Queensland Mining Industry Health and Safety Conference

Townsville, Queensland 26 August 2000

Hazardous Substances Management

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Introduction

In October 1994, a laboratory technician working in a palynological laboratory in a Perth suburb accidentally spilled about 150mL of anhydrous hydrofluoric acid (HF) onto his thigh. Hydrofluoric acid is a particularly hazardous substance, in that as an acid, it is not only corrosive, but it is also toxic. HF is readily absorbed through the skin and reacts rapidly with the available free calcium in the body to leave the individual severely calcium depleted (hypocalcaemic) and this loss of electrolyte is the major factor in fatalities involving HF. In this case, two weeks after the accident the technician died from multiple organ failure as a direct consequence of the accident. This is a particularly shocking example of the potency of some hazardous substances and of the necessity to adequately manage the risk associated with those substances.

The prime reason for the correct management of hazardous substances is the need to avoid the potential for adverse health effects as a result of exposure to those substances. The above example and the case studies given in the text below are indicative of some of the health effects of some exposures to hazardous substances.

In an even more recent - and somewhat bizarre - case, there is the account of an electrician who complained of intermittent abdominal pain and constipation. Initially, his doctor was puzzled as he could find no explanation for these symptoms. However, a blood test revealed surprisingly high levels of lead. Upon being questioned, it emerged that the electrician had chewed the plastic insulation of electrical cable as a substitute for smoking for at least 10 years. Smoking was prohibited on the building sites where he worked. The cable was readily available and according to the electrician, had a sweet taste and, he had taken to chewing approximately I metre of leaded electrical cable each day. Not surprisingly, as he was ingesting a significant quantity of lead each day, the electrician was displaying all the early symptoms of lead poisoning or plumbism.

The new Hazardous Substances regulations will provide a framework for managing hazardous substances in the workplace. The regulations use the risk management approach, which has three steps:

1. Hazard identification;
2. Risk assessment;
3. Control.

Based upon this approach, there are two basic thrusts underpinning the legislation:

1. The provision of information; and,
2. The prevention of exposure to those handling the substances.

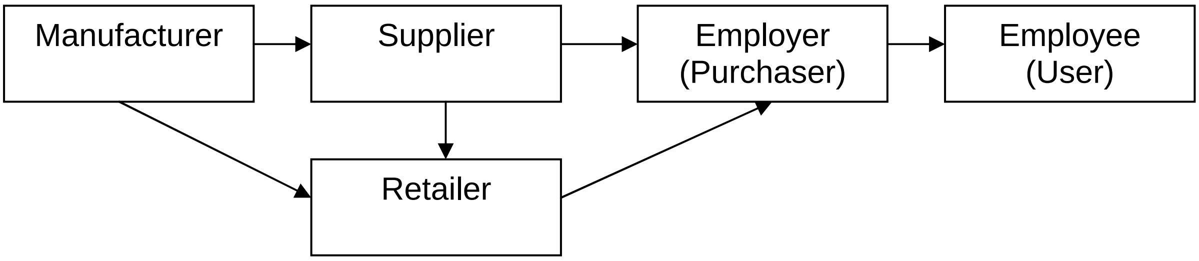
Information Provisions

Information is provided by the persons responsible for the substance – the manufacturer, or in the case of a substance brought into the country, the importer. This usually takes the form of a Material Safety Data Sheet (MSDS) or information on a product label. There are guidelines to ensure that the information is provided in a uniform and easily understood fashion. Nevertheless, to the lay person the terminology used can be confusing. For a start, people can confuse hazardous substances with Dangerous Goods, and to a lesser extent, with Poisons. All three categories are covered by separate pieces of legislation, the objectives of which are different. Dangerous Goods legislation applies to the control of the transport and storage of chemicals, and is intended to protect the community. Poisons regulations are designed to protect the consumers of the chemicals, especially those in the domestic environment. It is no coincidence that Poisons Information Centres are invariably located at major children's hospitals.

