

RISK ASSESSMENT AND CONTROL OF SMALL CHEMICAL SPILLS!

- WHAT THE BOOKS MAY NOT TELL YOU

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In this brief discussion a number of ideas will be presented; some may be a bit controversial and not necessarily total answers. There are few total answers to chemical spills because each chemical spill may have a differing set of parameters; hence a requirement for a rapid risk assessment in each case. The main danger in most small chemical spills is vapours. If the vapours can be controlled then so can most other immediate hazards including ignition.

One definition of a small chemical spill is "can you handle the situation safely without outside assistance?" Another definition is "an incident which results in an uncontrolled chemical exposure". Many spills involve waste which may be of unknown chemical composition. Spills involving waste can be caused by a slow gas pressure build-up with occasional spectacular aftermaths. Large chemical spills tend to be of known composition and are usually in industrial, transport or storage activities.

When attending a chemical spill one should remember the six "Kiplings" described by the famous "author". **WHERE ? WHAT? WHEN? WHY? WHO? and HOW?**

These need to be asked repeatedly. The first time is in the information gathering part of the response. Responses need to be carefully planned with the more accurate information you can obtain the better. "**Where?**" may sound a little obvious but not necessarily so. For example a multiple spill in a photographic processing room may have the capacity to generate cyanide gas. Such rooms are usually well ventilated with the next question being where to? An assessment which you need to make quickly: The air-conditioning system and/or exhaust ventilation: where will the vapours end up?? - To turn off or not to turn off and when, or to use portable auxiliary ventilation: a seminar in itself!

Another example could be in a cleaner's storeroom. A collapsing shelf has the potential to result in the mixing of incompatible chemicals. The mixing of chlorine water (a bleach/disinfectant) and the oxalate compounds used to remove water scale off toilets and showers may release chlorine gas. The mixing of chlorine water and ammonia cleaning chemicals can also generate poisonous gases.

Sometimes when you think that you know what the spill is, you may not. In Hong Kong there is an all too frequent practice of re-using containers with the original label intact. An example of this being an English label stating the contents as nitric acid and hand writing in Chinese stating the contents to be glycerol. A number of issues arise apart from what is it? A spill could arise from a vigorous reaction due to mis-use or as simple as is the new chemical safe to store in this container? [is it compatible with the materials used to manufacture the container?] This case may have been alright though one hopes that the refillers washed out the container properly before re-use. Thus go back to "**WHO?**" Local knowledge is imperative and local workers can often

provide valuable information towards your assessment. In your assessment there also needs to be an evaluation on how reliable is this "local knowledge"? If you do not know then you need to upgrade your response.

As a part of risk assessment for new laboratory research projects or for new processes, both spill potential of chemicals and waste disposal need consideration. The use of toxins is widespread in Biomedical research and regularly little is known about these compounds per se. Much of the safety information is derived from analogues. A toxin with an LD₅₀ of 5mg for a 70kg person makes that compound about 10 times more poisonous than cyanide. In this instance only 150µ gm in solution was available per container at a cost of HK\$2,500 which drastically reduces any risk.

In some cases where e.g. snake venoms are being purchased, the spill section of the Material Safety Data Sheet (MSDS) may read something like this "sweep up, place in a bag and hold for waste disposal". This may suffice in a tightly controlled laboratory system as a big danger is an allergic response from repeated exposure. A hidden danger is inoculation through a puncture wound, with the result perhaps being akin to a snake bite. One should ensure antivenin is obtained before the venom arrives.

A further part of research assessments comes back to "Who? Where? How?" This needs to be looked at because even when low concentrations of toxic substances are utilized, there may be a less experienced person measuring out these compounds from stock bottles. This is where the real danger is likely to occur. Our investigators must sign that they have and have read the MSDS for appropriate chemicals. Their team needs to understand the hazards.

This all goes back to planning and readiness, and knowing that knowledge is power. Every situation is different with a careful assessment is required for each spill.

In some laboratory spills, particularly in "biological" or "biomedical" situations there is the possibility of low levels of radioactivity being present and/or perhaps biologically active contaminants. I suggest that if you do not know, to treat the spills as if these conditions may exist. Basically the initial clean-up is as per a toxic chemical and later exposed surfaces can be decontaminated. As many disinfectants are strong oxidisers they can be dangerous for use on an organic / biological spill. Unless a special laboratory is involved, the Biological Safety Level should be at BSL II or less. Beware of trekking spills which spreads contamination.

Table I shows a suggested flow chart for spill clean-up methods and is NOT a safety level indicator. Use proper Protective clothing and consider the use of self contained breathing apparatus. SCBA is strongly recommended particularly for organic solvent spills and for spills of unknown compositions.

Fast planned clean-up lessens exposure and down-time. Proprietary spill "neutralising" kits require careful consideration. A likely scenario is the dropping of a 2.5 litres Winchester bottle. If you know the contents (the label may be destroyed) you are lucky. Check before proprietary spill neutralising kits are purchased that they have sufficient capacity for the type of spill that may occur in your location. Some may not!

Alternatively consider having separate sealed 3 to 4 kg containers of:

A: Soda ash -> add to acid spill till fizzing stops

B: Citric acid -> use the whole lot on 2.5 litres alkali spill

Initial diking and careful addition of water can be advisable.

