

Fire Protection for Solvent Extraction Plants

What we can learn from Olympic Dam

By Frank Rizzuto, CIPE

We will begin with some background information on solvent extraction (SX), an industrial process known predominantly for production of edible oils from the major oilseeds as well as from some animal products. This article focuses on the less publicized application of solvent extraction in the processing of copper and uranium ores and the associated challenge in terms of fire prevention and fire suppression.

Solvent extraction of non-ferrous metals may be less familiar to the fire protection engineer, but losses associated with fires in these SX plants by far exceed similar incidents in the oilseed industry in both drama and dollar value. Relatively little published information is available pertaining specifically to fire protection of SX operations in hydrometallurgy.

In October 2001, Western Mining Corporation's Olympic Dam copper and uranium mine located in South Australia experienced a fire in the SX area of the processing plant. The fire was originally reported to have started in the tank farm with prevailing winds carrying the fire to the settling ponds of the mixer/settler operation. The fire quickly spread through the ponds, although the area was highly automated and security was rigidly controlled, and a high level of fire detection and fire suppression was in place. The blaze was exacerbated by the use of plastic pipes to carry the flammable solvent.

Following a similar incident in 1999, which resulted in \$26 million damage to the facility and included a business interruption of six months, the plant was rebuilt with extensive modifications to address the fire's cause and to upgrade the fire detection and fire suppression systems. In spite of these measures, the cost of the 2001 fire has been reported by the news media at \$170 million, and the plant is still not operational. In addition to capital losses of equipment, the fire resulted in production losses contributing to the high overall cost to the company and to its insurance underwriters. The fire was the second major incident at the site since the official opening of a \$1.9 billion expansion earlier in 2001, and the second fire originating in the SX plant since 1999.

In addition to the fire losses, there were environmental concerns over changes in the concentration of uranium, iron, copper and lead in the surrounding soil that could be attributed to combustion deposits, as well as radiation issues associated with the smoke plume from the fire. The fire burned through electrical cables, cutting power to the homes of 4,000 people who live in the company-built township of Roxby Downs, more than 10 kilometres away.

Plumbing Engineer

To understand the lessons of Olympic Dam, three questions must be addressed: What really happened? Why did it happen? What can be done to avoid recurrence?

The process of extractive metallurgy

Solvent extraction as used in hydrometallurgy consists of contacting kerosene containing an active chemical ingredient with an aqueous solution containing a desired metal constituent. During the contact, the desired metal is transferred preferentially from solution in the aqueous phase to solution in the organic (hydrocarbon solvent) phase. After separating, the organic is stripped of its contained metal content and returned to the extraction circuit for reuse. The metal content is then further refined by means of electrowinning (SXEW) or other processing.

The metallurgical solvent extraction operation involves extensive flammable liquid handling including bulk solvent storage, pumps and piping, open ponds and agitator tank units known as settler/mixers, open launders, and

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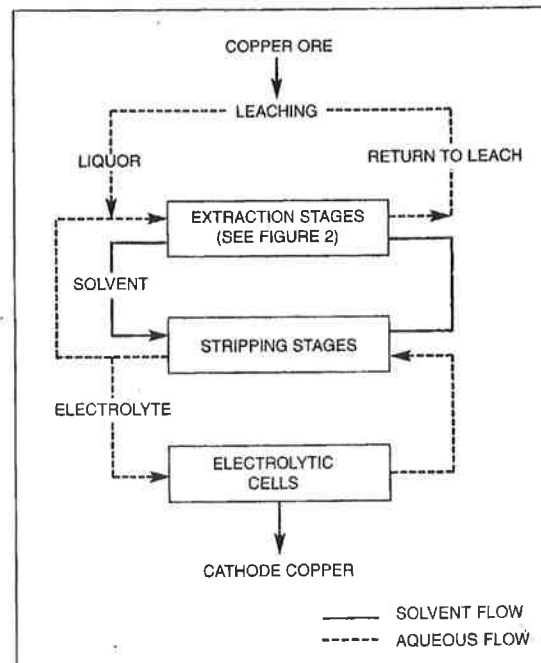


Figure 1 — Flow diagram of copper production using solvent extraction.