The Hazardous Substances legislation applies to those chemicals used in the workplace which have a certain adverse effect on the health of those exposed. A substance is classified as being hazardous if it is listed in the List of Designated Hazardous Substances or if it meets the Criteria for Classification as a Hazardous Substance. These criteria originated in the European Community (EC) and as they are now recognised by most of the major trading nations, we can be assured that substances imported from overseas should be appropriately classified. Even if a substance is not hazardous, the manufacturer should still indicate this on the MSDS with the statement to the effect that, "This substance is not classified as hazardous according to the criteria of Worksafe Australia", which indicates to the user that the requirements of the hazardous substances regulations. These effects or criteria may be:

- Acutely Toxic
- Irritant
- Sensitiser
- Corrosive
- Mutagenic
- Carcinogenic
- Toxic to reproduction
- Affect lactation
- Other toxicological properties

The key to the management of hazardous substances lies in the provision of information. There is a chain of information (see diagram below) commencing with the manufacturer; the person who should know the substance best – he knows the exact composition, the ingredients, the chemical and physical properties of the substance and he should determine the toxicological properties of the substance. This information forms the basis of the information on the product label and in the Material Safety Data Sheet (MSDS), which is passed on via the supplier, to the purchaser or employer and hence to the employee or end user.



Anyone allocated responsibility for managing hazardous substances needs a good working knowledge of toxicology, or the science of poisons. Paracelsus (1493 - 1541) enunciated one of the most basic tenets when he said,

"All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy".

Thus, a dose of something even as common as table salt can be toxic at a high enough dose, while substances such as cyanide or arsenic can be quite safe - at low doses. The toxicity of a substance is determined using terms by finding the quantity, or dose, capable of killing 50% of a population of a species. This is the LD_{50} for a substance, and is usually written giving the route of exposure and the species; the units are usually stated in terms of milligrammes of substance per kilogramme of the animal's body weight, thus,

$$\text{Parathion, } LD_{50} \text{ (Oral-rat)} = 50 \text{ mg/kg}$$

For inhalation toxicity, the lethal concentration is stated in terms of parts per million or mg/m3 of air over a period of time:

$$LC_{50} \text{ (inhal-rat)} = 50 \text{ ppm/4H.}$$

There are four main routes of exposure :

- Inhalation – breathing in dusts, gases, vapours, fumes, smokes
- Dermal – skin contact.
- Ingestion – swallowing
- Eye

Inhalation is the most common route of exposure in the workplace; dermal contact the next most common route of exposure may result in damage to the outer layers of the skin or direct absorption of the substance, while ingestion tends to be more of a problem with domestic consumers, where children can swallow toxic substances. In the workplace, ingestion tends to be a consequence of eating or smoking with contaminated hands; or poor personal hygiene habits, such as nail biting, sucking on pens or pencils, wiping ones mouth across one's sleeve or back of the hand and so on.

So, if a layman were to ask a toxicologist, "How toxic is this substance?", the toxicologist might use a rough rule-of-thumb approach , as shown in Table 1 to give a rough and ready indication. This gives a practical and useful means of gauging the inherent toxicity of a substance.

Table 1.
TOXICITY RATING CHART

TOXICITY RATING OR CLASS	**PROBABLE LETHAL ORAL DOSE FOR HUMANS**	
	Dosage	*For Average Adult*
Supertoxic	< 5 mg/kg	A taste (less than 7 drops)
Extremely toxic	5-50 mg/kg	Between 7 drops & a teaspoonful
Very toxic	50-500 mg/kg	Between teaspoonful & an ounce
Moderately toxic	0.5-5 g/kg	Between ounce & a pint
Slightly toxic	5-15 g/kg	Between pint & a quart
Practically non-toxic	>15 g/kg	More than 1 quart

Table 2, below shows the dosage of some selected chemicals to produce death in 50% of the treated animals (LD_{50}). Some will produce death in microgramme (③g or 10^{-6} grammes) doses and are regarded as being extremely toxic, while others, such as ethanol, can be ingested in relatively large quantities. This is not to say that ethanol is non-toxic; anyone who has ever had a hangover from ingesting ethanol as the active ingredient in their beer, wine or whisky can testify to the toxic effects of ethanol.

Table 2.
APPROXIMATE ACUTE LD50s OF SOME REPRESENTATIVE CHEMICAL AGENTS

AGENT	**LD_{50} (mg/kg)**
Ethanol	10,000.0
Sodium chloride (salt)	4,000.0
Ferrous sulphate	1,500.0
Morphine sulphate	900.0
Phenobarbital sodium	150.0
Picrotoxin	5.0
Strychnine sulphate	2.0
Nicotine	1.0
d-Tubocurarine	0.5
Hemicholinium-3	0.2
Tetrodotoxin	0.1
Dioxin (TCDD)	0.001
Botulinum toxin	0.00001

The dose of a hazardous substance is the amount absorbed into the body. It takes into account the concentration of exposure and the duration of the exposure, thus:

DOSE = Concentration of exposure x Time of Exposure

A dose may be either acute or chronic; an *acute* dose is a single, high concentration over a short period of time, typically seconds, minutes but rarely longer than a few

hours. With a few repeated exposures, or more prolonged exposure, say over the course of a shift, the dose is then said to be *sub-acute*. Such exposures may result in the worker showing signs or symptoms consistent with exposure.
A *chronic* exposure pattern is usually at a lower level of exposure, but over a much longer time span, often measured in months or years. The disease or illness associated with chronic exposure to a substance may often be significantly different to that from an acute exposure episode.

