so the flame spread rate increases to a limit set by the expulsion of unburnt gases ahead of the flame. [11, p237]. This limit is of the order of 2 m/s for a commercial settler of say 15 m x 15 m the escalation time from initiation to full involvement of the settler is of the *order of 5 to 10* ***second****s*. The implication from this is that any fire detection system needs to be accurate and very responsive to be effective.

To other vessels

Once a vessel (settler) is alight a large fire plume is formed which radiates large quantities of energy. From the radiant energy effect tables in the Appendix it can be seen that an unprotected pool of diluent will ignite at energy levels of around 10 kW/m^2. This radiant energy level occurs up to 55 m from the edge of the fire. Thus any near by settler (one or two meters away) will almost immediately become involved with the fire and catch alight itself.

The nearby settler can be protected for a period from this direct impingement by providing a roof with cooling sprays. The roof reflects much of the incident radiation while the water provides a heat sink for the majority of the energy directed at the other vessel.

5. INITIATION FACTORS

The initiation of any fire needs the usual factors of fuel, oxygen and an ignition source. Within an SX plant there is plenty of fuel and oxygen and the main control mechanism is the prevention of the ignition process.

5.1. IGNITION SOURCE

Once a flammable atmosphere has been created then any of the low energy ignition sources discussed later can cause a fire to begin. In many cases this can be an explosive initiation if the conditions are correct. The ignition sources under these conditions can be quite ‘modest’ in their intensity.

The ignition energy necessary to ignite a flammable gas atmosphere is low. Within the flammable range it can vary from a low of 0.3 mJ to a maximum of approximately 2.0 mJ. [10, p78]. The lowest energy is around midway between the upper and lower flammability limits.

One recent study [13] has shown experimentally that droplets and aerosols from a typical SX diluent can be ignited by low energy electrostatic discharges. The level of static charge that personnel sense is provided in Table 5.1

Spark Energy (mJ)	Response
1	Perceptible sensation
10	Distinct sensation
100	Unpleasant sensation (shock)
1000	Severe shock
10000	Possible lethal shock

Table 5.1: Static Electricity Felt by Personnel

As is evident from this table the ignition energy of 0.2 to 2.0 mJ is readily generated from personnel working in the plant environment.

5.2. STATIC ELECTRICITY

The most wide spread ignition issue for the whole of the plant is that of static electricity coupled with the production of mists and aerosols. The risks that are evident are a result of the combination of:

- Poor design elements
- Excessive energy input to the organic streams. This energy needs to dissipate as either heat or some static electricity
- Lack of appropriately designed drainage pathways for accumulated static charge.

This area is further detailed in the next section

5.3. WELDING AND GPO OUTLETS.

Provision of these items should not be anything other than via a fully considered risk assessment process.

5.4. LIGHTNING PROTECTION

Lightning protection needs to be 100% coverage for all areas of the plant that contain any organic

5.5. HAND HELD DEVICES

Hand held devises need to be controlled upon entry to the plant. Electronic equipment is not likely of itself to constitute an unacceptable risk. However items that can be dropped and their batteries fall out need to be eliminated as the spark from the battery disconnection can have sufficient energy to ignite a flammable atmosphere. Consideration needs to be given to total bans on:

- Mobile phones
- Radios that are not intrinsically safe
- Electrical equipment (inc testing equipment) that is not rated for the hazardous area
- Cameras
- Flash lights – Ex rated flashlights are commonly available; or install better permanent lighting that will eliminate the need to flashlights.

5.6. MECHANICAL EQUIPMENT

- Do not permit the use of vee belt drives in hazardous areas. The not only generate static but also can heat up to fire point of the rubber belts if jammed
- Use positive flushed mechanical seals on organic (Plan 11) not just cooled back faces
- Install low level cut out on tank levels
- Install temperature probes on pumps handling organic
- Mount most lighting on the lightning masts out of the hazardous area
- Reticulate small bore piping and eliminate hoses that may leak on to hot equipment.
- Tools should be non sparking – the coal industry has a good range of these for use in methane atmospheres.

5.7. PROCEDURES

Initiate procedures for elimination of ignition sources from:

- Hot work – permit system
- Smoking and lighters
- Good inspection and preventative maintenance on bearing and motors

- Petrol and diesel engines not rated for hazardous areas
- Spillage control
- Housekeeping
- Auditing and compliance
- Safe work practices for most day to day operational activities
- Training
- Availability of information on all of the above

6. CONTROL OF STATIC ELECTRICITY

6.1. STATIC GENERATION

The static electricity issues are significant for plants handling hydrocarbon liquids. There are relevant Australian and international standards [14] for the design of process plants to eliminate or minimise the generation of static charge. Mechanisms also need to be included to dissipate (drain or earth) any static charge that is created. Recommendations for grounding are contained in all the standards.

One important factor that is not generally considered is the generation of static in the separation process occurring in a settler. As the particles separate they can form static charge as they slip past each other. The presence of aqueous entrainment in the hydrocarbons is also a high generator of static charge as these droplets can create significant charge through their movement within the non conducting hydrocarbon. The lower the conductivity of the aqueous the greater is the generation of static electricity. The use of demineralised water for washing/scrubbing operations should not be contemplated; unless its conductivity is increased with the addition of acid or electrolyte.

Other charge generation occurs when any relative movement takes place. The higher the velocity and the greater the turbulence, the greater is the charge generation. Activities that can generate static include:

- Mixing of droplets
- Mixing or settling of solids
- Disruption of an interface
- Atomisation
- Splashing
- Flow past a fixed boundary eg pipe or vessel wall

Conductivity enhancement chemicals are available; particularly for the aeroplane fuels. These increase the conductivity of the hydrocarbon to levels where the static generation is minimised and dissipation is faster [13]. However there have been no plant trials, as there appears to be significant adverse effects on the phase separation process in the SX process.

The range of liquid conductivities, over which static charge generation is experienced, is 10^{-1} to 10^{5} pS/m. The maximum occurs with liquid conductivity of the order of 10 pS/m. The higher the conductivity the faster the generated charge flows to earth. It is unlikely that electrostatic discharge will occur for metal containers or pipes with liquid conductivities greater than 200 pS/m [13].

Some typical plant results for liquid conductivities are:

New diluent	1.0 pS/m

• Extractant (copper)	25 – 50 pS/m
• In circuit organic	80 – 200 pS/m
• In circuit organic (high metal loading)	>1000 pS/m

Simple spark discharge is common from conductive surfaces once an accumulated charge is grounded. However non conductive surfaces can discharge multiple times (brush discharge) as the charges on the non conducting surface have no mobility to the grounding point.

6.2. REMOVAL OF STATIC CHARGE

Conductive surfaces when grounded do not accumulate charge as the conduction allows the charge to be removed. There has been a move recently to provide conductive surfaces on FRP pipes and vessels to allow this charge removal to occur. ODO has led the way in this regard. However where lower grade stainless steel (316/316L) can be utilised for vessel fabrication, there is much greater opportunity for static charge grounding. In chemical environments where metal is not an economic option the use of conductivity enhanced FRP is a viable option, adding only 10% to 15% to the overall cost of the FRP.

However ungrounded (isolated) conductors (such as valves or instruments) can cause very high potentials to accumulate (up to tens of kilovolts). This can cause a brush discharge if the pipe or local volume is not full of liquid.

Charge dissipation in tanks is a function of whether the tank *bottom* can be grounded. If this is achieved then charge relaxation times (time to reach 1/e = 37% of its starting value) of *less than one second* can be achieved.

6.3. MINIMISATION OF STATIC GENERATION

Poor design elements are departures from the code of practice for control of static electricity. The major issues are:

- High level entries into tanks (loaded and/or stripped organic tanks)
- Free fall of organic from inlets to final levels with fall through surfaces (organic tanks and settler organic launders, coalescer overflow weirs etc)
- Excessive pipe velocities in organic lines from either/or/both pipe size too small or excessive available gravity head.
- Entrainment of air into the mixers and subsequent separation in the settlers
- Entrainment of low conductivity aqueous in organic streams from washing and scrubbing settlers

Most of these can be addressed to a greater or lesser extent with alternate equipment design:

- Tank entries at a lower level to keep the entry submerged
- Operation of weirs discharge launders at high level to minimise free fall heights.

In order to keep the incident vertical velocity to <1 m/s the free fall height in organic collection launders needs to be less than 50 mm.

- Provision of control valves to dissipate the available head in a controlled manner.
- The excess energy input to the organic has some limited opportunities for redress.
- The free fall into the tank farm area needs to minimised as illustrated in Figure 6.1

Figure 6.1: Low Head Difference Between SX and Tank Farm

- Extra energy added from any low hydraulic efficiency pump mixer and axial flow impellors. Modern high efficiency units should be used. This is also an issue with aerosol production.
- Any design feature that may induce energy dissipation needs to be redesigned and removed.
- High pressure cleaning using > 1 MPa should not be used, at it constitutes a risk of introducing static electricity via the high velocity nozzles used in the water blaster.
- Other sources of static charge are from personnel wearing PPE that can generate such charges. Non conductive artificial fibres are good for acid resistance but are also good generators of static electricity. Serious considerations should be given to changing the PPE requirement for the SX plant to cotton rather than polyester.
- Drainage of the static charge needs to be integrated into the plant and vessel design.
- Relaxation (dissipation) of the static requires both extended times and large areas of contact to achieve low voltages. This is best achieved with conductive vessels (and vessel internals). In all cases the conductive elements are to be earthed to dissipate the static charge.
- Loaded organic and coalescers tanks:
    - Line coalescers with conductive FRP veils
    - Line loaded organic tank with conductive FRP
    - Pipes to and from coalescers to be conductive FRP
    - Locate the tank feed to the bottom and select appropriate size
    - Add an aqueous entrainment transfer pump to remove de-entrained aqueous from the organic tank
    - Use of graphite conductive valve for flow control and energy dissipation.
- SX intra-plant organic pipes – use conductive FRP
- SX settlers:

  - Fit feed distributor vanes in conductive FRP
  - Use picket fences with non spouting design in conductive FRP
  - Organic weir use curved smooth flow weir in conductive FRP
  - Line with conductive FRP
- SX mixers:
  - Line with conductive FRP
  - Use high efficiency mixers

All of these elements are simply application of the relevant standards on minimisation and dissipation of static electricity. It is not rocket science and it is easy to do correctly. So often the plant layout is driven by other factors that are perceived to be more important. However the incidents at Olympic Dam have shown that static electricity is probably the most important ignition source that must be addressed by the design engineers.

7. FUEL CONTROL FACTORS

There are two fuel requirements for a fire. That needed in the initiation process to form the flammable atmosphere; and that required to sustain the fire in the longer term. Elimination of either or both of these fuel sources will break the fire scenario.

7.1. FUEL FOR INITIATION

The fuel for initiation needs to be in a form that can be readily ignited, and then maintained long enough for the local fire to escalate to involve the large settler pools. The presence of mists and vapours is a major source of potential ignitable fuel that can maintain a fire for the requisite period.

One of the easiest fuel control steps is to eliminate the atmosphere of droplets and aerosols that can form in partially full pipes. By *keeping the pipes full* there is no opportunity for an explosive atmosphere to form and minimal risk of ignition from any static charge generated.

All points where mists, vapours and aerosols are produced should be eliminated or minimised. Some of these aerosols are produced in prodigious amounts from:

- Stripped and loaded organic tanks if not fed correctly at the bottom
- Organic feed siphon break tanks
- Settler feed systems that induce turbulence
- Settler organic discharge launders
- Entrainment of air into mixers and subsequent release with entrained aerosols

Priority activities need to be directed towards the elimination and minimisation of aerosols in the plant. This will minimise the *continuous* availability of the ignition fuel sources.

7.2. LIMITING FIRE TIME

The fuel supply for any initiated fire is very large. Experience from other SX and large hydrocarbon fires is that removal of the fuel is a good method of limiting the time that the fire is able to damage assets. A fuel dump system from the process vessels could be integrated with a bund overflow handling system and stored in a modified environmental containment structure.

Vessel dump systems were an integral part of SX plants in the 70's and early 80's but have not been incorporated in recent times. Other operations with dump systems include Olympic Dam (retro-fitted) and Ranger Uranium (original design). New projects have included these systems as part of the overall risk management process.

Fire escalation scenario development planning is required to fully assess the effectiveness and timing required for a vessel dump system. This should be undertaken as a matter of course so that appropriate planning and design can be put in place. A fire plume analysis will be required to allow assessment of the time required to involve a near by settler from spontaneous ignition.

An integrated dump system with the bund overflow control system will minimise the cost impacts from separate systems.

Once decisions regarding the inclusion of dump system are made the implementation can become part of the larger issues of production continuity planning, settler long term maintenance, static electricity dissipation and operational performance. By integrating all of these functions a single coherent plan can be put in place with only one set of required outcomes.

8. FIRE PLUME AND RADIANT HEAT ISSUES

The fire plume and radiant heat release are important factors in analysing:

- The other assets that are at risk of being included in the fire
- The placement of control facilities (valves, foam tanks etc) so that they are serviceable in a fire event
- The distance that personnel can get to the seat of the fire for extinguishment activities.

A typical heat flux for a pool fire of 10 m diameter is shown in the Figure 8.1 for gasoline [12]. The lines represent different models used for fire plume.

a) Point source

b) Flame as a vertical rectangle

c) From a correlation of Shokri and Beyler of experimental data. They recommend a factor of safety of x2 to ensure that all data points are included. This indicates that the simple point source model can be used with some accuracy for first round approximations of heat flux from medium sized pool fires.

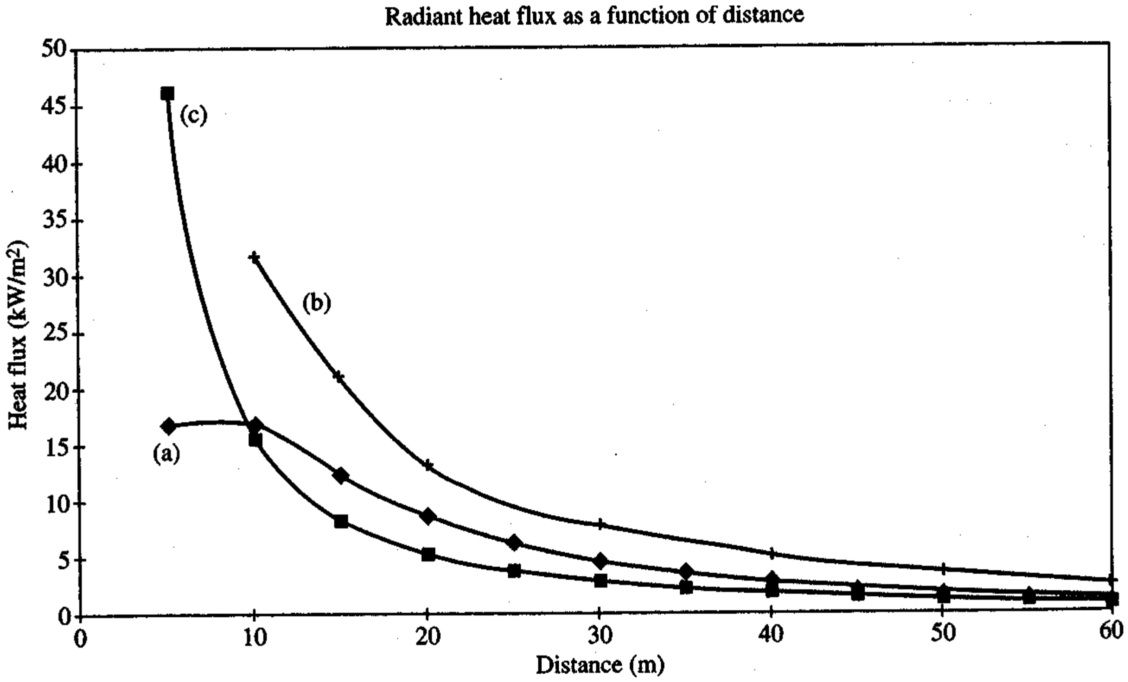

Figure 8.1: Heat Flux Models for Larger Pool Fires

The presence of a wind can severely distort the fire plume and extend the radiant zone down wind for a significant distance. A wind of 2 m/s (7.2 km/h) will distort the fire plume to 45 degrees. For open areas such as a settler fire the fire will tend to hug the ground for a distance of 0.5D down wind as well. [11, p145]. Both effects increase the exposure of down wind assets to the radiant heat flux.

In general the surface of the burning liquid is close to but just below its boiling point. For liquid mixtures the lower boiling fractions will tend to burn off first. The use of a tight boiling range diluent also has the benefit of limiting the liquid surface temperature as the fire progresses.

A more detailed list of radiant heat effects on personnel and materials is provided in the Appendix to this paper.

KW/m²	Effects
9.8	• An *exposed* pool of SHELLSOL will ignite spontaneously.
12.5	▪ 30% change of a fatality for long exposure. High chance of injury. ▪ Cause the temperature of wood to rise to a point where it can be ignited by a naked flame after long exposure. ▪ Thin steel with insulation on the side away from the fire may reach a thermal stress level high enough to cause structural failure. ▪ Generally it may be assumed that steel equipment will not require protection when exposed to a heat radiation level of 12.5kW/m² or less. At this radiation level the unprotected metal temperature stabilises at about 300°C, which is in itself harmless.
15	• PE piping will fail within 10-15 minutes.
23	• 100% chance of fatality for long exposure to people and 10% chance of fatality for instantaneous exposure. • Spontaneous ignition of wood after long exposure. • Unprotected steel will reach thermal stress temperatures to cause failure. • Pressure vessels need to be relieved or failure would occur. • Acceptable heat radiation level to steel (process) equipment/structures provided cooling is applied within 15 minutes.

32	• Unprotected steel equipment will quickly exceed the critical metal temperature (just above 400°C), which could result in the equipment losing its mechanical integrity and causing escalation of the fire emergency.
35	• Cellulose material will pilot ignite within one minute of exposure. • 25% chance of fatality if people are exposed instantaneously.
60	• 100% change of fatality for instantaneous exposure.

9. EXTINGUISHMENT

Liquid fires can be extinguished with foam, dry chemical agents, carbon dioxide, halogenated agents or water (with special fine mist applicators) [11 ch 6, p8-1].

The typical foam is an Aqueous Film forming Foam (AFFF), which spreads across the liquid surface excluding the air; and preventing the vapour from mixing with the air. As such it needs to cover the entire surface of the liquid until the fire is extinguished. There is no current theory for the performance of foams, and their characteristics need to be measured under standard conditions.

The point to keep in mind with foams is that they do drain and collapse both by film drainage and from evaporation of the film from the heat of the fire. Further foam loss can occur from entrainment in turbulent air or violent up-rising combustion gases. As a result foam needs to be replenished if the foam application does not immediately extinguish the flame. The drainage characteristic also implies that the foam will in time drain and expose the surface of the liquid to further possible ignition. This ‘burn back’ is also measured as a foam characteristic; and is generally in the region of 10 to 15 minutes, after the initial 5 minute application has ceased. [12, p 4-89]. The efficacy of foam is greater the sooner it is applied (especially to larger areas). A rapid-response detection system is recommended for initiation of the foam application. The aim is for liquid hydrocarbon fires to achieve a fire control time of 30 s and an extinguishment time of 60 s. For this reason alone the use of thermally activated systems cannot be recommended for SX plants.

The foam application rate can be tailored to suit the particular solvent being considered. Lower applications are possible with higher flash point fuels. However control and extinguishment times increase as a result. Typical application rates range from 1.6 L/min/m^2 to 6.6 L/min/m^2. The lower rates being more applicable to smaller spill fires in open locations such as aircraft carrier flight decks. [12, ch 4, p 4-109].

If a foam system is selected for use, then it needs to be of such a size and capacity that it can blanket the vessel in as short a time as possible – and maintain it for the required time to ensure extinguishment. For this reason multiple applicators are used on large settlers where the area is substantial. It is often possible to foam blanket a modest settler (less than 200 m^2) within a few seconds.

As was evident from the ODO experience, once a fire is set in a very large area there is little that can be done to extinguish it until the fuel has been consumed. The foam blanketing used did limit the active area of the fire (and thus helped to preserve some of the assets) but did little to actually extinguish it.

Much of the focus of conventional fire control is on the extinguishment step in the overall process. Using the sorts of analysis tools that are now available it is possible to review this focus and replace it with one based on a combination of:

- Fuel reduction
- Cooling and protection of other assets
- Prevention of escalation by bunding, enclosure (and cooling)
- Fast response knock down systems (foam or water mist sprays)

- Escalation scenario development and identification of high priority outcomes.

This latter tool is more fully explored in the next section

10. ESCALATION SCENARIOS ANALYSIS

Steel containers exposed to a liquid pool fire (without sprinkler protection) can fail structurally between two and eight minutes [x12, chap 4, p 4-115]. This period is very short in terms of getting external fire extinguishment systems initiated. The consequences of this are alarming and require significant ability to react quickly:

- Use of fast response detection systems
- Use of fuel minimisation strategies (ie dump system to a remote storage)
- Short fire life even of steel vessels and tanks
- The need for automatic systems that can respond rapidly to all the actions required – foam/water application, fuel dump, cooling of other local assets.

As a result of the short time periods, it is important to explore the various scenarios that can develop during a fire event.

A fire plume analysis will indicate which other assets may be at risk from the radiant energy from the very large fire plume. It is likely that the following assets can be at significant radiation risk.

- Adjacent settlers
- All the above ground fire water reticulation
- All near by foam addition systems
- Manual monitor stations
- Pipe rack between the SX and tank farms

Further information from a fire plume analysis will indicate if cooling water spray / curtains would be effective (and for how long) for protection of near by settlers and other assets.

From this analysis will arise an alternate asset protection / preservation plan that takes into account the very large fire plume likely to result from an SX fire. Some of the more ‘normal’ systems may be found to be of little value including:

- Manual monitor stations
- Over the settler deluge spray systems
- Total foam storage volume (in the light of experience from other fires)

The use of fire suppression and cooling water will place a significant load on the process bunding system. As such the disposal of the fire water becomes an integral part of the bund design and selection process. Without adequate bund overflow and containment systems uncontrolled overflow can occur with resultant running pool fires. These were responsible to a large degree in the escalation of the fires at ODO and Rossing. A similar situation did not seem to rise at Morenci, and further information would be welcome as to the reasons.

Systems Failure Risks

There are a number of risks of systems failures for operation of an SX plant. An in depth review of the systems in place needs to be undertaken to assess their effectiveness and the internal control and QA audit mechanisms in place.

Other potential issues are:

- Need of an emergency response team coordinator

- Need for operationally experienced personnel on the emergency response team
- Need for fluid isolation valve location information
- Need for known and easy access to the emergency response plan
- Need for emergency scenario developments and related response plans (the fight or flight decisions)

All of these items form an integral part of the systems needed to minimise risk and respond adequately to an incident.

11. MINIMISING BUSINESS INTERRUPTION

One of the largest consequences of an SX plant fire is the resultant business interruption. There is both the cost of replacing the facility and the lost production. This latter can be an order of magnitude more than the plant physical capital. As a result, one of the more effective management tools available is to integrate a business interruption plan with the plant design process. Alternatively, for an existing operation the interruption planning process can identify investment opportunities that will minimise the business interruption.

As was evident from the experiences of the known significant SX fires, the ability to get back into production quickly is a key part of the minimisation strategy. This was achieved by:

- Rossing - having the SX split into two separate trains. One of which could be preserved and maintain a high level of production.
- Morenci - preserving part of the SX plant and being able to reconfigure it to maximise production.
- Olympic Dam - having a second SX circuit that could be reconfigured to maximise production

This is in stark contrast to Mariquita and Gulf Chemicals where production loss was 100% until the plant was rebuilt.

A number of new projects have considered the business interruption (BI) planning process as an integral part of the engineering design of the plant. The BI analysis has highlighted the benefits of:

- Use of multiple SX trains to preserve a production capability
- Ability to reconfigure the remaining SX assets to maximise production
- Preservation of as many assets as possible both internal and external to the SX plant.
- Provision of plant separations
    - Primary:
        - ♦ SX train to SX train,
        - ♦ SX area to EW and other plant sections,
        - ♦ Electrolyte and crud treatment areas separate to SX tank-farms
    - Secondary:
        - ♦ Mixer-settlers to tank farm within a train.
- Fire break spools in all plastic piping crossing separation areas.
- Automatic cooling of nearby assets – especially other mixer-settlers. This requires that the fire be prevented from spreading by an ability to cool other assets within the fire plume
- Fire hydrants or monitors for cooling near by assets.

- Systems to handle the fire fighting and cooling water applied, to prevent creating running pool fires.
- Provision of a remote emergency dump area where a running pool fire could be directed.
- Provision of a remote dump area where vessel contents could be stored / removed from immediate fire danger.

Implementation of these measures has been included in three or four recent projects *without* major capital cost impact. By using the BI planning process the plant layout was changed to include these facilities without incurring extra costs.

- The biggest impact on fire development is the physical separation of the SX plant and the trains with it. All this needs is some extra piping.
- The provision of remote dump and fire water control ponds can be integrated with the overall site drainage and environmental management structures. There is no reason why the environmental dam cannot do double duty.
- The targeted provision of cooling systems is no more than is generally required for the fire fighting system in any case. Once again the fire system can perform two functions from the same reticulation. The only cost increase is a few more control valves to be able to more easily service the appropriate target.

Another recent project has included these aspects into a brown fields upgrade of their SX plants. The additional provisions on the site were:

- The dump ponds and
- The improved and targeted fire/cooling water reticulation.

12. CONCLUSIONS

The main SX fires have highlighted a number of failures of engineering and procedural controls. All these are well known in the hydrocarbon industries and need to be better appreciated in the mineral processing industries.

Fire prevention should be a paramount focus of SX plant design. This needs to include all the aspects of fuel supply, generation of flammable atmospheres, minimisation of static electricity and elimination of other ignition sources.

Many engineering companies have failed to ensure that all the available tools, standards and knowledge have been utilised in the design process. Some plants have been built without reference to even the most basic standards that should be in the toolkit of all designers.

Fire plume analysis and escalation scenario development are key tools in the understanding and minimisation of fire risk for SX plants. Both can provide significant benefits in eliminating risks (such as uncontrolled running pool fires) and involvement of other assets in a fire.

Business interruption planning needs to be made an integral part of the engineering control process. This ensures that the physical plant can be used after a fire event to maximise production and minimise the loss of cash flow.

Engineering controls are not enough for fire risk management. A strict system of risk management procedures and work descriptions needs to be in place and their use enforced and built into the site culture.

A significant number of SX plant fires can be traced to one or more failures of the operational management controls. Mostly this is related to a culture that is not focused on risk identification and removal, but rather adherence to set protocols that become burdensome and observed more in the breach.

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14. APPENDIX

HEAT AND THERMAL RADIATION CONSEQUENCES

Consequences of Heat Radiation

KW/m²	Effects
1.2	• Received from the sun at noon in summer.
2.1	• Minimum to cause pain in one minute.
4.7	• Will cause pain in 15-20 seconds and injury after 30 seconds exposure (at least second degree burns will occur).
9.8	• An exposed pool of SHELLSOL will ignite spontaneously.
12.5	• 30% change of a fatality for long exposure. High chance of injury. • Cause the temperature of wood to rise to a point where it can be ignited by a naked flame after long exposure. • Thin steel with insulation on the side away from the fire may reach a thermal stress level high enough to cause structural failure. • Generally it may be assumed that steel equipment will not require protection when exposed to a heat radiation level of 12.5kW/m² or less. At this radiation level the unprotected metal temperature

	stabilises at about 300°C, which is in itself harmless.
15	• PE piping will fail within 10-15 minutes.
23	• 100% change of fatality for long exposure to people and 10% change of fatality for instantaneous exposure. • Spontaneous ignition of wood after long exposure. • Unprotected steel will reach thermal stress temperatures to cause failure. • Pressure vessels need to be relieved or failure would occur. • Acceptable heat radiation level to steel (process) equipment/structures provided cooling is applied within 15 minutes.
32	• Unprotected steel equipment will quickly exceed the critical metal temperature (just above 400°C), which could result in the equipment losing its mechanical integrity and causing escalation of the fire emergency.
35	• Cellulose material will pilot ignite within one minute of exposure. • 25% change of fatality if people are exposes instantaneously.
60	• 100% change of fatality for instantaneous exposure.

THERMAL RADIATION HAZARD TO PEOPLE

How long can a worker continue to operate in an emergency situation whilst exposed to a given level of heat radiation?

API-521. Values for time to pain for exposed bare skin

Radiation Level (kW/m²)	Time to pain (seconds)
1.74	60
2.33	40
2.9	30
4.73	16
6.94	9
9.46	6
11.67	4
19.87	2

API-521. Worker appropriately dressed and will not remain static during a task

Radiation Level (kW/m²)	Conditions
1.58	Design flare heat release at any location where personnel are continuously exposed.
4.73	Heat intensity in areas where emergency actions lasting several minutes may be required by personnel without shielding but with appropriate clothing.
6.31	Heat intensity in areas where emergency actions lasting up to 1 minute may be required by personnel without shielding but with appropriate clothing.
9.46	Design flare heat release at any location to which people have access (eg. at grade below the flare or a service platform of a nearby tower).
15.77	Heat intensity on structures and in areas where operators are likely to be performing duties and where shelter from radiant heat is available (for eg. behind equipment).

Shell Research maximum design thermal radiation levels. Worker appropriately dressed and will not remain static during a task.

Radiation Level (kW/m²)	Exposure time limit
<1.5	Indefinite
1.5-1.8	Indefinite
2.2-3.0	15 minutes
3.0-4.0	5 minutes
4.0-6.3	1 minute
6.3-9.5	30 seconds
>9.5	Immediate

IGNITIONS FROM PEOPLE

Ignitions are produced by sparks from people when:

- A flammable atmosphere is present.
- There is a mechanism for generating charge on people such as:
    - Walking on an insulated floor covering or carpet.
    - Cleaning an object by rubbing.
    - Contacting another charged object.
    - Induction.
    - Sliding of a seat.
    - Removing clothing.
- The potential on a charged person may exceed 20kV and stored energy can be as high as 35mJ, therefore sparks can be incendive.
- People have a high resistance to earth so that charge can accumulate (ie. they are electrically insulated).

Sensitivity of People to Sparks

Spark Energy (mJ)	Response
1	Perceptible sensation
10	Distinct sensation
100	Unpleasant sensation (shock)
1000	Severe shock
10000	Possible lethal shock

STATIC ELECTRICITY – A DANGER INHERENT IN THE SOLVENT EXTRACTION PROCESS

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ABSTRACT

BHPBilliton Base Metals currently operate five copper SXEW plants; Escondida Oxide and Cerro Colorado in Chile, Tintaya in Peru and Pinto Valley and Miami in USA with a combined production of about 320kt/a cathode copper. In addition two new plants are in construction in Chile, at Escondida Sulphide Leach and at the Spence project. By the end of 2006 the total SXEW capacity of BHPBilliton operated plants will be some 700kt/a cathode copper.

The principles of fire prevention in SX plants were established at Nchanga over 30 years ago and these have remained virtually unchanged ever since. These are:

1. A system of permits for any work in the SX plant, especially for hot work, with established procedures, which included a risk analysis for each job. This is best reinforced by controlled access to SX areas.
2. Good earthing of the metallic SX roof structure to carry any lightning strike safely to earth. The Nchanga SX plant has operated for 30 years in an area with 150 lightning days/year without incident.
3. Rotating machinery located so that a fire, should it occurred, would not propagate. Pumps and motors should not be placed beneath organic lines, plastic pipes or other combustibles and metallic piping is used in the immediate vicinity of such equipment.
4. The use of high flash-point diluents to minimise the possibility of formation of flammable atmospheres.
5. The maintenance of high standards of housekeeping; ensuring that nothing that could form a wick remains in the SX area.
6. The submerged entry of organic lines into tanks to reduce turbulence and to prevent the flow of air in organic lines
7. The bonding of all metallic units (valves, flowmeters, metallic spools, structural members etc) to earth.

These principles have been followed in the design of recent BHPBilliton plants and in the design of current projects, however the recent fire events in the industry have again raised the spectre of static electricity as a potential source of SX fires. To be confident that the current designs were indeed safe in this respect BHPBilliton Base Metals engaged the services of Wolfson Electrostatics to survey the existing operations at Escondida and Cerro Colorado to confirm that electrostatic does not present a hazard in these operations and, by extension, that the SX designs in the current projects were sound.

1. INTRODUCTION

The well-established solvent extraction (SX) process for metals has generally been considered relatively safe from fire hazards. This is because SX plants normally operate well below the flashpoint of the organic solvents used. In recent years however, a number of serious solvent fires have occurred prompting investigations into the nature of the flammable atmospheres produced and the source of ignition.

Subsequent recent investigations have shown that the SX process can under certain conditions simultaneously produce sensitive flammable atmospheres at normal plant temperatures together with high levels of electrostatic charge – a lethal combination! Since it is impractical to fully eliminate these flammable atmospheres, hazard mitigation must concentrate on eliminating the electrostatic ignition source. This is not easy because the phenomenon of static electricity is both unpredictable and difficult to detect.

This paper identifies the sensitive flammable atmospheres and sources of hazardous electrostatic discharge (ESD) in SX. It presents data from measurements at two commercial copper mines in the north of Chile and considerers the practical measures adopted to minimise static electricity. The paper also challenges some of the traditional precautions employed to reduce static electricity.

2. FLAMMABILITY OF ORGANIC SOLVENTS – THE MYTH OF FLASHPOINT

The organic phase of SX is usually made up of an active 'extractant' dissolved in a carrier or diluent solvent. The fact that both of these materials can ignite and burn has been made dramatically apparent from recent fires around the world. Usually it is the diluent, a narrow-cut kerosene under brand names such as Escaid, Shellsol etc., that provides the fuel for an SX fire.

Common diluents have a flash point above 38C (100F) which puts them into the category 'Combustible' rather than 'Flammable'[1]. In fact, the flashpoints of diluents are often above 70C which is well above normal plant operating temperature. This fact can lead to a false sense of security. The flashpoint of liquids is measured by a standard laboratory technique[2]. The conditions in working SX plants however which may produce droplets, foaming surfaces and dense mists are far removed from the laboratory method.

The spark energy required to ignite flammable or combustible hydrocarbons in any form is temperature dependent. Under optimum conditions this can be as low as 0.2 milliJoules (mJ). Electrostatic discharges encountered in industrial situations may vary in energy up to 100 mJ(3).

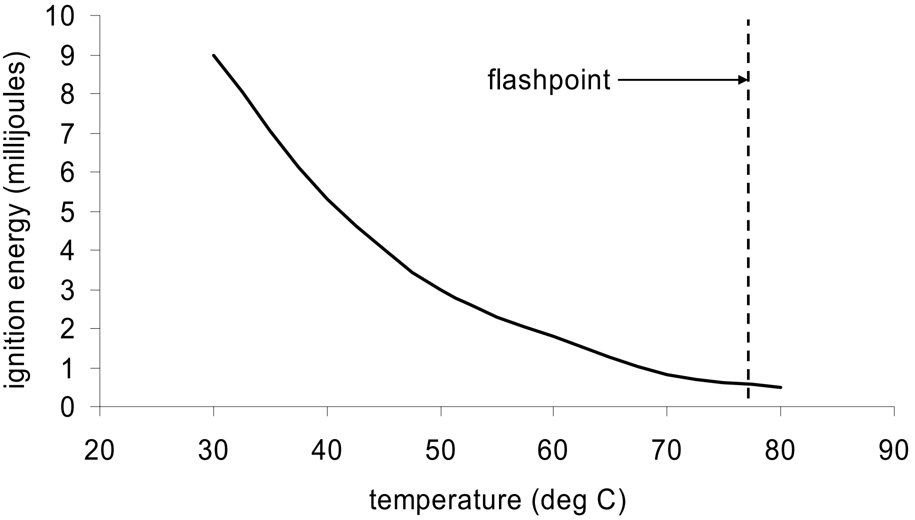

Figure 1. Ignition energy of a dense, fine droplet mist of SX diluent over the temperature range 30-80°C. Note that the liquid is capable of ignition below its flashpoint of 78 °C. A similar relationship will apply to froth on the surface of the solvent.

Figure 1 shows how a typical high-flashpoint kerosene can be ignited in the form of surface froth and mist at temperatures well below the quoted flashpoint temperature. Under such conditions, oxygen in the air can combine more readily with the combustible solvent and the low ignition energy of SX diluents in these forms puts them at risk from all forms of electrostatic discharge.

3. SOLVENT CONDUCTIVITY - THE SOURCE OF THE PROBLEM

Non-polar liquids such as kerosene have a low electrical conductivity and can exhibit significant electrostatic charge generation[4]. It is known that high levels of electrostatic charging occur as the result of high velocity flow in pipelines and agitation in tanks. Pouring, gravity fill and splashing are also charge generators but to a much lesser extent.

Charging of liquids in a pipeline, normally takes place because the moving liquid carries with it a loosely bound layer of charge leaving the other polarity attached to the inner pipe wall. This can occur in metal and plastic pipes but there are significant differences in the charging behaviour of liquids in each case[5]. The amount of charge generated on a liquid flowing in a straight pipe is generally limited by three factors:

- The conductivity of the liquid (low conductivity liquids produce higher charging)[6]
- The flow velocity (charging may increase exponentially with velocity)[7]
- The nature of the pipe wall.

The rate at which charge on a liquid dissipates to earth depends on its conductivity. It follows, therefore, that a highly conductive aqueous liquid cannot store charge on either the liquid or the pipe. A perfectly pure insulating liquid will not generate charge because there are insufficient disassociated ions present[8]. It is generally found that in plastic pipes the electrostatic activity associated with a liquid flow builds up as the conductivity increases, reaches a maximum when the liquid conductivity is in the range 10-50 pS.m^{-1}, then decreases with further increasing conductivity as the generated charge flows rapidly to earth. Generally, no significant charge generation is evident at conductivity levels above 250 pS.m^{-1} in plastic or metal (see figure 2).

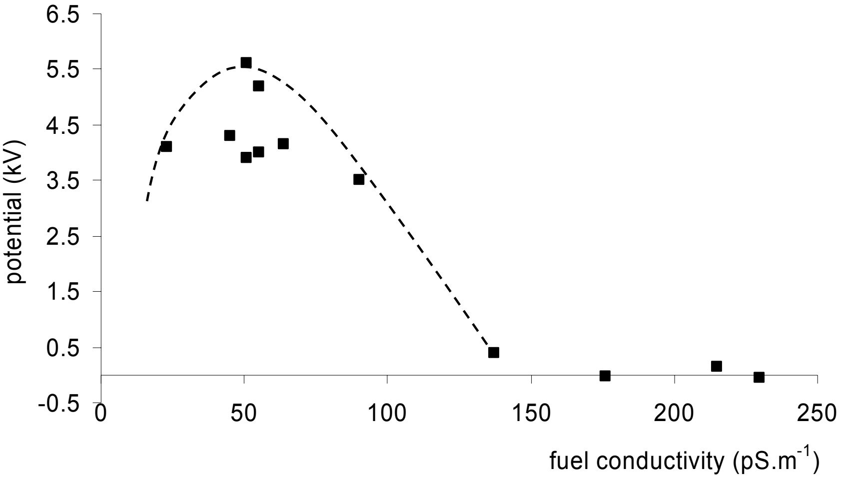

Figure 2. (a) Electrostatic potential in kilovolts developed on an ungrounded metal coupling during solvent flow at 2.8 m.s^{-1} through a plastic pipeline as a function of solvent conductivity[9]. Note: Dashed trend line is estimated.