C: Add the whole container of "a vapour absorb" carbon powder or carbon/graphite powder to absorb organic vapours (Messy). Do not put on oxidising substances. The proper use of "carbon" powder can be extremely effective on organic liquid spills. This traps vapours which are the prime causes of poisoning by inhalation and it is the vapour which catches fire. The flames and smoke generated from a fire of e.g. a 4 litre toluene spill are massive and have the capacity to rapidly deplete oxygen from the air.

The use of an appropriate foam fire extinguisher may temporarily control vapours. Special foam may be required for chemicals such as alcohols because the foam may rapidly break down.

Be particularly careful if spilled liquid is capable of forming acid gases which may be inhaled. You know how an acid burn weeps on your skin; in lungs, which are very sensitive the potential to kill is present, even with a spill of strong acetic acid.

Spills in chemical safety storage cabinets can be awkward to clean up. Risk assessments need to be done at the storage planning stage. Is the likely spill a small toxic liquids spill or a larger flammable liquid spill? For a small toxic spill one may consider to have absorbent socks placed at the bottom, or for the possibility of a larger release of chemical, the use of a false bottom and appropriate pump can make any spill clean-up less arduous and safer.

The use of absorbents such as sand, vermiculite and absorbent socks are all documented elsewhere. A couple of related ideas are of note. Where a substance such as toluene or thinner has spilt, and water is present, using small "oil boom" socks (skimmers) can be effective. If a solvent is flowing down a gutter with water, these skimmers will selectively absorb the solvent. With oily substances the use of treated wool cushions can be very effective.

Prevention is better than cure. A method of minimizing small spills is the use of "safebreak" or as I prefer "breaksafe" bottles. Commercially some 50 chemicals are available in "safebreak" 2.5 litre bottles. One process I have seen has the bottles coated with plastic at elevated temperatures (naturally before filling). Consumer cost resistance may be a major reason why these have not really caught on. Another reason may be some disappointment in performance that although the splashing is controlled the broken bottle may still leak. Actually this containment is a good start.

Many "nasty" chemicals do not come in these protected bottles. The Chinese University of Hong Kong "commissioned" for the lack of a better word a polymer consultant to develop an "in situ" coating solution. There are companies overseas who will cold-coat bottles/reaction flasks by dipping or wrapping - the catch is that the bottles have to be shipped to companies' factories. The new coating mixture, now Mark IV version, was developed in Melbourne and trials look promising. The bottles are not as aesthetically pleasing as the commercially available ones. The stability of the coating is still satisfactory after 18 months.

An interesting outcome is because the plastic coating is put over the existing label, in all ten tests the label remained readable: even if this is the only outcome from this project, the overcoating of labels maybe worthwhile of further research. This method may also help with the problems of loose and deteriorating labels in Dangerous Goods Stores. For this purpose we will trial the mixture with a smaller amount of thickener.

Who? cleans-up spills needs assessment. Persons who wear self-contained breathing apparatus need to be well trained, and be shown to be medically fit for the task. I believe that unless you have the time resources for regular training that you do not put your staff into air-tight "space" suits. The use of these suits are for highly trained, physically fit experts.

At the risk of being admonished under equal opportunity regulations I believe that pregnant women move quickly away from chemical spills as the "unknown" can cause worries later.

With regard attendances by the media I will again (and with good intentions) risk getting into hot water. There are reasons why control of the media at the site is essential. A spill may have absorbed and may leach out or ignite. Camera flashes can ignite organic vapours. If something goes wrong the area may have to be evacuated rapidly thus only the minimum number of experienced persons should be present. If it is decided to allow the media to enter, the numbers at any one time should be restricted.

There is concern that the press at the scene of an incident could, through over-enthusiasm, place themselves and others in danger. A system of coordination should be worked out that places safety first, while respecting the interest of the affected public's right to know. There is the further concern that some workers might, out of the fear of adverse publicity that could arise through possibly less than accurate reporting, choose instead to deal with potential hazards without seeking assistance.

Media questions are often demanding. Answers may not be immediately known. A further reason for giving careful replies is the possibility of making a legal admission. This is not an attempt at concealing information because eventually the facts will have to be revealed. One issue is if fault or blame is alleged and/or admitted your insurance company may abandon you! Read your policy! Another issue is it is wrong to admit or imply guilt at this stage. Your Public Relations staff should be involved at an early stage.

I finish by going back to the first question: "Can you handle the situation safely?" If not you must call in the experts (Fire Services) immediately and accept the fact that both fire engines and ambulances will attend. Also

accept that the media have excellent communication facilities and will arrive quite soon after your call for assistance. Not to call for appropriate assistance may later be classified as negligence. I suggest the best way to avoid the associated publicity is to minimise the potential for chemical spills and to have a limited in house self-help system available!

Table I.

Flow chart for choosing the suitable materials for clean up.

[This does not cover personal protective equipment (PPE)]

<i>At the edge of a liquid spill slowly squirt about 10ml from water squeeze bottle, or from a squeeze bottle of aqueous universal indicator</i>	
Observation	Probable major component
if water floats on top	Halogenated hydrocarbon
if spilled material floats on top	Petroleum like compound
if goes fizz/spat	Strong acid or strong base; may be anhydride (document fully if you spill e.g. acetic anhydride)
if water disappears (miscible)	Acid or base or polar substance e.g. alcohol
drop on a small pinch of a bicarbonate (in spill kit) strong fizz/spat	Acid spill

This should help you choose the most applicable clean-up material which you have available.