Control of Exposure

When using hazardous substances, the risk to the health of the person handling the substance must be assessed before the substance is handled. Using the information from the product label, the MSDS and any other sources of relevant material, the employer in consultation with the employees, must determine whether the risk to users is acceptable or otherwise. This requires a knowledge of the proposed usage of the substance as well as any process. For example, the level of risk associated with paint will vary, depending upon whether the paint is applied by brush, roller or by spraying. Spraying will generate an aerosol and hence create the greatest inhalation risk.

If the assessment indicates there is a risk of inhalation of the substance, the risk must be quantified by measuring the concentration of the airborne contaminant and this is assessed against a standard. Worksafe Australia has published a list of exposure standards which provide a guideline for comparison. A sample of the air in the worker's breathing zone sample is monitored for the contaminants in question, using an appropriate sampling device.

The air inhaled at work should not contain contaminants at concentrations that produce adverse effects on health, safety or well being. To assist occupational health and safety practitioners, employers and employees or their representatives, and regulatory agencies to secure workplace atmospheres which are as free as practicable from hazardous contaminants, exposure standards have been developed by expert working parties.

Exposure standards represent airborne concentrations of individual chemical substances which, according to current knowledge, should neither impair the health of nor cause undue discomfort to nearly all workers. Additionally, the exposure standards are believed to guard against narcosis or irritation that could precipitate industrial accidents.

These exposure standards are guides to be used in the control of occupational health hazards. They should not be used as fine dividing lines between safe and dangerous concentrations of chemicals. They are not a measure of relative toxicity and should not be applied in the control of community air pollution. An appropriately qualified and experienced person, such as an occupational hygienist, should undertake interpretation of the exposure standards.

There are three categories of exposure standards:
- 8-hour time-weighted averages (TWAs)
- Short-Term Exposure Limits (STELs)

- Peak Limitations or Ceiling Values

HAZARD IDENTIFICATION - The Walk-Through Survey

As a means of making a preliminary investigation into potential exposure problems, the walk though survey is a good first step in the consideration of the substances and processes involved. This is essential in recognising the hazards.

The components of such a survey would include:
- the process;
- the personnel likely to be exposed and their behaviour and their comments;
- the substances used, handled or produced;
- evidence of reactions, including energy inputs/outputs;
- controls in place - isolation, engineering, administrative;
- observation of general housekeeping conditions;
- workplace facilities for washing, eating, drinking, etc;
- sensory information - noise, odours, visible dust or mist; and
- personal protective clothing & equipment - type and patterns of use.

In addition to the above, certain further information will be useful, including:
- process flow charts or diagrams;
- inventory of substances;
- records of first-aid treatments, incident and accident statistics;
- production and other logs; and
- verbal information from relevant personnel.

To facilitate the walkthrough survey, it helps to break up the process into small sub-processes. For example, in chemical manufacturing industry, one would consider all the above points at each of the following steps:
- research & development;
- raw materials inwards;
- processing & handling;
- packaging;
- storage;
- transport;
- distribution;
- utilisation or consumption of product; and
- waste management, disposal or recycling.
- Other Factors

When assessing the risk from exposure to a substance, it should be recognised that some persons may be more vulnerable than others, due to the influence of certain factors such as:
- sex;
- age;
- predisposing medical conditions; and
- time (of day/year).

RISK ASSESSMENT - Preliminary Assessment

When assessing the risk of exposure to the worker from the hazardous substance in question, a number of factors need to be considered by way of a preliminary assessment:

- physical nature of the contaminant - this may be solid, liquid or an aerosol;
- toxicity of the contaminant;
- quantity of the hazardous substance present;
- number of people with potential for exposure; and
- likelihood of exposure.

Air Sampling

Where a preliminary assessment indicates a potential for exposure, the next step is to quantify this level of exposure in order to establish whether the exposure is acceptable.

This may be done by sampling the air that the worker inhales to determine an indication of the level of exposure or by taking biological samples to determine the actual level of exposure.