In the SX process electrostatic charge is generated primarily due to solvent flow. SX plants can contain a combination of metal and plastic pipelines and both will generate charge on low-conductivity solvent. Long pipe runs and large numbers of bends and constrictions generally result in increased charging. Turbulent flow produces more charge than laminar flow and pipes with rough internal surfaces tend to produce more charge than smooth surfaces, even when the roughness is on too small a scale to affect the state of turbulence[10]. In all cases, plastic pipelines can constitute an increased hazard over metal pipes because the charge can accumulate on the inner pipe wall.

Table 1 shows the electrical conductivity levels encountered at the Oxide Plant of Minera Escondida in the north of Chile together with the corresponding pipeline flow velocity and the level of electrostatic potential monitored on the pipe work. Similar results were obtained at Cerro Colorado.

	conductivity	*velocity*	*temperature*	*Electrostatic Potential*
Pure diluent Shellsol 2046AR	1-2	-	17	-
Pure extractant Acorga M56-40	38	-	16	-
Process liquor (loaded organic)	140-180	1.3-1.5	22	1.3 (HDPE pipe) 4.0 (metal fixture)
Process liquor (stripped organic)	210	1.3-1.5	29	0.2 (HDPE pipe)
	$pS.m^{-1}$	$m.s^{-1}$	^oC	*Kilovolts*

Table 1. Data obtained from the Copper SX process at Escondida Oxide Plant (October 2004)[11].

4. ELECTROSTATIC IGNITION

For an electrostatic ignition to occur, a flammable atmosphere must co-exist with a sufficiently energetic electrostatic discharge (ESD). At normal SX operating temperatures, flammable atmospheres may be generated within gravity-fed pipelines and possibly settler, intermediate and storage tanks where air is present and frothing or mists are generated. The low ignition energy exhibited by SX solvents puts them at risk of ignition from brush discharges (from charged plastic surfaces) and sparks from charged ungrounded objects.

Electrostatic brush discharges are low in energy; up to around 4 millijoules. Spark discharge energy depends on the size and potential developed on an ungrounded conductor and in practice in SX plants may reach several tens of millijoules.

4.1. PIPELINES

Electrostatic ignition hazards may exist in plastic pipe systems (eg. HDPE, FRP etc.) if the following conditions prevail:

- Air is admitted during or immediately following solvent flow
- The solvent conductivity is low (less than 250 $pS.m^{-1}$)
- The electrostatic potential on the pipe wall due to solvent flow exceeds 20kV (negative polarity)[12]
- Ungrounded metal components such as valves, couplings and fittings are incorporated in the pipeline

Since both metal and plastic systems can charge low conductivity solvent there is little if anything to be gained by the inclusion of grounded metal rings between HDPE pipe sections. In fact this may worsen the hazard by (a) creating turbulence, (b) providing a path for brush discharges from adjacent charged plastic and (c) introducing a source of sparking should the ring become ungrounded.

(a) *(b)*

Figure 3. Measurements at Escondida Oxide: (a) Liquid conductivity measurement. (b) Electrostatic potential of -3.72kV on isolated metalwork.

The photographs in figure 3 show measurement of liquid conductivity and static potential at a metal sampling fixture on a plastic pipeline in the Copper SX plant at Escondida Oxide. The object exhibits a potential of almost -3.7 kilovolts and an electrostatic discharge could be drawn from the object to the approaching meter. The energy of the discharge was estimated at around 0.2mJ and close to the minimum ignition energy of an optimum concentration of kerosene vapour in air. Measurements taken on the surface of HDPE lines generally gave low readings with a maximum recorded potential of +1.3kV.

4.2. STORAGE, INTERMEDIATE AND SETTLER TANKS

At Cerro Colorado and Escondida Oxide SX plants no measurable electrostatic potentials were recorded in any of the tanks including plastic-lined. This was borne out by performing simple calculations based on the liquid conductivity of the fluid as follows:

The rate at which electrostatic charge is dissipated from the surface of a liquid in a tank is given by the time constant RC; where R is the resistance path to earth and C is the capacitance of the liquid surface. The RC time constant is the time taken for the surface potential to decay to 1/e (37%) of its value at any time.

Considering both rectangular and cylindrical tanks with organic fluid floating on an earthed aqueous layer, the resistance is given by the equation $R = d/\sigma.A$ where σ is the conductivity of the organic in $S.m^{-1}$ (10^{12} $pS.m^{-1}$), A is the cross-sectional area of the tank and d is the depth of solvent.

The capacitance is given by the formula for a parallel plate configuration (organic surface to aqueous surface); $C = A.\varepsilon_o.\varepsilon_r/d$. The time constant therefore becomes:

$$RC = (d/\sigma.A) \times (A.\varepsilon_o.\varepsilon_r/d) = \varepsilon_o.\varepsilon_r/\sigma$$

The constant ε_o is the permittivity of free space (8.85×10^{-12} $Farad.m^{-1}$) and ε_r is the dielectric constant of the organic fluid and probably has a value of around 2.

From the above equation it is possible to easily calculate the charge relaxation time of the various fluids simply by knowing their conductivity. In the case of the organic process fluids at Cerro Colorado and Escondida Oxide, the lowest conductivity value was measured at 84 $pS.m^{-1}$. This gives a charge relaxation time of 0.21 seconds. Considering the liquid flow rate into the tank it is clear that electrostatic charge will not accumulate on the organic.

The above calculation applies only to tanks in which solvent is floating on an earthed aqueous layer, which is the normal situation in a Loaded Organic Tank where the aqueous layer is earthed through the aqueous return pump. In such situations the provision of a grounding electrode such as a submerged grid or plate does not provide any extra benefit.

5. CONCLUSIONS

It must be assumed that pipes and tanks in SX plant containing organic solvent and air may produce a flammable atmosphere capable of ignition by electrostatic discharge at normal operating temperatures. Good plant design, however, can greatly reduce this risk by minimising the production of mists and foams.

It has been determined in previous work that under certain conditions significant electrostatic charge can be generated by the flow of liquids of conductivity less than 250 $pS.m^{-1}$. The SX process organics at Cerro Colorado and Escondida Oxide are of relatively low conductivity and therefore able to generate electrostatic charge. It is therefore important to determine if hazardous levels of static electricity can be expected as a result.

In principle, the two areas where electrostatic charge can accumulate are on HDPE pipework and the liquid and plastic liners in tanks. Both were examined during the Cerro Colorado and Escondida Oxide investigation. Despite low conductivity solvents there were relatively low levels of charging observed on the pipes, which was considered principally due to low flow velocities and short straight pipe runs. The maximum potential recorded on HDPE pipework was +1300V. These levels will not give rise to electrostatic discharge (ESD).

A voltage of around -4000V was observed on an isolated metal component (drain point) in an HDPE gravity line at Escondida Oxide. Furthermore, an electrostatic discharge (ESD) could be drawn. The energy of the ESD was estimated at around 0.2mJ and close to the minimum ignition energy of an optimum concentration of kerosene vapour in air. This demonstrates the importance of the grounding of all such fixtures and this should be rigorously applied. As predicted, no measurable electrostatic potentials were recorded in any of the tanks.

From this work BHPBilliton Base Metals believes that their existing plants are basically safe from electrostatic hazards. The new projects of Sulphide Leach and Spence have been designed in accordance with the principles enumerated at the start of this paper and, as a further precaution, the Loaded Organic Tanks have been sited within the individual SX trains rather than in the traditional location of the SX tank farm. This greatly reduces the lengths of the organic lines and thus further lessens the potential for electrostatic generation.

Since no two SX plants share the same design, the findings from Cerro Colorado and Escondida Oxide may be expected to differ from other plants but the general principles covered in this paper will apply.

6. ACKNOWLEDGMENTS

Gratitude is extended to Pablo Amigo of Minera Escondida Ltda for his work in coordinating the measurements at Cerro Colorado and Escondida Oxide.

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DESIGN OF COPPER SX PLANTS TO MINIMIZE STATIC AND OTHER FIRE RISKS IN THE LIGHT OF RECENT INDUSTRY FIRES

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1. INTRODUCTION

The first two commercial copper solvent extraction (CuSX) plants were small scale plants built in Arizona for Ranchers Bluebird Mine and Bagdad Copper in the USA in the late 1960s for treatment of heap leach and dump leach solutions respectively and producing 5500-6500 stpa cathode copper. These plants were followed shortly afterwards by the very much larger scale CuSX plant for ZCCM at Chingola, Zambia, for treatment of tailings leach solution and producing approximately 100,000 tpa cathode copper. Since then, CuSX plants have ultimately proliferated on a world wide basis, providing largely continuing improvements in design and seemingly ever decreasing unit capital and operating costs as plant sizes have increased from an early low of around 5,000 tpa to up to a current maximum of 168,000 tpa (185,000 stpa) at the world's currently largest electrowinning (EW) plant at Morenci, Arizona[1] or the even larger 200,000 tpa capacity plant to be built for the Spence project under development in Chile[2]. However, it would seem that somewhere along this development path of continually reducing unit capital costs that an air of complacency inadvertently crept into the design process for certain plant configurations. For plants designed prior to 2002, it would seem highly likely that the risks of fire occurrence and control may not have been adequately addressed and minimized. It is possibly only for plants designed within the last 2-3 years that fire safety issues have now been closely examined and incorporated into appropriate low risk designs.

Certainly the two recent major CuSX fires at the Olympic Dam copper-uranium mine in South Australia on 23 December 1999[3] and 21 October 2001[4] and the subsequent two smaller scale, but nevertheless equally serious, CuSX fires at copper heap leach operations at both the Metcalf plant of the Phelps Dodge Morenci copper operations in Arizona on 16 October 2003[5,6], and nearby Mariquita SX plant of Minera Maria (a subsidiary of FRISCO) in Mexico on 18 March 2004[7] have provided a wake-up call to the industry and demonstrated the need for a serious and immediate review of current CuSX design policies for fire control. Detailed reviews of fire safety by plant owners, engineering companies, risk assessment companies, diluent and reagent suppliers, specialist process consultants, insurance companies, state mining regulators, lawyers and others have already occurred to varying degrees on the plants affected by the fires, but regrettably with only limited public reporting of the findings to date. The results of these and other reviews are being applied to the design of a limited number of new plants and possibly to the retrofit of selected existing plants in order to minimize the risk of fire in selected plants. Little is known about the status of any refit on many of the older CuSX plants that may possibly still be subject to significant fire risk.

Control of static and other fire risks in CuSX plants is addressed in this paper, primarily from a historic plant design review perspective, but also drawing on literature, public domain and Freedom of Information sources on fire events at Olympic Dam and other plants where available.

The authors of this paper have a chemical engineering background and have been involved for much of their careers in the development and process design review of CuSX and USX plants for mining companies, engineering companies, third parties as well as currently being independent consultants. Their experience has extended from the earliest days of SX design and development through to recent plant designs. This paper represents an attempt to share a process-orientated knowledge base with others so that new and/or existing plant designs can be modified, where required, at minimum cost to ensure greater fire safety in the industry.

Causes of fires in CuSX plants include static electricity, inadequate piping design allowing the formation of flammable vapours and mists inside organic drain lines, and human error during maintenance work. It is interesting to note that of the four fires that have occurred since 1999 all have taken place in relatively new plants owned by both major and junior mining companies and built by both major and small engineering companies. The risks of fires would therefore appear to be independent of the level of financial or technical backing of the mine owner or the engineering company, and to be more due to a culture that has been somehow insensitive to the real risks of fire in CuSX plant design, operation and maintenance.

2. HISTORICAL CUSX DESIGN DEVELOPMENTS

A paper[14] presented by the authors at Alta Cu 1977 in Brisbane, Queensland, Australia, evaluated developments and trends in commercial solvent extraction mixer-settler and contactors at that time. Key process issues relevant to fire risks, not necessarily identified in the same way in the earlier paper but specified more clearly in the current paper, include:

- Evolutionary changes with time in the selection of different materials of construction for mixers, settlers and interconnecting piping, based on targeting lowest possible capital costs for handling various site liquors (some containing high chloride levels unsuitable for stainless steel materials, especially in Chile) and generally increasing pregnant liquor flow rates, including the first use of various construction materials as follows:
    - FRP-lined concrete mixer-settlers (Ranchers, Arizona, 1968).
    - FRP free standing mixer-settlers (Cyprus Johnson, Arizona, 1976).
    - PVC Lined steel mixer-settlers (Anaconda Arbiter Plant, Montana, 1974).
    - Stainless steel free standing mixer-settlers (Bagdad, Arizona, 1970 and Twin Buttes, Arizona, 1975).
    - Stainless steel lined concrete mixer-settlers (Nchanga, Zambia, 1974).
    - HDPE lined concrete mixer-settlers (Codelco, Chile, 1987)
    - FRP interconnecting piping (Ranchers 1964 and Cyprus Johnson 1976, Arizona).
    - FFRP reinforced PVC interconnecting piping, Nchanga, Zambia, 1974.
    - Stainless steel interconnecting piping (Bagdad, Arizona, 1970, and Twin Buttes, Arizona, 1975)
    - HDPE interconnecting mixer-settler piping (Inspiration, Arizona, 1979, Codelco, Chile, 1987 and Krebs SX Olympic Dam, South Australia, 1988)
- Use of plastic construction materials that were known to be flammable (HDPE lining, HDPE piping, FRP lining and FRP piping unless impregnated with a fire retardant), but were still used because HDPE, the most common material, was generally considered to be very difficult to ignite and burn, until the two recent Olympic Dam CuSX plant fires.
- Relative humidity and temperature at the site and their effects on flammability.
- Number and spacing of SX trains and whether a CuSX mixer-settler affected by fire could be scuttled, or rapidly dumped, to a safe discharge area that would not allow fire to spread back to the rest of the plant.

- Plant layout changes with time including:
  - Initially an older style above-ground mixer-settler design with the settlers being supported by a steel, concrete or FRP structure well above ground, the mixers being supported on or slightly above ground, and the active level of organic in organic holding tanks being at essentially the same elevation as the active level of the organic and/or combined phases in the mixer-settlers. *In the opinion of the authors, this design would have resulted in:*
    - *Mainly full loaded organic lines, especially if a butterfly valve were included to control pressure drop and level in the loaded organic discharge weir box, and the line entered the loaded organic tank via a bottom entry.*
    - *Minimal air entry into the loaded organic line, provided that a suitable vortex breaker was located at the organic pipe inlet and a suitable pipe sizing had been selected, but still allowing burps of air to occasionally accumulate and release back in the organic weir.*
  - A subsequent “low-profile” modern mixer-settler design as pioneered by Holmes & Narver on the Cities Service Miami SX plant design in 1976, whereby in addition to shallow mixers and settlers located on ground level. a separate tank farm area containing the organic and other recirculating fluid tanks was located about 3-5 m below the ground level in an adjoining dedicated area*. In the opinion of the authors, this design would have resulted in:*
    - *Only partly full loaded organic drain lines and high organic velocities down those lines, unless a butterfly or similar valve were included in the drain line to control pressure drop so as to hold a full line, except possibly for the final drop of organic level from the upper entry point of the loaded organic holding tank into the lower level of the loaded organic holding tank via a bottom entry organic line or its equivalent.*
    - *Possibly significant air entry into the organic line unless a suitable vortex breaker was located at the organic pipe inlet and suitable pipe sizing had been selected, but still allowing burps of air to occasionally accumulate and release in the organic weir. If the organic entry to the loaded organic holding tank was located in an open air space above the operating liquid level, possibly significant amounts of air from within the holding tank could have entered the organic discharge pipe and mixed with the free falling organic to form an emulsion on the surface and organic mist in the vapour space as the organic transferred to the holding tank.*
  - Subsequent conventional mixer-settler designs involved on-ground settlers, or slightly above ground settlers supported by compacted earth fill which were initially close coupled to the loaded organic holding tank with a full operating tank level at the same organic level as that in the settler, but were later coupled to a more distant loaded organic holding tank situated in a tank farm located at a much lower operating fluid level than that in the settler. *In the opinion of the authors,* t*his design would have resulted in:*
    - *Mainly full loaded organic drain lines for the initial close coupled design.*
    - *Probably only party full loaded organic drain lines in the later tank farm designs, unless a butterfly or similar valve was included in the line to control pressure drop so as to hold a full line, except for the final drop of level from the upper entry point of the loaded organic holding tank into the lower level of the organic holding tank via a bottom entry organic line or its equivalent.*

- Air vents in the loaded organic drain lines to try to minimize air entrainment in those lines at two plants:
    - The Cyprus (formerly Anamax) Twin Buttes plant (1974), with one air vent located on the loaded organic drain line close to the entrance to the loaded organic holding tank. *This design apparently was intended to release any entrained air prior to the organic phase entering the loaded organic holding tank. The loaded organic tank ran at the same operating liquid level the adjoining settler, and was equipped for bottom entry so that settler, so that there was always a back pressure of organic in the air vent, thus preventing the ingress of air.*
    - The WMC Olympic Dam CuSX "conventional design" CuSX plants, in the 2002 fire and possibly also in the 1999 fire, at apparently two locations in each loaded organic gravity drain line for CuSX trains A and B. One air vent, the upper air vent, was located at the start of the loaded organic drain line shortly after the organic exited the settler. The other air vent was located at the end of the loaded organic drain line near the point where the drain line entered an organic holding tank in a below ground tank farm. *These designs apparently resulted in substantial mixing of air and organic and organic mist formation in partly filled loaded organic drain lines at both the start of the line and at the end of the line.*
- Static discharge rings consisting of electrically earthed metal flanges located at regular points along the length of the HDPE organic drain lines and protruding possibly as much as 2 cm into the 630 mm ID inner flow space of the HDPE piping were apparently installed within the loaded organic drain lines at Olympic Dam to try to minimize static build up within the organic flow. *Coupled with the effects of the air vents,* t*his design appears to have lead to:*
    - *Aggravated turbulence and air mixing within the loaded organic phase.*
    - *Numerous crud collection points on the immediate upstream side of the flange points along the entire length of the loaded organic drain line, which was only apparently about 60% full at maximum flow due to the large drop in elevation from the entry point to the exit point.*
    - *Organic flow velocities that were higher than the safe design levels for control of static.*
    - *Mists of air and organic plus foaming of the organic, that would appear to have led to a flash point that was much lower than the design flash point for a non-aerated organic.*
    - *Key points of high aeration within the pipe that would appear to have been vulnerable to ignition by an electrostatic discharge from a highly charged HDPE surface or the loaded organic liquid surface.*
    - *At some point during SX plant start-up and flow stabilization, a fire inside the part filled and aerated HDPE loaded organic drain pipe that was able to be sustained possibly by crud and HDPE burning at a highly aerated flange point near the discharge end of the pipe for a sufficient length of time so that the HDPE pipe walls became weakened by high temperature, collapsed by melting and subsequently ruptured to allow burning organic to escape through the molten and rapidly widening pipe void.*

- Some mixer-settlers were designed without covers in Arizona in the mid to late 1970s to secure capital cost savings, but with design provisions for adding a cover later if required (Cities Service, Arizona, 1976). Earlier plants and most, but not all, later plants included a cover as part of the original mixer-settler design and installation. *The covers were intended not only for dust control, but also for control of diluent evaporation and for containment of fire fighting foam that was designed to be rapidly applied to the organic surface to smother a fire through use of automatic fire fighting nozzles located above the top of the mixers and settlers in the more advanced fire fighting systems. The plants without settler covers were of stainless steel construction with stainless steel piping which would not have provided a supplementary flammable source of combustion throughout the plant.*
- Fire control design measures in most of the very early CuSX plants were relatively basic but effective and included:
    - Limiting organic line velocities to less than approximately 1 m/sec, for minimizing pressure drop in the lines connected to the low head pump mixers in each primary mix box and to minimize static generation in organic liquid flow.
    - Ensuring that organic lines were kept full to minimize air entrainment in the organic.
    - Use of materials of construction such as FRP with fire retardant or stainless steel for construction of mixers, settlers and interconnecting pipe lines.
    - Suitable lightning protection to ensure that lightning could not initiate an SX fire, even in an open settler.
- Static generation from organic flow and the possibility of fire occurring within the contents of an organic pipe from a static discharge did not appear to be a serious process concern in early CuSX plants.
- A fire in an electrical motor located above the organic in the primary pump mixer box or in an organic transfer pump or because of welding sparks during maintenance on an organic tank seemed to be regarded as the main area of risk in early plants where the materials of construction were essentially non-flammable.
- The flash point of the organic was considered to be high enough to avoid any real concern of fires from a low heat source such as a match. There was even the unusual demonstration of throwing a match onto the surface of the organic and noting that the match extinguished, to demonstrate that the organic was not easy to ignite.
- Even when HDPE usage for piping and tank lining became common, there appeared to be a general perception that HDPE, an organic material, was difficult to ignite. The potential consequences of unexpected ignition of HDPE were therefore not considered as seriously as they should have been in hindsight.
- CuSX plants that included low level tank farms for organic storage and recycle would appear in hindsight to have been the first CuSX plants to breach the 1 m/sec organic drain line velocity constraint for static generation, unless flow control devices were used in the loaded organic drain lines to constrain the velocity to less than 1 m/sec. If constructed of stainless steel piping, the risk of a fire within the organic drain line would have been minimal, even though the organic could still have become highly charged during its transfer down the partly empty drain line. If constructed of HDPE piping without any flow velocity controls, as would appear to have been the more common practice for plants constructed after 1988 through say 1992, the risk of fire from an electrical discharge due to static would have been much higher.

- The drawbacks to the design evolution of CuSX plants would appear to be the failure to consider at a much earlier stage of the design the application of the risk management processes used to ensure fire safety in the oil and gas, petrochemical and refining industries, where much larger volumes of highly volatile solvents are handled with much greater safety, except for the milestone disasters such as Flixborough in the UK and some similar high profile disaster events in the USA.
- The salutary and frightening conclusion to the SX plant fires has been that if the fire is not under control or isolation within the first few minutes of the outbreak that potentially the whole SX plant will be lost within the next 6-24 hours due to the size of the interconnected burning fuel sources and the intensity of the fire, no matter how many fire appliances might be available to try to control the fire.

3. STATIC

From initial references to static as a probable key cause of the 2nd fire at Olympic Dam[4] and also as a possibly contributing cause of the 1st fire at Olympic Dam[3] in the SA Metropolitan Fire Reports on those fires, and from the subsequent more detailed references to static in the two more detailed reports by the South Australian Mines Inspector on the same two fires, and obtained by IPDS under Freedom of Information provisions from the Department of Administrative Services of the South Australian Government, further historical as well as more recent references on static have been collected[10-13]. Relevant excerpts on static are reviewed below:

Designing solvent extraction plants to cut the risk of fires, Davy International Minerals and Metals Ltd, Gordon Collins et al, E/MJ December 1978[10]

- Pipeline Design:
    - Generation of static electricity is proportional to the flow velocity, which must be limited to safe values.
    - *API* 2003, "Recommended Practice for Protection Against Ignitions Arising out of Static, Lightning and Strong Currents, " October 1974 refers to 1.8 m/sec where the discharge is always below the tank liquid level.
    - A velocity of 1 m per sec is recommended for all SX piping to allow for variations at startup and during abnormal operations.
    - Piping material is also an important factor in calculating the generation of static electricity. Nonmetallic materials, fibreglass-reinforced plastic (FRP) and similar materials present more difficulty *with respect to charge dissipation.*
- Grounding for static electricity discharge:
    - Grounding is an important design consideration.
    - Pipes and equipment must be adequately bonded and grounded to prevent sparking from static buildup and accidental discharge in the presence of flammable liquid or vapor.
    - FRP pipe and vessels may be covered with conducting paint to dissipate any static that collects on the outside of the pipe lines .*(IPDS comment: external conducting paint may not significantly help dissipate static collecting on the inside of the pipe or in the organic phase flowing within the* pipe.)

Fire Protection For Solvent Extraction Plants, What We Can Learn From Olympic Dam, Frank Rizutto, Plumbing Engineer, July 2002[11]

- Static Discharge As Ignition Source:
    - Fire in the 2001 Olympic Dam fire was believed from public domain reports to have originated from static discharge within the piping network.

- Flow of a relatively non-conductive liquid through piping creates the probability of buildup of a static electrical charge in the liquid.
- Other potential ignition sources including electrical connections, electrical cable overheating, electrical motors, sparking tools, welding, and smoking were considered much less likely than static electricity.
- At Olympic Dam, relatively non-conductive liquid was flowing through non-conductive HDPE pipes.
- Kerosene has about six time the ability of gasoline to generate static.
- In the case of relatively non-conductive fluid flow through metallic piping, the static is readily discharged to ground when the piping and equipment are properly bonded and grounded.
- In the case of non-conductive fluid flow through plastic piping, the static cannot be readily discharged and accumulates within the fluid
- The generation of static is in itself not hazardous.
- The real danger was said to lie in the accumulation of static because in this way energy can be stored to create a spark capable of igniting a flammable vapor-air mixture. For comparison purposes, sliding across an automobile seat was pointed out to generate up to 15 mJ, while the energy level required for ignition of a flammable liquid mist was approximately 1 mJ.
- Sparks have been reported to be seen darting across the liquid surface of an agitation tank containing high flash point liquids.
- Sparks can also occur above the liquid surface.
- In the case of lower flash point products in other operations (Class 1 flammable products such as gasoline), vapors at the liquid surface may be too rich (above the upper flammable limit) to ignite and static charge tends to relax as liquid settles in a vessel after filling.
- In the case of CuSX operations, when flammable vapor or flammable mist is present at the solvent surface, it is more likely to be between its lower and upper flammability limits, and solvent in the mixer-settler circuit (*or presumably in a solvent holding tank*) remains at rest long enough to relax its static charge. In this scenario, the fire triangle can be revised from:
    - Fuel + air + ignition source = fire

      to:

    - *Fuel + air = fire*

      since all external ignition sources will have been eliminated. The fuel itself was suggested to provide the ignition source.

- The mixture of conducting and non-conducting materials (*presumably meaning the organic liquid and piping materials*) as well as turbulence caused by the metallic fittings and changes in direction, spillage into vessels, agitation, filtering and drainage promote the generation of static in the system.
- The problem of mitigating the static charge on the liquid surface reportedly cannot be solved by attaching any number of ground wires to it. Instead it is considered necessary to reduce or eliminate static generation, volume charge or surface charge.

- The most hopeful solution was felt to lie in the development of a non-contaminating additive that would lower the resistivity of the solvent to a value where static generation would be eliminated. (*IPDS understands from other sources that such an additive may have been found and patented by WMC for Olympic Dam.*)
- Mechanical measures to reduce the generation of static include:
    - Non-centrifugal transfer pumps that are designed to create the least turbulence.
    - Pressure reduction within the piping to the lowest values for efficient liquid transfer where possible.
    - Fluid velocity reduction, noting that the same volumetric flow rate of pumped liquid travels at a lesser velocity through a larger diameter pipe. *(IPDS comment: reduction of flow velocity in non-pumped or gravity flow lines will require a suitable control valve at the end of the line to keep the pipes full of liquid and to minimize air collection along as much of the pipe length as possible)*
    - Elimination or reduction of restrictions in the piping system that cause turbulence as much as possible. (*IPDS comment: this requirement would appear to include the elimination of multiple metallic static rings in piping, such as those used at Olympic Dam.*)
    - Selection of higher radius bends in piping runs.
    - Submergence of tank infeed nozzles. Avoidance of splash filling. The velocity of flow and the method of introducing the flow into a vessel should be such as to keep from stirring up water or other aqueous material which increase the ability of the solvent to generate static
    - Bonding and grounding of all metallic elements in the piping system, such as pumps and tanks, was considered to be a prerequisite to a program of static mitigation in the SX area.
    - The additional capital cost of suitable stainless steel (*or presumably other appropriate piping materials such as FRP with carbon and fire retardant impregnation*) over (*current HDPE)* plastic could well be justified in light of heavy dollar losses associated with fires in (*HDPE*) piping and equipment.
    - Static electricity should not be regarded as the cause of the fire. Rather the cause should be considered to be the condition that led to the formation of a flammable vapor concentration or flammable mist within or around the piping or equipment where a static spark was likely to occur.
    - Static-induced explosions and fire in flammable vapours and mists have reportedly even been initiated in non-CuSX plants (*at flanges or in vessels)* by operators who had previously removed a piece of clothing or descended a stairway while holding onto a plastic-covered handrail. The spark sequence and spark control solutions were suggested to include:
        - The wearer of insulating footwear acquires a charge, and a spark jumps from a hand-held tool to the open pipe or vessel allowing a flammable vapor or mist to be ignited.
        - Such sources of static-induced sparks cannot be entirely controlled, but the formation of a flammable mixture in air can be controlled.

    - It was considered to be better to shut off the pressure in a leaking solvent line and eliminate the flammable mist before tightening loose flange bolting to stop the leak.

- Specific recommendation on static control for new or upgraded facilities were noted to be:
    - Assessment of the piping network for causes of static build-up and methods of mitigating static charge in piping and equipment.
    - Implementation of solutions to reduce the volume of ignitable vapours present during normal and upset conditions.
    - Provision of electrical earthing (grounding) straps for grounding mechanical equipment and tanks.
- Other sections of the Rizutto paper covered important additional topics such as:
    - Flash point and the fire triangle.
    - Mechanical failure as contributing factor.
    - Vessels and tanks.
    - Piping.
    - Maintenance procedures for risk reduction.
    - Fire prevention and plant security.
    - Fire detection and suppression in SX units.
    - The Olympic Dam fires- what worked and what didn't.
    - Fire protection for new facilities and upgrading of existing plants.
    - Summary and conclusions.
    - References.

Electrostatic Hazards In Solvent Extraction Plants, Peter Haig and Jodie Maxwell, Shell Chemicals and Theo Koenen, Shell Engineering Ltd, ALTA Cu 2003, Perth, Australia [12]

This key paper provides a diluent supplier viewpoint of the risks caused by static generation in CuSX plants, based on experience with hydrocarbons in the oil and gas industry. It highlights the flammability of and ignitability of CuSX diluents compared with other solvents, the mechanics of electrostatic charging of the SX solvent, how charge accumulates, the different types of electrostatic discharges that can occur and the applicability of these issues to improvements to the safe design and operation of solvent extraction plants.

Key points include:

- The need for a heightened awareness of electrostatic hazards in CuSX plant design, management and operation to avoid major fire risk.
- The occurrence of many serious accidents in the oil and gas industry due to electrostatic discharge during large scale hydrocarbon processing and handling.
- The occurrence of numerous fatalities due to electrostatic discharge during filling of cars with gasoline at service stations in the USA (comment by presenter of the Shell paper at the ALTA 2003 conference)

- Insufficient attention given in past CuSX plant designs to the hydrocarbon handling risks through a tendency to think of the plants as simple aqueous handling plants without major fire risks.
- The heightened danger of electrostatic hazard in CuSX plants due to:
    - The extensive use in many CuSX plants of non-conducting HDPE, a flammable material with no fire resistance, for:
        - pipeline transport of solvent
        - liners of mixer tanks that mix solvent and aqueous phases
        - liners of settlers that separate solvent and aqueous phases.
    - The low conductivity of CuSX solvents as opposed to USX solvents.
    - Significant electrical charge generation as low conductivity solvent flows at high velocities over non-conducting surfaces.
    - Electrical charge accumulation in the solvent during pipeline flow.
    - Production of high electric field strengths and potentials of sufficient levels to result in electrical breakdown of the air in the pipe or tank.
    - Ignition of the solvent or solvent vapour where the discharge energy is high enough and the vapour is within upper and lower flammability limits.
    - The little know fact that potential ignition of solvent mists (suspended droplets in air) or solvent foams (aerated solvent) can occur at up to 20C below the flashpoint of solvent by itself (normally approximately 80C) if conditions are appropriate.
    - Mists and sprays being generated when hydrocarbons moved through high shear pumps and mixers and other turbulence creating devices are exposed to air.
- High flash point diluents used in CuSX plants having a typical volume percentage range in air of:
    - LFL (lower flash limit) of approx 0.7 vol% in air
    - UFL (upper flash limit) of approx 7 vol% in air.
- A saturated vapour composition of below the LFL being too dilute to be flammable and of above the UFL also being too rich to be flammable.
- The impossibility of combustion if the concentration of oxygen in the atmosphere is too low, such as achieved by:
    - keeping a CuSX organic line full of solvent during operations
    - inerting a vapour space with an inert gas such as nitrogen of carbon dioxide.
- An MIE (Minimum Ignition Energy) capable of igniting most hydrocarbons including CuSX organics of only 0.2 mJ versus the much higher spark energy of 40 mJ received when “zapped” from your car on a dry day.
- Electrical potentials of up to 20kV measured in CuSX plants where there is high shear mixing and pumping of low conductivity organic through insulating HDPE pipes. The current carried by the organic leaving the pipe is known as the “streaming current”.
- Electrostatic charges are generated by:
    - Relative movements of differing liquids such as aqueous and organic when agitated (The organic charges are left fixed in the bulk phase after settling of the aqueous)

  - Atomization or misting when an organic liquid is separated into fine drops, due to poor design of the piping system or excessive agitation.
  - Splash filling of the organic in loaded organic tanks.
- Hazardous potentials can be reached by all CuSX diluents through simply passing through a micro filter.
- Ignition of a flammable atmosphere by internal electrostatic discharge can take the form of three types of discharges:
  - Spark discharges that occur when:
    - The spark energy exceeds the MIE
    - The voltage exceeds 1kV for organic (e.g. a potential of more than 4 kV would be sufficient to cause an incentive spark from a 600mm internal diameter HDPE pipe where the stored electrostatic energy was 0.2 mJ).
  - Glow coronas from a single sharp conductor that has been raised to a high potential, but only for highly sensitive materials such as hydrogen and not for CuSX organic.
  - Brush discharge between blunt conducting electrodes and insulating materials such as solids or low conductivity liquids such as CuSX organic and characterized by:
    - Energies as high as 4 mJ
    - Ability to ignite most gases and vapours.
- Typical CuSX organic handling operations that can give rise to electrostatic ignitions include:
  - Filling tanks and containers such as sample buckets.
  - Circulating organic through partly filled tanks.
  - Road tanker deliveries of diluent.
  - Agitation of two phase mixture.
  - Settling of two phase mixtures.
  - Crystallization from low conductivity liquids such as loaded organic.
  - Passing organic through insulated pipes.
  - Passing organic through flexible hoses.
  - Filtering organic.
- Typical conductivities of fresh lab CuSX organics containing 0-10 % oxime or similar reagents are low and of the order of 20-30 pS/m, with a relaxation time of 150-200 seconds, versus high conductivities of the order of >200000 pS/m for USX diluents containing 5% tertiary amine.
- The addition of SDAs (static dissipating additives) to increase conductivity, as used for diesel and kerosene, has yet to be successfully applied for CuSX diluents due potential detrimental properties in CuSX plants for commonly know SDAs.
- Piping and lining:
  - Shell recommends against use of non-conductive pipes and non-conductive lined settlers such as HDPE due to accumulation of static charge and the lack of dissipation of that charge.
  - Shell recommends:

- Extra precautions to be taken if the piping and lining are made of HDPE including:
  - Earthed stainless steel grid to be applied in the loaded organic tank.
  - Flange earthing connections to be made in parallel, not in series, with a continuity of <10 ohms and checked at least 6 monthly.
- Tanks to contain:
  - conductive metal plates to the highest liquid level.
  - metal plates to be bonded and ground to earth.
  - metal plate surface area to be not less than 512 cm2 per 1000 litres (1 m3) of organic.
  - liquid not more than 2m distant from the nearest immersed part of the earthed metal plates.
  - incoming fill line discharge velocity not exceeding 1m/sec.
  - residence time of at least 2minutes for static dissipation.
  - fill pipes with a large diameter outlet that was directed to minimize turbulence, to discharge near the bottom of the tank, submerged to a depth of not less than 500mm of twice the ID of the pipe and not disturbing the water in the bottom of the tank.
  - spark promoters that have been grounded or else removed.
  - all conductive tank components that are grounded.
  - no conductive surface skimmers if metal plates are absent.
  - conductive material (e.g. stainless steel or conductive GRP) that lines the walls and is grounded.
- Mixer-settlers to include:
  - All of the above provisions for tanks.
  - Avoidance of excessive agitation of aqueous with organic.
  - Where mixer-settler are lined with non-conductive material:
    - Conductive plates <u>just below the liquid</u> <u>surface</u>.
    - Consideration of earthed stainless steel picket fences as an effective measure for dispensing some of the charge.
- Piping materials to incorporate:
  - Piping systems made of conducting materials such as stainless steel or conductive GRP or similar conductive materials.
  - **Lines filled with organic to avoid formation of a potentially flammable atmosphere where there are vapour spaces**
  - Avoidance of flow through filters and screens where possible.

        - Liquid flow velocity such that V2d shall not exceed 0.64 (where V= flow velocity in metre/sec and d = pipe diameter in metre).
        - Relaxation sections in non-conductive piping by insertion of a suitable length of earthed (enlarged diameter) metal pipe of length determined from:
            - l/V = (3x18)б

          where l = length of relaxation section in metres, V = flow velocity in section in metres/second and б = liquid conductivity in picoSiemens per metre (typically 30 pS/m in CuSX organics).
        - Relaxation section to include:
            - construction and connection to minimize organic turbulence within the section .
            - location along organic piping line:
                - close to organic receiving tank
                - downstream of any filters and coalescers.
        - All electrically isolated sections of metallic piping, valves etc to be bonded and grounded to earth.
    - Organic pumps to include:
        - Double mechanical seals with barrier liquid and seal supporting system.
        - No belt driven equipment operating above open sumps that could provide an electrostatic discharge from friction on the belt to ignite heavier than air vapours in the sump .
        - Direct drives only when operating above open sumps.
    - All solvent extraction plants to be audited:
        - to ascertain hazardous areas (Zones 0, 1 or 2).
        - to ensure that only electrical equipment that is rated for the respective zones is used in each zone.
    - Clothing, gloves and footwear to be carefully selected such that:
        - Clothing has a surface resistance of less than 5 x1012Ώ including:
            - Use of fibres such as cotton, flax and linen if the relative humidity is above 65%.
            - Avoidance of use of synthetic materials unless specially treated and regularly retreated.
        - Or, clothing includes conductive fibres in the fabrics.
        - Clothing, gloves and footwear is either conductive or anti-static, where there is an ignition risk.
    - Conductive surfaces such as metal grid flooring to be kept clean from insulating deposits where there is an ignition risk
- The following mechanism of static charging and ignition of flammable atmosphere by personnel:

        - Mechanisms for charging the human body include:
            - Walking on an insulated floor .
            - Cleaning an insulated object by rubbing.
            - Contacting another charged object
            - Induction in the vicinity of another charged object.
            - Sliding off an insulated seat.
            - Removing clothing especially when contaminated with organic.
        - A person that is charged and sufficiently insulated:
            - Will almost inevitably produce a spark when approaching an earthed object.
            - Can generate a potential of higher than 30kV.
            - Can store a charge that is as high as 90 mJ.
            - Can produce an incendive spark.
        - Ignitions will be produced by sparks from people when:
            - A flammable atmosphere is present.
            - There is a mechanism for generating charge on people.
            - People have a high resistance to earth (i.e. are electrically insulated) so that charge accumulates.
    - Risk management practices similar to those adopted in the oil and gas industry were expected to allow safe continued operation of CuSX plants with little or no risk to employees of the company if the risks were properly understood.
    - Actions recommended by Shell for safe CuSX plant operation included*:*
        - Consultation with relevant national and international regulatory requirements.
        - Ascertain the conductivity and electrical potential of the CuSX plant.
        - Review the materials of construction of the plant.
        - Audit to assess the hazardous areas of the plant.
        - Perform a "Risk Assessment Audit" to identify hazards such as hazardous ratings of electrical equipment.
        - Issue staff with appropriate clothing and footwear.
        - Maintain continual vigilance to the possibility of static build up and discharge.