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electrical power systems, as well as dry materials handling systems in the associated mill. In addition to extensive flammable liquid transfer operations, SX plants may contain a considerable amount of fire loading in the form of PVC jacketed electrical cable, high density polyethylene (HDPE) and other plastic pipe, oil filled electrical transformers, electrical motors and switch gear, hydraulic power units and hydraulic oil reservoirs, fibre-glass reinforced plastic (FRP) tanks, ducts and fan housings, FRP and rubber lined stainless steel tanks and other combustibles.

Figures 1 and 2 illustrate organic (solvent) flows versus aqueous (leach liquor and electrolyte) flows through the copper solvent extraction process to the electro-refining stage where the copper leaves solution in the form of cathode copper, to eventually be melted down into refined copper ingots. Points of concern for the fire protection engineer include the mixer/settler trains and the associated tank farm, transfer pumps and piping network.

A typical SX operation may incorporate one to four separate mixer/settler trains with two to seven mixer/settler units per train. In addition, there may be several SX operations, one for each metal to be extracted, such as copper and uranium. To give some idea of scale, each settler may cover a surface area of 4,000 square feet (370 square meters) to a depth of 3 feet (1 meter), exposing a considerable volume of solvent to atmosphere, and by implication, to whatever ignition sources may be present in the vicinity or carried into the area by wind or other means. The volume of organic present between the mixer/settler area and the tank farm in a typical SX operation may exceed 700,000 gallons (2,600 cubic meters). Where the tank farm is duplicated, as in the case of two separate SX operations side by side, this figure can be doubled.

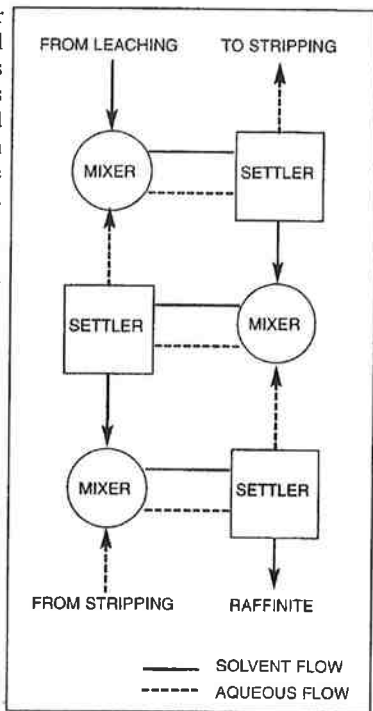


Figure 2 - Flow diagram for mixer/settler trains, as a part of the copper production process using solvent extraction (see Fig. 1).

In addition to flammable liquids, there may be thousands of linear feet of 14-inch (350 mm) diameter and 16-inch (400mm) diameter HDPE pipe transferring solution between the mixer/settlers and the tank farm, with the plastic pipe itself adding to the fire loading.

Static discharge as ignition source

It was originally reported that the most recent Olympic Dam fire originated in electrical power cable in the mixer/settler area, and later reports claimed the fire was carried into the SX area by wind from the tank farm. It is now believed to have originated from static discharge within the plastic piping network. Although the jury is still out on the actual cause of the blaze, investigators have concluded that there was no ready ignition source in the vicinity. Access to the SX plant was controlled, the process highly automated, and fixed fire protection systems were deemed adequate to detect and suppress, having been redesigned and upgraded after the 1999 fire.

Fire generation requires three basic elements for combustion: a fuel, oxygen and an ignition source. Fire prevention can therefore be simply defined as measures taken to prevent these elements from coming together to form the fire triangle.

The flammability of a liquid is defined in terms of its flash point, that is, the lowest temperature at which a flammable vapor formed above the liquid will sustain combustion when mixed with air and provided with a source of ignition. It is not the liquid itself that burns, but a vapor in air mixture that is created at the liquid surface due to the vapor pressure of the liquid.

In addition to a large surface of exposed organic in settlers and tanks, liquid contained and transferred under pressure or by gravity flow within the piping network may at times be at or exceeding its flash point. Lowering of pressure reduces the flash point of a liquid, therefore as atmospheric pressure decreases where SX plant is situated at altitude, it approaches the vapor pressure of the liquid, and a vapor rich atmosphere may develop at the surface of the liquid. SX plants are in operation with extractants or diluents that have flash points in the range of 59 F - 175 F (15 C - 79 C), with adjustment for temperature and elevation.

