

Chemical and Toxic Waste Disposal**Introduction**

There is no Australian Standard that applies to the handling of chemical wastes generated in a laboratory. There is legislation that applies to Dangerous Goods, Hazardous Substances, Radioactive Materials and Scheduled Poisons but chemical waste does not rate a mention. Generally the only information or guidelines provided are to comply with relevant Environmental legislation. The information in these notes is based on our experiences in collecting, transporting, storing and disposing of chemical wastes, especially those generated in laboratories.

Examples of Laboratory Generated Chemical Wastes

a) the first example is chemical waste generated as a result of a laboratory's normal activities and will include such things as “solvent wastes”, “organic waste” or “heavy metal wastes” etc.

b) second we have redundant laboratory reagents and deteriorated chemicals for example formaldehyde that has polymerised (ie turned to paraformaldehyde), or deliquescent or hygroscopic salts that have become wet and unusable as well as short life materials or bottles with no labels.

c) third is waste resulting from spills and accidents such as a broken mercury thermometer or absorbent used to mop up a spill. Broken or contaminated glassware and paper waste are also examples.

d) fourth is the big clean out of old and unwanted items from the chemical store, sometimes as a result of a purge by a newly appointed safety officer or lab manager, or the retirement of an academic who had a whole lab of strange and unusual research chemicals. This situation is very common in tertiary institutions and can present a wide range of unpleasant chemicals many in a state of deterioration or breakdown and is sometimes a very unsafe situation.

e) finally, we have chemicals for which a special licence or permit is required such as scheduled items or certain carcinogens and which are too much trouble to keep. Secondary schools for example have been issued lists of chemicals which are considered too dangerous to have in the school lab and the only option is to dispose of these chemicals. Examples are aromatic solvents, chlorinated solvents, mercury salts, arsenic and strong poisons like cyanides

All the above examples have in common the description: “Chemical Waste”. The disposal of these is subject to Environmental Legislation usually administered by a State

Environment Protection Authority or equivalent. Whatever the source of your waste chemicals, the handling and storage of these within the laboratory must be undertaken under the same rules and guidelines that the normal or non-waste chemicals are handled. We recommend strongly that the dangerous goods / hazardous class system is used for the correct storage, segregation and handling of waste chemicals.

It is most important to remember that the physical and chemical properties of your waste chemicals are identical with those of the "good" chemicals. Waste methanol is still a flammable liquid as is pure methanol and is still subject to the same set of rules you would follow when handling pure methanol or any other flammable liquid in the lab.

The Dangerous Goods / Hazardous Class System.

The most important criterion that has to be addressed when storing, transporting and generally handling chemicals including chemical wastes, is the hazardous chemical class of the individual chemical. The "class" of a chemical is an internationally recognised and utilised system for classification of hazardous and reactive chemicals as defined by the International Maritime Organisation (IMO), and the Australian Code for Transport of Dangerous Goods by Road and Rail. (the ADG code). All transport of dangerous goods within Australia is subject to the ADG code. The storage and handling of dangerous goods is subject to State level legislation. In Victoria it is the Dangerous Goods (storage and handling) Regulations. In common with both pieces of legislation is a recognition of the physical and chemical properties of chemicals that make them dangerous to transport and store. These properties include flammability, toxicity and corrosiveness. Because of these properties chemicals are assigned to a class from 1 to 9. Certain classes will be subject to segregation from one another because of potential reactions that result in a very dangerous situation such as an explosion, fire, or emission of toxic or corrosive gases. Any chemical or chemical compound that is assigned to one of the nine classes because of either physical and or chemical properties is by definition a "dangerous good". A dangerous good will have a class number, usually a "UN" number, a packing group and will require labelling that contains a hazardous class diamond. A working knowledge of the dangerous goods code is essential for anyone dealing with chemicals, including the storage and handling of chemicals in a laboratory and is *equally* applicable to waste chemicals.

The difference between Dangerous Goods and Hazardous Substances

Hazardous Substances legislation specifies how certain prescribed (ie listed) chemicals and chemical mixtures are labelled and categorised when actually being *used* within a laboratory and are more comprehensive and chemically specific as to the hazards of certain chemicals. The schedules of suspected and known human carcinogens are among the prescribed lists of hazardous substances. Risk and Safety phrases are required for labelling hazardous substances. Some chemicals are both dangerous goods as well as hazardous substances. Hazardous substances are generally an Occupational Health and Safety issue and the use of the material safety data sheet (msds) becomes mandatory.