What sparks danger in solvent extraction, Graham Hearn, Mining Magazine, pg 32, March 2005[13]

This more recent paper, based on experience gained from a review of the influence of static in the Olympic Dam fire, raises further points on risks and the evaluation of static electricity in SX plants and provides additional advice on how the causes of static can be avoided. Specific points include:

- With the correct approach, risks presented by static electricity can be quantified and controlled.
- Five general conditions are necessary for an electrostatic ignition to be present**:**

  - Presence of a sensitive flammable atmosphere
  - Generation of electrostatic charge
  - Accumulation of charge
  - Electrostatic discharge
  - Sufficient discharge energy.

Flammable atmospheres:

- An electrostatic discharge (ESD) is a low-energy ignition source and may produce only a few millijoules of energy (one millionth of the energy of a burning match).
- For ignition by an electrostatic hazard, it is only necessary to restrict investigation of flammable atmospheres to those sensitive enough to be ignited by electrostatic discharge, or usually flammable gases, solvent vapours and aerosols for SX plants.
- SX operations take place at temperatures well below the diluent flashpoint of about 80C and the vapour concentrations within the plant will therefore never reach the lower explosive limit.
- Foaming (fine droplets in air) of the solvent surface will however provide a sensitive atmosphere at normal plant operating temperatures and the solvent becomes sensitive to ignition at below the flash point.
- Foaming kerosene surface can be ignited with a spark energy below 10 mJ at 30C and below 1 mJ at 65C, both of which conditions have been observed in SX plants.

Electrostatic ignition:

- A fire caused by static energy is the result of a chain of events.
- The diluent and extractant in CuSX plants can have low electrical conductivity of the order of 1-10 pS/m for virgin diluent, 50-500 pS/m for typical organic process liquids.
- Studies for Olympic Dam by Wolfson Electrostatics have shown that the conductivity range producing maximum electrostatic activity in fuel flow through plastic pipes is 1-200pS/m, particularly at high speeds through long pipe runs.
- The level of charging in the organic is increased by:
  - Pipeline features causing by turbulence such as elbows and pipe constrictions.
  - Presence of an immiscible phase such as water droplets.
- Electrostatic charges will accumulate or dissipate depending on the conductivity of the liquid and the vessel of piping.
- Concrete, aqueous liquids and metals can be considered conductive in electrostatic terms.
- Polymers such as HDPE, glass fibre (GRP, FRP) and organic solvent may retain electrostatic charge for many minutes or even hours
- Electrostatic charges can accumulate on insulating surfaces such as plastics and also on ungrounded conductors, and both these situations can be equally hazardous.
- One example of an ungrounded conductor is a metal valve in an HDPE pipe.
- After static has accumulated to a certain level an ESD can occur.
- Two distinct types of ESD may be encountered in SX plants:
  - Spark discharge:
    - o Responsible for most industrial fires and explosions caused by static electricity.

    - Occur from conductive objects such as ungrounded metal fixtures and even personnel.
    - Typically 1-100 mJ energy
  - Brush discharge:
    - Occur from charged non-conductive surfaces such as highly charged plastic pipes.
    - May occur from the surface of a highly charged organic solvent
    - Maximum 4 mJ.
- Work at Southampton University has shown that both types of ESD are capable of igniting SX organics at temperatures well below the flash point, provided that certain conditions are satisfied.

Hazard Evaluation:

- The five conditions necessary for ESD hazard in CuSX plants are considered by Wolfson Electrostatics to most likely to occur in plants like the CuSX plants that were destroyed at Olympic Dam :
  - Within or around plastic (e.g. HDPE) pipes carrying organic solvent
    - Including gravity fed lines that may contain foaming surfaces and air in the presence of highly charged HDPE surfaces.
    - At small leaks in pressurized lines that may produce a most of solvent vulnerable to ESD at plant operating temperatures.
  - Possibly within HDPE-lined tanks.
- The ES activity in CuSX plants varies from one mine to another with the level of hazard depending on materials used, process parameters and plant layout.
- An ES safety audit will determine whether any measures are needed to lower or maintain the level of risk, including:
  - Monitoring the ES properties of the solvent and the static potentials at key points within the process.
  - Essential checking of the grounding of all metal work including:
    - Metallic components within plastic pipe, noting that metallic valves that have internal electrically insulated parts that may cause sparking.
    - The adequacy of existing provisions for relaxing charge from the organic surface of HDPE or other non-conducting lined tanks, noting that calculations based on liquid conductivity can be used to determine measures to be adopted.
  - Providing guidelines for implementation of key parameters such as:
    - Organic flow velocity.
    - Grounding maintenance procedures.
  - Identification of possible further safety improvement measures.

Investigation of Copper-Uranium Solvent Extraction Plant Fire at Olympic Dam-21/10/2001, MA Wilson, Inspector of Mines, July 2002[9]

This extensive South Australian State Government Department Report, obtained under Freedom of Information, provides an extensive review of virtually all aspects associated with the Inspector of Mines' investigation of the 2001 CuSX fire at Olympic Dam. Specific findings of the report of relevance to static electricity, crud presence, crud fire test, internal pipe conditions prior to fire, weather conditions, plant redesign recommendations of Shell, Hazop studies, other SX designs, Factory Mutual Global loss prevention, misting of solvent, fire consumables and factors and fire damage include the following:

- The direct cause of the fire was not known with absolute certainty
- The fire was believed to be due to static electricity igniting:
    - Flammable or combustible hydrocarbons within a deposit of crud, or
    - Misting and/or vaporized organic in the pipe and then crud
    - within an HDPE pre-scrub loaded organic drain line at a point about 10 m from the discharge end into an HDPE-lined loaded solvent (recirculation) tank.
- The loaded solvent tank was located under gravity feed at level in a below-ground tank farm well below the level of the organic in the organic weir of the mixer-settlers.
- The crud was apparently deposited on the circumference of metal flanges used to try to control static at uniform intervals down the length of the loaded organic drain line.
- HDPE piping had been selected for use throughout most of the SX plant rather than stainless steel because of its high acid and chloride resistance and low initial installation cost, rather than stainless steel which was used in limited sections but was expected to be subject to corrosion.
- HDPE piping is a combustible solid that will melt and flow in a fire situation
- The burning HDPE pipe just ahead of the loaded solvent tank allowed organic to fuel:
    - the fire on the ground and to spread away from the pipe rack into the tank farm below
    - the fire burning within the HDPE piping on the pipe rack back along the pipe rack towards the mixer-settlers and other upstream equipment .
- The selection of HDPE in the first place by WMC was reported to be based on a comment in a report by an engineering company that "it would be virtually impossible to set the pipe alight".
- The proposed future use of FRP as a replacement of HDPE for organic piping for the future SX plant rebuild was supported by its fire resistance behaviour at Olympic Dam including:
    - FRP piping used for inlets to the main solvent pumps and protected by sprinklers survived the fire.
    - FRP does not soften like HDPE at relatively low temperatures of around 90C.
    - FRP under sprinkler protection did not add to the fuel load of the fire.
    - FRP could be made conductive with addition of carbon and fire resistant with use of antimony.
    - FRP was apparently as durable to abrasion as stainless steel.
- 8,000 metres of earth strapping that was connected to every piece of structural steel, organic bearing HDPE piping and organic pumps was grounded to earth before the 2001 fire.

- The HDPE loaded organic lines, both pre-scrub and post-scrub, were found by testing by WMC after the 1999 fire rebuild to have static build up on the outside of the lines, with most build up occurring on the pre-scrub lines (the pre-scrub lines were the lines in which the 2001 fire started).
- The static build up was apparently attempted to be rectified by using conductive paint and bandit straps at 600-mm centres along the length, adjacent to the bend and fall in the 630mm ID HDPE pipes that had the higher static voltages.
- The static voltages were apparently considered insufficient by experts to start a fire in the solvent by static discharge from the external surface of the HDPE solvent lines, although evidence elsewhere is contradictory.
- Wolfson Electrostatics, an expert static consultant to WMC, reportedly showed that in smaller diameter pipes that the capacitive effect of metal around plastic pipe builds up the static charge and can lead to audible brush type discharges. However no explosive type sounds were reported as having been heard by any plant operator.
- Static electricity is generated in the diluent used in the organic in the CuSX plant but not in the same diluent used in USX plant, due to the addition of modifiers to the USX organic.
- Specific CuSX plant organic phase conductivities were reported to be:
    - 60 pS/m for pre-scrubbed loaded solvent (optimum for maximum static generation).
    - At levels that were well away from optimum static generation for other organic phases including:
        - either “non-conductive” (24 pS/m) so that not much static is generated
        - or else sufficiently conductive (380 pS/m) for the static to be dissipated by relaxation of solvent in the organic tanks.
- AS/NZS Standard 1020:1955 Control of undesirable static electricity. The conditions necessary for static to create fire or explosion and the measures required to minimize static are identified, including the following points noted in the Mines Inspector Report:
    - The high probability of static generation between the following parts of systems conveying liquids and earth objects:
        - Electrically isolated parts, which become charged by flowing liquids e.g. pipes and fittings.
        - Electrically isolated parts which become charged by induction e.g. floating objects.
        - Charged liquid.
    - Increase in charge generation without a significant change in conductivity due to dissolved general contaminants and inclusions.
    - Substantial increase in tendency for charge generation due to entrained water in refined and unrefined oil products.
    - Static generation increasing with pipe diameter for constant flow and with liquid velocity for constant diameter.
    - The unreliability of depending on earthing and bonding for dissipating static charges from non-conducting liquids, except where proven safe by long standing experience or substantial experimentation.
    - Maximum flows for non-conductive hydrocarbons of 1 m/sec for a 600 mm ID pipe (versus an indicative average 1.5 m/sec for the apparently 2/3 full organic drain pipe, excluding acceleration near the open end into the organic holding tank).

  - The presence of all conditions necessary for the development of problem levels of static in the loaded organic drain lines in the plant that caught fire in 2001.

- In an ironic twist and to show just how easy it is to be potentially misled by the risk of static electricity in any CuSX plant, apparently just 11 days before the CuSX fire in 2001 at Olympic Dam, a Wolfson Electrostatic expert is reported to have advised WMC by conference phone call in regards to a review of the about to be commissioned new CuSX plant that:
  - There was no risk of static igniting the organic liquid or the vapour at normal operating conditions (45C), due to the fact that:
    - normal operating conditions would not generate flammable levels of vapour (as opposed to mist, which was apparently subsequently defined after the fire to be highly flammable by Wolfson Electrostatics).
    - there has been no record of static electricity igniting a liquid where the flash point is in excess of normal room temperature.
  - Static discharges, probably brush discharges, were possible within partially full organic pipes.
  - Static generation was temperature dependent.
  - Conductivity additives to the organic, of the ppm level, should be considered to prevent static.
  - Steel pipes could generate more charge than plastic pipe.
  - FRP materials of construction would be expected to have minimal risk of fire in the proposed new CuSX plant.
- Wolfson also advised that CuSX diluent at conductivity levels or around 50 pS/m had the greatest electrostatic potential and hence the greatest risk of fire when measuring the potential in an electrofusion coupling test arrangement. The maximum electrostatic potentials were as high as plus 1-1.5 kV and minus 2.0-2.5 kV.
- Similar conductivity measurements of solvent with copper in solution were reported by the Mines Inspector to have been measured by Shell International (30 pS/m), WMC (50 pS/m) and by the Ian Wark Institute on a pre-scrub loaded organic sample taken by the Mines Inspector from extraction mixer-settler “ES1” (60 pS/m).
- AS 1020 Appendix B 1 was reported by the Mines Inspector to show that the Olympic Dam diluent, Shellsol 2046, has a vapour composition that was well below the lower flammability limit at normal plant operating conditions of 45C.

Crud presence:

- Crud, a term known to many, is the term used loosely to refer to a non-coalescing dispersion of organic, aqueous, solids and/or air that forms in mixer-settlers, and is present in most plants to varying degrees.
- Crud build up would appear to have occurred over an unknown period of time at the turbulence zone of the earthing annulus ring at the flange joints of the HDPE loaded organic line, with an estimate by the Mines Inspector that possibly as little as 1 kg in weight would have been all that was necessary to sustain a fire, once ignited. In a separate report, the SAMFS Investigator for the second fire also indicates very convincingly that crud adhering to the HDPE pipe surface was most likely a key fuel source for the fire, once ignited by a spark.
- The crud at Olympic Dam that forms between the interface of the solvent and the aqueous phases in the mixer-settlers leaves in the pre-scrub loaded solvent and precipitates out on the loaded organic settler weir was sampled and analyzed by the Mines Inspector. The assay indicated sulphate 38%, calcium 14%, silica 12%, iron 7%, and cerium less than 1%.

- The crud was referred to as jarosite, with colours of pale yellow, yellowish brown, brown, yellow ochre and yellow brown. Chemical formulae was said to be $KFe_33(SO4)_2(OH)_6$ and crystal type generally minute rhombohedral crystals
- The crud that built up behind the annular earthing rings in the loaded organic drain line was an orange brown solid, for which the colour was accentuated when soaked in organic for the fire test by SAMFS.

Crud fire test:

- A test was carried out on the burning of crud on a tray just inside the open end of a horizontal HDPE pipe section located in a fire test area at the Olympic Dam site by the South Australian Metropolitan Fire Services (SAMFS).
- One end of the pipe was blocked off.
- The crud was ignited
- After about one minute the burning crud had ignited the inside of the HDPE pipe as a small localized burning area, with little smoke evident and suggesting that any internal burning would not have been evident in the loaded organic tank or via the breather pipe near the discharge end of the organic drain line.
- The pipe continued to burn internally and was considered to have the potential to completely burn through the pipe from the inside, even though the test was not continued for long enough to do this.
- The pipe was also ignited and burnt fiercely on the outside at the same time as it was burning on the inside. The inside fire continued despite the strong competition for oxygen from the external fire.
- The externally burning HDPE fire produced molten HDPE drops which fell from the outside of the pipe as small fiery bombs, as described by a witness to the CuSX plant fire.

Internal pipe conditions prior to fire:

- The 630 mm HDPE loaded organic drain line pipes were expected by the Mines Inspector to be up to 2/3 full of liquid and 1/3 full of air, vapour and mist.
- The air space above the organic was considered to be sufficient to permit air flow and combustion.
- There was considered to be a possibility that a series of fires may have occurred in the pre-scrub loaded organic drain line that eventually led to the drain line failing and allowing the fire to spread externally.
- Adjoining organic drain lines were empty due to Train B being shut down since mid afternoon 18 October, although IPDS understands that there may have been several intermittent but unsuccessful efforts to commence flow in Train B on 20 October.
- Train A, the train in which the fire occurred, had been shut down since 18 October and was started up on 20 October but the flow had apparently not yet stabilized at the time of the fire.
- Trains A and B were both shut down for 36 hours on 18th and 19th October and the loaded organic drain lines would have been empty for a period that might conceivably have allowed a small fire to burn for a considerable period before plant startup.

Weather conditions:

- The HDPE piping in the area of the fire initiation was covered by the cable rack and would not have been heated to the surface temperature of 70-80C that would have occurred if it had been empty and in direct sun in summer.
- Organic temperature was normally around 45C.

- The temperature on the day of the fire was about 25C at 12 noon and was considered unlikely to have been a contributing cause to the fire.

Plant Redesign – Shell Services International

- In commenting on the limited changes that had occurred to the CuSX plant design for the rebuild after fire No 1 and prior to fire No 2, Shell International had a number of propitious comments and recommendations of 10 January 2000 which were unfortunately not addressed in the rebuild prior to the fire of 21 October 2001:
- HDPE piping tensile characteristics affected adversely by solvents, by temperature above 60C and by the absence of any barrier against a heat source touching the pipe.
- Escalation of the fire due to collapsing HDPE piping.
- Plant should not have been rebuilt largely as it was but should have had its design basis reviewed in the light of the fire investigation, including:
    - Suitable piping materials of construction specification.
    - Reduction or elimination of continuous solvent release from the solvent air vents in the loaded organic drain lines.
    - Location of rotating equipment and installation of secondary shaft seals.
    - Fire system design integrity.
    - Emergency shut down and isolation.
    - Inadequacy of fire separation distances.
    - Potential impedance of fire fighting by the large fire size.
    - Inadequate fire protection systems in the bunded areas around mixer-settlers and in the dump pond.
    - Inadequate cooling water back-up if the primary fire protection system failed to activate.

Hazop Studies:

- Hazop studies by an external consultant were conducted in 1997 (30% and 70% design points) and again in 2000.
- Such studies were considered to be weak at addressing multiple mode failures and strategic design weaknesses, according to an independent consultant, Risk and Reliability Associates.
- A Hazop recommendation for replacement of HDPE piping by stainless for pipelines traversing from the mixer-settler area of the tank farm was not adopted due to high cost and high corrosion concerns.

Other SX plant designs:

- 20 of the largest international SX plant designs reviewed by WMC were found to have no USX plant in series with the CuSX plant. but to have the following common features in many cases:
    - HDPE piping and tankage
    - Concrete tanks
    - Bonded roofing
    - No static precautions.

Factory Mutual Global, Loss Prevention:

- A 120 page guideline covering data sheets for mining and ore processing facilities, revised January 2000, includes a solvent extraction section which provides the following salient recommendations:
    - Use of FRP tanks instead of thermoplastic such as polypropylene due to softening and premature failure of thermoplastics under fire exposure.
    - Location of flammable or combustible solvent outdoors in a diked area.
    - Emergency drainage from curbed areas handling or storing solvents to run to a safe location with sizing and capacity based on guidelines provided by Factory Mutual .
    - Use of antimony trioxide for fire retardant for plastic equipment and liners where plastic is required to be used.

Misting of Solvent:

- The HDPE gravity drain return pipes to the pre-scrub and post-scrub loaded organic CuSX tanks were reportedly discharged below the fluid level in these tanks.
- Misting was not observable within the inside of HDPE pipe, but if it occurred it was expected by the Mines Inspector to have most likely occurred as a result of major turbulence generated at the elbow bend and corresponding 1.25 metre drop in pipe elevation at 10 metres from the discharge point into the two loaded organic tanks and then potentially dispersed within the vapour space in the partly filled pipe up to a few metres away from the discharge point.
- It was suggested that misting may have initiated and caused the fire to spread to the crud at the flange point in the drain line but there is no proof for such a scenario.
- The Mines Inspector report notes that an earlier report in February 1999 by Shell International noted the importance and risk of mist formation, pointing out that fine mist of Shellsol 2046 may ignite at temperatures below its flashpoint, due to the high surface area and mixing with oxygen.
- Unfortunately the potential interaction of the misting hazard within the HDPE drain line and internal sparking due to static electricity discharge within the same drain line was not considered a potential hazard at the time.

Fire Consumables and Factors:

- The fire impact was adversely affected by wind direction.
- Approximately 60 tonnes of HDPE piping and tank farm lining were consumed.
- Several hundred tonnes (thousand litres) of organic, principally Shellsol 2046, representing about 30% of the organic in the CuSX plant were consumed.
- An eye witness observed the start of the fire.
- The fire commenced at approx 12:15 pm, was nearly out but flared up with a tank rupture at 3.30 pm and was ultimately burnt out at approx. 11.00pm.
- More foam was activated on non-critical areas than was desirable and foam supplies ran low early on.
- The electric fire pump did not initially kick in as expected, but suffered a 4-5 minute delay.
- Fire reached the end of the pipe rack about 25 minutes after the fire first burst through the HDPE organic drain line.

- In the earlier 1999 fire, the automatic fire detection and related suppression systems were reported to be basically all off line within 2 minutes of the start of the fire, indicating that all automatic control systems were effectively useless within a very short time after the start of the fire. The fire was effectively unstoppable until all fuel sources accessible to the fire had been consumed.

Fire Damage:

- Severe damage to:
    - all tanks, equipment, electrical cabling, HDPE piping and motors in the CuSX tank farm.
    - a significant portion of the cabling, piping and support gantries in the pipe racks leading to the CuSX mixer-settlers and the downstream USX pulse column.
- No fire damage to the CuSX mixer-settlers or the USX pulse columns.
- Specific major CuSX equipment and/or piping items that were severely damaged or destroyed including:
    - 2 loaded organic tanks/train (pre-scrub and post-scrub) x 2 trains
    - Crud tank and crud processing* tank
    - Scrub solution* tank and spent scrub solution tank
    - Copper raffinate tanks
    - Solvent and electrolyte pipes
    - Electrical cabling
    - Skim filter backwash tank*
    - Electrolyte flotation*
    - 3 electrolyte filters*.

*damaged after the loaded solvent tanks caught fire

- The HDPE liner of the 1 ML waste dump pond within the CuSX tank farm area was also burnt out.
- The flooding of the tank farm area with fire water led to fire extending well beyond just the first set of fire affected CuSX tanks in the tank farm and to include the more remote copper electrolyte tanks and the copper raffinate tanks, still within the tank farm.
- The flooded/ fire affected area of the CuSX tank farm was approx. 100m x 60m.

Investigation of the Olympic Dam Copper and Uranium SX Plant Fire, 23 December 1999, Geoff Sulley, District Officer, Fire Cause Investigator, South Australian Metropolitan Fire Service[3]

This reference by the South Australian Metropolitan Fire Service provides helpful layout and elevation drawings for the Olympic Dam CuSX plant at the time of the first fire at 19:26 hours on 23 December 1999. Points of interest are:

- The fall in elevation in the HDPE loaded organic pipeline from the exit from the E1 CuSX settler to the top of the HDPE lined loaded organic holding tank in the tank farm would appear to have been of the order of 6 metres.
- The fall in elevation in the same pipeline to the bottom of the same organic holding tank would appear to have been of the order of 10 metres.
- The same fall in elevations are understood to have applied in the 2001 fire.
- The drop in elevation from the exit of the CuSX settler to a half-filled loaded organic tank would appear to have been of the order of 8 metres.

- The major drop in elevation would have led to a partly empty drain line, significant organic turbulence, air movement in the line, high organic velocities and consequently significant static generation, all of which were most undesirable.

As mentioned earlier, the combination of factors such as air vents at the start and end of the loaded organic line, the static earthing rings protruding into the organic flow at frequent intervals along the line, the collection of crud at the earthing rings and the rapid drop in elevation near the end of the line would have further contributed to the high risk of fire in the loaded organic drain line and the ultimate fire(s) that occurred in the CuSX plant at Olympic Dam.

4. PROCESS DESIGN RECOMMENDATIONS

Subject to the results of an audit of existing CuSX facilities or of proposed new CuSX facilities by appropriately qualified personnel, the following process design recommendations are considered to be the minimum necessary to reduce fire risks in future CuSX operations:

- Existing plants:
    - Ensure organic drain lines to the loaded organic tanks are kept full of organic to minimize any air or organic mist that could support combustion
    - Ensure bottom entry of organic to the organic holding tanks
    - Ensure organic velocity is below 1 m/sec and minimize turbulence in the organic piping
    - Change organic phase drain lines and interconnecting organic mixer-settler piping from HDPE to a suitable grade of stainless steel or FRP with conductive carbon and antimony oxide for fire resistance
    - Establish an organic scuttling system for rapid dumping of organic from mixer-settlers to a fire-safe area
    - Adopt safety protection equipment, clothing and safe practices to minimize static.
    - Adopt restricted personnel access practices for the SX area.
    - Avoid air breather pipes on organic drain lines.
    - Identify limitations of existing foam monitors and injection points under effects of strong cross winds.
    - Conduct a Hazop study including assessment of impact of multiple simultaneous failure events and other loss prevention measures.
    - Undertake modeling to assess the extent of the fire risk.
    - Install water curtains and/or firewalls, where appropriate.
- New plants:
    - Use loaded organic tanks that are close coupled to the corresponding mixer-settlers and at similar elevations to ensure drain lines are kept full of organic
    - Ensure bottom entry of organic to the organic holding tank
    - Ensure organic velocity is below 1 m/sec and minimize turbulence during flow in organic piping
    - Use appropriate grade stainless steel or FRP with conductive carbon, and preferably also antimony trioxide, for organic piping and for organic tanks and vessels

- Design an organic scuttling system for rapid dumping of organic from mixer-settlers to a fire-safe area
- Adopt safety protection equipment, clothing and safe practices to minimize static.
- Avoid use of air breather pipes on organic drain lines
- Select a plant layout to help minimize the risk of fire spreading significantly beyond its starting point, including consideration of potential wind direction during a fire, using fire flux modeling as a basis.
- Conduct several Hazop studies at different stages of design including an assessment of the potential impact of multiple simultaneous failure events and the adoption of loss prevention measures that have been proven from experience in the oil, gas and petrochemical industries
- Install water curtains and/or firewalls, where appropriate.
- Adopt safety protection equipment, clothing and safe practices to minimize static.
- Adopt restricted personnel access practices for the SX area.

Excluded from the above list are non-process design issues to ensure conformance with factors such as relevant national static and other fire safety standards; improved instrumentation and utilization of automatic/ manual control of fire fighting equipment; selection of the most appropriate water and foam storage capacity for the plant and other related issues.

Above all, the successful minimization of static and other fire risks in CuSX plants will require the adoption of new designs and operating practices that are more common in the oil, gas and petrochemical industries than the mining and metallurgical industry and will encourage a major change in attitude to the risks of fires in solvent extraction operations.

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SOLVENT EXTRACTION PLANTS – AN INSURER'S PERSPECTIVE

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ABSTRACT

SX technology is used for the production of more than 25% of the world's annual copper output, and this is set to increase as the technologies evolve for the leaching of sulphides. Unfortunately, as has been demonstrated by four major fires in last five years, SX presents some new challenges for the mining industry, and also its insurers. SX technology has been used for many years in the uranium industry with a good loss record, which is a distinct contrast to copper SX plants.

Devastating fires are avoidable, and provided that the appropriate fire prevention and fire protection measures are used, preferably right from the early design stages, the poor loss history of copper SX plants can be reversed. Comprehensive fire prevention and protection systems are essential for all SX plants and, provided that they are used, then copper SX plants can look forward to many years of operation without a fire. The essential features for fire prevention and fire protection are presented together with a discussion of the challenges of retrofitting these to an existing SX plant.

1. INTRODUCTION

Solvent Extraction is a mature technology that has been used for uranium extraction for more than 50 years with few major fires. With the current track record of four major fires in the previous five years, copper SX is different and the two most significant differences are:

- A different collector is used in the organic; this has a profound impact on fire prevention
- Copper SX plants are considerably larger; this has an equally profound impact on fire protection.

Managers of copper SX plants ignore either of these impacts at their peril.

2. FIRE PREVENTION

Essential features of fire prevention include:

- Effective management of static electricity so that generation and accumulation are minimised and the discharge of it is controlled
- Use Zone 0/1 electrical equipment at all times
- Eliminate heat sources
- Minimise organic mist and fumes

The petrochemical industry has developed methods for dealing with all of these fire prevention features but there are some unique aspects with SX plants that have to be considered when adapting these.

2.1. STATIC ELECTRICITY

Static electricity (static) is the unseen hazard in copper SX plants and has been the initiator in at least one of the four fires and probably one more. It is insidious because it is difficult to detect at the levels required to ignite organic if it is a mist or vapour.

It is also a misunderstood and under-rated hazard. The energy required to create a spark with sufficient intensity to ignite organic mist or vapour is very low; 1mJ is all that is required [1]. The spark that you witness as a result of sliding across an automobile seat is about 10mJ. Hence the energy levels that have to be managed to avoid a source of ignition from static are not perceptible to the human senses.

2.1.1. Generation of Static Electricity

The laws of physics state that when a fluid or mixture flows over a surface or through a pipe then static is ALWAYS generated. All we can do is manage the rate of generation, the amount of static that is allowed to accumulate and the rate of dissipation.

The rate of generation is predominantly a function of velocity and the empirical rule from the petrochemical industry is:

Fluid velocity, $v < 1m/s$ for all organic fluids flowing in a pipe [2]

Most, if not all, SX plant designers are now aware of this design rule and it is unlikely that a plant would be constructed with fluid flows that contravene this requirement.

For older plants an essential first check is to ensure that all organic flows have velocities of <1m/s. This check must include:

- Transient conditions when some of the pipes with gravity flow may be running at higher velocities than normal.
- Increases in organic flow rates above design to meet changed operating circumstances. The gravity flow lines do not run full, and hence can easily accommodate increases in flow rates if these are required to make the plant operate more effectively. There is close to a 1:1 relationship between flow rate and velocity for open channel flow in partially full pipes. Hence a 25% increase in flow rate will result in a 25% increase in velocity, which could then take the organic to a velocity where the rate of generation of static electricity is hazardous.
- The organic cleaning circuits where it is easy to increase flow rates, and therefore line velocities, simply by increasing the speed of pumps and suddenly static is being introduced to a facility that often is located in the heart of an SX plant or at least nearby.

A feature of flowing organic liquids is that the propensity for the generation of static increases when there is mild contamination of the organic with aqueous liquids, which is of course exactly what occurs in an SX plant.

2.1.2. Accumulation of Static Electricity

The rate of accumulation of static in a flowing organic is directly related to its conductivity, and this is the profound difference between uranium SX plants and the SX plants used for copper, nickel, cobalt etc. The conductivity of the collector added to the diluent in uranium SX plants is very high, and this combined with the use of metallic piping throughout these plants results in the dissipation of the static as fast as it is generated.

This contrasts strongly with copper SX plants where new organic (the combination of collector and diluent) has a very low conductivity, usually less than 50pS/m. In service there will be some contamination of the organic with the highly conductive aqueous solution and the conductivity of the organic will increase. If it remains below 200pS/m [3] then static is a major hazard and must be actively managed. Above 1,000pS/m [4] the conductivity of the organic is such that accumulation of static is unlikely to be a threat. Conductivities between these limits, which experience has shown to exist in copper SX plants, means that static generation, accumulation and discharge must be managed effectively if the potential for an ignition event is to be reduced to acceptable levels. NFPA 77 lists the upper limit at 10,000pS/m.

Conductivity measurements that IMIU is aware of show varying levels of conductivity in process organic in operating plants. Some have conductivities that are less then 200pS/m (personal communication) and others around 650pS/m [5].

Hence an essential fire prevention check for an SX plant is the electrical conductivity of the organic, because it is this property that determines the degree of accumulation in a flowing organic liquid.

2.1.3. Dissipation of Static Electricity

Managing accumulation requires frequent opportunities for dissipation. In some SX plants this occurs by default with sections of stainless steel pipe at frequent intervals that are connected to earth, either deliberately or by default. Plants that use HDPE almost exclusively are those most at risk of static accumulation and hence discharge with a spark of sufficient energy for ignition of mist or vapour.

Point discharge is to be avoided when static is being dissipated so that sparking does not occur. Having a long run of HDPE pipe with a short valve, elbow, flow sensor etc that is followed by another non-conductive run of HDPE pipe is probably the worst case for having a discharge of static, i.e. the creation of a spark with sufficient energy to ignite organic mist or vapour.

Establishing and maintaining robust connections to earth for all conductive pipes, pipefittings and tanks is essential. The effectiveness of these needs to be measured periodically to ensure that the resistance to earth is satisfactory, i.e. <10ohms [2].

A common method of construction for the organic surge tank is to have an HDPE lined concrete tank and hence the organic coming in, which may have accumulated a static charge, is not able to discharge this because the entire tank is insulated. Using a submerged grid fabricated from stainless steel that is connected to earth is one method that is used to dissipate the static charge from the organic as it moves around the tank.

Hazards in insulated tanks include any metallic instrumentation that can act as discharge point for the static charge causing a spark. If mist from entrained air in the organic is in the tank then the combination of an ignition source and a readily ignitable fuel and plenty of oxygen is present ready for a fire event to be initiated.

In summary, if there is the opportunity for static to accumulate then its dissipation must be managed to avoid discharge in the form of a spark.

2.1.4. Rules for Managing Static Electricity

Static is a complex issue and hence IMIU strongly recommends to all managers of SX plants that a recognised expert in this field is retained for at least an initial survey of your plant to ensure that static is not creeping in and waiting for the perfect combination of a spark and fuel in the right form for an ignition event to occur.

In summary the rules for static are:

- Restrict the organic velocities to less than 1 m/s
- Avoid short isolated metallic conductors in long runs of non-conductive piping
- Measure the conductivity of the organic
- Manage the dissipation of the static so that point discharge in a spark is avoided
- Retain an expert on static generation, accumulation and discharge to survey each SX plant to provide advice on where the vulnerabilities to static hazards exist

For SX plants that use low conductivity organics, the importance of adhering to these five points, and in particular the final point, cannot be over-emphasised if the likelihood of an ignition event is be suitably low.

2.2. ELECTRICAL PLANT

Electric motors and instrumentation are used throughout SX plants and hence have the energy available to ignite the organic if not installed and maintained properly. Fortunately we can draw directly on the rules and practices used in the petrochemical industry. The challenge for the metal extraction industry is to recognise the importance of these rules and then adopt them.

Commonly the electrical equipment and instrumentation that is installed in SX plants during construction is Zone 0 or Zone 1 depending on location. Ensuring that all future equipment that is installed during plant modifications meets these standards is the challenge for SX plant operators. Maintaining the equipment to this standard is also a challenge. Recruiting and training suitably qualified electrical staff is probably the single largest weakness in this regard so that the intrinsically safe status of the electrical equipment is maintained throughout the life of the SX plant.

2.3. HEAT SOURCES

Eliminating heat sources is similar to the electrical equipment, except that it usually involves the mechanical engineers and tradespeople. Pump seals are a vulnerable point and conventional mechanical seals can overheat and become potential ignition sources. The petrochemical industry has been handling low flash point liquids for many years and has developed the seals that avoid overheating even when failing.

2.4. ACCESS CONTROL

Control of access to SX plants is an important management tool for the avoidance of unexpected heat sources. SX plants are part of mining operations where, after passing through the front gate and being made aware of not going into the actual mine, there is little restriction on the movement of contractors, particularly those that are frequently onsite.

I have seen a wide variety of access control used in SX plants around the world, from nothing after the front gate, through to fully automated access control using proximity cards, CCTV monitors and turnstiles for all persons and the SX plant surrounded by a 2m high fence.

As a minimum, the SX plant should be fenced so that access is gained only through a gateway where signs can be used to remind persons entering the SX plant of the special hazards that are present. Even a chain and post fence to remind people that the SX plant is different from the remainder of the mineral processing facilities is better than nothing. Ensuring that access is only given to persons who have been suitably trained on the hazards should be the standard used. This has to be an active control rather than just advising people at an induction to not enter the SX plant area unless authorised.

2.5. MIST GENERATION

Mist generation is a major issue for SX plants and is one that does not receive the attention it deserves. Mist is the deadly link between low energy sparks and a difficult to ignite organic liquid. To date it is an issue that has been largely ignored by the metal extraction industry and this needs to change. The petrochemical industry has long recognised the significance of reducing mist and vapour generation and goes to great lengths to reduce them. With the current practices there is generation of substantial volumes of organic mists and this creates a level of hazard not normally seen in petrochemical plants.

The energy required to ignite mist is less than 1mJ and if there is an oxygen source available in say a vented pipe flowing under the action of gravity or in a surge tank, then there is a fire scenario waiting to occur.

The principal sources of mist generation are:

- At the weirs of the mixer-settlers
- At the discharge of pipes into tanks

Eliminating mist as a result of discharge of organic into a tank is easy – the outlets just need to be submerged at all times. This applies particularly to the organic surge tanks and in the crud treatment plants where liquid levels can vary considerably.

Figure 1. Organic falling +300mm at the weir of a mixer/settler with large amounts of froth generation. The mist created when the bubbles from the entrained air burst is very flammable and can be ignited with a very low energy spark.

Eliminating mist generated at the weirs is a much larger problem, particularly for copper SX plants that have very large mixer/settlers and hence long weirs. The mist is a direct result of the entrainment of air as the organic falls 300mm and more into the organic in the launder before running into pipes that deliver it to the next step in the process. Almost invariably the organic falls vertically after it flows over a sharp edged weir thus maximising the air entrainment and hence maximising the amount of mist generated. As the entrained air bubbles rise to the surface and burst, mist is generated as evidenced by the black stains on the leeward side of most copper SX plants. Not only is the mist a fire hazard, it creates some significant safety issues as it coats walkways, handrails etc.

Often the pipes are not completely full with the flow being under the action of gravity and hence there is a combination of mist and air in the pipe. If a static discharge occurs at some point then an ignition event becomes possible.

As an industry we need to develop effective weir designs that achieve the retention of the organic and radically reduce the generation of mist. Maybe involving civil engineers would be helpful because they probably have the best understanding of fluid flow over weirs and downstream of them. Without getting too specific about improving weir/launder design the following could be considered for improvements in this area:

- Minimising the fall. I have seen falls in various SX plants between close to zero to well in excess of 300mm. One of them was designed to be zero and used a valve in the pipe downstream of the mixer/settler to control the level of organic in the mixer/settler.
- Using gentle slopes on the weirs.
- Using a stilling zone after the weir to allow the entrained air to come to the surface before the organic moves onto the next stage.

Once mist is present in a pipe or tank and there is a static discharge, then an ignition event is ready to occur, possibly with sufficient energy to ignite the bulk organic and another large SX fire is underway.

3. FIRE PROTECTION

There are five overriding features of any fire protection system for SX plants. These are:

1. Minimise fuel availability.
2. Confine the fire.
3. Detect any fire while it is still small i.e. detect it early and automatically.
4. Hit any fire fast i.e. the response has to be automatic with the ER Brigade having to direct further response but not being required for major fire control.
5. Hit any fire with overwhelming force so that there is no opportunity for a fire to become a major fire. Once a fire exceeds the capability of the initial fire response then it will be very destructive and cause significant loss to the business.

