Safety with CORROSIVE CHEMICALS

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Introduction

The Factories and Commercial Premises Act 1981 requires occupiers to report to the Department of Labour any accident causing "serious bodily injury" that is, any injury necessitating an absence from work for 48 hours or more.

From these reports it is clear that corrosive chemicals, either acids or alkalis, are involved in the majority of chemical accidents. Although many of these accidents do not result in long-term absence from work, the potential nevertheless exists for severe injury.

Corrosive chemicals are used, in one form or another, in the majority of New Zealand factories. Thus many workers are potentially at risk.

This booklet outlines the various hazards posed by corrosive chemicals and the safe work practices necessary to minimise those hazards.

Effects on the body

The most serious effect of acids and alkalis is the burning and destruction they cause to body tissues. The eyes are particularly vulnerable to such damage. The severity of injury depends on the concentration of the corrosive material and the length of time it is in contact with the body. Thus concentrated acids and alkalis present a much greater hazard than dilute acids and alkalis.

Inhalation of the mists of corrosive chemicals or ingestion (swallowing) of liquids can also be

.

Worker wears face mask to avoid breathing dust while weighing solid caustic soda

harmful. Ingestion of corrosives causes burns to the sensitive lining of the mouth, gullet and stomach. Inhalation of corrosive mists (or dusts) causes irritation and burns to the inner lining of the windpipe and lungs.

In addition to the corrosive effects on the body, acids with oxidising properties, such as nitric acid, can also present a fire hazard.

Hazard assessment

In many premises where corrosive chemicals are used, workers fail to appreciate the hazards such chemicals pose. This may stem either from poor training and instruction, for which the employer must accept responsibility, or from an attitude of over-familiarity on the part of workers.

Clearly, employers and workers need to assess the ways in which hazardous chemicals in general, and corrosive chemicals in particular, are used within their premises as the first step towards deciding whether current methods of handling and use are safe.

They need also to take account of the nature of the hazards posed by each of the corrosives used and the first aid measures applicable when an accident involving that substance occurs.

Finally, they should assess whether protective clothing and equipment is adequate for the work, and whether it is being worn and used correctly.

This assessment of workplace safety can of course be extended to include many different hazardous situations. It is likely to be most effective if both management and workforce are involved together.

Transport and delivery

Large volumes of corrosives are most often transported in bulk tankers or tank wagons with capacities of 3000 litres or more. At the factory site, transfer is then made into large-capacity storage tanks.

The transport of bulk corrosives must be in accordance with the Toxic Substances Regulations, 1983 and its Amendment No. 1 (1986/363). These regulations relate to bulk tankers and tank trailers, fixed bulk storage vessels, labelling of these vessels and requirements covering transfer procedures.

The transfer stage represents the period of greatest risk. Workers can be splashed with corrosives during pumping or when connecting or disconnecting lines at the tanker or storage tank inlet valve. To avoid this:

(a) Care must be taken that pipes are connected to the correct valves so that the intermixing of reactive or incompatible chemicals is avoided.

(b) All equipment used in bulk transfers must be checked periodically by competent personnel. Items checked should include hoses, pipes, glands, clips and pumps.

(c) Workers must wear adequate and sufficient protective clothing and equipment.

(d) An emergency shower must be easily accessible. Its operation must be regularly checked.

(e) After the delivery, all equipment must be thoroughly decontaminated by washing with water.

Protective clothing is worn when unloading caustic soda from bulk tanker.

All containers used for transporting corrosive liquids must comply with the testing procedures set out in NZS 5433:1983 *Code of Practice for the Transport of Hazardous Substances on Land.* Containers must carry the appropriate labels.

Smaller quantities of corrosive chemicals are usually transported in plastic or glass carboys of up to 20 litres capacity. Under normal conditions these containers are robust enough.

Glass will not withstand rough treatment, however, and the combined effects of exposure to weather and contact with concentrated corrosives over a period of time can cause plastic containers to become brittle.

Glass containers must be transported in suitable carrying baskets made of wire or wood rather than carried by the neck. Containers must be handled with care and not dropped or manhandled.

Above: After delivery, all equipment is thoroughly hosed down.

