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ABSTRACT

Chemical reactivity is a major area of risk in high school laboratories. This paper reports on a study that has provided a research-based framework for risk management in Australian chemical education. The chemical practice model of risk management is considered with respect to kinetic factors; catalysts; concentrations and proportions; temperature; induction period factors; runaway reactions; pressure; exothermic reactions and explosions; agitation problems; adiabatic systems; thermal stability; and problems concerning chemical structures. The model includes a policy consideration of issues related to dusts and fibers in laboratories. Contains 30 references. (Author)

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Paper Summary: The Hazards of Reactive Chemicals in High School Laboratories

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Abstract

Chemical reactivity is a major area of risk in high school laboratories. This paper reports on a study that has provided a research based framework for risk management in Australian chemical education. The chemical practice model of risk management is considered with respect to kinetic factors; catalysts; concentrations and proportions; temperature; induction period factors; runaway reactions; pressure; exothermic reactions and explosions; agitation problems; adiabatic systems; thermal stability; and problems concerning chemical structures. The model includes a policy consideration of issues related to dusts and fibres in laboratories.

INTRODUCTION

- The research reported in this paper is concerned with the provision of a framework for risk management in Australian chemical education (Forlin, 1994).
- A formal definition for risk management is presented:

> *Risk management is the integration of policy alternatives and selecting the most appropriate response in the light of administrative, legal, and organisational* requirements (Forlin, 1994).

THE CHEMICAL PRACTICE RISK MANAGEMENT MODEL

- The 'chemical practice model' facilitates solutions to chemical risk problems. Chemical educators are encouraged to understand the problems associated with individual chemicals and chemical combinations. together with reactivity hazards.
- An uncertainty with this approach is that there are differences of opinion between chemical educators concerning many aspects of the problem, including acceptable levels for chemicals, among other contentious issues.

- Law intervenes in a chemical risk management system as does policy. International systems, including those that Australia has recognised and ratified, will also intervene in a system which will then come under pressure to change.
- No other way of specifying good practice can make any sense without reference to chemical practice and knowledge.

THE HAZARDS OF REACTIVE CHEMICALS

- Chemical reactivity is considered in this paper with respect to: **kinetic factors; catalysts; concentrations and proportions; temperature; induction period factors; runaway reactions; pressure; exothermic reactions and explosions; agitation problems; adiabatic systems; thermal stability; and problems concerning chemical structures**. The model includes a policy consideration of issues related to dusts in laboratories.

Kinetic Factors

- The reaction rate of a chemical reaction determines the rate of energy release.

The Effects of Proportions and Concentrations

- There are many examples where changes in concentration and/or proportion of reagents have affected the stability of what was previously regarded as an established, safe procedure (Bretherick, 1990).

The Effects of Catalysts

- The presence of a catalyst (normally used at 1-2%) may have a critical effect on reaction rate (Sittig, 1991). The presence of inhibitors may interfere with a reaction. An inhibitor may establish an induction period which increases the problems in controlling a reaction.

Induction Period Incidents

- If an inhibitor was present a reaction has usually slowed down. This induction period can interfere with the progress of a reaction.
- The reaction may be controlled by monitoring the addition rate of the reagents, or by controlling the reaction temperature.
- It is important, therefore, to monitor reactions, especially where large quantities of reagents are involved (Bretherick, 1990).

- Caunt, Tait and Davies (1983) used a gaseous poison, allene, to inhibit the rate of the polymerisation of purified propylene under a partial pressure of one atmosphere. The expectation that active centres would be affected and the reaction rate reduced, ultimately, to zero was not realised. What seems to have occurred is that only a fraction of the active sites were affected and after an initial drop to minimal rate, thereafter there was a slow increase in reaction rate which can pose safety problems if it is unexpected.

Temperature

- A 10 ^{0}C rise in temperature doubles or trebles the rate of a reaction. Temperature will rise as an exothermic reaction proceeds which, therefore, applies to many chemical reactions. Exothermic reactions should be cooled as they proceed (Bretherick, 1990).

Runaway Reactions

- The temperature effect on chemical reactions becomes critical when chemical reactions progress to runaway reactions, leading to intense heat generation and possibly explosion (Murti, 1988).

High Pressure Reactions

- The application of high pressure to chemical reactions and systems may cause instability. The energies involved in high pressure systems may be very great and have caused serious accidents. Such systems should be monitored carefully (Bretherick, 1990).

Dust Reactivity Problems

- Dust problems have occurred with a large variety of solids, when ground to a finely divided state (Manahan, 1991).
- The risk of dusts catching fire is considered much greater than the risk for the same material in bulk (Crawford, 1992; Grumer, 1991; see AS 3640).
- Dusts that have been involved with explosions and fires in laboratories are sulphur, phosphorus trisulphide, zinc phosphide, carbon, and rubber, among other dusts (Bretherick, 1990).
- Nagy and Verakis (1983) described the following materials that presented a dust explosion hazard: drugs; dyes; feeds; fertilisers; foods; grain; insecticides; meals; metals; paper; plastics; rubber; sulphur; soaps; spices; starches; wood; and coal or other carbonaceous materials.