Meeting the first of these is very challenging in an SX plant as a result of:

- Very large inventories of organic which is in open tanks (mixer/settlers).
- Close proximity between mixer/settler trains. This is often 10 metres or less.
- Close proximity of the tank farm to mixer/settlers.
- Extensive use of HDPE pipe, which is readily combustible and loses much of its strength at <100^{o}C. Hence it is very vulnerable to damage from radiant heat as well as direct flame impingement.
- SX plants are essentially gravity flow plants, and unless barriers are introduced then large quantities of organic will keep flowing downhill through the plant and continue to supply fuel to a fire. This can be exacerbated by pregnant leach solution coming into the plant under the action of gravity which assists with the continuing movement of fluids through the SX plant.
- Tank farms are often excavated below flat ground with no escape. All fluids that are liberated flow to here, and if burning create the potential for a massive escalation of the fire.

3.1. CONFINING THE FIRE - SEPARATION

As a minimum an SX plant should be divided into two completely separate halves. It is common for a four train system to be divided into two halves each with two trains. It is not common though for there to be anything but nominal separation between the two halves, and in the tank farm it is common for there to be a common space for the entire system. The better the separation, the cheaper the automatic fire protection system that has to be installed.

The principal aim of separation is to reduce the radiant heat flux that affects the portions of plant adjacent to a fire. The importance of separation can be seen from the table below.

Table 1: Heat flux contours of various heat flux levels that can be expected downwind from a pool fire of varying diameters with kerosene as the fuel. The contour distances quoted are the distances from the edge of the pool that is burning. Wind speed of 10m/s (36km/h). [6]

Pool Diameter (m)	1.1.1. Heat Flux Levels			
	2.5kW/m^2	4.7kW/m^2	12.5kW/m^2	23kW/m^2
	Distance from edge of pool (m)			
1	13	10.5	6	4.8
5	27	23	19	17
10	43	36	30	28
15	54	46	38	35

The distances from the edge of the pool fires is approximately halved for wind speeds less than 5m/s (18km/h).

At heat flux levels of 12.5kW/m^2 steel structures will reach a steady state temperature of 300^{o}C and hence will remain structurally sound. I have found no direct reference on the response of HDPE piping or the FRP/PE sheeting used to cover portions of mixer/settlers to radiant heat flux levels, but it is a reasonable assumption that the integrity of the piping or sheeting would disappear as a result of a prolonged exposure to radiation levels of 4.7kW/m^2 thus liberating large quantities of organic fuel.

When considering the options for fire protection on an existing plant providing adequate separation just using spatial separation is usually impossible to achieve. At some SX plants a water curtain has been installed to divide the plant into the trains, or groups of trains. This enhances the separation between sections, although on some plants the actual degree of separation achieved with the water curtains would be difficult to conceive because the mixer/settler trains are sometimes less than 2m apart.

3.2. RETENTION AND/OR SCUTTLING OF SPILT LIQUIDS

Organic liquors flowing unrestrained along open drains are a major potential for the rapid spread of a fire, particularly from the mixer/settler areas into the tank farm. The return lines from the mixer/settlers for the organic and aqueous liquor are normally set in a concrete channel that slopes towards the tank farm. If the flow of spilt organic is not halted then it will flow into the tank farm thus rapidly increasing the area affected by a fire if the organic is alight. The HDPE pipes also provide a readily combustible route for a fire to travel from the tank farm to the mixer/settlers with a similar expansion of the area affected by a fire.

When retrofitting a plant IMIU has seen two alternatives used:

- Construct a wall across the channel at the boundary of the mixer/settlers and the tank farm through which the pipes pass with a pipe stub and valve set into the wall that is normally closed and used to release the spilt liquids as required to the tank farm/sump. Where the pipes penetrate the walls *automatically* operated valves need to be installed that close whenever the fire protection system is activated. The closing of the valves then acts to retain all liquids above the tank farm once a fire has been detected.
- Construct a wall in the same location with the spilt fluids being held and diverted through an open drain or pipe to a sump where the fluid can burn without damage to other facilities. An essential feature of option is the installation of fire traps in the dump lines so that heat in the holding pond cannot flow back along the pipes to another part of the SX plant. Again automatically actuated valves need to be installed at the barrier.

Figure 2. An example of a deep pipe trench connecting the mixer/settler train with the tank farm. A wall needs to be built here to prevent spilt organic liquors flowing into the tank farm. This trench, together with the trenches around the mixer/settlers, has sufficient capacity to hold the potential spillage if all of the pipes are ruptured by fire and hence it is not proposed to divert the spillage to another location.

Figure 3. An example of a shallow pipe trench with a much higher density of HDPE piping. At this SX plant the pipes are almost at ground level at the mixer/settlers and it is proposed to install underground pipe drains that take the spilt liquor away to a disposal pond. A retaining wall at the junction of the trench with the tank farm is also to be installed.

In a new plant the ability to scuttle the organic liquors away from the portion of the SX plant affected by fire should be an integral part of the fire protection strategy. This means that once a fire has been detected in a section of the plant and the water/foam system activated, then scuttling valves in this section of the plant would be automatically opened and the liquors, or at least the organic portion of the liquors, drained through concrete or metallic pipes to a pond or holding tank well away from the SX plant. This has been installed in all uranium SX plants seen by IMIU, but only at one copper SX plant.

The pipes used to scuttle the liquors would normally be in a branch network feeding one or more trunk lines to the holding pond. Flame traps need to be installed on the branches so that the heat from burning liquor elsewhere cannot affect the remainder of the SX plant.

Sizing the pipes and valves in the scuttling system to achieve the emptying of a section of the plant within 15 minutes is a suitable design target.

3.3. HDPE PIPES

These are ubiquitous in copper SX plants and are a complete anathema to petrochemical engineers who have trouble comprehending why they are used at all. They lead to increased levels of static generation and accumulation, and if not carefully managed also increase likelihood of a discharge of static electricity. They also fail at modest temperatures, and if used in long runs move as a result of their high coefficient of expansion, and also are joined using a welding technique where the quality cannot be tested. However, they are cheap to install and do provide excellent corrosion resistance for acidic chloride solutions which occur even in the organic lines as a result of low levels of contamination of the organic.

HDPE pipes form natural conduits for fire including the pipes containing the aqueous solutions. Once the aqueous pipes rupture and the contents are discharged then the pipes burn vigorously and hence must be included in the fire protection plan if the spread of a fire is to be controlled quickly and before it reaches organic fuel.

A natural separation point in SX plants is between the mixer/settler trains and the tank farm, but the HDPE pipes create a direct conduit for fire between the two areas. If HDPE piping is to be used then IMIU strongly recommends the installation of 5m long metallic pipe spools at the weir walls that have been installed to separate the mixer/settler trains from the tank farm as a result of the recommendation in the previous subsection. It was the installation of these spool pieces that probably prevented the second fire at Olympic Dam from leading to the total destruction of the copper SX plant, instead of being confined to the tank farm.

3.4. TANK FARM

The tank farm holds large quantities of organic and also ignition sources as organic is moved using pumps through a myriad of pipes. It is also where three of the four recent fires have originated and hence is an area that warrants special attention.

One of the major hazards for the ER Team at both of the Olympic Dam fires was the sudden release of large quantities of organic into the general tank farm area from a rupture of one or more pipe outlets on storage tanks and, in the case of the second fire, from the collapse of one of the walls of the organic surge tank several hours after the fire commenced.

A design rule for SX plants needs to be:

- All pipework attached to a tank holding organic needs to be metallic so that if a fire occurs the organic cannot be released through a ruptured HDPE pipe or pipe spool. The metallic piping needs to extend up to the level of the organic in the tank so that no organic can be released from the action of gravity. All valves, gaskets and other pipe fittings such as flexible couplings also need to be fire rated.

In fact it is good practice for this rule to be extended to include piping on the aqueous tanks because a ruptured line that leads to the draining of the aqueous surge tank can result in severe corrosion damage of the lower levels of the steel structures in the tank farm.

It is *essential* that the application of the design rule extends to the pipe stubs cast into the organic surface tanks that are often from HDPE and then attached to stainless steel valves and pipework. Retrofitting stainless steel pipe stubs is difficult and will require a shutdown of the tanks. Another option may be to coat the HDPE with a thick fireproof coating that provides at least a two hour fire rating, as long as this includes the flange piece on the HDPE stub. This will require covering of the bolts, which will inconvenience the maintenance of the valve.

Figure 5. Arrangement of the organic pumps at the surge tank. Note the use of stainless steel for all pipe connections including the expansion/ isolation bellows on the discharge lines of the pumps. The stainless steel piping also extends up to the top of the surge tank.

The grave weakness of this arrangement is the use of HDPE stubs cast into the concrete wall of the tank. A fire in one part of the drain that runs underneath the stubs would release the entire contents of the surge tank with disastrous results.

3.5. EARLY DETECTION OF FIRES

The early and automatic detection of fires is an essential part of an effective fire protection strategy so that a fire can be fought while it is still modest in size. A combination of technologies is normally used to meet the different areas where a fire can occur. These must be robust and suitable for the acidic and open air environment in which these systems are used.

Due to the high cost of discharging large volumes of foam, and also the interruption to the process in the event of an accidental discharge, all detection systems need to have two systems from which a fire signal must be received prior to the automatic initiation of any active fire protection systems. Usually this is two of the same kind of detection, but sometimes a combination is appropriate.

3.6. FIRE PROTECTION IN MIXER/SETTLERS

Foam delivered through foam generators mounted in 2-4 locations around each of the mixer/settlers is the most common form of fire protection because it is ideally suited to pool fires. There is containment over a modest area and IMIU advocates delivering the foam at a rate that covers the surface within 60 seconds. Normally the foam system is initiated in a mixer/settler by a dual spectrum detector located in each mixer/settler. At Zaldivar the foam system is set-up so that a detection of flame in one mixer/settler initiates the release of foam in the mixer/settler affected and its two neighbours. Hence if the foam is only partially successful in the mixer/settler where a fire is first detected then the protective barrier is already in place at the neighbouring mixer/settlers.

3.7. FIRE PROTECTION IN THE PIPE RUNS OF THE MIXER/SETTLER TRAINS

Fire protection for the pipe runs amongst the mixer/settlers trains can be challenging, particularly when retrofitting. It should be automatically initiated and it needs to have comprehensive coverage in the train in which a fire has been detected. For those plants with the pipes set into deep concrete lined trenches, probably the most effective fire protection route is to use thermal detection wire to detect the fire that initiates the actuation of several high expansion foam units that rapidly fill the trenches with foam. This, combined with the retaining walls recommended to separate the mixer/settler trains from the tank farm, should result in the rapid control of any fire amongst the pipework in the mixer/settler train affected by the fire. The Fire Chief may then elect to fill the trenches of the adjacent train with foam. It was amongst these pipes that one of the four fires occurred.

Providing automatic fire protection is more difficult for mixer/settler trains where the pipes are on the surface and also more expensive. Foam will have to be used together with some form of retention for the foam, or the more general use of it and hence larger quantities being required. One of the challenges for SX plants with surface mounted pipework is the lack of a radiant heat barrier between pipes in adjacent trains that at least partially exists with pipes set in trenches.

4. FIRE PREVENTION AND PROTECTION BY COMPAÑIA MINERA ZALDIVAR

Zaldivar is a large SX plant located in the Atacama Desert inland from Antofogasta, Chile, and is owned and operated by Placer Dome Inc. Current copper production is more than 140,000tpa of cathode copper. It is a mature operation that had some reasonably good fire protection installed as part of the initial project. However, after the experience at Olympic Dam it was obvious that this would not be adequate to control a fire so that it would not lead to widespread destruction of the SX plant. In consultation with IMIU, Gerling Global and Marsh Risk Consulting, guidelines for a comprehensive fire protection system were developed that were suitable for retrofitting to the existing plant. As would be expected some compromises had to be made to suit the existing plant layout.

The Zaldivar SX plant has the following characteristics:

- There are four parallel trains each with four mixer settlers. These are known has Trains A, B, C and D.
- The trains and associated tank farm are divided into two groups of two, namely Trains A & B and Trains C & D. The separation between the trains in each group is minimal and the separation between the two groups i.e. between Trains B and C is around 15m

- The mixer/settlers are partially set into the ground and hence the pipe runs for the processing fluids from the mixer/settlers to the tank farm are all set in concrete trenches at a depth of around 3m in trenches that are 4m deep.
- The separation between the mixer/settlers and the tank farm is minimal and was determined by the angle of repose of the excavation rather than any concerns for fire protection
- The SX plant is located on flat ground and hence the tank farm is a large excavation that is entirely below the surrounding land with a depth of around 5m
- There is a pipe used to drain any spillage from the tank farm away to the barren raffinate pond that is at a lower level than the tank farm
- The bulk of the piping amongst the mixer/settlers is HDPE
- There is a combination of HDPE and stainless steel used for the piping in the tank farm. Typically all bends, spools, valves etc are in stainless steel and are connected using HDPE piping.
- All of the tanks are fully enclosed and from stainless steel as was all of the pipe connections to the tanks.
- There are large overhead HDPE pipes in the tank farm supported on elevated pipe racks that also support electrical cable trays above the pipes.
- The electro-winning building is downwind of the tank farm and quite close to it.

The initial fire protection system included:

- Automatic water mist fire suppression within the settlers using an array of nozzles, but these had a poor maintenance history as a result of internal corrosion of the distribution pipes. Naturally staff were reluctant to test them.
- Large high-expansion foam generators had been installed in the pipe trenches amongst the mixer/settlers. However the time required to fill the trenches was excessive.
- Fire protection in the tank farm was manual using the hydrant network that had been installed. Similarly general fire protection amongst the mixer/settlers was provided from the hydrants and manually operated fixed monitors that had been installed around the perimeter of the SX plant.
- Water supply was very large and robust, with water for fire protection being provided by a pipeline from the water supply reservoir used to provide water for the entire operation. Pressure relief valves had been installed along the pipeline to keep the pressure at the SX plant to acceptable levels for manual fire fighting. There had been problems with the set-up of the pressure relief valves under low and no-flow conditions, but these had all been resolved prior to the commencement of the new fire protection project. The backup water supply was provided by dedicated reserve in a tank on Cerro Mocho, a nearby hill. Water pressure and flow at the SX plant was all by gravity.

Following the establishment of the design objectives, a specialist fire design contractor (Fire & Safety Systems, Brisbane, Australia) was retained by Placer Dome to provide detailed design, some procurement, documentation of the work packages for fire protection contractors, commissioning tests and documentation of the procedures required for the ongoing maintenance. The design, approval, installation and commissioning took almost 3 years and more than USD5million. This also included an upgrade of the fire alarm system for the SXEW plant.

4.1. FIRE PREVENTION AT ZALDIVAR

Additional fire prevention steps at Zaldivar have included:

- The installation of water-cooled seals on all organic pumps along with thermocouples that have alarm and trip points for the pumps.
- Conducted a detailed testing programme for all of the earth points in the SX plant. Most of the stainless steel piping and tanks in the tank farm had an earth attachment. The testing programme ensured that these all had very low resistances to earth.

4.2. FIRE PROTECTION UPGRADE PROJECT AT ZALDIVAR

The fire protection systems at Zaldivar were completely revamped starting with the water supply. The steps in the project were:

- Objectives nominated by the engineers from engineers attached to insurers and the broker in January 2002.
- Appointment of experienced fire engineering consultant for preliminary design and estimates.
- Review by engineers from insurers and the broker, along with detailed review by Placer Dome.
- Detailed design by the fire engineering consultant.
- Approval for funds.
- Implementation through a combination of specialised procurement done by the fire engineering consultant, and installation using local contractors
- Commissioning in February 2005 that was witnessed by an insurance representative.
- Training of operators and ER Brigade, still largely to be done.
- Establishment of a comprehensive testing programme that uses the requirements of NFPA 25 as minimum standards.

The objectives and details of the fire protection upgrade at Zaldivar were based almost entirely on the guidelines provided in the various NFPA standards relevant to automatic fire protection using private facilities. The main standards used were:

- NFPA 11A Standard for Medium- Expansion and High- Expansion Foam Systems 1999 Edition.
- NFPA 13 Standard for the Installation of Sprinkler Systems 2002 Edition.
- NFPA 14 Standard for the Installation of Standpipe, Private Hydrant and Hose Systems 2000 Edition.
- NFPA 15 Standard for Water Spray Fixed Systems for Fire Protection 2001 Edition.
- NFPA 16 Standard for the Installation of Foam-Water Sprinkler and Foam-Water Spray Systems 1999 Edition.
- NFPA 20 Standard for the Installation of Stationary Pumps for Fire Protection 1999 Edition.
- NFPA 22 Standard for Water Tanks for Private Fire Protection 1998 Edition.
- NFPA 24 Standard for the Installation of Private Fire Service Mains and their Appurtenances 2002 Edition .

4.2.1. Features of the Fire Protection Upgrade at Zaldivar

4.2.1.1. Separation

The aim was to have an SX plant with two halves so that in the worst case only half of the production capacity would be lost. To achieve this there are three main features:

- A water curtain was installed between trains B and C to reduce the radiant heat flux between the two groups of two trains.
- Construction of a large ‘speed hump’ barrier within the tank farm between the two halves so that any spilt organic would be held in the half where the spillage occurred.
- Installed sprinkler protection over the grates in the undercover drain that runs the length of the tank farm and out to the barren raffinate pond. This is to prevent a fire spreading from one half of the tank farm to the other through the drains.

Within each half, the separation between the mixer/settlers and the tank farm was substantially increased by:

- Installing full height retaining walls at the ends of open trenches that held the piping at the junction between the trench and the excavation for the tank farm. This is to retain any spilt liquors from the mixer/settlers in the trenches so that any fire in them can be dealt with using the high-expansion foam dispensers that were installed.
- Installing 5m metallic spool pieces in all of the pipes where they penetrated the wall.
- Installing auto-closing valves on one end of the metallic pipe spool pieces at the walls.

Further separation is obtained by all tanks in the tank farm being made from stainless steel along with all pipework from the tanks up to a level at which the organic cannot flow from the tank under the action of gravity.

4.2.1.2. Fire Detection at Zaldivar

Detection is done using a combination of devices depending on the location. The detection methods used are:

- Infrared detection inside the settlers. These were used in the initial fire protection system and have proven to be robust in service and not susceptible to false alarms in this location. The settlers are fully enclosed and hence the detectors do not pick up reflected sunlight that may give false readings. There are two in each settler and both have to detect a fire for the foam to discharge into the settler affected.
- Thermal wire detection around the pipes in the trenches around the mixer/settlers. The thermal wire has been installed at the lower and upper levels of the trenches and both must generate an alarm for the foam system to be initiated.
- Dual spectrum detection around the tanks and pumps in the tank farm. Both UV and IR spectrums have to pick up a fire signal for the fire protection systems to be initiated. This limits the possibility of a false alarm and has proven to be robust in other outdoor applications.
- Thermal wire detection in the pipe racks in the tank farm. Again the thermal wire has been installed at upper and lower levels and both must generate an alarm signal before the water and foam fire protection systems are initiated. Hence if a wire is broken during maintenance then an alarm will be generated but the systems will not discharge.
- Infrared detectors inside the tanks in the tank farm.

All of these systems are automatic and continuous in detection duties and hence will provide early warning of any fire.

4.2.1.3. Applying Overwhelming Force at Zaldivar

The primary water source for fire fighting is a 70Ml (18,000,000 US gallon) reservoir set in an elevated position. A single 400mm buried HDPE line brings water to the SX plant via a bypass line around the fire water tank on Cerro Mocho. To control the pressure of the water that would otherwise exceed 2,000kPA (300psi) there are four pressure reducing valves. These have been selected to operate under no flow and low flow conditions as well as full flow.

The secondary water source is a 380 kl (100,000US gallon) steel tank on Cerro Mocho. The fire reserve in this tank is 350 kl.

A 320 l/s (5,100 USgpm) diesel pump is used to take the water from the tank on Cerro Mocho to provide a constant pressure to the new SX fire protection systems.

The actual fire protection equipment applying water and/or foam to the fire zones covers the following areas:

- **Tank Farm**
    - Open head deluge fire sprinkler protection over the SX delivery pipe rack which also contains the electrical reticulation. The fire sprinklers are activated by dual (parallel) thermal wire detection. Both wires have to be in alarm before the sprinkler valve is opened. Detection is provided above and below the piping to ensure no false alarms due to maintenance and also to confirm a 3-D fire. Fire protection using sprinklers is provided to the legs of the racks.
    - Automatic water sprays over the open grate manholes in the tank farm drainage pipe
    - Automatic open head deluge fire sprinkler exposure protection around the perimeter of all tanks containing organic solution. This is initiated by dual spectrum detection. These tanks are from stainless steel and the water sprays are to keep the tanks and their contents cool
    - Low expansion foam (type 2 entry) into all tanks in the tank farm containing organic solutions
    - Automatic open head deluge fire sprinkler protection over all process pumps transferring organic solution also initiated by dual spectrum detection
- **Mixer Settlers**
    - Automatic open head deluge water spray curtain situated adjacent to the Train B separating the mixer/settlers trains into two zones, one with A & B trains and one with C & D trains
    - High expansion foam discharge into all 16 mixers and settlers and associated launders. A 600mm thick layer of foam can be placed across the settlers affected by fire within 2 minutes. Actuation is by existing infrared detectors
    - High expansion foam discharge into all trenches around the mixer/settlers. The foam is produced at a rate that fills the trenches of a train affected by fire within 2 minutes. Actuation is by thermal wire
    - Low expansion foam into all mixer tanks. Type 2 entry is used.
- **Adjacent Rectifier Transformers**
    - Two of the three rectifier transformers at the EW plant are close enough to the tank farm to be considered vulnerable to loss from a fire within the tank farm. Automatic open head water curtain sprinkler systems have been installed adjacent to all three rectifier transformers to provide a robust radiant heat barrier. Actuation is by thermal wire.

4.2.1.4. Fire Protection Combinations

Various fire scenarios were considered as part of the original design process and the fire protection system has been set-up to actuate in the following manner:

- **Detection of a fire by two sensors in the mixer/settlers will activate the following:**
    - Water curtain between Trains B & C providing a radiant heat barrier between Trains A & B and Trains C & D

  - Process shut-off valves of appropriate trains to prevent pregnant solution coming into the plant
  - Process shut-off valves between the mixer/settlers and the tank farm
  - Appropriate trench high expansion foam system
  - Actuation of the foam and/or water system for the area where the alarm occurred

- **Detection of a fire by sensors in the Tank Farm will simultaneously activate the fire sprinklers over the pipe rack for either Train AB or Train CD**

The system is designed to cope with the water demand for all fire systems associated with

- SX Trains A & B plus the water curtain, or
- SX Trains C & D plus the water curtain, or
- Tank Farm AB plus EW rectiformer plus Pipe Trestle for AB, or
- Tank Farm CD plus EW rectiformer plus Pipe Trestle for CD
- A fire hose stream allowance of 63 l/s (1,000USgpm)

All fire protection systems have been provided with orifice plate or regulating valve to balance the systems.

There is a 100% redundant foam supply. The initial automatic 15 minute foam supply is backed up by a second 15 minute supply available by remote actuation by the ER Brigade from any of the three control centres. Although this is in excess of the NFPA requirements, it is considered to be prudent with the very high consequences that are possible, and the modest level of manual fire fighting resources that are available at this remote location.

4.2.1.5. Fire Protection Control System

The aim is of the fire protection control system is to provide a completely automated response to any fire within the SX plant once two sensors have detected it.

The existing fire alarm systems were completely replaced as part of the installation of the new fire alarm systems. The new system includes:

- An addressable loop system
- A MFIP (Master Fire Indicator Panel) situated in the EW control room
- Two SFIP’s (Site Fire Indicator Panels) located at the Foam Control Centre and the SX operators’ site office. The fire protection systems will also be operable from the two SFIP locations.

4.3. PHOTOGRAPHS FROM ZALDIVAR FIRE PROTECTION UPGRADE PROJECT

Figure 6. Retaining wall at the end of the trench for pipes from mixer/settlers. Note the stainless steel spool pieces penetrating the wall and the automatically closing isolation valves on all pipes on the downstream side of the walls. The separation of the SX plant into manageable areas through the installation of containment walls results in lower costs for the fire protection equipment and a much high likelihood of success in limiting the extent of the damage from a fire.

Figure 7. Cerro Mocho Pump. This is capable of 320 l/s (5,100USgpm) and is connected to the back up water supply.

Figure 8. Rear view of the container housing the Fire System Control Centre (FSCC). All of the foam, foam valves and pumps, and deluge sprinkler valves are housed in this container together with the main control panel for the fire protection system.

Figure 9. Interior view of one end of the FSCC. The storage tanks for the low-expansion and hi-expansion foams are shown on the right and the bank of deluge valves are shown on the left.

Figure 10. Lo-Expansion foam valves in the FSCC.

Figure 11. Discharge test of the tank farm exposure sprinklers. At Zaldivar all tanks are from stainless steel and the water provides cooling in the event of a fire to maintain the structural integrity of the tanks. Low-expansion foam is discharged into the interior of the tanks.

Figure 12. Discharge test for the low-expansion foam in the organic surge tanks in the tank farm. The foam generator has been turned around and a test piece attached to discharge the foam onto the ground. Tests such as these need to be done at the frequencies specified in NFPA 25 as a minimum requirement.

Figure 13. Hi-expansion foam generator installed above one of the trenches in a mixer/settler train. These are initiated by thermal wire detection in the trenches and once initiated can fill the trench of the mixer/settler train affected within a few minutes. The operation of each group of these was tested during commissioning along with the capability to fill the trenches with foam within 2 minutes.

Figure 14. One of the hi-expansion foam generators for the settlers during commissioning tests. Note the that the generator has been removed from the aperture in the side of the settler where it normally sits so that the foam is discharged into the pipe trench below. During commissioning the testing of the capability of the foam generators was tested in one of the settlers to ensure that a 600mm thick layer of foam was placed in the settler within 2 minutes.

Figure 15. Discharge test of the water curtain that has been installed between trains B and C. This acts as a radiant heat barrier between the two trains effectively dividing the SX plant into two halves. The distance between these two trains is approximately 15m which is insufficient to prevent radiant heat from a major fire in one half from adversely affecting the integrity of the plant in the other half, particularly the HDPE piping.

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USING PRINCIPLES OF INHERENT SAFETY FOR DESIGN OF HYDROMETALLURGICAL SOLVENT EXTRACTION PLANTS

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1. ABSTRACT

An Inherently Safe (IS) facility relies on the reduction or elimination of hazardous materials or processes through changes in the chemistry, physics and physical design of a process rather than by relying entirely on layers of add-on protection. The mainstream chemical processing industry (CPI) has adopted guidelines and Best Practices to better apply IS when designing or modifying facilities against fires and explosions. The mining industry has not embraced IS nor are there published Best Practice Guidelines that promote IS in this industry. This paper addresses IS principles in general and explores specific IS opportunities for fire protection of hydrometallurgical SX plants using the concepts of intensification, substitution, attenuation, limitation of effects and simplification/error tolerance.

2. INTRODUCTION

Hydrometallurgical solvent extraction (SX) processes – featuring large quantities of combustible or flammable organic solvents - are common in the mining industry for recovering non-ferrous metals such as copper, nickel, cobalt, uranium, tungsten, iodine and lithium. Recent fire loss incidents and the widespread use of sub-grade tank farms and piping trenches, plastic piping, poor drainage, and closely spaced buildings demonstrate opportunities to improve the use of IS concepts for this industry.

The mining industry has designed and constructed facilities with an emphasis on personnel safety, production efficiency and cost effectiveness. The use of IS to eliminate or minimize property fire exposures has not seen widespread practice. Lessons learned from the mainstream CPI have not been communicated or applied.

As an example, copper SX plants have consistently used design of gravity flow as a cost and production-effective solution for transferring liquids and minerals through a process. In fact, Jergensen1 recommends to “utilize gravity to the fullest extent possible” in design of SX plants. This philosophy has been achieved by laying out SX plants with process equipment at different grade levels so that solutions can flow “downhill”. Because of the use of large quantities of flammable liquids and the potential for these liquids - if released – to flow unimpeded into other areas – gravity SX processes represent severe inherent fire consequences unless costly barriers, drainage and channeling are also provided. It appears that little thought has been given to the fire protection consequences and challenges of this design feature during the evolution of SX plants and most copper SX plants constructed today use some form of a sub-grade processing area (tank farm) and one-way gravity flow.

While this layout is used to assure a cost effective operation it has resulted in significant exposures to high value production. The use of sub-grade production units is an inherently unsafe layout where flammable liquids are used and is a layout that would rarely if ever be used today by the mainstream CPI.

Gravity-assist layout is only one example where copper SX plants have been designed and constructed without IS in mind. The use of combustible and frangible corrosion-resistant materials – such as glass, wood and plastic - for flammable liquid storage, processing and piping systems has significantly increased the hazards of these facilities. These materials of construction are not rigorous and allow for rapid failure and release of flammable contents during fire exposure. The use of combustible or frangible systems to handle or transport flammable liquids is not a practice seen today in the CPI.

Another example of inherently unsafe layout is in the popular use of sub-grade trenches to carry solvent piping. Access to trenches for fire fighting is usually limited and the trenches often drain directly into the lower grade tank farm areas. Trenches encircle solvent-filled cells, have open grated coverings, and represent severe fire exposure to production processes such as mixer-settlers (M-S). Trenches also offer low spots for vapors or liquids to collect unnoticed and may require mechanical ventilation systems to prevent flammable vapor accumulation. The use of plastic piping in trenches further increases the hazard. The CPI long ago discontinued the use of sub-grade trenches for carrying flammable materials and uses instead elevated, easily accessible and well ventilated piperacks.

The CPI – having experienced many fires and explosions of great impact to the industry and to the public – has begun to embrace IS principles in the design phase of new facilities. Inherent safety is being promoted through corporate standards, public domain Best Practice publications, seminars, and at the chemical engineering university level. In many companies IS has become part of the design and chemical engineer's consciousness and has resulted in a safer industry.

This paper provides the reader with some concepts and ideas on how to design SX facilities with IS principles in mind, hopefully without sacrificing cost effectiveness of operations.

3. FIRE LOSS EXPERIENCE IN SX PLANTS

The need for improved fire prevention and protection is strongly supported by historical and recent fire losses in global SX plants. Seven hydrometallurgical SX plant fire loss examples have been abstracted in Table 1 from public domain sources and private communications. Improper plant layout, spacing, drainage, protection, and use of combustible or frangible pipe and vessel construction materials were all major factors in the loss severity in these incidents. Conventional fire protection systems were seriously challenged in many of these incidents due to poor layout and materials of construction and in some cases entirely failed to limit fire impact.

Fig 1 Copper SX plant fire in Mexico 2003 (Source: Internet News Services)

Table 1 SX plant fire incidents. Estimates are indexed to 2004US currency.

Location	Date	Process	Fire Protection	Incident	Cause	Results	Reference
Norway	1972	Cobalt-nickel SX using kerosene. Glass piping. Indoor process	Manual response with water hoses	Solvent spill into pit below M-S. Glass piping failed under fire exposure.	Hot work	Three fatalities. Plant destroyed. US$75 M damage. Six months production outage.	2
US	1975	Rhenium-Tungsten SX using mineral spirits and perchloric acid. Plastic piping. Indoor process	Automatic Sprinklers over process area. Manual response with water hoses	Small solvent spill spread into M-S cells and through plant Additional solvent fed by failed plastic pipes.	Perchloric acid reaction	Plant destroyed. . Excess US $10 M damage. Six months production outage.	Private Files
Namibia	1978	Uranium SX using kerosene. Outdoor process. Plastic piping.	Manual response with water hoses	Solvent leaked form plastic pipe. Additional solvent fed by failed plastic pipes.	Electrical	Total plant damage. Excess US $50 M damage. Four months production outage.	Private Files
Australia	1999	Uranium-copper SX using kerosene. Outdoor process. Plastic (HDPE) piping.	Partial foam-water sprinklers. Manual response with foam - monitor nozzles	Solvent release at plastic pipe. Fire spread throughout local area Additional solvent fed by failed plastic pipes.	Not reported.	Partial plant damage. Reported in excess US $40 M damage. Nine months production outage.	3, 4
Australia	2001	Uranium-copper SX using kerosene. Outdoor process. Plastic (HDPE) piping.	Partial foam-water sprinklers. Manual response with foam - monitor nozzles.	Solvent release at plastic pipe. Fire spread throughout wide area. Additional solvent fed by failed plastic pipes.	Possible static ignition inside non-conductive plastic pipe.	Widespread plant severe damage. Reported in excess US $100 M damage. Two years production outage.	3,4
US	2003	Copper SX using kerosene solvent. Outdoor process	Unknown	Solvent fire involving M-S cells	Not reported	Four M-S cells partially damaged. US $5 - 10 M reported by AP	4, 5
Mexico	2003	Copper SX using kerosene solvent. Outdoor process	Unknown	Solvent fire involving M-S cells	Not reported	Not reported. See Fig 1 (photo) for fire in progress	Internet News services

4. GENERAL PRINCIPLES OF INHERENT SAFETY

The classical and common approach to loss prevention for industrial facilities has been to accept a hazard and to protect against it. This approach usually requires expensive and sophisticated add-on protection systems, which are subject to failure during the life of the plant. An inherently safer plant has eliminated or reduced the hazard to where protection systems may not be needed or can be reduced, saving initial installation cost, lifetime maintenance and testing, and potential loss costs should systems fail.

There are four tiers or “layers-of-protection” (Fig 2) usually applied to loss prevention of a chemical processing facility[6]:

- *Inherent safety* (IS) - A protection layer that relies on the reduction or elimination of hazardous materials or processes through changes in the chemistry, physics and physical design of a process. Examples of IS systems are described further in this paper.
- *Passive* - A protection layer that requires no mechanical device or system to actively function to limit or prevent the loss. The most favorable aspect of a passive system is its performance reliability because it is not prone to failure upon demand. Examples of passive systems are non-combustible materials of construction, physical space separation, dikes, drainage systems, and fire walls.
- *Active* - A protection layer that requires a mechanical device or system to actively detect and respond to limit or prevent the loss. An active system must be:
    - reliably designed to work when intended
    - installed according to strict installation rules
    - maintained and tested over its entire life.
    - operate upon demand

  An active system is more prone to failure than a passive system and may cost more over the life of the plant. Examples of active systems are fire detectors, automatic sprinklers, automatic closing valves, pressure relief systems, and process safety interlocks.
- *Procedural* - A protection layer that requires human response to limit or prevent the loss. Because of the need for human reaction and response this form of protection is highly subject to failure or improper action. Examples are an operator pushing a control button to close a valve or a fire brigade hearing an alarm, responding and attacking a fire with hose streams.

These systems can be shown as representing rings or layers of protection that guard the facility from fire and other exposures. Failure of an inner layer can sometimes be overcome by outer layers, albeit often at higher cost and larger potential loss.

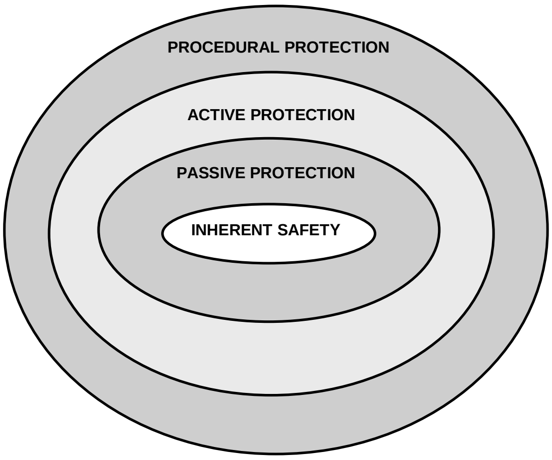

Fig 2 Layers of Protection

A chemical processing facility usually has some features of all of these protection layers but the best protected facilities heavily rely on the inner IS and passive protection layers - which can be built in during initial design and are highly reliable - rather than the outer active and procedural protection layers - which are usually more costly and are more subject to failure-upon-demand..

Opportunities exist to reduce the risk at a chemical facility at many stages of its life, but the primary opportunity exists during new technology development, early in a project design or during major changes. At these stages, IS opportunities can be explored economically.

According to Kletz [7, 8], there are five approaches to the development of inherently safer plants:

- Intensification
- Substitution
- Attenuation
- Limitation of Effects
- Simplification and Error Tolerance

Intensification – Reducing the presence or amounts of a hazardous material. This is also called Minimization.

In one CPI intensification example, a process required large quantities of flammable feedstock. In the past it had a large day tank within the process unit. This tank was fed from bulk storage tanks located many hundreds (meters) of feet away. The day tank was found to severely expose the production unit to fire, and in fact was originally installed only as a production convenience if supplies were temporarily cut off from the larger tanks (due to a pump failure, for example). The day tank was eliminated and spare pumps installed for reliability. The plant was able to operate as efficiently without the large volume hazardous inventory within the production unit.

Substitution - Replacing a hazardous material with a non-hazardous or less-hazardous material.

The classic example of substitution is the use of water as a coolant instead of combustible and highly corrosive thermal oil. The advantage is obvious. Water is both nonflammable and non-corrosive. Fire protection will not be needed for the water coolant alone, which could have been the case for the thermal oil. Obviously in this example, water would need to provide the cooling specifications required and it in itself not increase the hazard due to some other (i.e., water reactivity) exposure.

Using non-combustible materials instead of low flash point hydrocarbons is another example such as the substitution of supercritical carbon dioxide instead of hexane solvent in the extraction of caffeine from coffee beans. The hazards of fire and explosion from the solvent are eliminated. A possible trade off is the high pressure operating conditions required for supercritical extraction and the use of a toxic gas like carbon dioxide.

Substitution can apply to non-chemical systems as well. Use of noncombustible construction in buildings, use of electric cables inside metal conduit instead of exposed plastic insulated cable, and use of stainless steel instead of plastic or glass for piping systems handling flammable corrosives are all examples of this element of inherent safety.

Attenuation - Using less hazardous process conditions or a less hazardous form of material.

Attenuation is commonly achieved by using lower temperatures and pressures. It may be achieved through process chemistry (i.e., a new process with less potentially energetic effects). It might also be achieved by using less flammable or corrosive materials.

The 1974 Flixborough explosion incident[9] was caused by a release of cyclohexane, a hydrocarbon used to make nylon. Hundreds of thousands of pounds (kg) of cyclohexane above its boiling point were present in the system at high pressure. This was the standard way of producing this intermediate product. In the incident the boiling cyclohexane flashed to vapor and an outdoor vapor cloud explosion occurred which destroyed the plant. Another company discovered a way to produce nylon using cyclohexane in a process below its boiling point. The fact that the material is below its boiling point eliminates superheated vapor formation and reduces the chance of an outdoor vapor cloud explosion.

Another common example of attenuation is using refrigerated storage of hazardous materials, such as ethylene oxide or chlorine. Ethylene oxide stored at ambient conditions can form flammable vapor clouds if released. If stored as a refrigerated liquid, essentially no vapor cloud can form.

At one plant, a combustible metal dust presented an unacceptable explosion risk. The dust had a very high energy potential and conventional explosion venting systems would not be effective in reducing overpressures should the material ignite. The solution was to mix and dilute the combustible dust by addition of an inert dust, a process called phlegmatization. This was done immediately at the point of dust liberation prior to any large or important collection systems. The resultant mixture was rendered noncombustible and the explosion hazard was eliminated. This is a common practice in some coal mines where an inert dust is layered over combustible coal dusts in tunnelways. If an explosion occurs the incipient blast wave lifts and mixes the inert dust with the coal dust rendering the ensuing mixture non-combustible.