Storage and transfer

Important rules for storage are:

(a) Containers should be stored in an area secure from the possibility of physical damage and with good natural ventilation.

(b) Containers must be stored out of direct sunlight.

(c) Containers should be stored at a convenient height for handling; high shelving increases the risk of containers being dropped.

(d) Containers of incompatible chemicals must be separated in storage.

(e) All containers must be clearly and indelibly labelled.

Take special care when decanting from bulk containers into smaller vessels. These vessels should

Below: 20 litre plastic carboy commonly used for storing corrosives.

be closed receptacles rather than open containers such as buckets. Experience has shown that corrosive liquids in an open container can be easily spilt during transfer.

If liquid corrosives are stored in drums, use a drum pump for transferring the liquid to a secondary container. This method ensures a closed system between the drum and the container.

When planning work procedures, ensure if possible that corrosives are stored within a reasonable distance of the site where they are to be used.

If buckets are used for conveying corrosive chemicals, the following basic rules should be followed:

(a) The distance a worker is required to carry a bucket of

Above right: Drum pump (electrically powered) ensures the safe transfer of corrosive liquid from the drum to container.

Below: Glass container is put into rubber bucket for safe carrying.

corrosive chemical should be minimal (preferably not more than 3 metres).

(b) Workers must wear protective overalls (preferably all cotton), rubber boots, PVC gloves and safety glasses.

(c) The operation should not be hurried. The supervisor must not only ensure the worker has sufficient time to do the job safely, but must provide adequate training (see below).

(d) Buckets should not be filled more than half full.

(e) Caustic soda on gloves, boots or floors produces *a very* slippery surface. If spills occur they must be cleaned up immediately.

Where a worker is using more than about 20 litres of corrosives er shift, management should provide a pump and pipeline to replace the bucket operation.

Protective clothing and equipment

Adequate protective clothing for use when handling corrosives will include some or all of the following items, depending on the nature of the work being done:

Gloves

These should be of PVC, neoprene, rubber or other acid-resistant material. Fabric gloves, e.g. of cotton, provide no protection against corrosive liquids.

Footwear

Rubber of PVC gumboots are appropriate for handling bulk liquids. Otherwise, strong safety shoes with

Above: Worker wears full protective clothing, i.e. face shield and goggles, rubber gloves, PVC suit and gumboots.

Facing page: Eyewash operated by pressure from forehead, leaving hands free to remove contaminated clothing.

soles resistant to attack by corrosive liquids are more practical. Do not tuck leggings into gumboots or other footwear.

Facial protection

Depending on the work, safety glasses with side shields, goggles, or a face shield with a movable visor may be appropriate. It is essential that good vision be maintained by regular cleaning or replacement.

Body clothing

For bulk work, such as the unloading of tankers, a PVC suit is essential. Otherwise, PVC aprons should be worn when handling smaller quantities of corrosives.

It is important that all necessary items of protective clothing are worn, even when there is no apparent danger.

Eyewashes and showers

Eyewashes and emergency showers are essential items of equipment for workers who have to handle corrosive chemicals.

Emergency shower, operated by lever action

Eyewashes should be of a type which operate automatically, leaving both hands free so that the eyelids may be held open and rinsed thoroughly. Such devices usually work by pressure from the forehead on a bar.

Emergency showers should be well signposted and the surrounding floor kept clear of obstructions. Showers may be operated by a simple chain or lever action or, preferably, by standing on a pressure plate. In the former case the valve should lock in the "on" position so that once activated the water flow will continue, leaving both hands free to remove contaminated clothing.

Eyewashes and showers must be tested and maintained regularly to ensure they will work properly in an emergency

Dealing with spillages

These are the steps to take when corrosives are spilt:

(a) Wear appropriate protective clothing.

(b) Remove bulk contamination by pumping if possible or by absorption with inert material (e.g. vermiculite). Dispose of the used inert material safely e.g. by burial in a landfill area.

(c) Neutralise the residue, having regard to whether it is acid or alkali. A suitable neutralising agent for an acid spillage is soda ash (sodium carbonate). For an alkali spillage, dilute hydrochloric acid is appropriate.