Air sampling of the workplace atmosphere may be done by means of static samplers to obtain a general or area sample, or it may be done by means of a personal sample, which is collected in the breathing zone of the worker. This is usually collected with the worker using a personal monitor.

For the purpose of ensuring that the sample is genuinely representative of the worker's exposure, a sampling strategy must be developed to encompass a number of factors:

- collection techniques;
- analytical techniques;
- where to sample;
- whom to sample;
- when to sample;
- how long to sample;
- how many samples to collect; and,
- required accuracy and precision.

Following analysis, a result of the exposure concentration is found and is usually expressed as the quantity of contaminant for a given volume of air; for example, mg/m3, ppm or f/mL. This figure is also expressed as a Time Weighted Average (TWA) for the entire period of the time of sampling. Ideally, this period should be the full time in which the worker is potentially exposed, i.e., the full length of the shift.

CONTROL

When exposure monitoring indicates unsatisfactory levels of exposure may be occurring, then this must be reduced. While there are various ways in which this may be achieved, a hierarchy of controls has been established, listing methods in their order of effectiveness.

Elimination - if a hazard exists then the most appropriate control is to eliminate it completely by not using a particular substance. For example, it may be possible to eliminate the use of chemical adhesives by fastening items together with screws or nails.

Substitution - when it is not possible to eliminate the use of a chemical substance, it may be possible to use a safer alternative, for example, using a water based paint instead of a solvent based paint.

Isolation - the exposure may be reduced by the use of a substance in an area which is remote to the rest of the workplace (isolation by distance) or by carrying out a process during quiet hours when fewest people are likely to be exposed (isolation by time).

Engineering methods - a process may be modified in such a way to minimise the release of aerosols, for example, by enclosure or by means of local extraction ventilation systems.

Administrative methods - this could include the development of standard operating procedures to limit exposures, or by restricting access to areas of high exposure.

Personal protective equipment (PPE) - this is generally regarded as being the least effective method of reducing exposure, as the hazard still exists in the workplace and PPE is open to misuse or abuse by the wearer.

Case study
Choose your controls carefully

One morning, at a plant which manufactured organophosphate pesticides, a plant operator collapsed. He showed the classic symptoms associated with poisoning by organophosphates: increased salivation and lachrymation, sweating, nausea and abdominal cramps and constriction of the pupils. He was rushed to hospital where this preliminary diagnosis was confirmed by a severely depressed blood cholinesterase level. He was treated with atropine sulphate, the antidote to organophosphate poisoning, and he recovered uneventfully after a few days in hospital.
Meanwhile an investigation was carried out by plant management to determine how this accident could have occurred. The controls associated with the handling of this product were very stringent and the workforce were well trained in their use. This was a well run plant, which prided itself on its health and safety performance and this incident was taken very seriously by all concerned.
At he time of the accident, the plant operator had been working on the formulation of a product which contained phosdrin as the active ingredient and hexanone as the solvent carrier. As phosdrin is readily absorbed through the intact skin, it was hypothesised that this was the probable route of entry,

caused by an inadvertent splash. However, the operator's clothing did not reveal any indiation of splashing, nor could he recall any such incident.
Finally, it was noticed by the hygienist that at the time of the accident, the operator was wearing PVC gloves. He knew that PVC is not suitable for use with ketone solvents such as hexanone, as it is highly permeable to ketones. So, it was apparent that the solvent would have passed through the glove material, carrying the active ingredient with it and hence bringing it into direct contact with the skin. As a consequence of this incident, the entire glove management programme was reviewed.

This case study highlights a number of points:-

- The need for a complete risk assessment of a job with input from a competent person;
- That PPE is very much a last choice of control measure;
- The need for constant vigilance in the use of controls - this could have been picked up in an audit, had one been done.

RECORD KEEPING

Because of the nature of the health effects incurred from exposure to some hazardous substances, eg cancer, it is possible that there will be a long latency period between actual exposure and the onset of symptoms. In some cases, this may be 20, 30 or more years. For this reason, records kept relating to working with hazardous substances must be retained for at least 30 years.

CONCLUSION

The Hazardous Substances Regulations will provide a framework for the systematic management of substances hazardous to health of those exposed to them. As these are based upon model Regulations developed by the National Occupational Safety and Health Commission (Worksafe Australia), the requirements are essentially uniform across the country and across jurisdictions. This will ensure that employers are not faced with costs of complying with differing requirements in different States and that employees are adequately protected, whether they are employed in the mining or non-mining industry sector.