Exothermic Reactions

- Exothermic reactions may result in explosion. This release of energy takes only a few microseconds, creating projectile and fire hazards. Gerlovich (1992) stressed that school science departments should develop and implement safety plans for conducting these reactions at low temperatures.
- Pressure release procedures are considered critical in the control of runaway exothermic reactions.
- There are many examples of pyrophoric materials. Finely divided metal powders may be pyrophoric. Factors that have affected the pyrophoricity of metals are particle size, presence of moisture, mass, hydrogen content, stress, purity, and presence of oxide, among other factors (Bretherick, 1990). It has been possible to handle these materials, safely, only in low concentrations of oxygen.

Explosions

- Many chemicals are explosive or burn very rapidly.
- "Burning chemicals can emit fumes so toxic that they will kill a person long before the flames ever reach them" (VCE, 1991, p.57).
- Bretherick (1990) defined explosibility as "... the tendency of a chemical system (involving one or more compounds) to undergo violent or explosive decomposition under appropriate conditions of reaction or initiation" (p.1590).
- Mechanical detonation risks should also be considered. Chemical 'flash points' should be well documented (see AS 2106-1980).
- Where the flash point for a chemical is below room temperature, the chemical constitutes a fire hazard.
- There is a correlation between flash point and the probability of fire even where liquids are maintained at temperatures below their flash points during procedures conducted at lower than atmospheric pressures (Bretherick, 1990).
- The rate of flame propagation through a mixture depends on the temperature, the pressure, and the mixture composition (Grumer, 1991).
- When combustible gases and vapours are mixed with air or oxygen, in appropriate proportions, they have ignited if exposed to a source of ignition (Grumer, 1991).
- The following ignition sources are recognised: electrical sparks and arcs; open flames such as bunsen burner flames, matches, lighters, some hot water heaters; hot surfaces, hot vessels, exposed light filaments; lasers; catalytic and pyrophoric materials; and spontaneous or self heating reactions (source: Grumer (1991)).
- An obvious method of reducing fire has been to minimise the amount of oxygen in an atmosphere by dilution with inert gases such as nitrogen and carbon dioxide (Grumer, 1991).
- Once a reaction has reached explosion point it is unlikely that there is sufficient time available to have applied inert gases.

Agitation Problems (Incomplete Mixing)

- Problems with chemical reactivity have occurred through incomplete mixing or by the absence of mixing. This may have occurred when reactions were conducted between phases of different densities (Bretherick, 1990).

Adiabatic Systems

- Adiabatic and near adiabatic systems, which are thermally unstable, are considered as potentially hazardous and require great care (Bretherick, 1990).
- Particularly dangerous are those systems which possess a self-heating capacity.

Polymerisation Incidents

- Uncontrollable polymerisation reactions have lead to potentially serious incidents

Self-Heating and Ignition Incidents

- An extensive literature is accessible in relation to adiabatic self-heating incidents (see Bretherick (1990), p.1793).

Thermal Stability

- There may be a safety margin of only 10-20 ^{0}C between stable and runaway reactions (Bretherick, 1990). This may be controlled through minor modifications such as better catalysts or less agitation.

Specific Problems With Chemical Structures

- Evidence has been established of a relationship between the chemical properties of a substance, its chemical structure, and its toxicity (Rodricks, 1992; Manahan, 1991).
- Members of certain classes of compounds (for example organic compounds, grouped together because of structural similarities) have been shown to have caused similar problems (Rodricks, 1992).
- Bretherick (1990) conceded, however, that there are limited possibilities of predicting reactivity and stability merely from composition and structure.
- Instability in individual chemicals and reactivity in chemical combinations has often been associated with particular structure configurations "... such as high proportions or local concentrations of oxygen or nitrogen" (Bretherick, 1990, p.xxiv).

- How structure has contributed to toxicity is a new science and poorly understood.
- A significant issue has been that very small variations in chemical structure have resulted in quite significant differences in toxicity levels.

Health Problems Related to Dusts

Dust Contamination

- Many dusts are hazardous to health following inhalation
- Crawford (1992) claimed that certain dusts cause carcinomas; chronic lung disease; and respiratory complaints such as asthma
- Some dusts are fibrogenic having caused fibrotic change to lung tissue and having eventually poisoned the body systems. Examples of fibrogenic dusts are silica, cement dust, and certain metals, whereas toxic dusts include arsenic, mercury, beryllium, and lead, as well as cadmium, aluminium, antimony, copper, selenium, and zinc (Ryding, 1992; NOHSC, 1989).