The days of storage of your laboratory chemicals according to alphabetical order should be over. The layout and design of a chemical store, especially one servicing a laboratory, must be based on the segregation and appropriate storage guidelines as stipulated in the ADG code and AS 2243 now advises this.

Becoming familiar with the dangerous goods code is really only the first step in becoming a safer chemical user. A knowledge of the actual chemicals that you deal with is also important because within single classes, there are incompatible items. The best example is that of acids and alkalis. Both are class 8 (corrosive materials) which when mixed will usually produce a very vigorous reaction. Acids and alkalis must not be stored next to each other or allowed to come into contact with each other. Other examples show that some chemicals within the same class have different reactions, such as class 4.3, dangerous when wet. Sodium, sodium amide and sodium borohydride are all class 4.3 but all have different reactions with water. Sodium reacts almost explosively with evolution of hydrogen, sodium amide emits ammonia on contact with water and sodium borohydride emits hydrogen and may catch fire. The message here is "know your chemicals" which is part of assuming a *proactive* approach to laboratory safety as far as handling chemicals is concerned.

Naturally not all chemicals are dangerous or hazardous and these are termed "non hazardous." The ADG code does not apply to such chemicals and therefore there are no transport, packing, labelling or segregation rules that need to be applied. Chemical wastes can still be non hazardous however and the EPA requirements must still be met (see later)

How do you determine whether or not a chemical is a dangerous good or a hazardous substance? These days laboratory chemicals will have all DG and hazardous substance (where applicable) information on the label. The absence of this is usually indicative of a chemical being non-hazardous. Older chemicals were not always well labelled so be careful. An excellent source of information on laboratory chemicals is the Ajax Fine Chemical Reference Manual and its equivalent publication from Merck. These are free and available from your laboratory supplier and now are available on disk. Most laboratory chemical suppliers have catalogue and safety information available on disk. Also the ACTDG two volumes list a great many chemicals that are transported by road, rail, sea and air and is the reference of choice for industrial chemicals. Remember that many laboratory chemicals are also handled in bulk so information about virtually any chemical in use should be found in the ACTDG. Non hazardous chemicals are *not* listed in this volume however. Proprietary software products such as InfoSafe, ChemAlert and Safety Label Pro are also available at a price.

Chemical Wastes by Class

a laboratory is a workplace, not a storeroom. Chemicals and chemical wastes generated in the laboratory are best stored in an area dedicated to storage. As waste chemicals generally retain the same properties that made them hazardous when fresh, they must also be stored according to their hazardous class.

class 1-Explosives

The storage and handling of explosives is beyond the scope of this lecture however some chemicals do become explosive or form explosive compounds on storage or ageing. The two most common examples are dry picric acid and the peroxidation of ethers. Both situations are controllable once some knowledge of the reactions involved is gained. Picric acid is an explosive solid when dry. It must be stored and transported, by law, containing at least 30% by weight of water. When wet it is a class 6 toxic solid. When dry it is an unstable explosive. Metal picrates are especially unstable and picrates and dry picric will explode on heating or on contact causing friction such as can occur when a ground glass stopper in a reagent bottle is twisted to open it. Picric acid is readily soluble in hot water and any dry crystals on a bottle can be washed off. Ethers on storage can form explosive peroxides that appear as white crystals. Never use ether that appears to contain such crystals. Oxidation occurs due to exposure to air and as the reaction is a free radical one, it is accelerated by UV from sunlight. Store ether in dark glass or metal containers. Ethers that are reused and redistilled are most at risk as the peroxides tend to concentrate. Store your ether with a reducing agent if possible or in a metal tin. Use copper gauze or ferrous sulphate or hydroquinone. Test for the presence of ethers using a 10% solution of potassium iodide. Peroxides will oxidise the iodide to iodine giving a brown colouration. Use of starch indicator will highlight the iodine. There is also a method on page 23 of AS 2243.2 for peroxide detection. Diisopropyl ether is reputedly much more prone to form peroxides than diethyl ether. Petroleum ether is not an ether but usually different boiling range blends of hexane. If you suspect that you have explosive compounds in your laboratory, make contact with the appropriate authority in your state. Fire brigades are not trained to deal with explosives. Usually there is an explosives branch of the Victorian Workcover Authority.