Limitation-of-Effects - Designing a facility to minimize the impact of a release of hazardous material or energy.

The most common example of Limitation-of-Effects is proper siting and location of facilities. Space separation can reduce the impact of an energetic release at one location from impacting another by minimizing radiant heat and explosion-generated pressure effects and projectiles. Other examples are providing drainage (which channel flowing liquids to a safe location) and considering prevailing winds and meteorological conditions in design

As an example, a typical older chemical processing unit has equipment located inside the unit as shown below. It is congested, has poor drainage patterns, and has limited fire fighting access. This arrangement will allow for more damage should flammable liquids be released and requires extensive and expensive automatic fire protection. It also is ideally suited to promote an explosion.

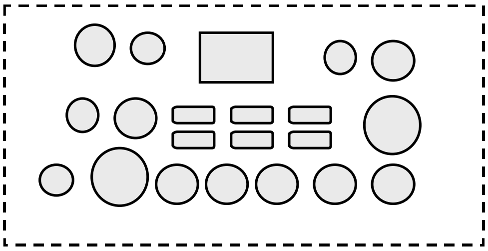

Fig 3 Older style chemical process unit

A newer plant using the IS principle of Limitation-of-Effects has positioned processing equipment with high volume flammable materials around the outside perimeter of the unit. The unit is long and narrow with heavily sloped liquid drainage toward the outside of the unit. These features ensure that all vessels with significant quantities of flammable materials are accessible for fire fighting from outside the unit. Upon a release, the materials flow outward from the unit away from other critical equipment and can be more easily controlled. Damage will be limited to peripheral equipment. Less extensive automatic (active) fire protection systems are needed. The potential for explosion has also been reduced by “opening up” the unit and minimizing confinement.

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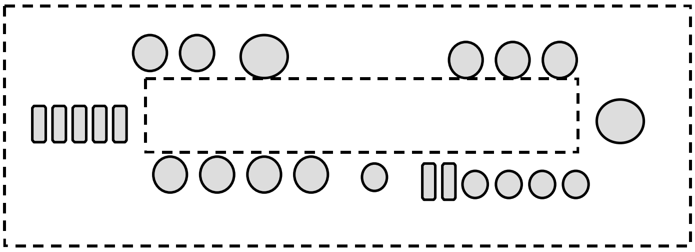

Fig 4 Modern chemical process unit layout

Another approach to Limitation-of-Effects is to limit the magnitude of a process deviation should one occur. For example, the rate of addition of a material to a vessel can be limited by sizing the feed pump so that it cannot possibly exceed the safe addition rate or pressure. This also can be achieved by use of smaller piping or restrictive orifice plates in pipes or by using pipe reactors instead of large volume vessel reactors. This is classically demonstrated in the manufacture of nitro-glycerin. Older processes featured manual addition of nitric acid to glycerin in large vessels of hundreds of gallons (cu m) volume. If one ingredient were added at the wrong time or in too large an amount the mixture in the vessel would explode destroying the production area, the building, and causing fatalities. This happened many times. Finally a process was developed whereby the two ingredients were added remotely by process controls and interlocks into a small pipe of only a few gallons (liters) in volume. The materials reacted instantly, the potential for explosion was minimized, and the consequences of the explosion should it occur were significantly reduced.

Another example of Limitation-of-Effects is provision of blast barriers or containment of a hazardous material or process. This has been used effectively by the chemical and nuclear industries for energetic and toxic materials.

Simplification and Error Tolerance - Designing a facility so that operating errors are less likely or the process is more forgiving if errors are made.

This can apply to many operating conditions within a plant. Where pumps are used to transfer flammable liquids, pumps without seals or double-sealed are preferable. Piping should be non-combustible and welded if possible, flexible couplings minimized or eliminated, and glass level devices eliminated. Sample points should be avoided, but should have double valving and collection pots if necessary.

Another example is ergonomic design of control systems and control panels. The easier it is for an operator to respond and find the correct shutoff button (for example) the better chance of an orderly safe shutdown. Alarm management (which helps discriminate nuisance alarms from critical alarms) is an example of Simplification and Error Tolerance.

At one chemical plant under design, the facility was simplified by reducing the number of vessels and equipment needed to run a similar but older plant by sixty. The complexity of running the plant and thus potential for loss was substantially reduced.

5. APPLYING INHERENT SAFETY IN SOLVENT EXTRACTION PLANTS

Many modern copper producing SX plants have a ‘typical” layout shown by Figs 5 and 6. While there are many variations, typically multiple side-by-side M-S cells are located below a pregnant liquor solution (PLS) pond which in turn is located below a heap leaching operation. Encircling the M-S cells are pipeways, often in sub-grade trenches, which feed a lower grade processing area, often called the “tank farm”. At a grade below or adjacent to the SX plant is an Electrowinning (EW) Cell House where final product cathode copper is electrically recovered (“won”) from solution. In many cases the entire process is based on gravity flow of liquids downwards which saves on cost and process complexity. In some plants a solvent release at one level can flow to a lower level unimpeded by physical barriers. In one facility visited by the author a solvent spill in the M-S area could potentially have flowed all the way into the EW building via open pipe channels and cable tunnels under roadways.

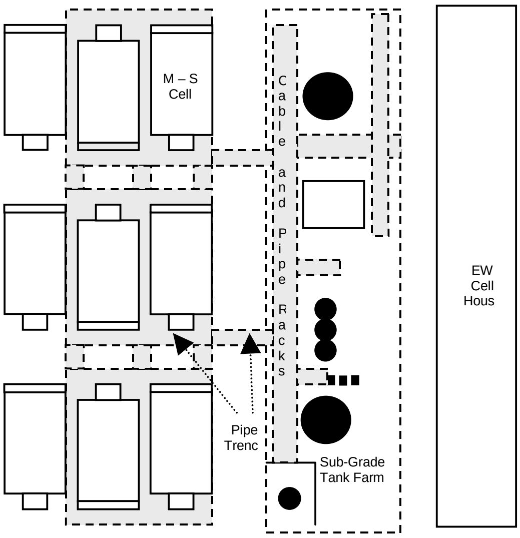

Fig.5 Plan View of “typical” copper SX plant layout

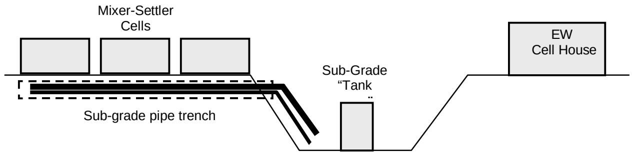

Fig 6 Section view of “typical” copper SX plant layout

Piping systems and vessels in SX plants require corrosion resistance due to presence of acids in solution. Piping and vessels in older copper SX plants are often stainless steel. The use of glass piping has been mostly discontinued except for some rare metal solvent processes. Piping and vessels in newer SX plants are usually high density polyethylene (HDPE), polyvinyl chloride (PVC), polypropylene (PP), or glass fiber reinforced plastic (FRP/GRP). These materials of construction are chosen due to low cost, ease of construction, and good corrosion resistance.

The use of plastic – especially soft thermoplastics such as HDPE, PP, some forms of PVC and rubber flexible fittings (Fig 7) on steel piping – creates conditions for rapid failure and release of solvent contents during fire exposure. These systems are also non-conductive and present difficulty in eliminating static build-up caused by solvent flow in pipes. Black plastic pipes in hot climates also can cause solvents to heat – by solar radiation – above flash points.

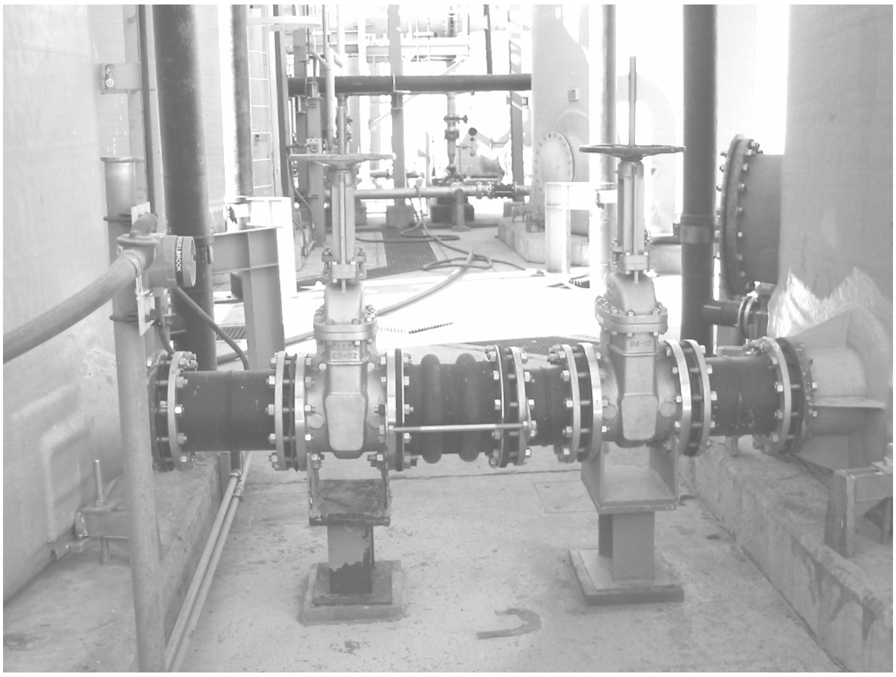

Fig 7 Rubber couplings on a piping system connecting two solvent tanks. Should a small solvent fire occur and burn through the rubber couplings the entire contents of both tanks would be fed uncontrollably to the fire.

"Typical" flammable solvents used in copper SX processes are midweight petroleum products (usually a grade of kerosene) with flash points in the 100 to 140^o F (38 to 60^o C) range. At sea level these are classified as Class II Combustible Liquids [10]. At very high elevations (like in the high Andes) flash points significantly decrease due to lower barometric pressure and can cause a solvent to enter a Class I Flammable Liquid classification[11]. This may influence their ignitability as well as flammability and require more rigorous electrical equipment design and classification. Flammable liquid mists – which are created by free-falling liquids or pressurized sprays - are easier to ignite than quiescent liquids and have been known to explode when confined inside vessels or buildings. Although the ignition sensitivity of kerosene solvent is less than lower flash point materials once ignited it will burn similar to lighter hydrocarbons, producing about 20,000 BTU/lb (46.4 kJ/g) of energy[12].

The traditional response to fire protection of a "typical" copper SX plant is to add on multiple layers of passive, active and operational protection systems once process and layout design has been determined. Fire protection design is often done months after initial layout design and little impact on basic design is possible. This usually involves provision of high volume water or foam-water deluge systems in all areas including inside M-S cells, over launderers, inside sub-grade pipe trenches, along elevated pipeways, inside solvent tanks, over pumps, etc. It may also involve provision of hydrants and monitor nozzles with foam injection capability, sophisticated fire detection systems, large dedicated fire water pumping or storage systems, and barriers or special drainage systems. It also requires a well equipped emergency response capability often in remote areas [3, 11, 13].

Properly designed and reliably installed protection systems supplemented by passive barriers and emergency response will certainly adequately protect SX facilities against severe fire damage and should be provided where and when needed based on a hazard risk assessment. However, because a flammable liquid fire presents a severe and fast acting hazard, all protection systems must act together rapidly with very high reliability or the fire might gain control overtax the protection system. If high volume flammable liquid storage, piping or processing systems fail under fire exposure and release additional fuel the protection system design-basis may be exceeded. Once a flammable liquid fire has grown beyond a controllable size, fixed protection systems may not be able to limit damage. Further, active systems have a defined failure rate and may not be available upon demand over the life of a facility.

As a result a facility that has to rely on fixed fire protection will usually have a higher inherent damage potential than one which has designed in IS features.

While add-on protection is often the only economic solution for existing plants, there are opportunities to lower the overall hazard of new SX plants through inherent safety.

The ideal IS approach to this industry would be to completely change the technology or process chemistry of SX plants. The extent to which this could be technically or economically achieved is not known but some ideas are:

- Develop and use a non-flammable organic solvent (Intensification)
- Develop and use a less flammable organic solvent (Substitution)
- Find an additive that lowers the resistivity of the solvent to eliminate the potential for static electricity generation (Attenuation) [3]
- Develop a new process to extract minerals by significant reduction in quantities and flow of solvent and eliminate large open pools of flammable liquids (Intensification)

Given that the basic science and technology of a well established process cannot always be economically changed and that combustible solvents will likely continue to be used in large quantities potential IS opportunities should focus on changes to design and layout concepts. Some ideas are:

- Stop or reduce the practice of gravity flow in SX process (Simplification and Error Tolerance)
- Install all equipment and processes at the same grade level rather than using lower rade tank farms (Fig 8) (Limitation-of-Effects)

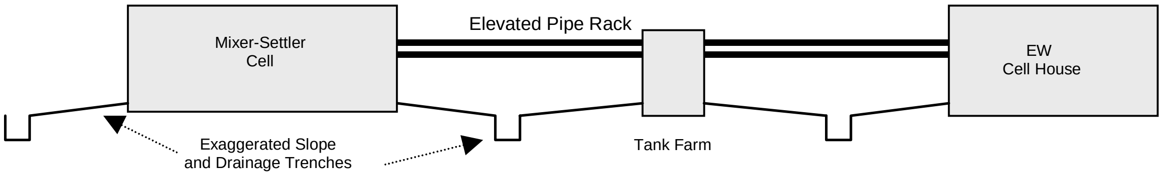

Fig 8 Example of IS design in an SX plant. In this "hypothetical" IS design sub-grade trenches and tank farms are eliminated, all processes are at the same grade with high volume channeled drainage systems, buildings are well separated and pipes (all steel) are on elevated pipe racks for easier response and inspection.

- Eliminate the use of sub-grade trenches for piping; place piping on elevated piperacks located away from solvent storage or drainage discharge areas (Limitation-of-Effects)
- Separate buildings, vessels and process areas by physical distance based on a risk assessment that includes the impact of radiant heat, wind effects and drainage patterns (Limitation-of-Effects)

- Lower mixer-settler roofs to rest on or near the top of the liquid layer to minimize or eliminate space for flammable vapor accumulation (Intensification)
- Provide liquid barriers such as walls, curbs and dikes between buildings, vessels and process areas (Limitation-of-Effects)
- Provide high capacity drainage systems for spilled solvents with discharge to a safe, remote area. (Limitation-of-Effects)
- Provide high capacity emergency dump systems for mixer-settler cells and other vessels with large quantities of solvents with discharge to a safe, remote area. (Limitation-of-Effects)
- Locate solvent pumps outside of dikes or sub-grade areas enclosing solvent tanks and other equipment (Simplification/error tolerance)
- Separate process control and safety interlock instrumentation from power cables (Limitation-of-Effects)
- Use robust, fire resistant conductive materials (like stainless steel) for piping and vessels rather than combustible, frangible, or non-conductive materials like thermoplastics or glass. When steel cannot be used consider use of a more durable and fire resistant structural thermoset plastic such as FRP/GRP with a conductive lining. (Substitution)
- Eliminate polymeric materials such as rubber for flexible connections on piping and pumps (Substitution)
- Use seal-less or double sealed pumps for solvents (Substitution)
- Find methods to reduce static or mist generation in solvent systems such as submerging in-feed nozzles, minimizing bends and restrictions in piping, reducing solvent flow velocities, and using low turbulence pumps (Intensification) [3]

As a final thought, it is important to note that not all IS solutions will provide obvious assurance that they are the best approach and there will always be trade-offs.

An example is the use of gravity flow versus the use of pumps to transport flammable liquids. While gravity flow presents unique fire protection challenges due to flowing flammable liquids the use of pumps can increase the likelihood for release and ignition due to mechanical parts and friction. Use of gravity systems can reduce the complexity of a transfer system.

When considering which approach is best all failure mode and hazard scenarios must be considered by using modern and rigorous risk analysis and assessment techniques. The impact (consequences) of a release with ignition versus the likelihood (probability) of the release occurring must be balanced based on the operator’s tolerance for risk. Ultimately it may be better to use a gravity flow layout and provide greater space separation, barriers and channeled drainage (all passive systems) rather than increase the number of pumps and thus increase the chance of a release.

Conversely, by using seal-less or double sealed pumps and properly siting and protecting the pumps the potential for release and escalation of a fire can be significantly reduced below that of a gravity system.

The CPI long ago discontinued the widespread use of gravity flow in chemical plants and chose instead to improve the reliability of pumping systems.

6. CONCLUSIONS

This paper has explored the use of inherent safety concepts for design of chemical plants. Inherent safety elements have been defined and examples of IS that have been applied in the CPI have been presented. Opportunities for using IS in hydrometallurgical SX plants have been specifically explored.

As long as flammable or combustible solvents are used in SX plants reliance on traditional passive, active, and procedural protection systems will be needed to detect, react to and suppress fires in addition to IS.

With creative thinking, motivation and a willingness to effect change the IS principles of intensification, substitution, attenuation, limitation of effects and simplification/error tolerance can be applied to eliminate or reduce the hazard and minimize the need for costly and less reliable add-on fire protection. This is best done at the design or pilot plant level or a project.

The degree to which this can be done is in the hands of the process designer, the mining engineer and the accountant. The use of IS should never limit or impede technology, design or operation and cannot always be economically achieved. However, without the knowledge that IS can be designed in – if carefully considered in the earliest conceptual stages – it will never become part of the mining industry's consciousness and best practices.

As final thought it is recommended that this industry:

- Study new SX technologies that reduce or minimize the fire hazard
- Form global working groups to study possible improvements to SX plant design and inherent safety
- Publish Best Practice guidelines on SX plant loss prevention design including use of inherent safety
- Support seminars and symposiums on SX plants with focus on loss prevention

7. APPENDIX

Suggested supplemental reading on Inherent Safety:

- CCPS 1996. *Inherently Safer Chemical Processes – A Life Cycle Approach*, New York: Center for Chemical Process Safety of the American Institute of Chemical Engineers
- CCPS Guideline G-18, 1992. *Guidelines for Hazard Evaluation Procedures*, New York: Center for Chemical Process Safety of the American Institute of Chemical Engineers
- CCPS Guideline G-4, 1988, *Guidelines for Vapor Release Mitigation*, Chapter 2, New York: Center for Chemical Process Safety of the American Institute of Chemical Engineers
- Englund, S.A., ''Inherently Safer Plants: Practical Applications'', Process Safety Progress, Vol 14 No 1 pp 63-70, Jan. 1995
- Englund, S. A., ''Opportunities in the Design and Operation of Inherently Safer Chemical Plants,'' Advances in Chemical Engineering, 15, pp 73-135, 1990
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2. Hoy-Petersen, R., *Fire Prevention in Solvent Extraction Plants*, Proceedings of the 1st International Loss Prevention Symposium, The Hague/Delft, the Netherlands, May 1974
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9. The Flixborough Disaster, *Report of the Court of Enquiry*, HMSO, 1974
10. National Fire Protection Association, NFPA 30, *Flammable and Combustible Liquids Code, 1996,* Quincy MA USA
11. FM Global Loss Prevention Data Sheet 7-12, *Mining and Ore Processing Facilities*, 2001, Factory Mutual Insurance Company
12. FM Global Loss Prevention Data Sheet 7-32, *Flammable Liquid Operations*, 2000, Factory Mutual Insurance Company
13. Collins, G., Cooper, J.H., Brandy, M.R., *Designing Solvent Extraction Plants to Cut the Risk of Fires*, Engineering and Mining Journal, Pgs. 58 – 64, December, 1978

9. LIST OF TABLES AND FIGURES

Fig 1 (Photo) Copper SX plant fire in Mexico 2003

Fig 2 Layers of Protection

Fig 3 Older style process unit

Fig 4 Modern style process unit

Fig 5 Plan View of “typical” copper SX plant layout

Fig 6 Section view of “typical” copper SX plant layout

Fig 7 (Photo) Flexible rubber fittings

Fig 8 Example of IS layout design for an SX plant

Table 1 SX plant fire history.

10. LIST OF ABBREVIATIONS

AIChE	American Institute of Chemical Engineers
CCPS	Center for Chemical Process Safety
CPI	Chemical Process Industry
EW	Electrowinning
FM	FM Global or Factory Mutual Insurance Company
FRP/GRP	(Glass) Fiber Reinforced Plastic
HDPE	High density polyethylene (plastic)
IS	Inherent Safety
M-S	Mixer-Settler
NFPA	National Fire Protection Association
PLS	Pregnant Liquor Solution
PP	Polypropylene (plastic)
PVC	Polyvinyl chloride (plastic)
SME	Society for Mining, Metallurgy, and Exploration
SX	Solvent Extraction

FIRE HAZARDS IN SX PLANT DESIGN – SOME UPDATES

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ABSTRACT

This paper updates an earlier Aker Kvaerner paper on fire hazards in SX plant design. It deals with new situations arising from increased use of plastic materials, the introduction of more organic compatible foam systems, newer plant layout concepts and greater awareness of the dangers of static electricity generation and discharge. Fire incidents in various solvent extraction facilities over the last forty years are discussed.

1. INTRODUCTION

This paper is an extensive updating of a much earlier Aker Kvaerner paper “Solvent Extraction Plant Design – Safety Aspects with Particular Reference to Fire Hazard in Hydrometallurgical Plants”, G. Collins, S. Cooper and M. Bandy, Symposium on Safety in Solvent Extraction Plants, Fire Research Station Boreham Wood, England, April 1977. Since those early days the industry has seen the introduction of much more plastic materials, AFFF foams, new plant layout schemes and an awareness of the dangers of static charge. A general update of this very good paper now seems appropriate to suit the new plant design conditions, from a major engineering company’s point of view.

The record of solvent extraction plants with respect to fire outbreaks is very good but several incidents (over the last thirty years) show how disastrous such a fire can be. Because of the small number of reported incidents and the wide variation of protective equipment installed on existing plants the formulation of a policy for essential requirements is somewhat a matter of opinion rather than established fact. It is the purpose of this paper to present the hazards which may occur and the methods of minimising the risks by proper design bearing in mind the compromises imposed by economic considerations. It will also suggest the necessary precautions for the wide variety of SX plants and ambient conditions to ensure that the fire risk is minimal and the fire fighting installation is adequate. The author’s involvement has been mainly in the metallurgical industry using gravity mixer settlers and the statements in this paper will generally apply to this environment. The final section of the paper deals with some typical installations and incidents.

Solvent extraction in the metallurgical industry means the treatment of impure pregnant liquor, perhaps derived from leaching ores, with an organic solvent to extract the desired metal. This is followed by treatment of the solvent with an aqueous stripping liquor to give a pure concentrated solution of the metal from which it can be recovered by electrowinning or by various salts and hydroxides precipitation. The stripped solvent is recycled to the extraction stage.

This operation is generally performed in mixers and settlers which vary in size according to throughput. The process is now well known and does not need much further explanation.

There appears to be a philosophical error of which most of us in the industry, both engineer/designers and operator alike, have been guilty – we have always thought of these plants as metallurgical extraction facilities with some corrosion problems not as very large hydrocarbon handling plants operating with designs and practices that would not be permitted on most petrochemical sites.

Metallurgical solvent extraction plants can be inherently dangerous operations and they require that adequate attention is paid to various operational and design aspects from the outset.

Experience and design modifications arising out of the fires of the past few years indicate that all of us may have been very lucky for a long time.

2 CODES AND CLASSIFICATIONS

Because of the combustible nature of these organic solvent fluids and the information on sporadic fire events that have destroyed SX plants in the past, classification of SX areas regarding fire protection has become a controversial issue for projects. This section is intended to provide guidance for proper classification of the solvent extraction organic fluids.

There are several sources of origin for fire that may affect an SX metallurgical complex, of which the following are identified as having a realistic potential for becoming actual fire sources:

- Hazard created by operator manoeuvring or maintenance.
- Mechanical or electric energy released from equipment in any form (sparks, friction).
- Static electricity build-up.

Internationally there is now a large group of standards which address problems that various industries encounter in matters related to fire protection and hazard classification. These include the following:

National Fire Protection Association – NFPA (USA)

NFPA 10	Portable Fire Extinguishers
NFPA 11	Low Expansion Foam and Combined Agent Systems
NFPA 12	Carbon Dioxide Extinguishing Systems.
NFPA 13	Installation of Sprinkler Systems
NFPA 14	Installation of Standpipe and Hose Systems.
NFPA 15	Water Spray Fixed Systems.
NFPA 16	Deluge Foam – Water Sprinkler and Foam – Water Spray Systems.
NFPA 20	Centrifugal Fire Pumps
NFPA 24	Installation of Private Fire Service Mains and their Appurtenances
NFPA 25	Water – Based Fire Protection Systems
NFPA 30	Flammable and Combustible Liquids Code
NFPA 36	Solvent Extraction Plants
NFPA 70	Electrical Code.
NFPA 72	National Fire Alarm Code.
NFPA 77	Recommended Practice on Static Electricity
NFPA 78	Lightning Protection Code
NFPA 325	Guide to Fire Hazard Properties of Flammable Liquids, Gases and Volatile Solids.

- NFPA 497 Recommended Practice for the Classification of Flammable Liquids, Gases or Vapours and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas.
- NFPA 2001 Clean Agent Fire Extinguishing Systems.

and several general publications:

- Fire Protection Systems: Inspection, Test & Maintenance Manual
- Fire Protection Handbook

Other relevant standards would be:

National Electric Code – NEC (USA) – Article 500
American Petroleum Institute – API (USA) – RP500 Recommended Practice for Classification of Locations for Electrical Installations at Petroleum Facilities.

British Standards Institute – BSI (UK) – BS5345 Parts 1 and 4
BS1259 Intrinsic Safety
BS229 Explosion Proofing
BS5958 Static Control

In addition to these industry standards there may be corporate standards such as the following from Codelco-Chile considered amongst the most rigorous in the industry.

NCC N°20	Estanques de Almacenamiento de Líquidos e Inflamables.
NCC N°21	Seguridad, Prevención y Protección contra Incendio en Instalaciones Eléctricas.

Although there are slight variations principally in nomenclature amongst the various national standards they are all based on similar classifications

"Class" – defines the generic type of hazardous materials
"Group" – a list of materials of similar hazard.
"Division" – an indication of the probability that a combustible or flammable concentration of material may be present.

A fundamental criterion for combustible liquids is the <u>flash point</u>. This is normally defined as the minimum temperature of a liquid at which sufficient vapour is given off to form an ignitable mixture with the air near the surface of the liquid or within a closed vessel. That is to say it corresponds to the lower flammable limit when a flammable vapour mixture is formed.

There are two main test methods for the flash point: open cup and closed cup which gives lower values and is used in the paper. These methods are standardised for pressures corresponding to sea level, and kerosenes are typically more flammable by 1°C/300m above sea level. The flash point lowering is offset to some extent by reduced oxygen in the atmosphere at higher altitudes. A general equation would be:

Actual flash point °C = sea level flash point °C + 6.07 - 0.015 atmos. press. mm Hg.

This means for example that the flash point can fall by 15.5°C by moving to an altitude of 4200m. In general if the closed cup flash point is greater than 54°C at sea level combustible air mixtures will not be generated up to 3040 m.

From the above codes and the knowledge of flash point a classification of liquids can be developed:

Class 1- Division 1 – ignitable concentrations of flammable gases/vapours exist under normal operating conditions.

Division 2 – ignitable concentration of flammable gases/vapours could exist but normally do not because flammable material is handled in containers or flammable conditions could only arise during equipment disturbance in maintenance or failure.

Class 2 – Combustible Dusts

Class 3 – Flyings.

There is now a further subdivision originating in the European Codes of

Class 1 – Zone 0 – ignitable concentrations of flammable gases/vapours are continually present and over long periods of time (usually greater than 10%) and precautions must be taken to prevent ignition by electrical apparatus.

Zone 1 – Ignitable concentrations of flammable gases/vapours exist in normal operation.

Zone 2 – Ignitable concentrations of flammable gases/vapours exist only for short periods.

Thus we now have

IEC Zone 0, Zone 1 = U.S. Division 1
IEC Zone 2 = U.S. Division 2

In the codes definition of liquids is set by their flash points:

A combustible liquid has a closed cup flash point of greater than 37.8°C. This is then subdivided into:

Class II	– closed cup flash point 37.8°C – 60°C
Class IIIA	– closed cup flash point 60°C – 93°C
Class IIIB	– closed cup flash point above 93°C

And it is generally considered that a combustible liquid will only form an ignitable mixture when heated above its flash point.

A flammable liquid has a closed cup flash point of less than 37.8°C.

In solvent extraction plants, particularly for copper the diluent kerosene is a Class III A combustible material with a closed cup flash point above 60°C but less than 93,4°C. Most organic phases in SX plants (diluent plus reagent) operate at under 40 – 45°C which is well below the closed cup flash point of the diluent.

A key consideration to determine the potential for inflammation of the SX fluids is the classification of the mixture of diluent vapour and air found above every surface of organic in plants. The following quotes are excerpts from section 4-1.1.1 of the NFPA's code section n°77 (1993 Ed.), supplemented with facts from copper SX industry practice:

"If the liquid temperature is below its flash point, the mixture above its surface will be below the lower flammable limit, or too lean to burn. A liquid handled at or somewhat above its flash point is more likely to have a flammable vapour-air mixture at any free surface". The flash-point temperatures for SX-grade diluents are typically higher than 72°C, and for copper-extractant reagents are higher than 62°C. The flash point for organic will be no less than the lower of the two previous ones, while the maximum temperature the organic stream can reasonably reach ever in normal operations in a copper SX plant is less than 45°C (SX strip section).

"If the vapour mixture is below or above the flammable limits, it will not ignite, even should an incentive spark occur". The flammable RVP limits for fluid temperatures between 20°C and 40°C range between 0.7 kPa and 4 kPa (at 40°C) and 2.1 kPa and 11.2 kPa. Within these flammable limits, fluids need to be handled with proper care (preventing static discharge, proper ventilation) as will be described later.

Based on the above analysis, neither special nor restrictive design requirements (grounding of HDPE piping and or lining, Class II classification for design, etc.) appear necessary from a technical point of view for metallurgical solvent extraction facilities.

For many years copper SX plant designers and operators have complacently accepted this situation as inherently non-hazardous and solvent extraction plants have been designed with minimal or no fire protection systems.

In spite of the fact that neither the organic stream nor its components (reagent and diluent) will ever likely reach temperatures closer to their respective flash-points in SX plants, corporate standards have dictated restrictive designs regarding fire protection in most recent SX projects in Chile. Now with a better understanding of fire events in some SX plants such design requirements may now seem fortuitous.

3 CHEMICALS INVOLVED IN METALLURGICAL SOLVENT EXTRACTION

A range of active extractant reagents are used such as phosphinic acids, amines, versatic acid and oximes. The majority of solvent extraction facilities of large size are in the copper industry. Here ketoximes and aldoximes are the usual choice together with various modifiers. These are water insoluble mixtures of substituted oximes which form water insoluble complexes with metallic ions.

Such mixtures generally have a flash point of 65 - 85°C and a fire point of 92°C. In solvent extraction processes the active reagent is normally used at up to 40% v/v in a diluent such as kerosene. This is usually a high flash point kerosene of mainly (>85%) aliphatic character.

The fire point is the temperature at which a steadily heated liquid and vapour will combust spontaneously.

Liquids are classified according to flammability. As we have seen under NFPA code flammable liquids are defined as having flash points below 60°C and a vapour pressure not exceeding 272 kPa abs at 38°C. NFPA Class I combustible liquids have flash points below 38°C, Class II 38-60°C, Class III above 60°C.

In uranium extraction a tertiary amine is often used. This reagent has a flash point of 179°C and a fire point of 210°C. But again it is used as a 3 to 5% solution in a diluent such as kerosene with 4% of a modifier such as isodecanol. The latter has a flash point of 104°C.

The diluent is therefore an important consideration in both the above processes from a flammability viewpoint. In the copper industry the tendency has been to use a diluent which is manufactured to a closely controlled specification to have a narrower boiling range and high flash point (79°C) compared to commercial kerosenes.

During the apartheid era, because of import restrictions, uranium practice in South Africa used heating and illuminating kerosenes. These have a minimum flash point of 43°C and typical figure of 48°C. Such low flash point material was a significant contribution to the Rossing uranium SX plant fire. Similarly the diluent used in the Kristiansand cobalt refinery in Norway which was destroyed by fire had a flashpoint of 42°C (108°F). Also the fires in Soquimich (SQM) iodine SX plants in Chile were aggravated by the use of low flash point lighting kerosenes.

An important consideration in SX fires is the replacement of the organic solution. Apart from its cost there is the manufacture and delivery time so that the fire fighting method should be compatible with preserving the organic solution and minimizing lost production.

4 SX DESIGN PARAMETERS AFFECTING FIRE RISK

4.1 OPERATING TEMPERATURE

In general a higher operating temperature improves reaction kinetics and rate of transfer of metal to extractant and also improves the rate of settling and separation of the phases. In many cases the temperature of the pregnant liquor feed to SX is approximately ambient having been derived from leach liquors which have cooled in the solid separation step in thickeners for example or emanate from heap leach operations. The cost of heating these liquors above about 25°C to improve kinetics and settling characteristics is generally not justified. So that except in cold climates heating of the pregnant liquor is not usual.

However when a combination of CIX and SX is used as in uranium extraction the SX pregnant liquor is the eluate from the CIX plant which could be operating at 50°C. In this case a heat exchanger operating with eluate to the SX unit and raffinate from SX would be needed and possibly a water cooled exchanger to maintain a reasonable operating temperature in the SX plant. The choice of operating temperature in this case is a compromise between the greater safety at lower temperatures and the better operating characteristics at higher temperatures which of course implies smaller less costly equipment for the same duty.

In the stripping section of a copper SX process the stripping liquor will normally be the EW plant spent electrolyte which is normally at about 35 to 50°C dependent on current density and other EW operating parameters. Again a heat interchanger between spent electrolyte and advance strong electrolyte is needed to maintain a reasonable solvent extraction operating temperature.

If the solubility increases markedly with increasing temperature there is an incentive to operate at higher temperatures to increase the total metal extracted per pass through the extraction stages thereby employing the reagent to its full capacity and reducing both plant and inventory costs.

4.2 ENCLOSING OF EQUIPMENT

Evaporation losses of kerosene and extractant reagent are dependent on operating temperature and whether the equipment is open to atmosphere or enclosed. Dependent on the location and climate it may be necessary to cover the units because of rainfall, heat losses from the system or protection against dusty conditions or insects. There are also the operational requirements of the control of levels within weirs, inspection for ‘crud’ formation, checking phase continuity etc. The practice generally adopted is to enclose the equipment but not necessarily in a gas tight manner and to provide inspection hatches where visual examination is necessary. This increases the hazard because the vapour space below the cover contains a concentrated flammable vapour mixed with air capable of being ignited more easily than the liquid, possibility with explosive violence. Radiant heat from the sun also tends to keep the temperature higher than ambient in this vapour space. The roofing scheme used at Girilambone in Australia for example attenuated this by the use of white FRP panels. There are several installations operating in Arizona with open mixer-settlers and an interesting compromise is the system used at Gibraltar, Cerro Dominador, BHP Tintaya and soon at Spence of locating the ‘open’ settlers inside one large building covering a whole mixer settler train.

4.3 ENTRAINMENT REMOVAL

A well designed SX plant should have low organic entrainment values in the streams leaving the mixer-settlers which are raffinate and strong electrolyte for copper systems. However even small entrainments can build up in plant sections associated with the SX plant and increase the fire hazard in these areas. For instance the entrainment in the strong electrolyte disengages in after settlers/surge tanks prior to filtration and if filtration is inefficient, or fails, appears in the electrolytic cells forming a layer of organic on the cell which can be ignited by electrical sparking when removing or adjusting cathodes under load. In fact the risk of fire in many plants with poor electrolyte filtration is much higher in electrowinning rather than solvent extraction! These tanks with films of organic on the surface must not be forgotten in the fire protection scheme. It is noteworthy that the only tanks which exploded in the Rossing fire were those which supposedly only contained aqueous phase (but had accumulated organic by entrainment) and no fire protection was provided.

4.4 PIPELINE DESIGN

The SX plant has a considerable amount of piping associated with the equipment. The interstage and recycle lines carrying both organic and aqueous fluids are designed for low pressure losses consistent with the pump impeller system. However, a number of lines have pumped supply and could be designed for relatively high velocities to minimise piping costs. The generation of static electricity in any system is proportional to the velocity and this must be limited to safe values. The generally accepted figure given by API code is 2m/s where discharge is always beneath the tank liquid level. A velocity of 1m/sec is recommended for all SX piping to allow for variations at start up and during abnormal operation. Chemical engineers will be familiar with these recommendations for petrochemical service. Here the materials being conveyed are much more flammable but the piping is usually metallic. Thus the piping material is important also in static generation, the non-metallic materials, plastics etc, being more conducive to charge generation than metals and less easy to dissipate. Such static discharges were important in the more recent fires where HDPE linings and pipe are widely used. The recent events have shown that design of pipe systems must be done such that these organic pipelines especially under gravity flow must run full to prevent explosive mixtures with air being generated.

4.5 PLANT LAYOUT

Economic design calls for the mixer-settlers to be arranged relatively close together to maintain piping runs short and consistent with the low pressure drops allowable. This proximity increases the fire hazard and means that added precautions are necessary to prevent any fire spreading to involve the whole plant. Access for fire fighting must also be taken into account.

4.6 LIGHTNING

The design of an SX plant must consider the possibility of a fire being caused by lightning. Such a high voltage high temperature source is almost certain to set even the high flash point diluents ablaze. It is the same danger as arcing over surface organic in an electrolytic cell on a more dramatic scale. For this reason it is usual to arrange earthing conductors at the high points of the equipment to discharge any strike to earth. In areas prone to thunderstorms a system of electric wires above the hazardous areas which are then grounded is required. Plants at high altitude in the Andes such as Collahuasi and Quebrada Blanca are subjected to violent electrical storms and such provisions have been of paramount importance in their designs.

4.7 ELECTROSTATIC DISCHARGE FIRE RISK

Based on fire events that have occurred in the last few years this aspect warrants discussion in depth. Electrostatic charge can accumulate and discharge as an ignition point. There have been two fires in SX plants attributable to static discharge and many plant operators report seeing arcing at night – enough to send a chill up your spine!.

There are five conditions which must occur for an electrostatic ignition hazard to be present:

- A flammable atmosphere
- Electrical charge generation
- Electrical charge accumulation to produce high field strength
- Electrical breakdown of the insulating material and discharge
- Sufficient discharge energy

Sensitive Atmosphere

As we have seen depending on the temperature and flash point, flammable liquids can form explosive vapour/air mixtures that can be ignited by an ignition source. The degree of hazard inherent in a liquid relates strongly to its flash point, its ignition point and the upper and lower explosive limits.