Any fluid passing through piping generates a static electrical charge. For comparison, kerosene has about six times the ability of gasoline to generate static. In the case of metallic piping, the static is readily discharged to ground when piping and equipment are properly bonded, however, when a fluid is passing through plastic pipe, because of the mode of generation it cannot be discharged and accumulates in the fluid. Since iron pipe is unsuitable for transfer operations within the SX area due to corrosivity of the liquids involved (H_2SO_4 mixed in with the kerosene) and the acidic atmosphere around the mixer/settler operations, and stainless steel represents a significant increase in capital investment, HDPE and other plastic materials are selected over electrically conductive materials.

The generation of static in itself is not hazardous. The real danger lies 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 may generate up to 15 millijoules (mJ), while the energy level required for ignition of a flammable liquid mist is approximately 1 mJ.

It is known that sparks can dart across the surface of a tank containing high flash point liquids. Such sparks have been seen in agitators and there are places where sparks can occur above the liquid surface. In the case of lower flash point products (Class I flammable liquids such as gasoline), vapors at the liquid surface may be too rich (above their upper explosive limit) to ignite, and static charge tends to relax as the liquid settles in a vessel after filling. In SX operations, when flammable vapor is present at the surface it is more likely to be between its

lower and upper explosive limits, and liquid in the mixer/settler circuits seldom remains at rest long enough to relax its static charge.

The mixture of conducting and non-conducting 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 within the system. The problem of mitigating the static charge on the liquid surface cannot be solved by attaching any number of ground wires to it. Instead, it is necessary to reduce or eliminate static generation, volume charge or surface charge.

Some mechanical measures that can reduce the generation of static include:

- Select transfer pumps designed to create the least turbulence in the liquid handled. Centrifugal pumps tend to create high turbulence.
- Reduce pressures within piping to the lowest values required for efficient liquid transfer.

- Reduce fluid velocity. The same volume of liquid (gpm) travels at lesser velocity through a larger diameter pipe than through a smaller one.
- Eliminate or reduce restrictions in the piping system as much as possible.
- Select higher radius bends in piping runs.
- Submerge tank infeed nozzles. Avoid 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 increases the ability of the solvent to generate static.
- Bonding and grounding of all metallic elements in the piping system, such as pumps and tanks, is a prerequisite to a program of static mitigation in the SX area.

Of course the most hopeful solution lies 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.

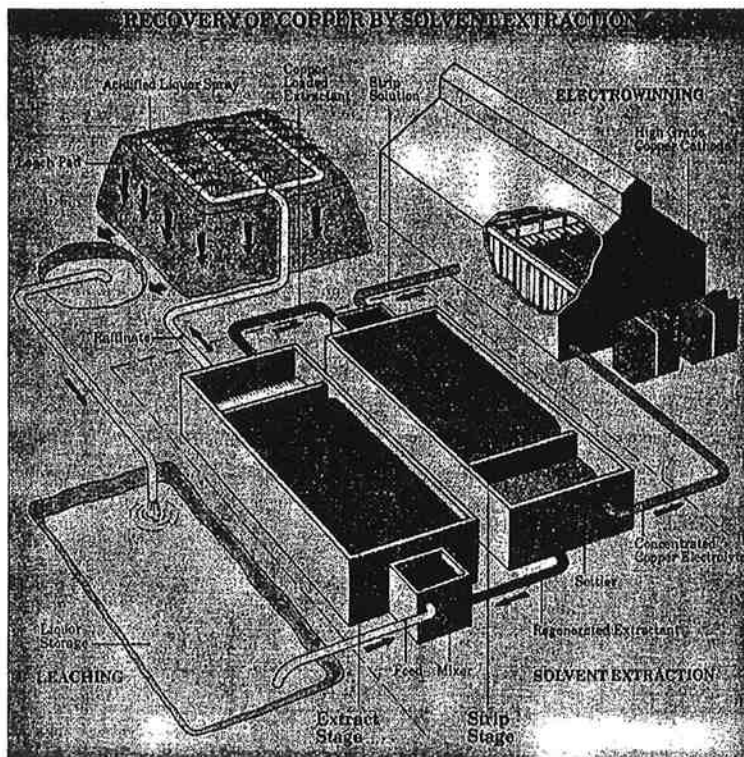


Figure 3 - Typical solvent extraction plant layout. Diagram courtesy of Aveica, Inc.