class 2-Gases in cylinders

Cylinders must be secured in an upright position and chained or clamped. Use only the appropriate regulator and piping. The use of copper tubing for acetylene for example will result in the formation of explosive copper acetylide. This is a brown powder which is very unstable and will explode. Consider having all incoming gas lines bunched together so that a quick shut valve that shuts off all lines at the same time can be installed. Remember also that gas cylinders are easy targets for vandals so secure them in a tamper proof location. We recommend that you do not purchase any rare or unusual gas cylinder without a guarantee that the seller will take the empty or partly empty cylinder back. The disposal of gas cylinders is a specialised and very expensive exercise and can be avoided.

class 3- Flammable liquids

These should be stored in a flame proof cabinet that is capable of retaining any free liquid from a leaker and that is explosion proof. Venting of vapours from the cabinet should ideally be external rather than back into the lab. If a whole room or large dedicated storage is used any lighting within the room must be flame proof. Do not store flammable liquids inside a refrigerator unless the fridge is specifically flame proofed. The flash point of diethyl ether is about minus forty degrees Celsius while a fridge normally runs at four degrees. You have not made the storage of the ether any safer. It should be stored in flame proof surroundings. Class 3 compounds are not compatible with any class 4 or 5 compounds, so do not store the sodium and potassium in the flame proof cabinet. These cabinets are also not

suitable for storage of class 8 corrosive liquids although the two classes are compatible with the exception of nitric acid which is a secondary class 5 oxidiser.

class 4.1 Combustible solids.

examples are sulphur, naphthalene, charcoal, red phosphorous etc. They will not catch fire but will burn if ignited. Therefore store away from the flammable liquids and ignition sources.

class 4.2 Spontaneously combustible solids

white phosphorous is the most common member of this class and will catch fire on contact with air. It must be stored under water and preferably stored away from all other hazardous goods in a flame proof environment. Secondary packaging such as inside a metal keg is advisable. Treat 4.2 compounds as flammable but do not store them anywhere near flammable liquids. White and yellow phosphorous are the same compound.

class 4.3 Dangerous when wet.

do not store these in an area protected by water sprinklers. They are incompatible with classes 5 and 8. They are best stored in metal containers. Some of these compounds have different reactions with water ranging from explosive with emission of flame to emission of a poisonous or flammable gas. Be aware of the potential reaction. Do not store sodium and potassium under kerosene; use paraffin.

class 5.1-5.2 Oxidisers and Organic Peroxides.

these compounds are incompatible with all other classes except toxics (class 6). They must never be allowed to come into contact with organic materials such as oil, solvents or even paper as a fire will result. They are generally very reactive and can cause explosive reactions especially strong oxidisers such as perchloric acid. They must be kept away from sources of heat and ignition and are best stored in a separate area of the store or in a separate store or cabinet. Common oxidisers include nitrates and nitrites, dichromates, bromates and chlorates and calcium hypochlorite (swimming pool chlorine).

class 6- Toxic or Poisons

These are incompatible with corrosives if the corrosive is an acid and the toxic is a cyanide. Otherwise they are compatible with other classes and can be used as buffers between incompatible classes for small stores. They can be stored on shelves rather than in dedicated cabinets although it is advisable to store strong poisons such as cyanides, arsenic and mercury salts in locked cabinets. This class includes infectious and biologically active materials.

class 7- Radioactive Materials

. Radioactive wastes often are mixed with a solvent or poison whose properties are of more concern than the radioactive emission. The isotope, half life and particle emitted is essential information when dealing with these materials. The type of radioactivity indicates the type of shielding required and it is not enough to assume that lead for example will shield radiation. Lead will only shield gamma radiation eg X-rays and is ineffective for beta and high energy alpha emitters. Observe the "holy trinity" of radioactive safety ie time, distance and shielding. Minimise the time of exposure, remember that the inverse square law applies to the distance travelled by radioactive particles and use the appropriate

shielding. Beta particles are shielded by aluminium, alpha emitters are shielded by concrete or brick and usually only travel short distances. In any case look up the isotope. Many uranium and thorium salts are class 7 compounds as well as class 6.

class 8- Corrosives

The main concerns with storing these compounds are the irritating and corrosive vapours they emit and their usually vigorous reactions. Most are also hazardous substances. They should be stored in an area vented externally to enable dissipation of vapours and in a cabinet inert to acids and able to retain any liquid spill. The class 8 compounds are compatible with class 3 compounds but it must be noted that some class 8 acids, specifically nitric and perchloric acids are also strong oxidisers and therefore incompatible with class 3 compounds. Mercury is a class 8 compound because of its corrosive reaction on metals and metal alloys especially aluminium.

class 9- Miscellaneous.

these are compounds with dangerous properties but that do not fit into any one of the lower classes. The most common class 9 compound is polychlorinated biphenyls (PCB). Dry ice or frozen carbon dioxide is also a class 9. There are no special storage requirements for class 9 materials.