For a gas/air mixture or vapour/air mixture to be flammable the ratio of the concentration of flammable material to the concentration of air must lie between the lower and upper explosibility limits. Flammable hydrocarbon vapours when present in concentrations roughly mid way between their upper and lower flammable limits are very sensitive to spark ignition. Some have very low ignition energies that can be below human perception. It is generally thought that the vapour mixture present above a liquid is only flammable if the liquid temperature exceeds the flash point – however in the presence of organic mists or aerosols these act as a finely divided carbon source in air and ignition is possibly independent of the bulk material flash point. Owing to their low heat capacity the temperature of liquid droplets in aerosols can rise very rapidly above the flash point. Not only mists of solvent produce conditions for ignition below the flash point. Any situation producing an increase of the liquid/air interface such as frothing from splashing, foam generation in pipelines by intermittent flow or turbulence can produce a hazard.

Atmospheres above the bulk organic may be above the upper explosive limit but opening an inspection hatch may dilute it down to a dangerous condition.

An atmosphere could be considered flammable if the concentration of the flammable vapour is more than 50% of the lower flammable limit. But if the concentration of oxygen in this location is low combustion is impossible. Consequently maintenance work using nitrogen or CO_2 blankets can be useful.

Pipes and tanks in the SX plant containing the usually safe organic solvent and air can then produce under certain conditions a flammable atmosphere capable of ignition by static discharge.

Charge Generation and Accumulation

Regarding the build up of charge, this is related to the conductivity of the organic liquid, the pipeline and equipment materials, grounding provisions and line velocity.

Electrostatic charge accumulates on insulating solvent, insulating plastic pipework; plastic tank linings, metal items insulated from ground, personnel with non-conductive footwear or non-conductive flooring.

An organic liquid is considered of low conductivity if the conductivity is less than 10^{-8} ohm.m. Many reagent/diluent combinations are beyond this requirement and generally can be considered safe. Adding polar solvents can improve conductivity.

However the narrow-cut kerosenes used as SX diluents have very low electrical conductivity and are prone to electrostatic charging and can be ignited with low energy discharge. Pipelines with this material with or without the extractant present may generate high levels of charge and a sensitive flammable atmosphere. The usual extractant oximes are also of low conductivity but are less flammable.

Recent years have seen the move away from the traditional design using conductive 316L stainless steel construction for mixer settlers and tanks. Here Aker Kvaerner must own up to some culpability – it was our plant at Inspiration (now Phelps Dodge Miami) that used HDPE as piping for the first time proving its resistance to organic solutions. Because of the price differential over 316L stainless HDPE was soon being promoted and used for all SX tank lining and piping. This move was accentuated in Chile where the leaching of atacamites introduced chloride ion into the corrosion equation and the costs of suitable metal equipment and piping escalated. Almost all recently designed plants use HDPE or FRP as their primary material of construction in contact with organic and aqueous fluids in the plants.

It is now recognized that continuous movement of organic in a pipe, especially a pipe which is of non-conductive plastic, produces a moving stream of charge which can raise potentials between the pipe and the fluid at discharge points to amazing levels (20 kV). Charge can accumulate on the pipe wall and any isolated metal fittings. It does not occur on grounded metal pipe or plastic pipe with some form of grounded inner layer or conducting FRP.

The accumulation of static charge is increased if the organic liquid contains an immiscible component (such as “entrainment”!) or suspended solids.

Olympic Dam produced very high potentials due to pipe velocities, long pipelines and turbulence but other plants with lower velocities and short pipe runs and lower operating temperature have much lower potentials.

Charge developed on the human body is dangerous as a person is mobile and can transfer charge into hazardous areas plus the body can produce spark discharges.

The bad news continues as we look at mixers and settlers. The relative movement of the two phases will produce static charge as in a mixer box or the movement of the phases down the settler. This is accentuated by the charge which may be entering the plant item on the organic phase even if it is leaving a grounded conductive pipe.

As the metallurgical SX processes use low temperature and high flash point diluents the vapour concentrations in the plant never reach the lower explosive limit and they will not normally ignite. However the formation of fine droplets by foaming of the surface can provide a sensitive flammable atmosphere at normal plant temperatures at up to 20°C below their flash points. Here the importance of flash point is diminished and the solvent becomes sensitive to ignition – tests at the University of Southampton showed that a foaming surface can be ignited by less than a 10mJ discharge at 30°C and less than a 1mJ discharge at 65°C – Such conditions are observed in many metal extraction SX plants.

Thus the most dangerous areas are splashing, organic droplet development and misting. This may occur on a too violently agitated mixer box or a badly designed/operated organic weir or splash filling of organic surge tanks.

Thus the move to these HDPE and FRP based systems has increased the dangers of these plants related to static electricity build up. Fire safety is affected as the plastic materials themselves are combustible and HDPE has no fire resistance.

Electrical breakdown and discharge

An SX plant has three potential sources of electrostatic discharge, namely charged plastic surfaces such as pipelines and tank walls, electrically isolated metal items and from the liquid surfaces in large tanks. All of these can have sufficient energy to ignite any surface froth of organic or organic sprays.

Energy levels in a static electricity spark discharge can range from 1 – 100mJ in comparison to a match which releases 10^6 mJ per second. These small sources are dangerous and important in areas where sensitive flammable mixtures are present.

In operating facilities with HDPE piping systems potentials on the lines have been measured at 680 – 1300 V and an electrostatic discharge is not likely.

Because of the low mobility of charge carriers in an insulator it is impossible to remove the charge by grounding. Spark discharges are possible inside plastic pipes in the presence of solvent and air.

Earthing for static electricity discharge is an important design consideration and adequate means of bonding and earthing of pipes and equipment is necessary to prevent any sparking which may result from static build up and accidental discharge in the presence of flammable mixtures of liquid or vapour.

Consideration should be given to painting FRP and HDPE pipes and vessels with conducting paint to dissipate any static which may collect on the outside of the pipes. Another alternative is to use the new carbon fibre based conductive FRP pipe systems. Much of this static and earthing problem disappears if designers would simply ensure all organic piping is metal. If, because of chlorides etc, this metal has to be rather exotic this decision should be seen in the light of the total project costs where the additional expenditure will be marginal and will probably be offset by lower insurance premiums.

5. REQUIREMENTS FOR SAFE DESIGN

5.1 WHAT NEEDS PROTECTION

In a typical metallurgical SX installation the following items need consideration in design to avoid fire initiation and provision of fire extinguishment equipment:

- Mixer settlers, after settlers, organic surge tanks, strong electrolyte tanks.
- Crud treatment equipment
- Diluent storage tanks
- Filter backwash tanks
- Coalescing devices on loaded organic
- Pipe trenches
- SX plant sumps
- Fire pump station

- Control room
- Substations and electrical rooms

5.2 MINIMIZATION OF FIRE RISK

The requirements for a safe design based on the above discussion can be summarized as follows. The flowsheet and operating parameters need to be chosen such that an acceptable compromise between maximum plant efficiency with minimum cost and safety of operation is reached. The operating temperature and diluent selected are important factors in this compromise. Note that additional capital investment in fire protection is often offset by lower operating cost in insurance premiums. (General compliance with standards such as NFPA 10, 11, 13, 15, 16, using equipment that is UL listed or FM approved with attention given to areas known to problematic for SX fire incidents should satisfy most insurance companies).

Sources of ignition, such as electrical equipment, static electricity discharge, lightning storms, operating and maintenance operations and personnel, (by way of smoking or welding etc.) must be controlled and allowed for in the design.

During design clear simplified layout drawings should be produced showing the classified areas with the demarcation points set to be physically recognized points for operator benefit.

Obviously the SX plant will be designated a ‘Non-smoking area’ and to ensure this rule is not broken inadvertently, suitable warning signs should be erected and a 15m free space allowed around the SX plant area enclosed by a perimeter fence.

Design and construction has to be thoroughly monitored to reduce to a minimum any requirement for construction modifications after start up or loading of organic.

The effect of upstream and downstream plant sections (e.g. electrowinning, CIX etc) on the SX plant must be considered and heat exchangers, coalescers, surge tanks etc provided as necessary.

5.3 REAGENT SELECTION

Normal diluents used in SX facilities are narrow band high flash point aliphatic kerosenes, with flash points at sea level above 75°C. They are classed as “Combustible” not “flammable” liquids and are inherently safe in most locations. Stories abound in the industry folklore of operators extinguishing cigarettes in settler organic for example. (Recent fire incidents suggest such tales are apocryphal!). This simplified view of the situation led many of us to conclude that the three requirements for ignition: fuel, oxygen and ignition source, could not be encountered in these plants and many are built with almost no fire detection or extinguishment provisions.

As we have seen earlier in the paper there is now a realization that poor design or operation can negate the advantages of these high flash point diluents but they still remain the principal protection against serious fire incidents.

It should be remembered that the mixture flash point when the extractant reagent and/or modifiers are added can be somewhat lower that the diluent flash point.

5.4 REDUCTION/ELIMINATION OF IGNITION SOURCES

The foregoing sections have indicated the origin of ignition and for electrostatic discharges, the topic is discussed in more detail below. Generally no mechanical equipment with motor drives should be located under or close to mixer settlers or organic surge tanks. Similarly no spillages should pass under the mixer settler units.

5.5 DESIGNING TO REDUCE ELECTROSTATIC RISK

Following from the earlier discussion we can recommend that the design to reduce the possibility of all the requirements for an electrostatic discharge generated fire occurring should consider the following:

- Ground all equipment items
- Ground isolated metal items such as valves
- For organic fluids use conductive pipe and ground it. (either metal or carbon impregnated conductive FRP)
- Provide grounding plates and grids in tanks with non-conductive surfaces and settlers.
- All pipelines running with chargeable organic liquids must run full to exclude the possibility of explosive mixtures occurring in the vapour space.
- All organic lines should operate at less than 1m/s flow velocity. This applies particularly for any partially full lines or lines discharging into tanks.
- Reduce the length of organic phase lines to the minimum especially those flowing under gravity.
- Check potential on non-metallic pipes periodically with non-contact electric field meters.
- Check liquid (especially organic) conductivity. Consider adding conductivity improvers to get conductivity over 500 pS/m.
- Lines discharging organic into tanks should have the discharge submerged and terminate in “tee” pieces or 45° cut ends.
- All plastic lined/plastic tanks should have a bottom aqueous layer and grounding plates. Conductive carbon impregnated FRP should be used for organic surge tanks and settlers if metal construction is considered too expensive.
- Operators should use anti-static footwear.
- Use conductive materials for walkways, handrails.
- Use intrinsically safe instruments.
- Organic mists must be prevented so avoid splashing.

5.6 MIXER SETTLER DESIGN AND PLANT LAYOUT

The plant layout and proximity of adjacent plots is important from the safety aspect and API RP500 “Classification of Areas” offers advice on this. Drainage and collection of accidental spillage to a sump located in a safe position and bunding of the SX area should be considered, particularly if the plant is to be built in an earthquake zone and damage can be expected.

If the plant uses settlers elevated on columns rather than placed on fill, the surface below the mixer settler tanks should be kept clear of all machinery. It should be finished with a surface impervious to kerosene and graded so that any spillage drains away from beneath it to an area where it can be disposed of without danger. It should be noted that in the Rossing fire, a temporary line leaked material to a sump outside the “classified” area, where a motor spark ignited it. The subsequent uncontrolled use of hose water to extinguish the fire floated the burning organic material back up beneath the FRP mixer settlers whose contents then boiled so spreading the conflagration.

The mixer settlers should be designed with a weir system and sufficient freeboard above the normal liquid level to ensure that in the event of abnormal conditions organic solution will not overflow the unit. Before the advent of AFFF foam systems when large volumes of water were needed, this was achieved by considering the hydraulic balance in the equipment, which required the added precaution of an overflow weir behind the aqueous weir which allows the aqueous phase to overflow preferentially before the organic phase reaches the top of the freeboard allowed. This consideration was of special importance when water sprays were used for settler firefighting in which case the water could be applied directly into the mixer settler without fear of spreading the fire by overflowing organic phase. In today’s plants, the blanketing effects of high expansion AFFF foams mean much smaller volumes of water are required and this overflow weir can usually be dispensed with.

Increased separation between mixer settler trains of around 35m is now being considered in the large multi train plants in design.

Some of the newer designs such as Tintaya and Spence locate a battery of reverse flow mixer settlers without roofs inside a building for each train, and in the case of Tintaya and several others in design space restrictions have indicated locating the SX mixer settler train inside a common building with the EW cells. The two areas are separated by a concrete fire wall with minimum 1 hour fire rating.

Some uranium plants have considered building fire walls of brick of concrete between the mixer settlers and between mixer settlers and organic surge tanks.

For the new multi train plants each train should have a liquid containment wall around the outside of the train. This should be of reinforced concrete more than 100 mm thick with a 2 hour fire ratting.

Pipe supports in steel within 5m of combustible material are recommended to have a concrete protective cover with 2 hour fire resistance.

Mixer settler designs which avoid pits (for mixers) are preferred with above grade construction for the mixer and settler either on columns or fill.

5.7 ELECTRICAL DESIGN

- Any cables running above ground to motors or control valves close to the mixer settler or organic surge tanks need a fire resistant cable coating or armouring.
- Where cables enter and leave control and switchgear rooms or underground conduit, fire resistant mortar should be used for grout.

- Cable trays should be preferentially run a safe distance from pipe bridges and trenches.
- On the loaded organic surge and diluent tanks, there should be FM listed electrically operated fire rated valves on the inlet and outlet steel flanges. These should fail safe closed if a maintenance signal from the fire detection system is lost.
- Electrical equipment must comply with recognized codes of safe practice. It is recommended that all are suitable for Class I Division I.
- Use flame proof/explosion proof motors, enclosures and light fittings in the mixer settler and organic tank areas. Strict application of the codes indicates that motors more than 1m from the combustible liquid can be simply TEFC but if there is a possibility of organic mists, exposed surfaces with foam and turbulence such a recommendation needs review and spark proof motors will be a safer choice.

5.8 INSTRUMENT DESIGN AND SELECTION

In a similar fashion to motors a case can be made for not selecting intrinsically safe instruments. However the same caveats apply.

Intrinsically safe design restricts the available energy in a flammable atmosphere to a level where ignition of the material is not possible. It is very suited for Division 1 hazardous areas. Because the available energy must be low it is limited to application to equipment requiring low levels of available energy and so it is well suited for instrumentation with circuits commonly running at 4-20mA at 24 Vdc.

Compared to explosion proof housings it has been estimated that if the probability of ignition from an explosion proof housing is 10^{-9} that for an intrinsically safe system will be 10^{-17}. However as there are no recorded events of an explosion proof housing leading to a fire incident the two systems can be considered equivalent. There are some interesting differentiations however in the effects of human operators – explosion proof housings may be dropped and damaged or badly replaced by maintenance crews. Intrinsically safe instruments and fittings avoid this as a hazardous situation cannot arise. Additionally intrinsically safe systems have lower installation cost as the wiring can be installed as per any normal location but explosion proof systems require conduit. Similarly intrinsically safe systems have low maintenance costs as shut off of the plant section is not required for adjustment or maintenance.

6 EXTINGUISHMENT OF A KEROSENE FIRE

6.1 DEVELOPMENT OF TECHNIQUES

The most straightforward approach to dealing with fires in these large surface areas to volume kerosene tanks has always appeared at first consideration to be by means of firefighting foam. As the tanks are almost always provided with some kind of roof, this would most conveniently be applied by means of fixed or semifixed systems.

Fire fighting with foams was first introduced in the 19 century to extinguish coal oil fires. Such early foams were “chemical foams” where a chemical reaction generated gas bubbles. In contrast modern "mechanical" or "air" foam introduce atmospheric air into a liquid mixture of water and a foam concentrate.

The foam is a blanketing and cooling agent which carries water to the fire and the fire is extinguished by:

- Smothering the fire by preventing air foam mixing with flammable vapour.
- Reducing the release of flammable vapour.
- Separating the burning material from the fuel source.
- Cooling the fuel.

Several types of foam are encountered in fire extinguishment operations.

- Protein
- Fluoroprotein
- Aqueous film forming foam (AFFF)
- High expansion foams
- Alcohol resistant foams.

Foams and Water

There are aspects other than those directly connected with firefighting which have had considerable bearing on the selection of fire extinguishment method, namely:

- Some solvents are adversely affected by many foams and would have to be replaced after contamination at the expense of working capital and loss of production. High protein foams with water were installed at several uranium plants. A 3% protein low expansion foam was used. Degradation of the materials was slow and charge lives of up to 20 years were experienced. Accidental discharges did occur and times as short as 15-20 seconds could produce stable emulsions. These would gradually dissipate and in general most of the organic was recovered after 2 days of settling. Following the discharge of foam the loading capacity of the organic phase fell by up to 50% for some hours.

- Foam possesses a minimum of the coolant properties which are most desirable when dealing with the higher flash point kerosenes. With high flash point hydrocarbons considerable heat intake is required before they can liberate sufficient vapour to support combustion, so that conversely, even after fire flame extinguishment, before complete extinguishment is achieved considerable cooling of the fuel is needed and foam does not perform well in this regard.

To counter these points various treatments including CO_2 application were considered.

Systems employing carbon dioxide flooding of the vapour space in the mixer-settlers, supported by external watersprays are used in solvent extraction plants in other industries, but have the disadvantages that there can be no guarantee that the roof will remain intact in the event of a fire, and that it is not considered a practical system for large mixer-settlers.

Currently there is new interest in gas extinguishment. Several companies are extending the area of use of halon replacement gases, known as "Clean Agent Fire Protection". This is the discharge of a blanketing compound as a gas into the space above the fire for a short period of around 10 seconds. The gas remains in the space for a long enough period to achieve fire extinguishment and prevent re-ignition. Such materials extinguish the fire but do not damage the organic phase, are safe for any personnel in the area and, as a gas, no clean up is required after the fire has been extinguished.

However similar caveats apply as to carbon dioxide regarding settler roof integrity as the gas needs to be released into a relatively closed environment. There are interesting possibilities and the systems may offer a cheaper alternative to foam based systems.

Direct injection water sprays however seemed good at extinguishment and were effective as cooling medium. These cooled the organic below its flash point and created an organic aqueous emulsion.

In the early days of solvent extraction, when organic compatible AFFF systems were not proven Aker Kvaerner came to the conclusion that the use of internal watersprays as a medium both for cooling and extinguishing provided a solution to the various problems and was applicable throughout the range of solvents in common use in the hydrometallurgical industries for conventional gravity mixer-settlers.

This system of direct spraying onto the liquid surface also incorporated overflow weir type settlers to prevent the fire water entering the settler from displacing organic phase out of the settler as the overflow weir ensured the preferential overflow of the aqueous phase. Typical application rates used were 0.6 m^3/m^2h. and could be varied in concentration throughout the settler.

At this time protein foam systems were considered as a last resort but the possible loss of the organic inventory through contamination would not be as disastrous as the loss of the plant and inventory through fire. Also the extracting agents would probably be thermally degraded in any case.

Investigations showed that fluoroprotein foams have almost no long term effect on the organic combustible phase and they would be an effective extinguishment medium in solvent extraction applications.

The fluorochemical surfactants in foams allow the water to float on the organic phase and are resistant to emulsion formation. This forms a cohesive layer which renews itself if broken by agitation. This property allowed the development of AFFF (Aqueous Film Forming Foam). Here there is a controlled drainage of solution from the foam blanket which forms a thin layer of aqueous under the foam blanket. This rapidly reduces the flames but is also one of the reasons why such foam blankets do not rapidly cool the fuel material.

High expansion foams such as Jet X provide capacity for total inundation of the fire. Such foam systems employ air aspirating devices to produce foam expansion of 100-1000:1. Consequently large volumes of foam can be produced using small volumes of water.

The commonly encountered foams in use with solvent extraction plants are "light water" AFFF high expansion foams such as FC600, Jet X, FC203 used in 3-6% concentration.

Most systems today in metallurgical solvent extraction are hybrids. Foam is the principal extinguishment medium over the mixer, settler, organic surge tank, sump surfaces with water sprays to cool the tanks and vessels externally and on their roofs and for the adjacent structures. Large volumes of water can also be supplied as water curtains between the trains to reduce radiated heat.

6.2 DESIGN OF THE FIRE EXTINGUISHMENT NETWORK

The aim of the firefighting system must be to extinguish any fire within about ten minutes and to ensure that the adjacent mixer-settler units are cooled sufficiently to prevent extension of the fire. If a fire with the kerosene type liquid is not extinguished in this period then it is most probable that serious and extensive fire damage will result putting the plant out of operation for a long period. The attainment of high temperatures during prolonged combustion will make the fire especially dangerous as the aqueous layer beneath the organic layer will boil and generate large quantities of steam which may eject burning organic droplets.

For preference the water supplies should be reserved for fire fighting purposes only and should be sufficient for at least 2 hours at full pumping capacity with automatic make up if required.

It is interesting to note that in some developed countries where fire brigade services are near to plants the requirements for the on site service may not be extinguishment but containment until the official service arrives.

The system involves a number of considerations, such as:

Water Reticulation System

The provision of adequate water supplies to all parts of the installation by a ring main system is essential. The system should be suitably sized for treating three mixer-settlers (ie one which is ignited and the two adjacent units) together with an allowance for use with manual and portable equipment possibly including additional foam producing facilities.

The piping should be of corrosion protected painted carbon steel or 316L stainless steel in severe corrosion areas such as around mixing boxes and discharge weir boxes. To avoid damage by maintenance vehicles, etc. or a fire incident the ring main pipe should be buried except in earthquake zones where it is best run on the surface. Generally pipe diameters greater than 200mm are used for the principal ring main pipe work. Gaskets must be of non-combustible material especially for any dry risers for piping in a possible fire zone.

The design of the system should include adequate drains for washing and resetting the system periodically and good access for fire fighting equipment. If the system is extensive it should be designed to allow sections to be isolated for maintenance without taking the whole system down.

Pumping

Unless the topography offers the chance of using an elevated tank to give assured gravity flow, the ring main will normally be fed by the emergency fire water pump system.

This will comprise an electric motor driven pump, a back up of a diesel driven pump with double battery banks for starting and a jockey pump to maintain the line pressure usually around 630 kPag. When operating the system pressure may rise to over 1000 kPag but it is worth noting that the jockey pump maintained pressure should not differ by more than 70-100 kPa from the fire pump discharge pressure to avoid water hammer problems on starting which could damage the system.

Each of the fire pumps should be able to deliver the full flow required at around 880 kPag (with pressures at spray heads of around 140 kPag). For each group of electrically driven fire pumps there should be a diesel standby capacity. There must be a standby bank of batteries for the start of the diesel pump. Its fuel tank is commonly sized at 5L/kW + 10%. (the use of an emergency generator on the electrically driven pump is an alternative but most insurance companies will not accept this option).

If there is positive feed from the fire water tank the pumps should be horizontal centrifugal but if pumping from a river or lake as the fire water reservoir a vertical centrifugal design is recommended.

All cabling up to the fire water pumps must be in fire protected cables. The pumps should be housed in a non-combustible building with its own sprinkler supply. Preferably the pump station must be at least 25m from the nearest tank with combustible fluids.

Opinions differ on the rating for the flow capacity of the water pumps but generally this flow is arrived at by the total of:

- Need foam on burning mixer settler and the mixer settlers on each side
- Need foam on walkways each side of the burning settler.
- Need water sprays on roof and side walls of burning settler and units on each side.
- Need water and foam for two monitor units.

Foam Supply

Foam systems are designed to NFPA 11 and 16.

The mixer settler units, loaded organic surge, diluent storage and prefiltration electrolyte tanks are foam protected internally. A bladder tank supplies the foam concentrate water mixture to foam chambers (usually 2) discharging at around 850 k Pag into the settler sides above the organic phase level. Rapid high volume discharge occurs from these chambers and deflector plates push the foam blanket down and over the organic phase surface.

The bladder tank can be a dedicated unit for each mixer settler or organic surge tank. This is usually much cheaper (around 30%) than a central bladder tank and water sprays. All foam chambers are to be made from corrosion resistant materials such as 316L stainless steel and for security should be at least 15m from any organic containing unit. The strictest standards call for standby bladder tanks.

As an alternative to bladder tanks a balanced pressure proportioning system is available using a foam concentrate injection pump with a foam concentrate storage tank at atmospheric pressure. The foam concentrate is pumped directly to the proportioning positive displacement pumps. This would overcome the slight disadvantage of bladder tanks in that they must be taken off line for refilling.

Foam should be applied by this flooding system to settlers and organic storage/surge tankage but by sprays above mixing boxes, walkways, pipe trenches and so on.

Subsurface injection of foam is not usually recommendable as this destroys the foam as it picks up hydrocarbon contamination as it passes through the “fuel” layer.

Typical application rates from the foam chambers are 0.4m^3/m^2h of surface to be blanketed in the mixer settlers and 0.25m^3/m^2h of the surface to be blanketed in the surge tankage. This would apply to individual roofed settlers or the new designs with each train inside a building and typical minimum application times as set by NFPA for the foam would be 10 – 15 minutes for mixer settlers and 30 minutes for tanks. (note that Factory Mutual and other insurers normally want to increase this to 2 hours). Foam sprays could provide 0.4 m^3/m^2 h for the organic surface.

Deluge Curtains and Sprays

More attention in being given in current designs to the use of deluge water curtains at least between trains in multi-train plants and even between mixer settler units. These significantly increase the water flow requirement in the fire water pipeline system but reduce the amount of radiant heat around any fire.

The curtain sprinkler heads should be approx. 2m above the normal level of organic liquid in the tank being protected. Each mixer settler could have an independent system which operates separately from the foam system. Details can be found in NFPA 13 and 15.

The water deluge rate is commonly set at 0.6 m^3/m^2h with provisions for a 2 hours supply. Sprinklers can be rated at 0.6 – 1m^3/m^2h.

Monitors and Hydrants

Monitor units can be employed to protect open areas, emergency tanks and ponds, sumps, pipe trenches, organic pumps which may be outside the overall foam blanketing areas. They can be combined with hydrants to connect fire hoses.

They should be on two systems so they can supply foam or water by connection to the fire water loop feeding the dry riser system. Rates commonly used are 0.4m^3/m^2h of the area to be covered. The spacing between monitor units is commonly 80-120m and they can be remote controlled oscillating units. Flow per monitor of water is typically 60m^3/h.

Detection and Initiation

The settlers, if roofed, need to be provided with fire detection equipment inside the vapour space. This can be infrared flame detector based or thermal rate compensated/fixed temperature sensors. The detectors of the thermostatic heat type activate an alarm system when the set points of temperature and/or rate of temperature rise are exceeded and annunciate the area of incidence to the control room. The firefighting system, consisting of

AFFF or water sprays inside the settler for both extinguishment and cooling, may be started automatically or manually from the control room and the valves in the spray headers actuated. At the same time the circulating pumps and pump mixers will be stopped and isolating valves on process lines shut.

Automatic initiation alone of these systems is problematical. It may not be desirable as the system may be rendered inoperative and it is difficult to test. It may be better to send detector information and alarms to the control room where there would be remote initiation switches. It is desirable to provide manual actuation additionally for any automatic system.

The system should start only after 2 sensors in the particular equipment item or area are triggered. A delay period of up to 45 seconds could be introduced from detection signal being received to system initiation to allow possible override from the control room.

This type of system is fitted in all mixer settlers, loaded organic tank, diluent storage tank, pre-filtration strong electrolyte tank and the SX plant pumps.

Closed head systems are preferred by most insurers rather than open head deluge systems. With the closed head system the application rate can be calculated to handle just one mixer settler at a time as the sprays, flooding system cannot be initiated by horizontal heat transfer from the mixer settler that is on fire to the next. A simple closed head system uses a wet riser pipe arrangement where the entire system is charged with water and initiation occurs by the melting of the fusible link in the spray head. Foam injection can be incorporated for each individual mixer settler.

However if winter temperature can cause freezing a closed head dry riser pipe system is used. The loop is buried and charged with water but the above surface distribution system is dry. In the event of a fire being detected the valves supplying water to the distribution piping spray heads and foam chambers are opened but with the final release of the water/foam mixture into the area of the fire detection still dependent on the melting of the fusible link in the spray heads in the fire area.

For the settlers, organic surge tank, after settler, pre-filter tankage the spray heads are based on a lead coated quartzoid glass feasible link. For the areas above the mixer boxes and organic weirbox the heads are of 316L stainless steel.

7 DESCRIPTION OF OPERATING PLANT FIRE PRECAUTIONS

7.1 OPERATING & MAINTENANCE HAZARDS

The probability of fire in a hydrometallurgical solvent extraction plant is low because the flash points of the kerosene used are generally high and the chance of ignition is low

The normal process hazard is low because the operating temperature is below the flash points. However, hot spots may be produced by solar radiation. Possible sources of ignition are sustained organic phase leakage into motor enclosures and motor or gearbox fires close to organic lines or tanks and now especially static electrical discharge into flammable air organic vapour filled spaces. Other hazards are lightning strikes and maintenance, particularly if welding is required on organic tanks or lines. The firefighting crew must be put on full alert during plant maintenance. Several small fire incidents have occurred due to rather foolhardy welding activities on operating plants. All work inside the SX plant area should require permits and entry into this area should be controlled.

Plants must maintain the highest standards of housekeeping and all ignitable waste materials and spillage clean up must be removed from the area.

In the words of an authority from the seventies and eighties "the more I learn of incidents in these plants the more I get the impression that their maintenance staff are determined to destroy them".

7.2 URANIUM PLANTS

In these plants a typical organic extractant used is 5% v/v Alamine 336, 4% nonanol, 91% v/v kerosene diluent with a flash point of 50°C. Fire detection consists of temperature sensors in the vapour space above the liquid level near the weir box inspection hatches. These give an alarm for high temperature or fast rate of temperature rise conditions and the solvent plant is shut down manually and the firefighting is by means of water sprays inside the settlers, hand fire extinguishers, and as a back-up, mobile trolley unit with foam generators and monitor capable of producing a jet or spray.

However, there were uranium plants in South Africa and Namibia which were potentially more hazardous. The tertiary amine extractant used illuminating paraffin due to lack of high flash point diluents. This has a flash point of 43°C minimum by the standard method but a flash point on site of approximately 38°C since most of these plants are built on the Transvaal Plateau at about 1500m above sea level. One plant contains mixer-settlers inside a building which is not well ventilated and another has minimal free space around the SX plant with the control room approximately 3m from the nearest mixer-settler. A number of these plants employ CO_2 for fire extinguishment. As explained earlier the Rossing fire was largely a result of these types of conditions.

7.3 COPPER PLANTS

Organic diluents in these facilities usually have a flash point of 75-80° C. The fire protection system usually consists of thermostatic detectors which automatically start a foam or water spray system inside and outside the mixer-settlers.

The high flash point of the diluent and low likelihood of fire have led many plant operators and designers to feel that no fire protection is necessary and they may think any reductions in their insurance premiums are not worth the cost. However the origin of recent major fire disasters, stemming not from direct ignition of the organic liquor but rather static discharge and ignition of organic vapour air mixtures, may be changing this opinion.

8. SOME FIRE INCIDENTS

Kristiansand, 4 May 1972

This fire incident totally destroyed the solvent extraction cobalt refinery at Falconbridge Nikkelverk in Kristiansand Norway.

In the process nickel cobalt hydroxides are dissolved in hydrochloric acid and cobalt is extracted by solvent extraction. Salient points about the operation were

- Diluent had a closed cup flash point of 42°C
- Plant was fabricated from rubber lined equipment for aqueous service and a reinforced phenol formaldehyde resin for the solvent extraction equipment with glass piping.
- Mixer settlers and tanks were on several levels interconnected by the glass pipe with the whole plant located inside a building.

The plant was starting up after a shutdown and organic had been drained down into a lower surge tank. Some had overflowed into a sump so a layer of organic was floating on the surface of the aqueous in the sump. A welding project nearby started a small fire and a burning rag fell into the sump. This acted as a wick and increased the local temperature of the diluent to above the flash point. The film of organic caught fire and burnt one of the timber structural members; this burst one of the overhead glass pipelines.

Fire fighting using large volumes of hose water spread the burning organic over a large area. The fire burned until all the organic fuel material was gone.

The rebuilt plant separated the SX mixer settler and tank area and a new drainage system allowed all the tank contents to be drained outside the building to a large concrete sump tank with an organic trap overflow. Mixer settlers were changed to FRP lined steel and the piping system to glass lined steel.

A complete sprinkler system was fitted over the mixer settlers and tanks rated at 12.5 L/min m^2.

Codelco Chuquicamata 1gpm Pilot Plant

This fire destroyed the small pilot plant copper SX unit at Chuquicamata. It originated from a domestic room heater used to heat a room adjacent to the plant where some organic samples were stored. The mixer settler units were located close to this room and the fire spread directly.

Anamax Arizona 1972

This was a fire in the organic entrainment in a raffinate tank, all the organic burnt and the fire was extinguished when all this fuel was gone.

Anamax Arizona September 1975

This fire occurred during maintenance operations to weld a patch on a mixer box (while it was in operation!). The fire system activated but no sprays were fitted over the mixer box and extinguishment occurred by back flow of the water from the settler. The incident lasted less than ten minutes.

SQM María Elena 1980

Iodine is produced by Soquimich (SQM) in Chile by true solvent extraction into kerosene. Their plant at María Elena between Antofagasta and Tocopilla is a three stage counter current extraction plant using FRP mixer settlers. This was destroyed by fire. This fire originated from maintenance welding on the mixer settler support structure when some weld splatter fell on organic oozing out of a crack in a FRP mixer box. Note that at that time these plants used lighting kerosene with a flash point around 40°C. This low flash point was further aggravated by being used at 1000 m altitude.

A similar incident occurred at the SQM Pedro de Valdivia unit.

Rossing Namibia

This fire completely destroyed the solvent extraction section of the Rossing Uranium Limited plant in Namibia.

Here a temporary line carrying organic dripped organic which ran into a sump outside the classified area. The motor on the sump pump sparked and the fire which started was fought with hoses. The flow of water pushed the burning material back up the drainage gutters to under the mixer settlers. The aqueous in the mixer settlers boiled, overflowing the mixer settlers causing the conflagration.

All the mixer settlers were destroyed but the fire protection water spray system protected most of the tanks. However tanks which had accumulated entrainment organic were not adequately protected and were destroyed.

The rebuilt plant featured

- All sumps overflowed to an earthen berm well outside the plant area.
- The plant sump was sized at 1.25 times the volumes of the settlers and mixer boxes.
- All mixer settlers and sump were provided with foam protection.
- Foam system was automated with manual override in the control room.
- A water spray system was provided to cover the outside of the mixer settlers and roofs, settler support structure, cable trays. This also had automated starting with manual override.
- Organic surge tanks were fitted with fail closed on power failure or fuseable link fire stop valves.
- Any pipelines under settlers were 316L stainless steel.

As explained previously a principal contributor to this fire was the use of low flash point diluent.

Olympic Dam, 23 December 1999

This fire at Western Mining Corporation, Olympic Dam is reported to have started in a sump near the loaded organic tank. An overheated pump caused the organic in the sump to burn. This then caught the overhead HDPE piping and HDPE lined tanks.

The fire was extinguished when all the fuel was gone.

Olympic Dam, 21 October 2001

The official reports on this fire conclude that static discharge was the cause of this fire that destroyed a copper solvent extraction plant train at the Western Mining Corporation, Olympic Dam facility.

The fire started internally in a gravity fed HDPE pipe in a piperack above the loaded organic tank. All the organic in the tank burnt plus the surrounding tanks and pumps, the overflow pond and all the piping in the piperack.

The reports conclude the following:

- A sensitive flammable atmosphere resulted from kerosene froth and surface foam or with droplets and air in a partially filled pipe.
- The pipe was partially filled as it was a line combining two gravity flows one from each train and one train was shut down. Thus the long line was operating under launder conditions with 25-50% of pipe section as vapour space.
- Intermittent high temperatures from the desert location around and within the black-plastic pipe made the internal atmosphere more sensitive to ignition and heated the organic.
- Too high velocity flow (up to 8 m/s) and the long pipe run with turbulence from bends and grounding rings caused high levels of charge to build up inside the plastic pipe. These may have been up to 20 kV.
- Cable trays were located above the pipe runs.
- There were grounding rings every 4m between flanges. Crud or jarosite build up in the circulating organic covered the grounding rings protruding into the flow and insulated them. But with the line flowing as a launder the ring above the organic level remained as conductive metal. Thus these were converted into fire contributors by:
  - not grounding the charge in the organic,
  - possibly acting as wicks drawing the organic from the bulk flow,
  - providing in the space above the organic a metal section that collected the spark that went from the organic surface
  - simply caused turbulence which generated more static charge.
- Turbulent flows entering and within the pipe caused organic misting and splashing.
- Air inlets which helped to form the sensitive atmosphere were two breather pipes which were intended to allow air to escape when the pipe was full.
- The fire fighting deluge system would not start properly as the electric pump kept tripping out.
- None of the foam or deluge systems was activated by the fire.
- The plant was located in a single large bund and this contributed to the fire spreading as there was no organic stopping overflow system. Compartmenting of the bund was recommended.
- The fixed monitor throws fell short of the fire and their jets were affected by strong winds.
- A locked gate in the SX plant fence prevented easy access of fire fighting equipment.

Metcalf 2003

The official investigation into the fire at the Morenci property of Phelps Dodge Corporation has not been released. There are several rumoured causes.

One is that the fire started in a pipe trench near a hydraulic pump system for a hydraulically actuated valve. This was in a line carrying organic mixed with crud from the settlers to the crud treatment plant. The fire spread from the trench to the adjacent settler and from there to the other two mixer settlers in the train. The two other trains were not affected. They were located some 20m away. The fire burnt until the organic was exhausted.

Another story is that a piece of rotating equipment overheated and burnt an organic line starting the fire.
There are also reports that when the plant was shut down because of the fire there was air trapped inside an organic line which blew back and ejected organic outside of that settler and this spread the fire.

Mariquita 2004

This recent fire occurred at the Mariquita property of Minera María operated by FRISCO and destroyed the solvent extraction plant. It started from an electrical short in piping near a holding tank and the fire spread back along HDPE piping to the mixer settler and surge tankage. All the tanks, pumps and mixer settlers were destroyed except for tanks in stainless steel.

9. CONCLUSION

The risk of fire in these hydrometallurgical solvent extraction plants employing high flash point kerosene as the diluent for the extractant is low, but nevertheless precautions must be taken. The designer and owner must be aware of the flammability/combustibility of the materials involved, how poor operation and/or design can create hazardous situations and the practice in other industries such as petrochemicals where fire has always been a strong factor in design.

Operating plants employ various fire protection systems depending on the opinions of the operator, local regulations and the demands of the company's insurance assessors. Knowledge of fundamental good design in diluent selection and use, piping materials, electrostatic hazards and configuration will help to avoid a fire starting which of course must be supplemented by the best economic scheme possible to put it out.

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TRADITIONAL FIRE SYSTEMS FOR EXTREME FIRE HAZARDS

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ABSTRACT

A paper outlining a process to provide effective fire solutions to critical hazards, such as solvent extraction plant, using the techniques of risk assessment, hazard analysis and fire modelling to better understand the role, selection and design of automatic fire systems.

1. INTRODUCTION

For a fire solution to be effective in combating an extreme fire hazard, understanding the physical and chemical processes employed by the fire extinguishing system is essential; however so is an appreciation of the nature of the fire hazard, the fuels involved, the production process and construction materials. Combining risk analysis processes with fire system application and design can be the means to provide an effective fire solution.