The Olympic Dam fires - what worked and what didn't

Analysis of the Olympic Dam fires is useful in determining the future approach to fire protection for new SX plants as well as how to approach the upgrading of fire protection for existing SX operations. The 1999 fire destroyed the tank farm and the 2001 fire destroyed the rebuilt tank farm, as well as the mixer/settler area. In light of the high dollar losses and a correspondingly more conservative attitude being taken by insurance underwriters, non-protected or minimally fire protected facilities may in the future not be able to purchase insurance.

All of the Olympic Dam mixer/settlers had four foam outlets that covered the top of the solution rapidly, automatically simultaneously initiated by UV-IR detectors. Automatic foam suppression was also installed within the organic surge tank. The systems functioned as intended, nevertheless the fire resulted in an almost total loss.

A better approach would have been

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to replace the foam chambers with permanently installed high expansion foam generators at opposite ends that would discharge a synthetic detergent type foam yielding expansion ratios up to 1000:1, rather than foam chambers and AFFF foam with expansion ratios of less than 10:1 and much slower foam distribution across the surface of the burning liquid.

One of the contributing factors to the fire was the lack of fire protection

the HDPE piping between the tank farm and the mixer/settler area to create a fire break. This appears to have been the single most effective fire protection measure in whole fire scenario.

Monitors were installed around the perimeter of the tank farm and around the mixer/settler area. These proved to be of limited value as the range of the monitor closest to the fire was insufficient. Wind direction and velocity being a significant factor, it is impor-

plant operating philosophy.

3. Building construction should be non-combustible. Concrete and steel beams and columns should be provided with approved fire resistive coatings. Wherever possible, process areas should be located under cover only (open sided) to prevent accumulation of vapors and to permit manual fire fighting by hose streams from yard hydrants.

4. Flame arrestors should be provided on bulk organic tanks and on all batch tanks located within process areas. Provide adequate ventilation of all vessels and enclosed spaces where flammable vapors are likely to occur. Provide lightning protection for large bulk storage tanks.

5. Containment curbing, trenches and drains connected to a remote storage tank or drained safely to a separate spill containment area should be provided in areas where flammable liquids are pumped, piped or utilized in process equipment. Design of bulk solvent storage tanks should include spill containment by means of concrete containment walls or earth dykes, with adequate separation from exposed buildings and structures, in accordance with the recommendations of FM 7-88. Provide an approved means of solvent unloading with adequate provision for spill containment.

6. Fire separations are imperative between the SX and tank farm areas. Pony walls should be constructed to full height and 15 foot long (5 meter) metal spool pieces installed where HDPE piping penetrates the wall. Water curtains should be provided between separate SX trains.

7. Ensure that all electrical equipment located within SX areas and in the tank farm meets National Electrical Code (NFPA 70) Class I Division 1 (explosion proof) requirements. Replace any substandard electrical motors, switchgear, junction boxes and other non-conformant components, and any field electrical connections. Steel wired armoured electrical wiring should be provided with earth leakage detection. Instrumentation and control elements should be pneumatic rather electrically operated wherever possible.

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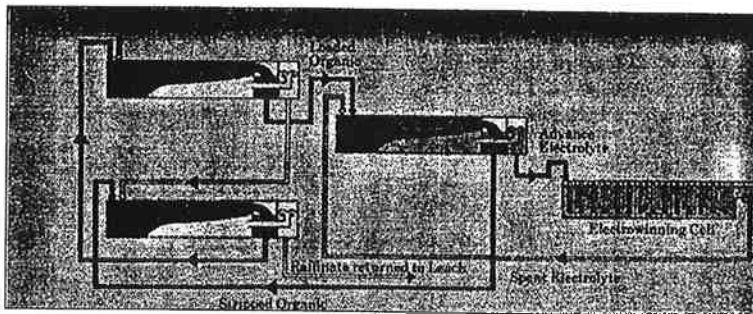