Labelling Requirements

One of the biggest problems encountered when collecting waste chemicals for disposal is the labelling. The purpose of a label is to provide information, in an unambiguous manner, on the contents of a bottle. Anyone reading the label should be able to understand and read it whether or not they have a training in chemistry. The essential elements of a label are the name of the chemical, not the chemical formula. The use of a formula is optional and is secondary to the chemical name. The concentration, solvent if applicable, date of preparation, identification of preparer, any warnings applicable and an ingredient list if applicable. Hazardous substance labels also require risk and safety phrases and first aid information. The importance of the date of preparation would be applicable in the case of an ether for example. The label must be affixed in a permanent manner. Code words or labels that only the preparer can read are not acceptable. Remember that one can't put too much information on a label and the reverse is on many occasions the case. In our experience the worst labellers seem to be tertiary institutions and the best are secondary school laboratories.

Examples of bad labels we have encountered are " ?", " this is stuffed" (and variations), " Dr Jamiesons' Brew", " Contains acid", " no idea what this is at all" , "this belongs to Mary", "potassium something". The worst label of all however is the label containing the wrong information. Other bad labels which are very common are the old favourites " Solvent Wastes" and "Organic Wastes".

The use of second hand bottles and containers to hold waste is common as is the practice of leaving the original label unaltered on the bottle!

Chemical Spill Kits.

For any liquid (except mercury) we have found that the best all purpose single use absorbent is vermiculite. It is non reactive, inorganic and absorbs both aqueous and solvent based liquids as well as oils, acids and alkalis. Sand is not absorbent at all and has no real place in a laboratory. Vermiculite can be made more appropriate for specific chemicals with the addition for example of soda ash for acid spills, or citric acid for ammonia spills. Commercially available spill kits are available for many chemical types but their main disadvantage is that they are single use and single chemical type. For mercury spills we have found some of these spill kits to be good although most seem to simply provide a container in which to store the mercury. The use of sulphur for mercury spills is a waste of time as sulphur does not actually react with the mercury and only creates a bigger mess. Fine zinc granules can be used in the absence of a proprietary absorbent; a solid zinc amalgam will form on contact which can be easily collected. When collecting mercury, use a container that is appropriate. A plastic winchester for example, not a glass coffee jar. Mercury should have some water placed over it and be stored in an air tight container. The contents of many commercial spill kits consist of readily available items such as disposable gloves, plastic bags, goggles etc. These can be obtained for a fraction of the cost and together with vermiculite and a neutraliser if necessary a cheap alternative can be put together.

Waste Containers.

The use of glass is generally not recommended. Plastic pails with lids are fine as are heavy duty plastic carboys, especially those that are approved to hold dangerous goods. These types have a stamp either on the top or base if they are DG approved. If metal drums are to be used try to use heavy duty types such as those that have contained a chlorinated solvent. Chlorinated solvents that contain water will generally produce free chlorides which will corrode normal metal drums such as alcohol or xylene drums. Do not place any waste acids into any metal drum or container. Always prepare a new label for any second hand container and remember to remove the old label.

Legislation Requirements for Waste Disposal

All States now have an Environment Protection Authority or equivalent administering an Environment Protection Act. In common with most States is the requirement for transporters of prescribed wastes to be have permitted vehicles, for a docket system to be in place to enable the “ cradle to grave “ philosophy for waste tracking and licensed disposal sites. In Victoria such legislation was the first in Australia. It is an offence to use a transporter that does not hold a permit to transport prescribed chemical waste and the disposer is as much an offender as the transporter. The waste must be transported to a disposal site that is licensed to accept that type of waste. In Victoria such sites are Schedule Four sites and include incinerators and landfills. The responsibility for the waste remains with the disposer until the disposal site has disposed of the waste. NSW is doing away with the docket tracking system in 1999. All other States use the a docket based tracking system. If you do not receive the appropriate copies of the docket when your waste is collected then the transporter is most likely to be unlicensed and everyone is breaking the law. Laboratory chemicals are a prescribed chemical waste as is contaminated soil or a broken thermometer.