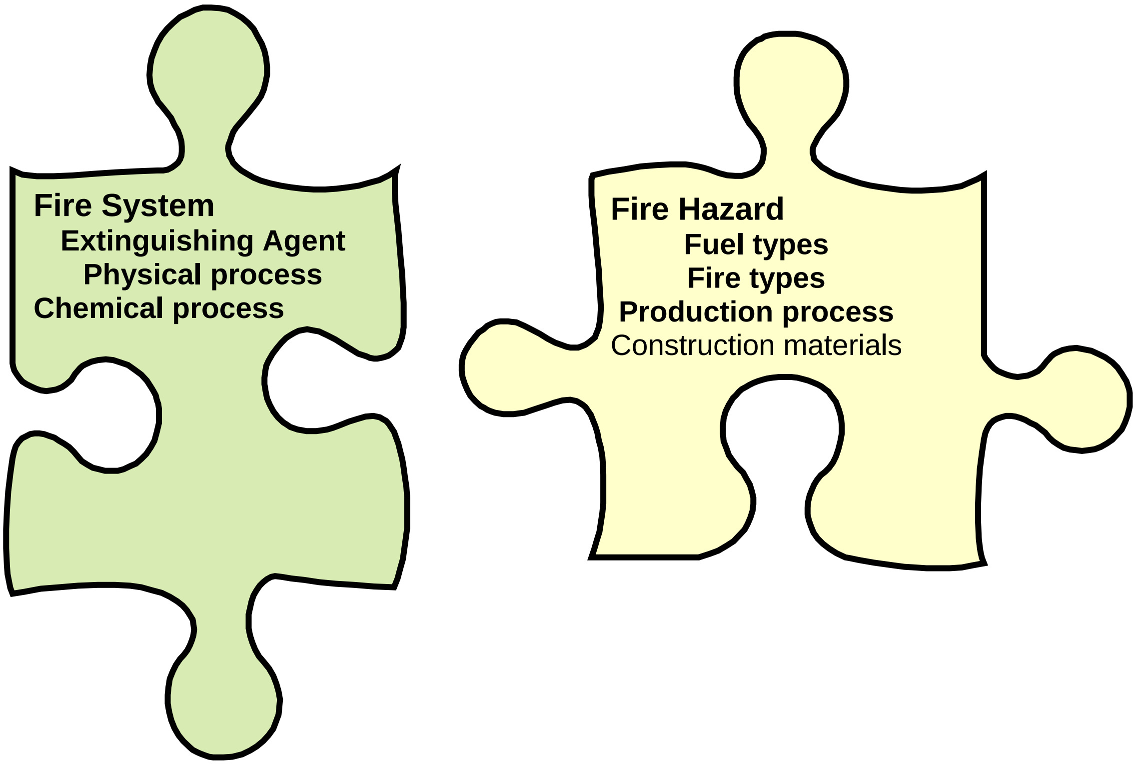

Figure 1

Fire protection engineering is a fairly obscure part of the engineering industry, combining elements of fire science, fluid dynamics and chemical processes of our extinguishing agents, with mechanical engineering. We are “systems people” who provide automatic fire protection that doesn’t require manual intervention to achieve its goal, and at the same time assist expert fire teams to fully extinguish the fire.

Successful operation of plant and equipment is proven during the commissioning process; however while fire systems are commissioned, they are only proven when a fire occurs. Traditional fire systems (such as automatic sprinklers and water spray) have a broad scope of application, have been proven through the test of time, many over 50 years, and are tolerant in their application design; however when protection involves extreme fire hazards there is little room for error. Some systems just aren’t suitable while many new systems have, in practice (such as water mist), a narrow band of application with critical design limitations that must be observed.

In our field, experience helps but the necessary expertise comes from understanding the fire hazard and the extinguishing process involved in the fire system.

2. RISK ASSESSMENT & HAZARD ANALYSIS

It is vital that the fire protection engineer focus on risk, i.e. the likelihood and consequences of an event, to arrive at a value for money fire solution. The risk analysis process also requires the potential fire hazards be identified and understood before considering any strategy to mitigate the risk the hazards may present. Removing or reducing the fire hazard's critical elements such as fuel load or likely ignition sources is often not possible. In other words the hazardous process remains, the fire system's task is therefore to reduce the risk of the hazard to an acceptable level.

2.1. HAZARD ANALYSIS

So what are the elements of a fire hazard are important to the fire protection risk analysis process? Most would expect we would include:-

a) FUEL: fire class A, B, E, D, oxidizing etc, quantity, fire load per m^2, storage method, ease (energy) of ignition, volatility, auto-ignition, flash point, boiling point, polar or non-polar, rate of combustion, heat release rate, smoke and toxic emissions, environmental impact.

b) FIRE: pool fire, spray fire (atomised), 3D cascading fire, gas cloud or vapour, flame spread, shielded, high piled storage, open or confined.

These are some of the key elements for extinguishing agent selection, ie water, foam, powder, aerosol, gaseous agent etc. Equally import though is an understanding the indirect elements contributing to the fire hazard:-

a) PRODUCTION PROCESS: enclosed, indoors, outdoors, communicating, fixed, moving, energy input - heated, pressurised, electrical or static, climatic or environmental conditions, operator error, automatic or manual shut-downs

b) CONSTRUCTION METHODS & MATERIALS: combustibility, impact on fire load, strength during fire, separation and boundaries, drainage and bunding, fire fighting access, lightning.

These are some of the key for fire system selection when combined with the FIRE and FUEL elements of a fire hazard.

2.2. FIRE MODELLING

Establishing the above key elements is sometimes quite a task however understanding their simultaneous impact is yet another and although, as I said before, experience helps, one way to better understand the dynamics of a fire is fire modelling.

Although we are a long way from modelling the performance of water spray patterns and densities against practical design fires, there are however two very important tasks fire modelling can achieve.

2.2.1. Sprinkler Response Times

The first is the ability to evaluate sprinkler and fire detector fire response times to the internationally standardised parameters of response time index (RTI) and C factor. In fact NFPA 13 now provides guidance for modeling sprinkler response times, where concealed sprinklers can be considered equivalent to pendent sprinklers (having similar thermal response sensitivity) installed 300 mm below smooth unobstructed ceilings.

Software models such as LAVENT model sprinklers in compartment fires including the effects of ceiling jet and upper layer of hot gases. Inputs are compartment and sprinkler geometry, ceiling properties, fire elevation, time history of fire heat release rate, area of fire, ambient temp, RTI, and activation temperature. Outputs are ceiling gas and device temperatures over time and time to activation.

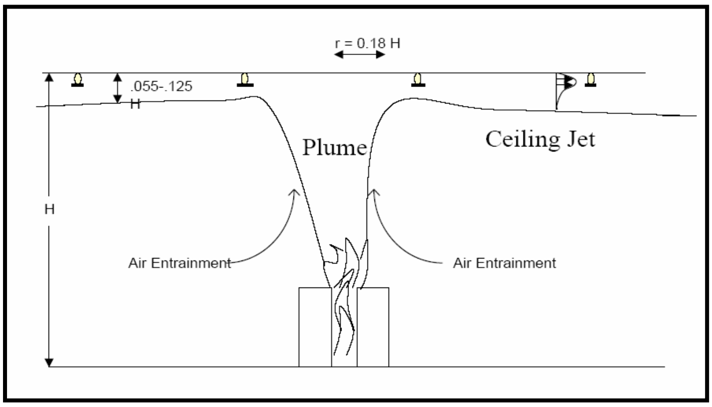

Figure 2 - Lavent Fire Model

2.2.2. Radiant Heat

The second task is the ability to predict radiant heat transfer between flames and nearby solid surfaces, as well as evaluate the effects of a steady film of water provided by water spray system cooling the solid surfaces.

Software models such as the Fire Dynamics Simulator (FDS), developed by NIST, is a large eddy simulation type, computational fluid dynamics (CFD) model. The software solves numerically a form of Navier-Stokes equations appropriate for low-speed, thermally-driven fluid flow with an emphasis on smoke and heat transport from fires.

An example of the use of these fire-engineering tools is provided below where, after determining a ‘worst credible’ fire scenario and the resultant ‘design fire’, the effectiveness of one fire protection solution in preventing fire spread to adjacent process trains at a set distance away, was compared to having no fire protection. The design fire assumed a complete process train of a solvent-extraction (S-X) plant to be fully involved in the fire.

Burning of the organic/diluent is based on the properties of kerosene with a heat of combustion of 40.0MJ/kg at 0.8 kg/litre and a burning rate of 5mm/min. Using a bunded fire area of the process train of approx 5,000 m^3, the heat generated from the organic solvent fire was estimated to be a massive 13,400 MW.

The following table of heat radiation will assist in assessing the fire modelling results.

Radiant Heat Flux kW/m^2	Intensity Effect	Guideline
0.8 – 1.2	Approx. summer noon sun	No protection required
1.6	Level pain can be felt	Maximum for residential areas
5.0		Brief exposure if protected by water spray
5.0 – 8.0	Will cause pain in 20 secs	
12.5		UK limit for building separation distance
20.0 – 25.0	Uninsulated steel thermal stress can cause failure	Suggested maximum process separation when protected with water spray
75.0	Fatal in 5 second exposure	

Table 1 - Heat Radiation Effects and Guidelines

The FDS fire modelling output values of the incident heat flux received and the radiant heat temperatures of the exposed surfaces are given below for both the proposed fire protection solution and without fire protection.

Model Feature	Heat Flux Range (kW/m^2)	Wall Temperature Range (°C)	Roof Temperature Range (°C)
Train C	35 – 55	180 – 430	200 – 350
Train A	10 – 15	Ambient – 75	Ambient – 75
Mixer Tanks	0 – 3	Ambient (Protected by fire Wall and Sprinklers)	n/a

Table 2 - Proposed Fire Protection Solution

Model Feature	Heat Flux Range (kW/m^2)	Wall Temperature Range (°C)	Roof Temperature Range (°C)
Train C	30 – 40	200 – 300	100 – 225
Train A	20 – 30	160 – 250	100 – 250
Mixer Tanks	20 – 30	220 – 230	n/a

Table 3 – Without Fire Protection

These results have also been represented pictorially in 3D colour image.

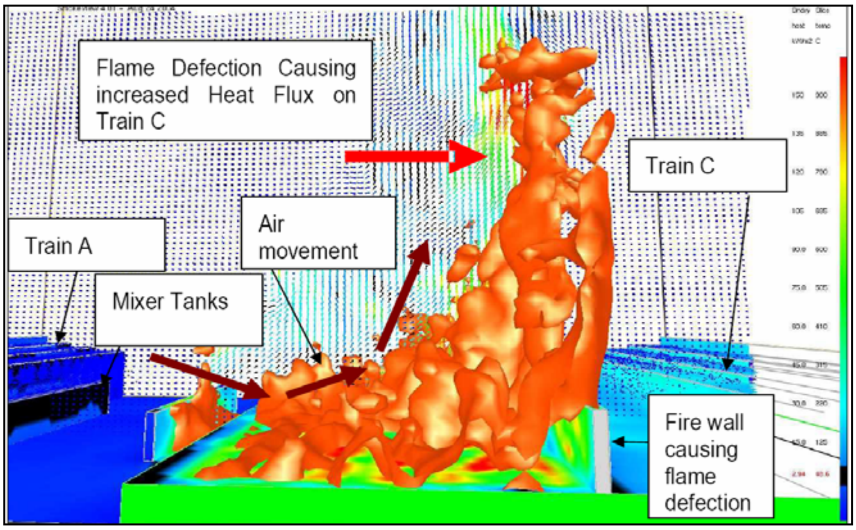

Figure 3 - Proposed Fire Protection Solution

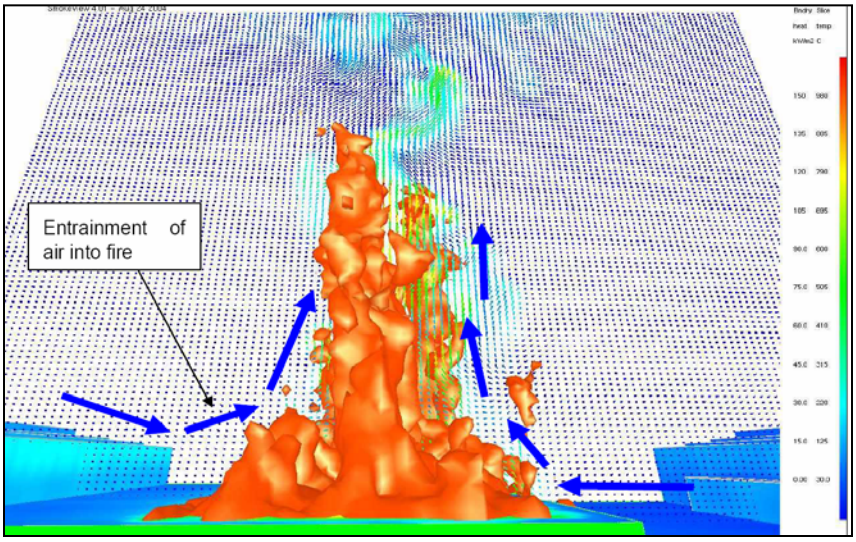

Figure 4 – Without Fire Protection

Comparing the results in Tables 2 & 3 on the previous page, it can be seen that the radiant heat flux ranges for Train A and the Mixer tanks were significantly reduced by the proposed fire solution to 3.0 kW/m^2 and 15 kW/m^2 respectively. Both of these results can be considered acceptable when referencing Table 1 Heat Radiation Effects and Guidelines. However note that the radiant heat for Train C increased rather than reduced. The modelling predicted that the proposed fire wall would cause a deflection of the flames towards Train C due to blocking of entrained air into the fire. A valuable inside into the fire's burning characteristics which was able to demonstrate the ineffectiveness of the proposal.

2.3. STATISTICS

Statistics relevant to a specific process are sometimes difficult to obtain; however once the key elements of the fire hazard are understood, the statistics can be found relevant to a number of different processes. For example there is a surprising similarity between Class Society statistics for marine machinery space fires and our own Wormald statics for mining equipment machinery space fires.

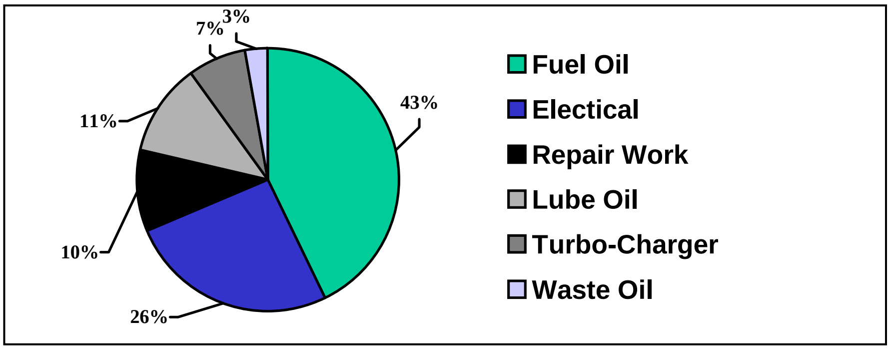

Figure 5 - Japanese Class NK Engine Room Fire Statistics 1980 – 1992

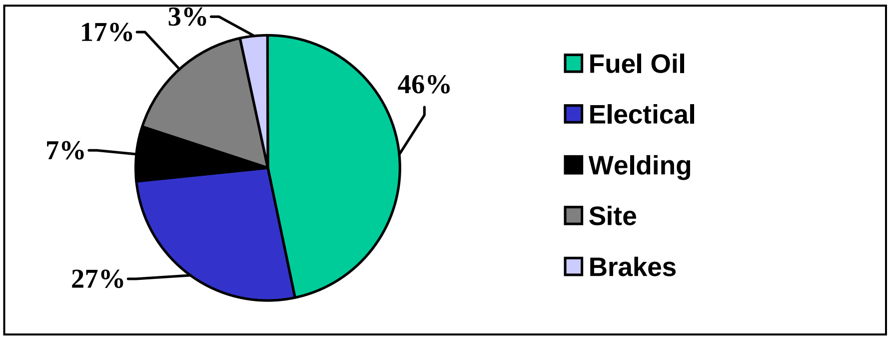

Figure 6 - Wormald Mining Equipment Fire Statistics 2003

3. EFFECTIVE FIRE SOLUTIONS

Having identified the critical elements of fire hazard, the processes of developing an effective fire solution can begin; however there are one or two prerequisites to ensure the outcome is both cost effective and practical.

3.1. ELIMINATE THE CAUSE

The first of these is to evaluate the possibility of eliminating the cause and the familiar fire triangle of HEAT – FUEL – OXYGEN still provides the best starting point. Examining the options available to change the design or other aspects of the production process to remove one of these elements can quickly provide an understanding of what is practical and cost effective.

Eliminating the hazard is the most positive approach; for example, a change in the material of construction might cost more but reduce the fuel load and allow higher levels of heat to be tolerated. Alternatively, modifying process procedures also helps to reduce the possibility of an event occurring but provides a less positive solution, as safe work procedures can always be ignored. For example reducing the speed of the process might help reduce energy input, such as static electricity, but later on the finer points of fire protection design might be lost production objectives.

3.2. CONTAINING THE LOSSES

The second is to isolate the hazard. Whatever the outcome of the above hazard reduction process is, isolating the hazard allows the extent of any further fire protection to be determined, and when isolation becomes more and more difficult then the scope of other measures will increase. The goal of hazard isolation is to reduce fire exposure to neighbouring plant and limit fire spread. It is best provided by passive means such as fire resistant barriers and construction, radiant heat separation distances, and boundaries such as bunding and drainage etc. Alternatively, fire systems can also provide exposure protection when passive means are not feasible; however limits apply.

3.3. PROTECTION IN DEPTH

From the fire engineer’s ‘side of the fence’ we are often asked to respond to comments like:-

a) My process doesn’t need a fire system – This is a case for RISK assessment.

b) The system is too expensive – This is a case of RISK vs COST of reduction.

c) They are unreliable and make a mess – This is a case for system SUITABILITY

System suitability introduces a number of issues all of which impact on the **goal** of the fire system. Is the goal occupant safety where safe evacuation is the key concern, such as in the building code of Australia, or is property protection also of concern with the aim of reducing building and infrastructure fire losses? Critical facilities, in addition, often consider the time element, as fire losses due to business interruption can easily outweigh property losses. Extreme fire hazards just raise the stakes to be able to achieve the fire system's goal, particularly for fire a solution providing protection against business interruption.

Protection in depth is the key strategy for providing protection against business interruption. The greater level of risk reduction the more layers of defence are required. Importantly though the performance of the whole should be greater than the sum of the individual parts:-

a) FIRE ISOLATION - fire rated construction (FRL), fire stopping, separation distance, bunding, drainage, fuel dumping, ie limiting the extent of the fire hazard.

b) PROTECTION – exposure protection, fire control, suppression or extinguishment.

c) DETECTION – early warning detection, manual alarms, process monitoring, interface shut-downs, direct brigade alarm, ie fire growth vs response time.

d) BRIGADE APPLIANCES – remote controlled, isolating and manual fire monitors, fire hydrants, reliable water supply, fire hose suction and booster points.

e) FIRST AID – fire extinguishers and hose reels.

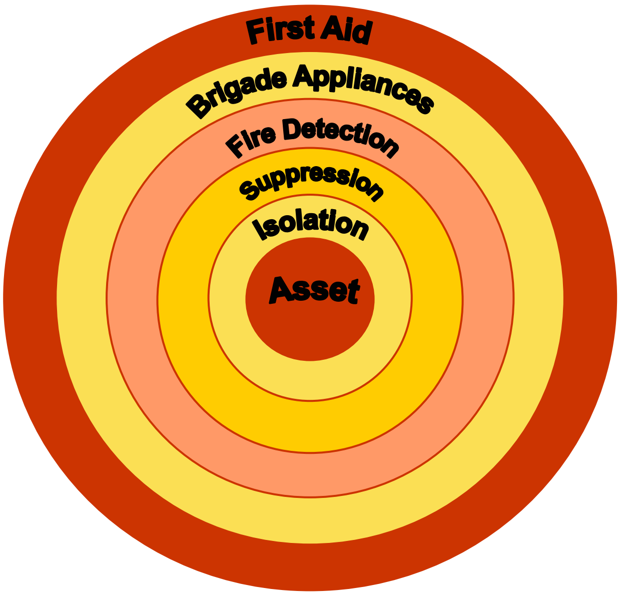

Figure 7 - Protection in Depth

3.4. RELIABILITY, REDUNDANCY AND MAINTENANCE

The reliability of each these measures is as important as their intended effectiveness ie, where a particular layer is critical to the fire protection goal then its reliability is also critical.

A system will be vulnerable to failure if intricate system components require high levels of maintenance that might be inconsistent with the production priorities of the manufacturing plant or its environment. For example Factory Mutual have recorded the reliability of high pressure gaseous agent systems, that strive to fully extinguish a fire, at less than 70%, while automatic sprinkler systems, which are only designed to control a fire, have a much higher reliability record in Australia of over 100 years at 99.5%, Therefore a fire system with a lower level of fire performance might be considered more suitable, due to its higher level of reliability and lower, more acceptable, maintenance requirements

Secondly, to balance the reliance on each layer of protection, the level of redundancy of the fire measure within each layer should be considered, ie the provision of duplicate water supplies are a requirement for high hazard sprinkler systems. Alternatively, were one layer of protection to fail then the protection in depth model could be designed with sufficient redundancy to be able to cope with this and still achieve its goal. Therefore the impact each layer of protection has on the other is import if only to ensure the whole is greater than the sum of the individual parts.

Minimising fire system false alarms or accidental activation is a major factor in judging the suitability of a system for a particular application; however system maintenance is also fundamental to the decision as reliability is often improved by providing more sustained levels of system maintenance. On the other hand, if the impact of the false alarm or activation is not severe, the benefits of a more sophisticated, higher performance, system may be worthwhile, eg a gaseous agent system for a process control room business interruption protection while retaining the property protection with automatic sprinklers.

4. FIRE SYSTEM APPLICATION (SUITABILITY)

Weighing up the key elements from the fire hazard analysis, with the extent of protection and risk mitigation required, as well as the preferred fire protection goals, can seem impenetrable; however the task is greatly assisted by the use of fire protection codes and standards.

4.1. SYSTEM STANDARDS AND CODES OF PRACTICE

Fire system selection is really a process of weighing up the strengths and weaknesses each fire system against the key elements of the fire hazard, and fire standards provide information regarding the ire hazard and help identify system selection options.

NFPA codes of practice and FM Global data sheets provide advice on fire protection solutions for particular applications, and once the mix of fire systems and other protection elements have been decided, Australian, ISO and NFPA system standards provide guidance and minimum requirements for the design and installation of each type of system.

Extreme fire hazards are seen to exist where industrial processes or products have a high likelihood of fire with a high fuel load of fast burning, high heat output fuel, and are typically found in industries such mining, oil & gas, power generation and the like. Extreme hazards include steam and gas turbines, flammable liquid storage facilities, fuel transfer & loading operations, industrial machinery & processes using flammable product, flammable liquid stores etc.

Fortunately the insurance and fire industries have been providing advice for hazardous processes, and SX plants are no exception. Relevant publications include AS1940 storage and Handling of flammable and combustible liquids, FM 7-30N (NFPA36) solvent extraction plants, FM 7-32 flammable liquid operations, FM 7-83 drainage systems for flammable liquids.

4.2. FIRE PROTECTION SYSTEMS

Understanding the physical and chemical processes employed by the various fire protection systems, as well as having an appreciation of each system's strengths and weaknesses, is the means to enable the most appropriate system to be matched against the critical elements of fire hazard.

4.2.1. Water Spray systems

Water spray systems are used to provide protection to fire hazards that cannot be effectively protected by standard sprinklers. The performance objectives that can be achieved with water spray systems are dependant (amongst other things) on the flash point and viscosity of the fuel, and include fire extinguishment, fire suppression or fire control. Exposure protection from radiant heat of adjacent fire is also a key objective of water spray.

The protection mechanisms of water spray are:-

a) Emulsification: by direct impingement spray emulsifying the surface oil to form a smothering blanket.

b) Cooling: by heat extraction of the flame, the pyrolysis gas and the fuel, as well as protection via wetting of the surrounding area.

c) Smothering: by steam production, reducing oxygen levels at the flame zone.

d) Dilution: of pyrolysis gases at the flame zone and fuel gasses enveloping the protected area

Fire hazards that can protected by water spray systems may be broadly divided into three categories:

a) GROUP 1:- Hazards that involve such products as heavy and medium oils, paints, greases etc, where extinguishment is achieved by cooling, vapour dilution and emulsification.

b) GROUP 2:- Light Oils, such as Kerosene and similar products where emulsification is not possible, and extinguishing is achieved by cooling, smothering and dilution of volatile vapours above the fire.

c) GROUP 3:- Plant and equipment, in which highly flammable liquids and gases are employed, as normally associated with the petrochemical industry, where extinguishment is neither possible nor desirable and other such applications where control burning and/or exposure protection is required.

To deal adequately with the various types of hazards, two basic types of water spray nozzles have been developed; medium velocity and high velocity sprayers.

High velocity sprayers discharge a coarse droplet spray, of uniform density, at velocities of approximately 5 m/s. They are effective at distances up to 3.0 m to 5.0 m height and require direct impingement 'cone' coverage of the protected equipment. The coarse, high momentum, spray is used on fires involving Group 1 heavy and medium oils, and is able to penetrate the flame zone to reach the surface of the burning oil where an emulsion formed on the surfaces of the oil. The effects of vapour dilution, cooling and smothering, give secondary assistance to extinguishment.

High velocity systems are able to protect outdoor hazards, extinguishing oils or fuels with a flash point above 66^0 C that are sufficiently viscous to emulsify, such as transformers, circuit breakers, diesel engines and diesel storage tanks, turbo alternator, lube-oil systems, oil-fired boilers and similar hazards.

Medium velocity sprayers discharge finely divided droplets at a medium velocity of approximately 2.0 m/s, which due to these smaller droplets have a high heat absorption rate. This makes the sprayer ideal for the protection of hazards involving Group 2 light oils and Group 3 flammable liquids with a flash point below 66^0 C, where emulsification is not possible. These same discharge characteristics are also desirable where controlled burning and/or exposure protection is required.

Medium velocity systems employ the area density and area coverage design technique similar to sprinkler systems; however performance objectives of extinguishment or fire control are limited to indoor hazards only. On the other hand, the fine spray makes medium velocity system ideally suited for exposure protection of equipment in any location, with the proviso that the nozzles are spraying no further than 600mm from the protected surface.

4.2.2. foam systems

The Australian Standard AS 1940 defines firefighting foam as “a stable aggregation of small bubbles, of lower density than oil or water, whose properties are such that the foam may be used as a flame-smothering blanket to prevent the entry of air or to suppress vapour”.

Foam is made by mixing air into a solution of water that contains foam concentrate proportioned at a fixed percentage, usually 1, 3 or 6%. Such foams flow freely over the surface of burning liquid and form an air-excluding continuous blanket that both cools off the surface of the fuel and seals volatile vapours from contact with air. It resists disruption from wind, drafts, heat or flame, and is capable of resealing in case of mechanical rupture. Firefighting foams are able retain these properties for relatively long periods of time.

Foams are defined by their expansion rate and are divided into three expansion ranges:-

a) Low-expansion foam — expansion up to 10.

b) Medium-expansion foam — expansion from 20 to 200.

c) High-expansion foam — expansion from 200 to approximately 1000.

Low expansion foam offers the most stable foam blanket and robust flame ‘burn-back’ resistance, as well as being able to retain its vapour suppression properties for many hours. Its low expansion rate means the higher water content adds to the fuel cooling capacity. When seconds count however, low expansion foam can be comparatively slow to achieve full coverage, while medium expansion foam with its higher expansion rates is able to flood large bund areas more quickly to provide a vapour seal.

High expansion foam is only suitable for indoor applications; however it is extremely frugal in its water consumption and has a rapid spread time. Typically, the entire building can be flooded in minutes, and burn-back of the light foam is simply overwhelmed by the high foam flooding rate.

Foam concentrates can be divided into two categories, protein based concentrates verses synthetic concentrates, and there is sometimes divided opinion, depending on the manufacturer, as to which is the better.

Protein foams are heavy and stable and are available as Protein (P), Fluoro-protein (FP) and film-forming fluoro-protein (FFFP) concentrates. Protein foams are manufactured from hydrolysed proteins and iron salts (hoof & horn chips), and FP concentrates contain glycol ether solvents, such as hexylene carbitol, to help retain the ingredients in solution and provide stability. Fluorinated surfactants (F) are added to assist in forming a film on the fuel surface by fuel shedding and reducing viscosity.

Synthetic foams create a rapid film across the fuel surface sealing flammable vapours, and are available as aqueous film-forming foam (AFFF) and alcohol resistant concentrates (ARC) for use on polar solvents (water loving) such as ethanol. Synthetic foams contain hydrocarbon foaming agents as well as the glycol ethers (butyl carbitol) for stability and fluorinated surfactants for fuel shedding & viscosity. Alcohol resistant concentrates contain water-soluble polymers such as polysaccharides to provide a protective membrane around the fuel to limit the water in the foam being taken up by the polar solvent.

Rather than rely of the marketing brochure, firstly ensure the foam concentrate is approved to a foam-testing standard. For example, surfactants are approved to much lower testing standard but are offered by some 'environmental foams'.

Foams for storage tank protection should be tested and approved to UL162, as this standard will only approve foams with high burn-back resistance against hot metal walls and mechanical rupture of the blanket. On the other hand, the aviation foam testing standard ICAO "b" encourages foam with fast film forming coverage for major spill fires as well as requiring high burn-back resistance.

4.2.3. System Zoning

Limiting the area or extent of protection of an entire installation by dividing the fire system's total protected area into a set of zones will provide operators and fire fighters with more options during the emergency. As well as the flexibility zoning offers it also provides for a more economical use of the available water supplies or foam storage capacity.

Zones must of sufficient size to limit fire spread during the early stages before fire control has been fully established; also operation of adjacent zones will provide exposure protection and some security against ignition of adjacent hazards. The extent of communication between one fire hazard and the next will assist in the zoning arrangement and decision regarding simultaneous operation of adjacent zones. Fig 8 demonstrates, where a single fire scenario, in one case can be attended to by simultaneous operation of fire zones 2 and 3, while in the other, all four zones would be required to operate.

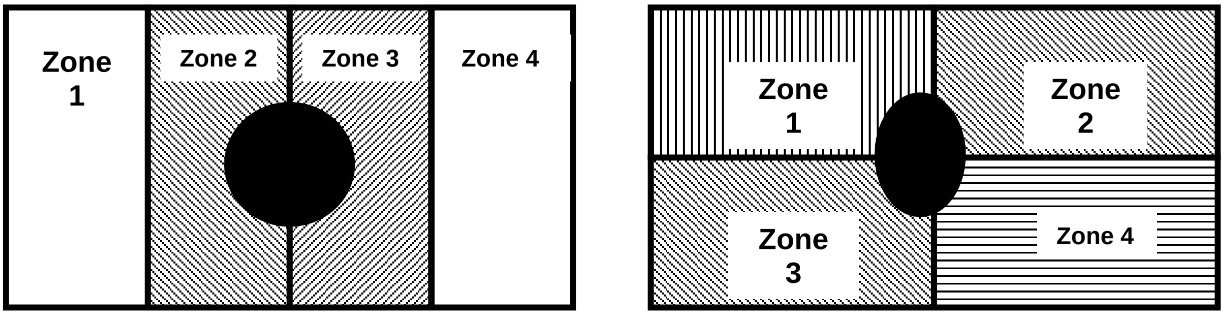

Figure 8 - Fire System Zoning

4.2.4. Water Supply

If the pipework and nozzles are the heart of a fire system then the water supply would be the legs, because without a reliable and adequate water supply there are many examples where a fire has quickly re-established itself due to a water supply failure.

Duration is dependent on the goal of the fire system. If the fire system has the capacity to rapidly extinguish the fire, then a much shorter water supply can be considered. If controlled burning is the fire system's task with final extinguishment by the fire teams, then a much longer duration will be required. In either case, but particularly a controlled burning fire scenario, there will need to be sufficient quantity of water for simultaneous demand of the fire fighting teams and any exposure protection demands. The quantity of fuel anticipated being available to the fire, the arrival time of fire team and their expected role in the extinguishing process, will all be factors in considering quantity and duration. In any case many of the fire standards and code provide minimum water supply requirements.

The benchmark reliable water supply is a single town main as this provides a limitless capacity and constant supply with the highest reliability. When boosting of the supply pressure is needed and a pump is to be provided, dual, 100% capacity pumps should be considered, one compression engine driven and the other electric driven, to offset the reduction in reliability from a town main supply to a pump boosted supply. Similarly, water storage tanks should be divided or split tanks with outlets interconnected should be used to ensure that at least a limited duration supply is available when the tank is to be emptied for routine maintenance. Note that automatic tank infill will offset the limited duration, or the tank could be reduced in size by the amount of infill expected during the system operation time.

Lastly, again for reliability, the water supply feed main to the fire system should be protected against exposure in fire hazard areas or run underground with suitable corrosion protection.

5. COMMISSIONING

To establish the various fire systems' complete functionality and performance, a full discharge and operational commissioning test must be conducted. Preparation of a 'Cause and Effect" chart capturing all system interface interconnections, fire detection, alarms, shutdowns etc, as well as the sequence of these events, are all critical to the system's successful commissioning.

Due to the impact of some extinguishing agents may have on the operating plant and equipment, a commissioning test proving the functionality and adherence to the cause and effect matrix may be considered; however it should be remembered that a system's performance to specification is only demonstrated when running under full load. Discharge commissioning will enable the system's performance to be measured against specification.

Successful operation of production plant and equipment is proven during the commissioning process, however while fire systems are commissioned, they are only proven when a fire occurs.

Water Mist Fire Protection for Copper Solvent Process and Other Industrial Hazards

By

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1. Project Basics

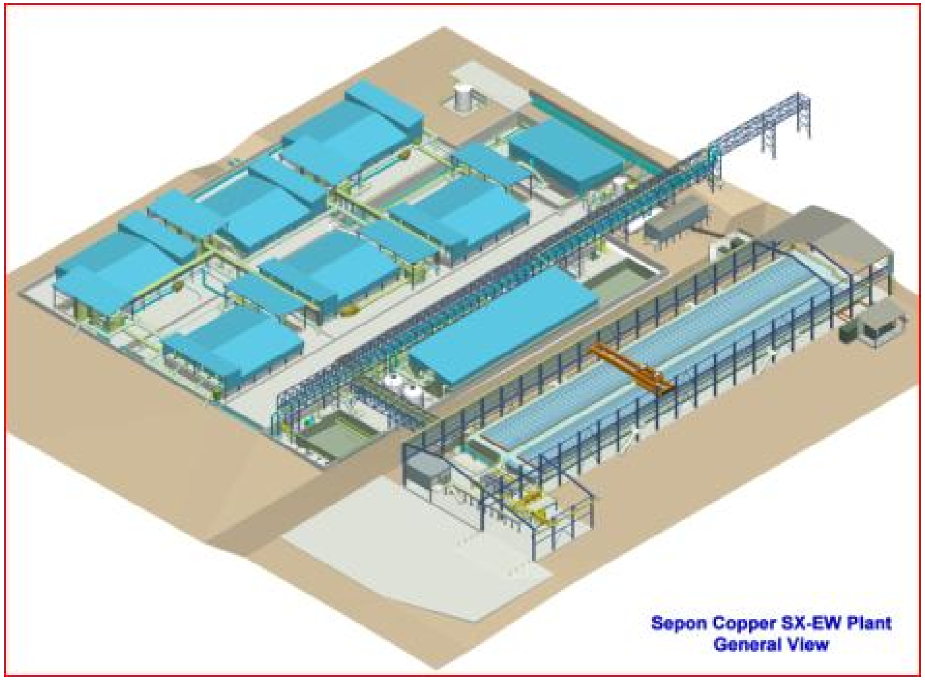
The Sepon Copper Project in Laos is a development of natural resources and associated infrastructure. Copper production capacity is 60,000 tonnes/annum of London Metal Exchange (LME), Grade A copper cathodes through Leaching-Solvent Extraction and Electrowinning phases of the process.

Project name:	SEPON COPPER PROJECT
Client:	OXIANA Resources NL, Melbourne, Australia
Owner/Operator:	Lane Xang Minerals Limited, unit of OXIANA Resources Group
Contractor:	Outokumpu Technology for technology and material supply for SX / EW areas
Plant areas:	Leaching, Solvent Extraction, Tank Farm & Electrowinning

SEPON COPPER PLANT

Protected areas:

- 3 x extraction mixer-settlers
- 2 x stripping mixer-settlers
- 1 x organic washing mixer-settler
- 1 x loaded organic tank
- DOP ("Dispersion Overflow Pump") Units
- Spirok mixing units



Sepon Copper SX-EW Plant
General View

2. Risk of Fire at SEPON COPPER

Outokumpu Technology makes in design significant actions to minimize the risk of fire, for example:

- Pipe & launder dimensioning is based on low linear velocities → low friction and less static electricity
- Motor and gear box design factors are high → low superficial temperatures of motors and gear boxes
- Both DOP and Spirok tanks are covered → less evaporation and less air into the system (in dispersion) → less organic mist in settlers
- Less agitation in DOP tank dispersion surface and not at all in Spirok tanks → less evaporation in these tanks
- Stainless steel sections in organic pipelines
- Organic pipelines are ensured to be full

……. However, there is always risk of fire due to following reasons;

2. Risk of Fire at SEPON COPPER

Possible source of ignition / fire at SX plants (lots of flammable liquid)

- Static electricity
- Overheating of electrical or mechanical equipment
- Short circuit in electrical equipment
- Lightning
- Hot work at site
- Smoking / naked fire

3. Fixed Fire Protection Systems

Light & Ordinary Hazards

- Fire in solid materials
- residences, offices, hospitals, public buildings, ...

Conventional sprinkler

Industrial Hazards

- Fire in liquids & gases, plastics
- Refineries, oil&gas, power generation, flammable liquid storages, …

Water, CO_2, inert gas, halocarbon, foam, dry powder

HI-FOG® water mist fire protection is positioned in both segments

3. Fixed Fire Protection Systems

Industrial Hazards

Hazard (Risk) = Probability x Consequences

Industrial hazards are characterized by the following factors:

- Fire loads are heavy
- Personnel could be exposed to danger
- Valuable equipment and buildings could be exposed to danger
- Consequential damage or risk potential is significant
  - People
  - Environment
  - Infrastucture
  - Lost production
  - Reputation

4. HI-FOG Water Mist Fire Protection System at the SEPON COPPER Plant

Protected by the Marioff HI-FOG MT3 System

The HI-FOG MT3 system is a high pressure water mist system engineered for large machinery spaces

ie. spaces where the fire risk is predominantly flammable liquids and/or gas

The HI-FOG MT3 system is tested and approved against very strict test procedures and approval criterias set by IMO.