Figure 4 - Settler/mixer flow diagram from a typical solvent extraction plant. Diagram courtesy of Aveica, Inc.

over the pipe racks. The solvent transfer pump suction and discharge piping was metallic up to the overhead pipe rack where a transition was made to HDPE pipe runs, designed to prevent the solvent flowing out of the surge tank under gravity if a discharge line ruptured or melted. Although the metallic piping withstood the fire, the plastic piping melted and collapsed, adding more fuel to the blaze. It was assumed at the design stage, that since there were no identifiable ignition sources in the vicinity of the pipe racks, no fire protection was needed, hence no sprinklers over the plastic pipe. All plastic piping runs and all piping runs carrying organics should have been fully sprinklered on a deluge water spray system, using conventional smoke/heat detectors, UV-IR detectors, or linear heat detector wire to actuate the deluge system and to initiate remote alarms. Once a fire is generated, it will propagate along open trenches, spilled organic accumulations, and along combustible plastic piping. With or without a combustible liquid present, HDPE itself is a combustible material and should be protected.

Metallic spool pieces were fitted in

tant to install a sufficient number of monitors to ensure that water is available at least to cool tanks exposed to fire in adjacent tanks. A fire department connection should be installed at two or more points on the header to allow pumper trucks to pressurize the monitors from opposite directions depending on the prevailing wind. It is important to consider this aspect early in the design stage when laying out the site plan for new facilities.

Over four hours of stored fire water was available for fighting the Olympic Dam fire, well in excess of the recommended volume of fire water for the site. Nevertheless, the fire burned out of control.

Fire protection for new facilities and upgrading of existing plants

Of all the health and environmental hazards involved in SX plant operation, fire is by far the most sensational. Following are 25 recommendations that can be applied in the design of fire protection for new SX plants and when assessing existing facilities:

1. Access to SX areas should be strictly controlled.

2. Establish fire-safe housekeeping procedures as an integral part of the

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8. Motor control centers (MCC rooms) containing oil-filled switchgear should be fully sprinklered. Cable spreading areas and areas containing electrical cable trays stacked two or more tiers high should be provided with automatic sprinklers to prevent fires from spreading beyond lower trays. It is prudent to provide automatic sprinklers on a preaction system in all electrical and MCC rooms. Stripping of the outer PVC jacket from armoured electrical cable is not a very effective means of reducing fire loading, as another PVC jacket is present beneath the armour.

9. Electrical power transformers should be isolated from areas likely to contain flammable vapors or areas expected to experience spills or leaky piping and equipment, and should be located in fire-rated enclosures or vaults depending on the type and rating of the transformer. Oil filled transformers should be provided with spill containment and automatic sprinkler protection.

10. Electric reheat coils in HVAC ductwork, electric unit heaters, and electric heating elements in process equipment should be evaluated for safety. Steam or circulating glycol is a preferred method of space heating.

11. Assess the piping network for causes of static build up and methods of mitigating static charge in piping and equipment. Implement solutions to reduce the volume of ignitable vapors present during normal as well as upset conditions. Provide electrical earthing (grounding) straps for grounding mechanical equipment and tanks.

12. Tanks, piping and solvent transfer equipment should be designed for the solvent, working pressures and stresses involved in their operation. Pumping systems should be provided with pressure relief circuits. Pumps should be located on ground floor level wherever possible. Double pump seals should be installed and other mechanical measures taken to reduce the possibility of atomizing sprays issuing onto nearby ignition sources. Wherever possible, piping should be welded (or HDPE fused) and connections to tanks and vessels should be

bolted flanges. FRP tanks and FRP or rubber-lined tanks and plastic piping should be labelled as such.

13. Provide automatic shutoff valves to stop organic flow into and out of the SX area. Shutoff valves may be of the fusible link self-closing type or electric solenoid operated (explosion proof) safety shutoff valves, de-energized to close so that organic flow will be automatically shut off in the event of power loss, or by means of a fire detection system interlock.

14. Ensure that the plant fire alarm

The generation of static in itself is not hazardous; the real danger lies 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.

system is functional and that proprietary alarms annunciate at a constantly (24/7) manned location. Upgrade to fire resistant control and alarm cabling throughout the SX plant.