Summary

A working knowledge of the IMO/ADG system of dangerous goods chemical classification forms the basis of safe transport, storage and handling of chemicals. The system is equally applicable to chemical wastes, both at an industrial level and at the laboratory level. All users and handlers of dangerous goods and hazardous substances including chemical wastes are well advised to acquaint themselves with the specific reactions of any chemicals they commonly use and handle in their laboratories. Correct storage facilities coupled with the ADG code guidelines will lead to a safer working environment for all concerned. Take a proactive approach to chemical safety as accidents do and will happen.

SELECTED BIBLIOGRAPHY

Commonwealth of Australia

Australian Code for the Transport of Dangerous Goods by Road and Rail. 6th edition 2 vol
(also available on CD-Rom)

Pitt and Pitt Handbook of Laboratory Waste Disposals (Ellis Norwood p/l)

Bretherwick L. Handbook of Reactive Chemical Hazards (Butterworths)

ibid, Hazards in the Chemical Laboratory (Butterworths)

Porteous A. (*ed*) Hazardous Waste Management Handbook (Butterworths)

National Research Council (USA). Prudent Practices for Disposal of Chemicals from
Laboratories (National Academy Press)

Armour M.A. Hazardous Laboratory Chemicals Disposal Guide (CRC Press)

Lewis R.J. Hawleys Condensed Chemical Dictionary (Van Nostrand Reinhold)

Diberardinis L.J. *et al.* Guidelines for Laboratory Design (Wiley)

Ajax Chemicals Fine Chemicals Reference Book (available from suppliers)

Lunn and Sansone Destruction of Hazardous Chemicals in the Laboratory (Wiley)

Treatment of Some Laboratory Wastes , In-House.

the following methods should only be attempted by experienced and preferably qualified personnel. A general outline of the method is given and complete detailed methods will be found in some of the books listed in the bibliography. Prior to attempting any treatment of laboratory wastes, it is strongly advised to study the reactions that will be occurring.

acids and alkalis : can be treated simply by dilution or by neutralisation. Do not attempt either with perchloric acid or concentrated sulphuric acid. Dilute acid streams can be treated with sodium hydroxide solution at 10% concentration or solid sodium carbonate. Ammonia solutions can be easily neutralised with citric acid. The use of hydrochloric acid to treat ammonia results in the copious white ammonium chloride fumes which are harmless but their appearance is startling to the unwary. For hydrofluoric acid use calcium carbonate rather than sodium hydroxide. Insoluble calcium fluoride will precipitate. Do not attempt to dilute or neutralise the following: acetic anhydride, acid chlorides, chlorosulphonic acid, any fuming acid, concentrated sodium or potassium hydroxide.

metal solutions: many metal solutions can be precipitated as insoluble inert sulphides eg. mercury, arsenic, lead, zinc, cobalt and barium. Nickel, iron, manganese, copper and magnesium can be precipitated as insoluble hydroxides. The sulphides are precipitated using sodium sulphide solution at alkaline pH, the hydroxides using ammonia solution. Some metals will precipitate with either reagent although mercury is best precipitated using sulphide. Thioacetamide in hydrochloric acid is used for arsenic compounds. (See Armour : Hazardous Laboratory Chemicals Disposal Guide).

organic solvents : little can be done in the laboratory apart from keeping halogenated solvents separate from non-halogenateds. Evaporation in a fume hood of small volumes of volatile solvents can be attempted but be careful with ethers and peroxides and don't use direct heat.

cyanides: treatment with aqueous chlorine in alkaline solution is very effective provided you have a good spot test for cyanide to test for completion of reaction.(Silver nitrate is good provided there are no free chlorides otherwise use the longer and more involved Prussian blue method) The cyanide must be made fairly strongly alkaline prior to addition of chlorine which can be in the form of fresh sodium hypochlorite or solid calcium hypochlorite. The former is preferable as it is not an oxidiser.

oxidising agents: a simple reducing mixture for oxidisers is ferrous sulphate and dilute sulphuric acid. Other good reducing agents are sugar for permanganate solutions and sodium metabisulphite for chromium VI, nitrites and chlorates.