Fire testing has been witnessed by FMRC and the approval is pending.

The HI-FOG MT3 system has superior extinghuishing capabilities in large spaces. It also has an excellent cooling capacity and it prevents re-ignition in the protected zone(s).

4. HI-FOG Water Mist Fire Protection System at the SEPON COPPER Plant

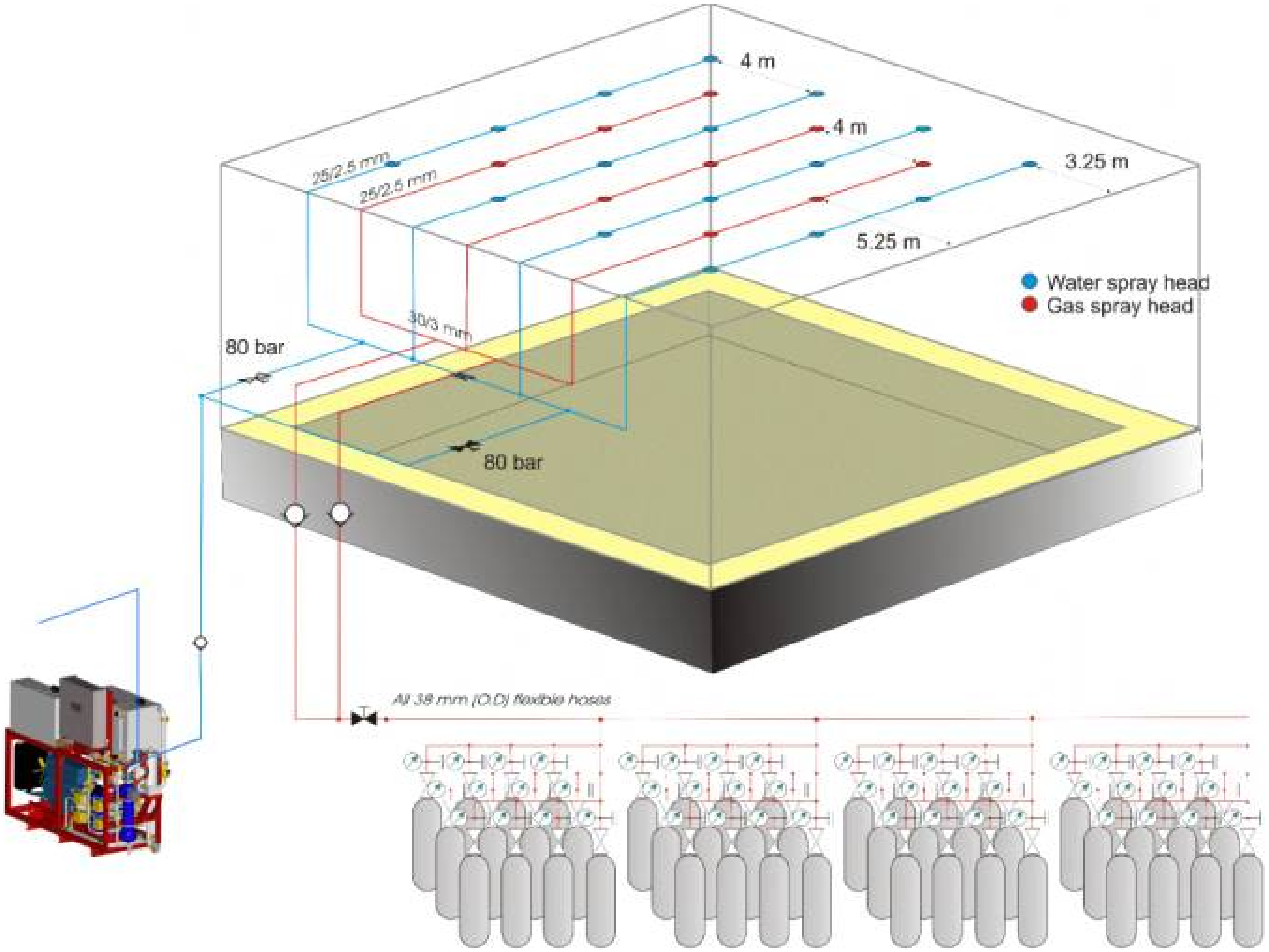
The installed HI-FOG MT3 system contains the following main components;

- 2 x SPUD Diesel pump units, installed within an air-conditioned container
- Nitrogen cylinder bank
- Section valves
- HI-FOG spray heads
- Stainless steel tubing network

The HI-FOG system is integrated with a Siemens fire detection / control system at SEPON COPPER Plant

4. HI-FOG Water Mist Fire Protection System at the SEPON COPPER Plant

Typical HI-FOG MT3 installation



SPUD Pump Unit

4. HI-FOG Water Mist Fire Protection System at the SEPON COPPER Plant

The HI-FOG MT3 Total Flooding System, Operational Principle

Water Mist Distribution

- **Two pump units, comprising 2 diesel engines and 16 high-pressure pumps, are provided as the basic system**
- **A standby pressure is maintained in the wet part of the water distribution network, up to section valves using a pneumatic pump (wet pipe, 25 barg). There are 13 sections at the SEPON COPPER plant**
- **Section valves are located in an accessible area close to , but outside, the protected zone and capable of local manual operation. Each valve is complete with an electric solenoid, flow indicator and a pressure gauge**
- **Section valves can be opened by a signal from the fire detection system, or manually, - lowering standby pressure starts the Diesel Pump Unit automatically**
- **High pressure water is discharged through the specially engineered HI-FOG spray heads to deliver fine, high speed water mist in a form that ensures effective fire extinguishing**
- **Typical flux density: 0.15 L / min / m3**

4. HI-FOG Water Mist Fire Protection System at the SEPON COPPER Plant

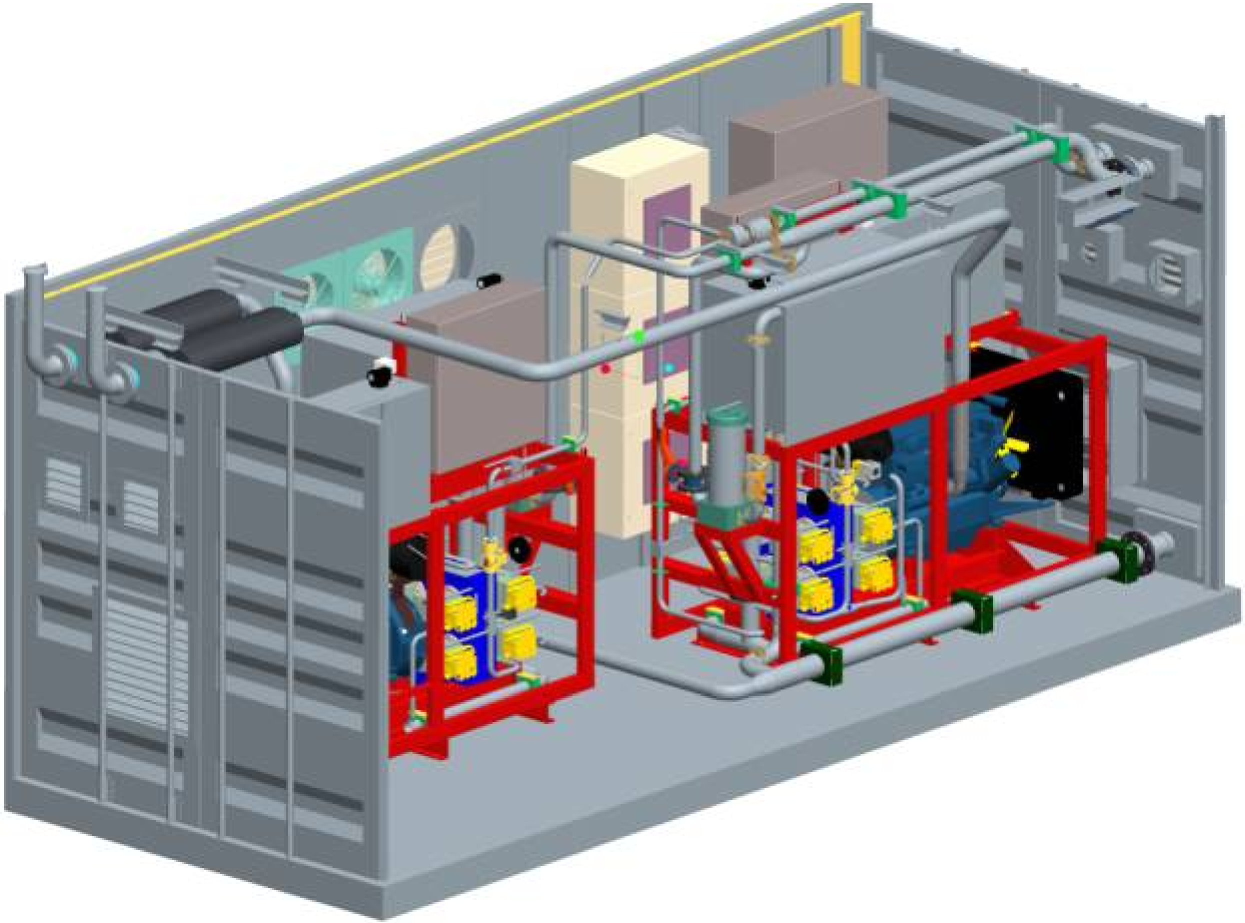
The HI-FOG MT3 Total Flooding System, Operational Principle

Gas Distribution

- **The Nitrogen cylinder units consist of high pressure cylinders arranged in pre-engineered racks (nitrogen banks). The number of cylinders and their rack arrangements are project specific. – 3 x 30 cylinder banks at SEPON COPPER plant**
- **Nitrogen is discharged by opening an electrically activated valve. Gas released upon activation opens a flow passage of distribution from other cylinders in a cascade manner.**
- **Nitrogen is delivered into the protected space through special engineered HI-FOG spray heads, similar to water mist spray heads.**
- **The Nitrogen bank(s) are discharged after a 3 minutes delay to avoid gas loss in case of faulty activations**

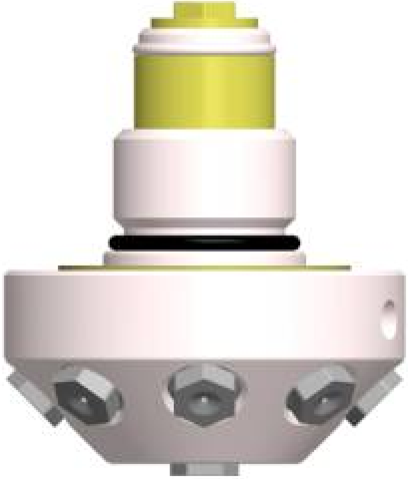
4. HI-FOG Water Mist Fire Protection System at the SEPON COPPER Plant

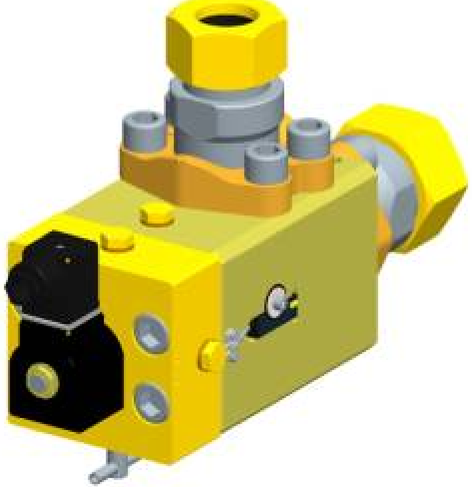
The HI-FOG SPUD pump units within their container



4. HI-FOG Water Mist Fire Protection System at the SEPON COPPER Plant

Other HI-FOG components

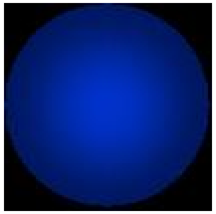
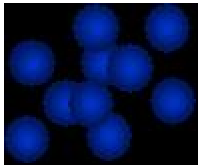
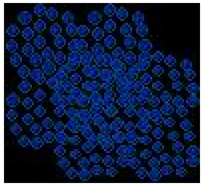




4. HI-FOG Water Mist Fire Protection System at the SEPON COPPER Plant

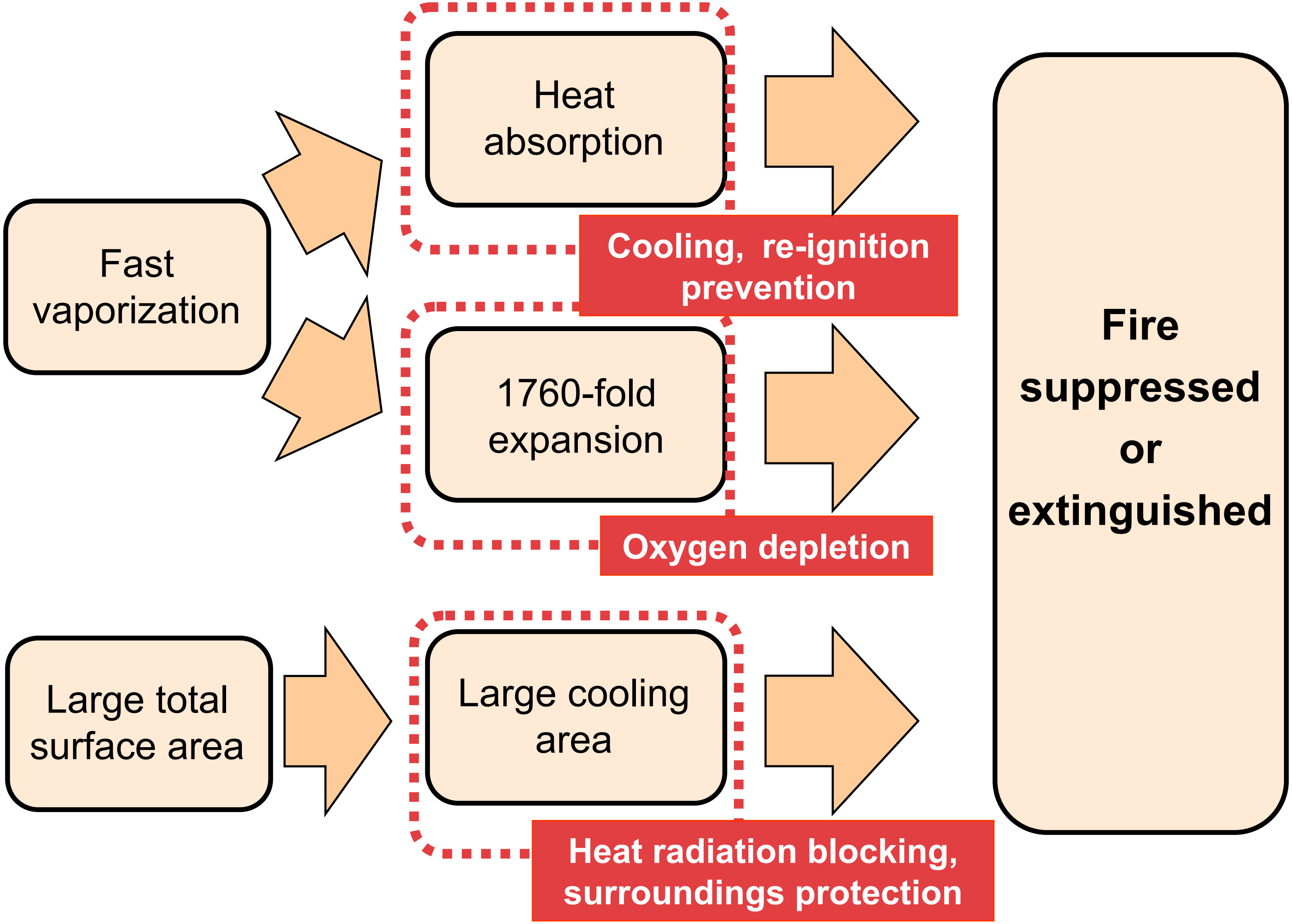
The HI-FOG test discharge

5. HI-FOG - Fundamental Principles

		Drop size (avg µm)	No. of drops	Surface area	Vaporisation rate
	**Sprinkler**	> 1000	1	1	1
	**Low pressure Mist**	300	40	10	0.1
	**HI-FOG®** water mist fire protection	**50**	**8000**	**400**	**0.003**

Decreasing droplet size by 10 increases surface area by 10 and the number of droplets by 1000

5. HI-FOG Fundamentals



Fast vaporization

Heat absorption

Cooling, re-ignition prevention

1760-fold expansion

Oxygen depletion

Large total surface area

Large cooling area

Heat radiation blocking, surroundings protection

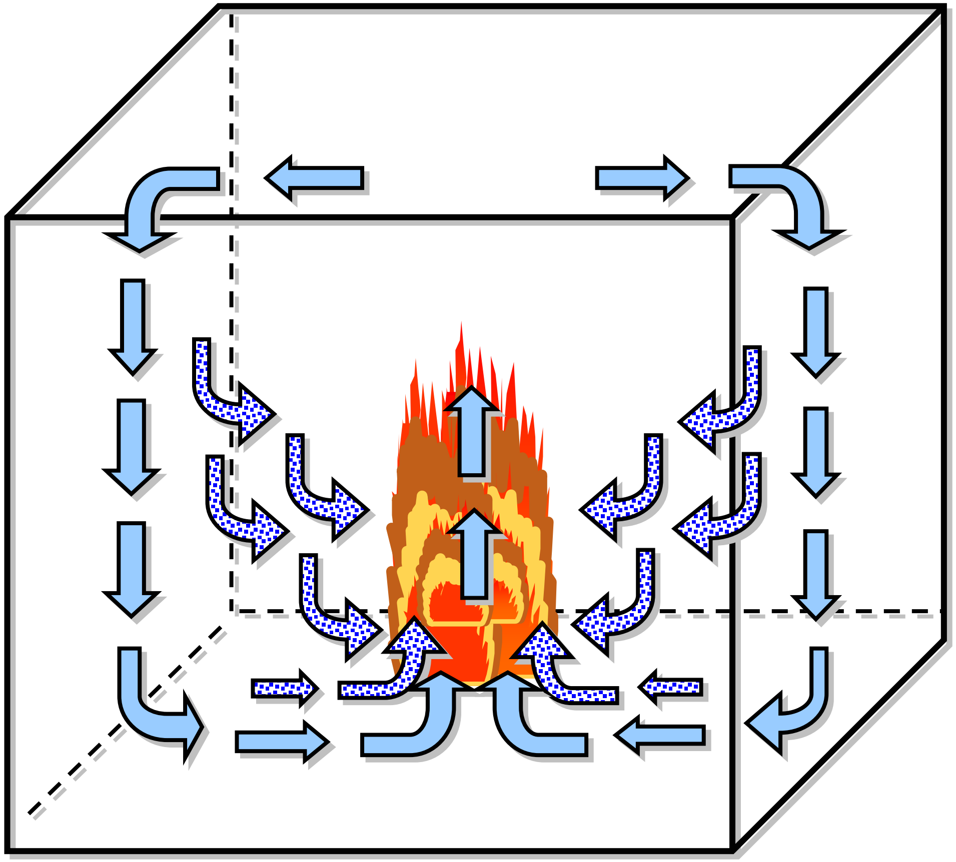
Fire suppressed or extinguished

5. HI-FOG Fundamentals

Water mist entrainment into fire
”3-D function”

Water mist

Air



”Room Effect”

HI-FOG Benefits

- Superior Extinguishing Capability
- Superior Cooling Capability
- Fast activation
- Prevents re-ignition
- Low Water Consumption
- Harmless for the Process
- No Chemical Additives
- No Corrosion Problems
- Low Maintenance & Re-fill costs
- Environmentally Friendly
- Easy to Test

6. Other HI-FOG Applications

Applications

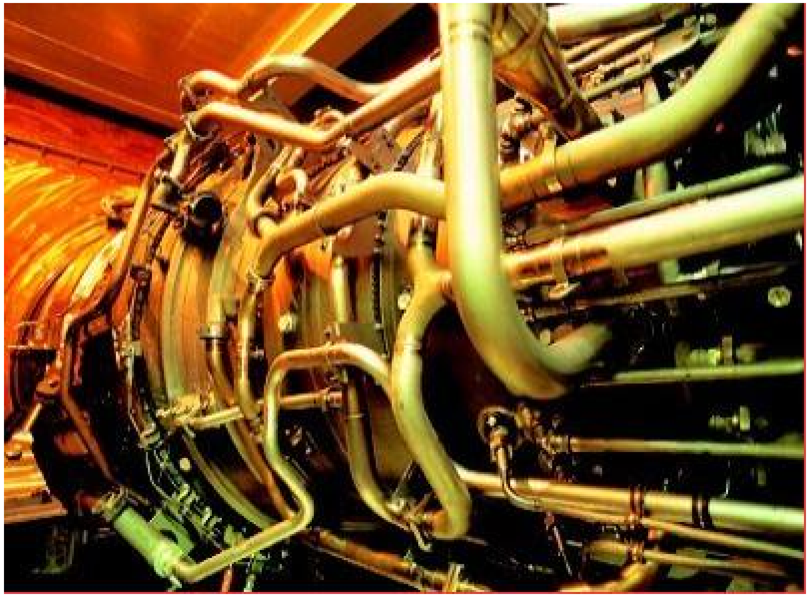
Rotating Machinery

- Diesel engine gensets & pumps

Applications

Rotating Machinery

- Gas turbine gensets
- Gas turbine mech. drive sets



Applications

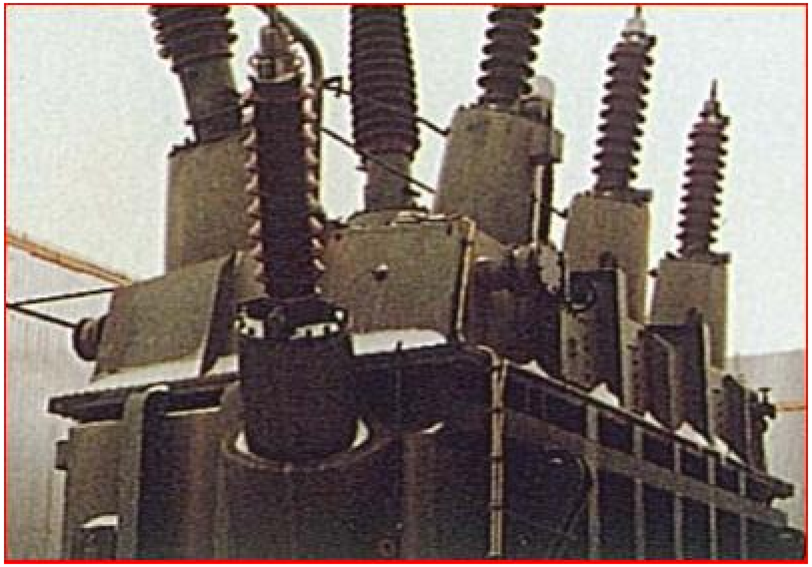
Electronics

- Cable Tunnels

Applications

Electronics

- Switchgear
- Transformers (including outdoors)



Applications

Computing and Telecommunication

- Control rooms
- Data storage areas
- Telecom centres

Applications

Mining

- Copper ore processing
- Conveyor belts
- Emergency power
- Administration & ammenities

Applications

Paper Industry

- Inside the hood
- Over the coater
- Hydraulics
- Drives and gears
- Pulp dryer

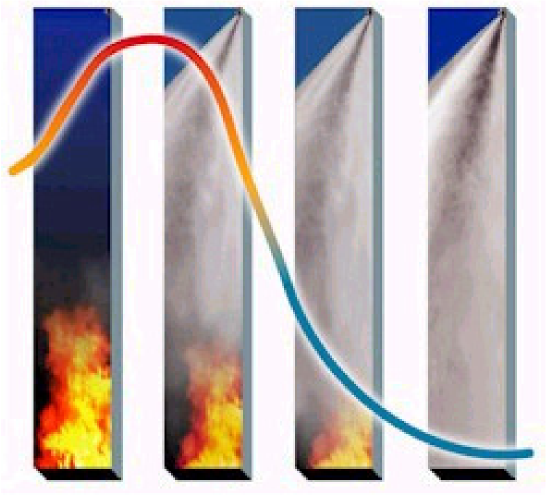
Applications

Manufacturing

- Wet benches
- Oil baths
- Food (ovens, deep fat fryers, ducts)

Main Features

- Fire protection performance
- Cleanliness
- Water consumption
- Installation
- Testing, maintenance
- Smoke handling



- Continuity
  - fire
  - smoke
  - water
  - other
- Safety
  - personnel
  - equipment
  - environment
  - reputation

HI-FOG® Systems

- Self-contained Cylinder Units
- Pump Units
- Flexibility in powering
- Flexibility in duration
- Continuous discharge

COPPER SX FIRE HAZARD MANAGEMENT
- THE PHELPS DODGE EXPERIENCE

By

Tim Robinson –Phelps Dodge Mining Co.
Debra Burkardt – Fluor Daniel Wright

Presented By

Tim Robinson
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Introduction

- Safety Share
- Objective of Paper
- Preliminary Review and Report Development
- Interim Research
- Development of Hazardous Classification Procedures
- Static Electricity
- Radiant Heating
- Misting
- Flashpoint and Conductivity
- Metcalf Incident
- Conclusions

Objective of Presentation

- The intent of the presentation is to share findings with the industry in the spirit of PD’s ‘Zero & Beyond’ safety culture
- Fire safety is an industry issue
- Our culture requires that we share information that could make our industrial environment safer
- It is within the spirit of that commitment that this presentation is being made

PD’s SX Fire Hazard Review

- Phelps Dodge (PD) initiated a SX fire hazard review in spring of 2002 following fires that occurred at the Olympic Dam Mine near Roxby Downs, SA
- This presentation reports the sequence and methodology of the review
- A small team of engineers visited 13 operations in North And South America and filled out check lists , including climactic conditions
- From this preliminary review it was decided that additional interim research was required

Interim Research

- This effort was aimed at addressing concerns such as hazard classification, static electricity accumulation, radiant heat contribution, flash point and conductivity
- Impacts of flash point and conductivity varied from site to site depending on types and mixtures of diluents and extractants
- Flash point information is required to determine minimum temperature at which an organic vapor can be ignited
- Conductivity information was necessary to assess the feasibility of static charge build up to cause ignition

Development of Hazardous Classification Procedures

- A procedure for the classification of hazardous locations for electrical installations at SX facilities at PD was prepared
- Document was an interpretation of various codes and guidelines specific to copper SX
- Flashpoint information is required
- Published flashpoint information is available for diluents and extractants but not for their mixtures
- NFPA defines Class II liquids as flashpoint between 100 and 140 F and Class IIIA between 140 and 200F
- Higher plant elevations also affect Class

Static Electricity

- Static electricity due to lightning and stray currents was not addressed
- Another investigation began describing the theory of static charge accumulation in fluid systems with specific relation to piping and SX EW unit processes
- Static builds up when charge recombines through a path with resistance
- This is known as relaxation or decay time and is exponential
- Key issue in SX plants is vapor ignition leading to fire
- Not typically a concern with conductive solutions such as PLS and electrolyte in bonded and grounded metallic systems as decay time is so fast
- Can be an issue with non conductive SX organic liquids in non metallic systems
- NFPA defines non conductive liquid as <50 pS/m and that will accumulate static charge

Radiant Heating and Misting

- Calculations were done on the effect of radiant heating of organic solution in a partially filled black vessel with worst case static conditions
- Theoretically 150F seems possible
- NFPA 497 also states that mists arising from splashing can ignite below flashpoint
- NFPA recommends adding 15F to account for affects of misting
- Maximum threshold temperature of 165F was then evaluated

Flashpoint and Conductivity

- Research found
  - published flashpoint data on pure liquids but not mixtures
  - All diluents used were non-conductive
  - No published information for extractant conductivities or these mixtures
  - that both conductivity and flashpoint of a mixture may not be weighted or the mathematical average of the two pure liquids and that these mixtures required laboratory measurement

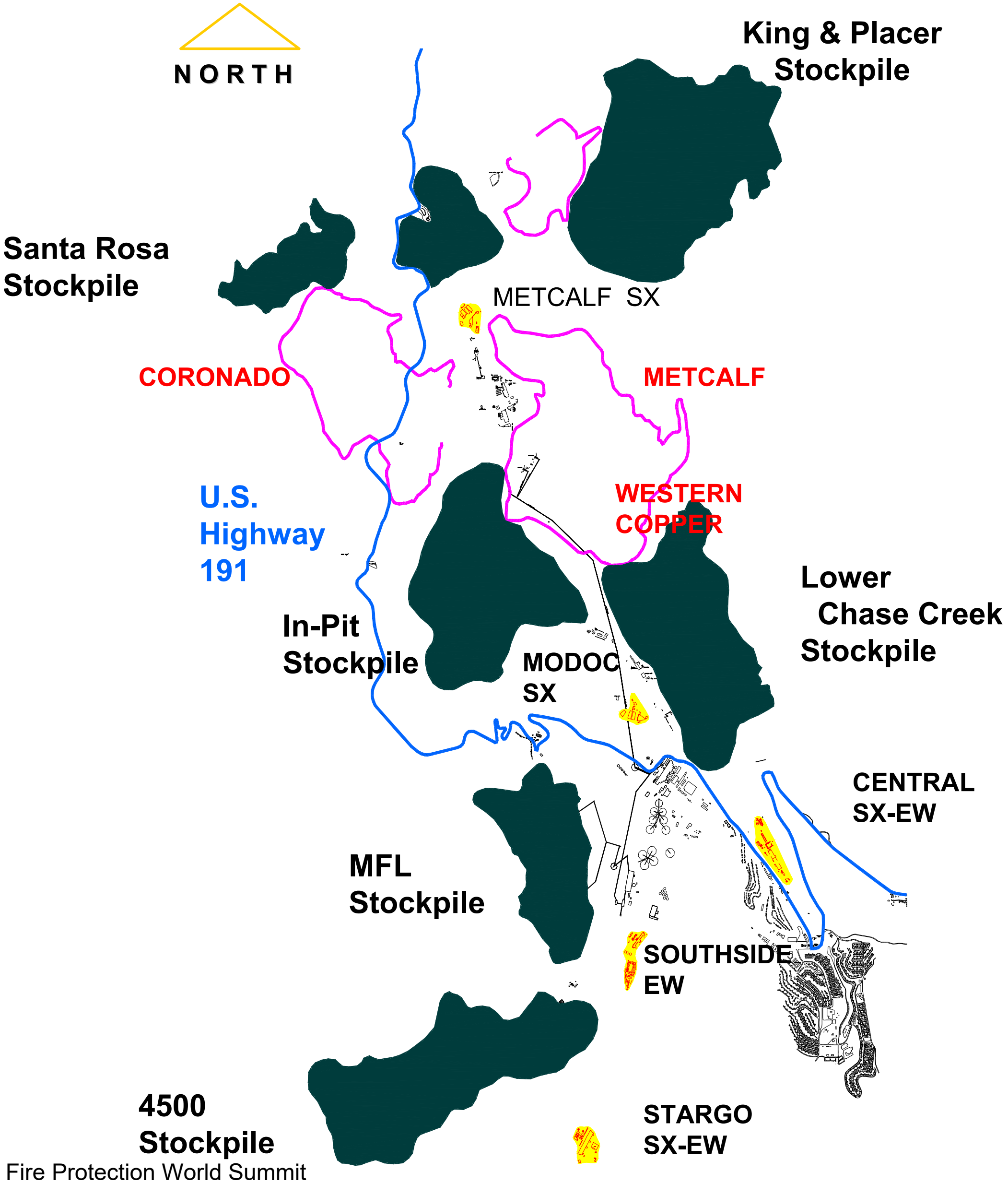
Testwork

- PTC prepared and delivered pure and mixed solutions to an independent expert laboratory
- Results indicated that extractant dictated the conductivity of the mixture and the diluent the flashpoint

Metcalf Fire

- PD Morenci Metcalf SX caught fire on October 16 , 2003
- Fire lasted approximately 4 hours and involved three mixer settler units
- The facility was originally a two train system piped as a 2 by 2 by 1 series parallel with wash stages
- These settlers were located in the 1997 expansion portion of the plant that enabled the operators to hydraulically isolate the plant
- Required the assistance of numerous PDMI departments and community resources
- It should be noted that all involved with fighting this fire are to be commended as there were no significant injuries and the major portion of the SX plant was not damaged
- After the incident an immediate forensic study was initiated

Morenci District Map



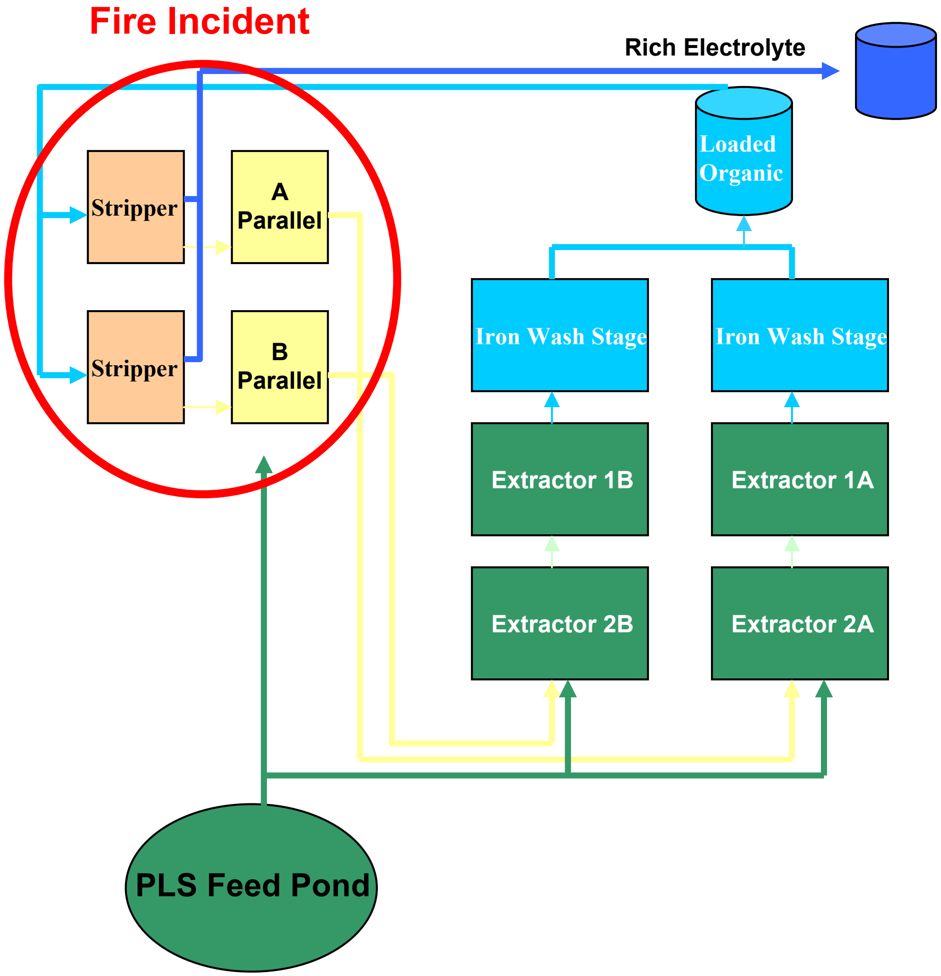
Metcalf SX Plant

METCALF SX Parallel and Strip Stage Settlers

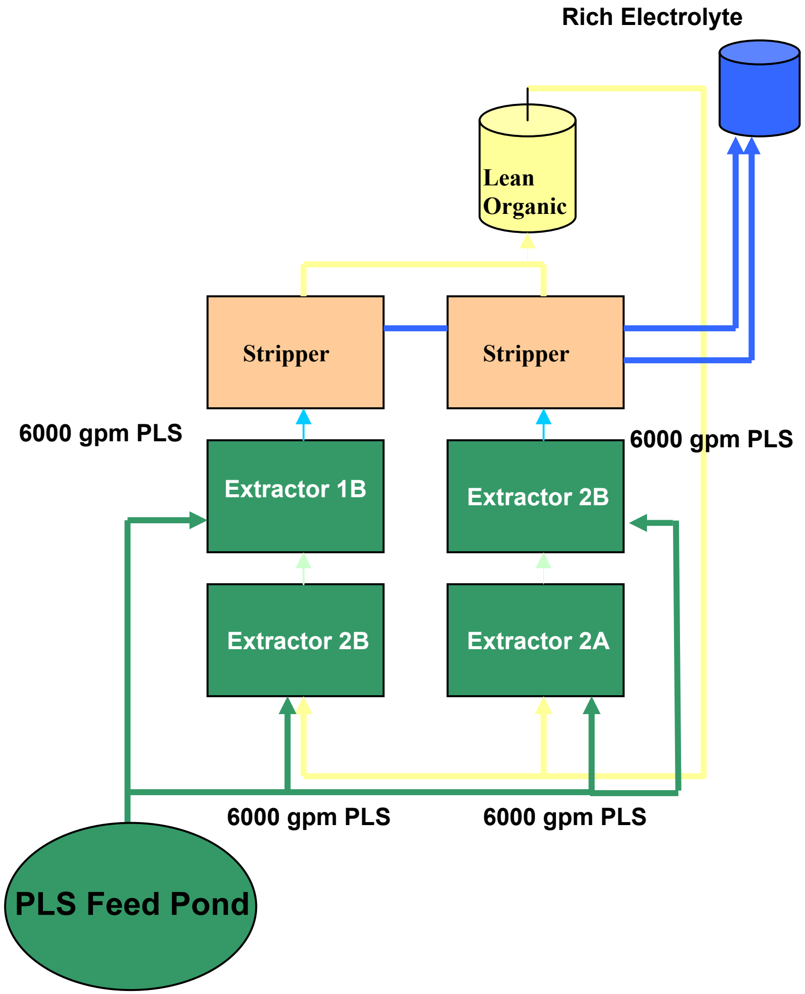
Metcalf SX Facility

Metcalf Plant Fire

Metcalf Plant Current Configuration



Metcalf Plant New Configuration



Metcalf Fire Forensic Study Conclusions

- Forensic study concluded that the source of the fire was at the heat trace connections (used to mitigate the risk of freezing temperatures) in a junction box that had been exposed to some organic material

- This ‘shorting’ and overheating started a small fire which in turn ignited organic in a containment ditch adjacent to the settler

- Recommendations from the forensic report were:
  - All heat trace circuits should be protected with a GFIC circuit breaker
  - All instrumentation power circuits should be reviewed to ensure a design that minimizes any potential exposure to organic material

Further Discussions

- Further discussions after the event included noting that;

- The FRP roofs on the settlers limited the ability to fight the organic fire in the settlers
- Maintaining PLS flow could have been maintained to the plant to attempt to provide additional cooling
- Overflowing the settler weirs may have removed the organic from the fire

Conclusions

- Interim research with a SX Fire hazard review concluded that flashpoint, conductivity, static electricity accumulation, misting and radiant heat from sunlight should all be considered
- Conductivities and flashpoint of mixtures required measurement not calculated estimation
- A forensic study into the Morenci Metcalf fire concluded that the source of the fire was at the heat trace connections in a junction box that shorted. This lead to overheating which also led to a small fire which in turn ignited organic in a containment ditch next to the settler