15. Where fixed foam systems are not provided, automatic sprinklers or deluge water spray systems should be installed over all areas where organics are present in process equipment, over solvent pumping systems and piping networks, over organic bulk and batch tanks located in buildings and process areas, and over settlers. Particular attention should be paid to sprinklers over HDPE piping and over organic transfer pumps. Sprinklers should also be provided over rubber belt conveyors in the associated mill, FRP tanks and plastic piping containing non-organics, hydraulic power units, oil

filled air compressors and vacuum pumps, electrical switchgear and power transformers, and throughout electrical cable spreading areas.

16. A fixed fire fighting foam system should be installed at bulk storage tanks, and over open vessels, pipework trenches and launders, and curbed containment areas likely to contain flammable liquid spills, on all other organic tanks, filter feed tanks, coalescers, crud treatment tanks and systems, and diluent tanks. Foam generators should be installed at all mixer tanks and settlers, and a water curtain installed between mixer/settler trains.

17. The plant fire water supply should be assessed for capacity. Fire water distribution piping should be extended in a looped configuration fed from opposite ends of the site and zoned such that impairments can be isolated to affected portions of the loop and the system remain pressurized. The reliability of existing fire pumps in case of power loss should be determined and a diesel-driven backup fire pump installed or a second electric driven fire pump installed on a backup generator set. Care should be taken that only underwriters approved fire pumps and controllers are installed and that equipment is regularly tested.

18. Class II fire hose stations should be located throughout the plant with access to all levels in accordance with NFPA 14. Where trained fire crews are available, Class III hose stations may be installed. Hose stations should be supplied by a standpipe header independent of any sprinkler system control valve. Within SX areas, AFFF foam concentrate may be introduced into the standpipe system by means of a bladder tank and proportioner installed downstream of a deluge valve. The system should be a semiautomatic pre-action type, with pneumatic manual release valves at each hose station. The system should be designed for a minimum 15 minute foam discharge followed by water. An approved portable dry chemical fire extinguisher, minimum 20 lb. (9 kg) rated 10A:60B:C should be located at each fire hose station.

19. Yard hydrants should be located

to provide hose coverage throughout process areas that are open sided, and to provide coverage to the outside surfaces of all buildings and structures. Provide a fully equipped metal or masonry hose house including extra hose, couplings, straight stream and fog nozzles, wyes, wrenches, crow bar, and fireman's axe at each hydrant.

20. Permanently mounted monitors should be provided around all bulk solvent storage tanks for cooling in case of fire in adjacent tanks, and for

better. Reserve a sufficient inventory of self-contained breathing apparatus (SCBA).

22. If the plant maintains an in-house fire brigade, conduct a skills assessment survey to determine training needs. Establish or revise an existing emergency response plan to implement appropriate fire fighting methodology both fixed and mobile.

23. Mobile equipment is a major player in fighting fires. The plant should purchase and maintain at least

as detailed in FM 7-43/17-2, *Loss Prevention in Chemical Plants*, should be implemented. A Hazop (hazards and operability analysis) review should be conducted of the SXEW facility and a Hazan (management control document) issued to ensure changes to process are reviewed with the appropriate personnel. Provide training for electrical and other maintenance personnel with a focus on fire safe methods and procedures.

Unless the fire is detected and extinguished in the incipient stage by automatic fixed fire suppression systems, manual fire fighting efforts may have relatively little effect in limiting the damage.

covering the mixer/settler trains. Ensure that monitors are automatic swivel type and provided in sufficient numbers and proximity to tanks to afford coverage under all foreseeable conditions. A fire department connection should be installed at two or more points on the independent header to allow pumper trucks to pressurize the monitors from opposite directions depending on the prevailing wind.

21. As well as increasing the available water supply, provide an increased supply of foam concentrate stored in a secure location. Observe the expiry dates of foam stock and replace as required. Coordinate foam stocks with other SX plants in the vicinity and with local municipal or airport stocks. During a fire, significant amounts of foam are used. Although the volume of fire water and the amount of foam concentrate available to fight a hydrocarbon fire are not as important as the timing and manner in which the foam and water are applied to the fire, nevertheless, there is no upper limit to the volume of water or foam that may be required to fight the fire; the more available, the

one metropolitan type fire tender vehicle or more depending on the scale of the operation, including trucks equipped with ladder and snorkel as well as water and foam tanks. There are many reasonably priced vehicles on the pre-owned market as well as opportunities for taking ownership of used trucks from decommissioned mining operations at practically no cost other than transportation to the new site.