Minimising Exposure to Respirable Dusts

- Grantham (1991) suggested a framework as first, substitution by a less hazardous substance; second, engineering out the hazard; and third, ventilating the workplace (see also Stranks (1992), Dewis (1991), Sherson and Breum (1991)).
- There is no theoretical ignition temperature for dust combustibility.
- Dewis (1991) recommended that it may be possible to dilute the particles by inducing large volumes of air to flow through the contaminated area. A problem with respirable dust is that not all dusts have been assigned exposure standards.
- NOHSC (1991) recommended that where no exposure standard has been assigned to a substance, which is considered to have a low toxicity and to be free from toxic impurities, the accepted exposure standard should be 10 mg/m^3, measured as inspirable dust (NOHSC, 1991).

Occupational Health Data in Relation to Dusts

- It has been demonstrated that the inhalation of mineral particles can lead to problems ranging from simple inflammatory reactions to fibrogenesis, or to carcinogenesis (Jolicoeur & Poisson, 1988).

Coal Dust

- The body has no method of metabolising coal dust and the health effects of inhalation may be pulmonary fibrosis and massive fibrosis (Grantham, 1991). The only known treatment is the removal of an individual from an exposure area.

Silica Dust

- In reported cases where silicon dioxide (SiO_2) was inhaled, a reaction from the pulmonary tissues has been triggered. This has caused pulmonary fibrosis, tuberculosis, or silicosis (Crawford, 1992; Sittig, 1991; Friedberg & Schiller, 1988).
- Exposure to crystalline silica may cause silicosis which may develop after a few weeks of very high exposure or after many years of lower exposures (Sittig, 1991). The disease may be progressive and fatal. According to Sittig (1991) very fine silica is even more hazardous.
- There has also been an increase in the incidence of lymphoreticular tumours in rats inoculated with silica particles (Friedberg & Schiller, 1988). The only known treatment is the removal of persons from an exposure area.

Asbestos Particles

- Health hazards associated with asbestos dusts have been reported from ancient times, however, many of the early warnings were ignored.
- Asbestos occurs in the forms commonly referred to as chrysotile asbestos or white asbestos, together with crocidolite (blue asbestos), amosite (grunerite: brown asbestos), tremolite, and some other forms such as anthophyllite, and actinolite
- Roggli, Pratt, and Brody (1992) confirmed earlier findings by Friedberg and Schiller (1988) that despite the dangers associated with chrysotile fibres, they did not accumulate in lung tissue to the same extent as other types of asbestos fibres and were more easily cleared from lung tissue.
- Friedberg and Schiller (1988) confirmed that the extent of cytochemical interactions between the fibres and the cellular matrices are in the order amosite> crocidolite> chrysotile.
- Sittig (1991) synthesised available studies on asbestos fibres and concluded that the size and shape of the fibres were important factors. Fibres less than 0.5 micrometres in diameter were most active in producing tumours.
- There has been wide agreement that no safe level of exposure to asbestos can be stated.
- There has been significant evidence of its carcogenicity (Crawford, 1992; Sittig, 1991; Friedberg & Schiller, 1988). Diseases such as asbestosis, mesothelioma, cancer, bronchial carcinoma, and bronchial-intestinal carcinoma occurred in individuals who had been exposed to relatively large amounts of asbestos fibres for extended periods of time (Boulle & Parks, 1993; Crawford, 1992; Roggli & Pratt, 1992; see also (83/477/EEC), Annex II).
- The fibres are deposited in tissues by sedimentation, diffusion, impaction, and interception in airways (Friedberg & Schiller, 1988).

- According to Crawford (1992) these diseases tended to occur when the dust particles were less than five micrometres in size.
- Another problem associated with asbestos is non-occupational exposure. According to Greenberg and Darcey (1992) the most important source of non-occupational exposure has been the release of fibres from existing asbestos structures, often in schools.
- The induction period for some asbestos related diseases may be as long as 40 years (Ryding, 1992; Quinlan & Bohle, 1991) and therefore, for many people, regulation may be too late.
- Disposal of asbestos has posed a major problem and no satisfactory method has been identified.

Synthetic Mineral Fibres

- The term synthetic mineral fibres (SMF) has embraced a variety of fibrous inorganic materials . Examples are fabrics, yarn, industrial textiles, insulation fibres, glass wool, and many more.
- They have been used as replacements for asbestos in some situations.
- Fibres are solid particles which are known to have caused skin irritation, but surprisingly with little evidence of lung disease (Harrington & Gill, 1990).
- Harrington and Gill (1990) conceded that a recent international study of SMF workers has failed to resolve the issue of whether these fibres are carcinogenic or not.

CONCLUSION

- Any chemical facility needs to be managed with special care.
  There is a patchwork of legislation in the area of chemical risk management.
  It is impossible and impractical to provide a summary of safety practices for handling and working with all chemicals in the educational laboratory.

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