24. Wherever possible, establish mutual aid agreements with nearby fire departments. It took 30 trained members of the mine rescue team plus approximately 100 extra personnel all with varying degrees of experience in fighting a major hydrocarbon fire, to cope with the Olympic Dam fire. SX operations are made even more hazardous by the volume of H₂SO₄ mixed in with the kerosene. This is a challenging scenario even for fully trained professional fire fighters with all the most advanced apparatus at their disposal.

25. Due to the involvement of large quantities of flammable liquids, a process safety management program,

Summary and conclusions

To answer the questions posed earlier, what happened (cause of the blaze) at Olympic Dam has yet to be definitively announced; why it happened can be attributed to the failure of the fixed fire suppression systems to cope successfully with the blaze in its incipient stage; what can be done to prevent a recurrence has been the focus of this article.

The 2001 Olympic Dam fire illustrates the value of early detection and fast suppression of hydrocarbon fires. Unless the fire is detected and extinguished in the incipient stage by automatic fixed fire suppression systems, manual fire fighting efforts may have relatively little effect in limiting the damage. The concept of utilizing automatic fire suppression systems to control a fire until it can be extinguished by the responding fire brigade is not an effective fire protection strategy when it comes to large scale flammable liquid operations. Once the fire grows beyond the design of the fixed fire suppression systems, the emergency response team may have little to do other than become spectators until the fuel is fully consumed.

References

Note that NFPA, IRI and FM standards pertaining to solvent extraction focus specifically on the commercial scale extraction processing of animal and vegetable oils and fats by the use of Class I flammable hydrocarbon liquids. While solvents used in extraction of metals involve Class II flammable liquids, many of the recommendations also apply to hydrometallurgical oper-

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ations. The following is a list of useful reference texts, codes and standards.

SME Mineral Processing Handbook, Society of Mining Engineers, 1985.

Handbook of Solvent Extraction, Lo, Baird and Hansen: John Wiley & Sons Publisher, 1983.

Fire Protection Manual For Hydrocarbon Processing Plants, Charles H. Vervalin, Editor, Gulf Publishing Company, 1973.

What Went Wrong? Case Histories of Process Plant Disasters, Trevor Kletz, Gulf Publishing Company, 1994.

Improved Chemical Engineering Practices, Trevor Kletz, Hemisphere Publishing Company, 1990.

API RP500, *Classification of Locations for Electrical Installation*

of Petroleum Facilities classified as Class I, Division I and Division II.

FM 5-1, *Equipment in Hazardous (Classified) Locations.*

FM 7-30, *Solvent Extraction Plants.*
FM 7-32, *Flammable Liquid Operations.*

FM 7-59, *Inerting and Purging of Tanks, Process Vessels and Equipment.*

FM 7-83, *Drainage Systems for Flammable Liquids.*

FM 7-88, *Storage Tanks for Flammable and Combustible Liquids.*

IRI 17.23.1.14, *Solvent Extraction.*
NPPA 36, *Standard for Solvent Extraction Plants.*

NFPA 69, *Standard on Explosion Prevention Systems.*

NFPA 70, *National Electrical Code.* □

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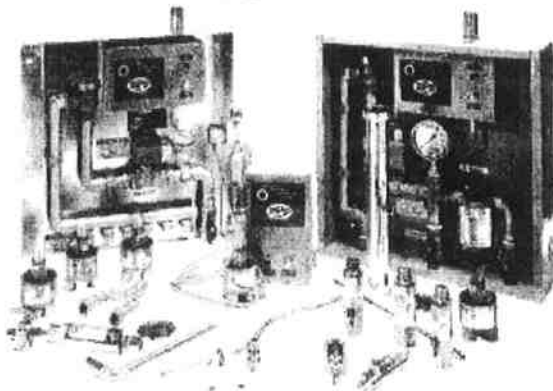
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