(d) After removal of most of the material, wash the contaminated area with copious quantities of water, flushing it to the drain.

(e) Adequately ventilate the decontaminated area.

(f) Clean up and decontaminate all protective clothing and equipment, and replace in store.

(g) If the spillage situation becomes unmanageable, call the Fire Service.

(h) Consult local authority bylaws to determine what particular provisions apply, if any, to the disposal of corrosive wastes.

It is important that personnel are fully trained in the procedures to adopt in the event of spillage.

Notes on common corrosives

Brief notes on some of the more commonly encountered corrosive chemicals' are given below with emphasis on their uses, particular properties and hazards.

Sulphuric acid

Sulphuric acid is used extensively in New Zealand in the fertiliser industry,

First aid measures

Basic first aid measures for accidents involving corrosives are:

Eyes

Wash out with copious quantities of water for a minimum of 15 minutes. Always get medical attention after eye contamination.

Skin

Remove contaminated clothing. Drench the affected area directly and as rapidly as possible with copious quantities of clean water. This is best done using the emergency shower. Obtain medical attention.

Ingestion

If conscious, the affected person should be made to drink large: quantities of water- to dilute the effect of the corrosive. Vomiting should not be induced. Obtain medical attention immediately.

Inhalation

Mists of corrosive liquids, and sometimes dusts, are hazardous if inhaled. Move the exposed person to fresh air immediately. Start artificial respiration if the victim's breathing has stopped. Obtain medical attention.

and is usually manufactured on site, starting with raw sulphur.

Other uses for this acid are in tanning processes, electroplating, soap manufacture, general industrial chemical processes and as the electrolyte in storage batteries.

Concentrated sulphuric acid is a heavy, oily liquid. Containers of sulphuric acid can be deceptively heavy. This has resulted in the dropping and fracture of containers and workers being splashed with acid.

Like most common acids, sulphuric acid reacts readily with many metals, giving off hydrogen gas. Mixtures of hydrogen and air can explode on ignition.

Concentrated sulphuric acid has a very strong affinity for water and much heat is evolved when the acid is diluted. For this reason *always add acid* to water-never the reverse.

The concentrated acid is hazardous in contact with all oxidising and reducing agents, organic chemicals-especially those soluble in water, and all alkalis. In many cases the reactions will be very violent. Sulphuric acid must be stored separately from these substances.

Nitric acid

Nitric acid has a wide range of uses in industry: examples are in electroplating, pickling of metals, etching, production of nitrates, chemical oxidation reactions, and as a general laboratory chemical reagent.

It is a colourless or pale yellow liquid which liberates choking brown "nitrous" fumes into the air, particularly when highly concentrated. Addition to water evolves heat but not to the same extent as sulphuric acid. The same rule applies, however-always *add acid* to water.

A powerful oxidising agent, nitric acid constitutes a serious fire hazard if allowed to come into contact with organic substances such as wood, sawdust, straw, paper and sacking

It reacts with most metals, usually releasing brown nitrogen dioxide fumes, but can also liberate hydrogen gas, especially when dilute.

Hydrochloric acid

Hydrochloric acid has many industrial uses, including tanning and metal pickling; the manufacture of glue, casein, dyes, fluxes, pharmaceuticals and certain foodstuffs; as a boiler descaler; and in cleaning brickwork and concrete.

It fumes on exposure to air, liberating choking fumes of hydrogen chloride which irritate the eyes, nose and throat. Hydrochloric acid is strongly corrosive and attacks many common materials. Most metals react with hydrochloric acid, with the evolution of hydrogen.

Phosphoric acid

The main industrial use of phosphoric acid is as a rust inhibitor in metal treatment solutions. The treatment is carried out before painting or other surface treatment.

Phosphoric acid is a colourless, corrosive liquid which evolves fumes of oxides of phosphorus if heated until it decomposes. It is a particularly effective dehydrating agent and is often used in chemical laboratories for this purpose.

Perchloric acid

Although not used to any major extent in New Zealand, perchloric

acid is a widely encountered laboratory reagent. It may also find use in medical analyses and in specialised electroplating processes.

Perchloric acid is a strong and corrosive liquid. Combustible materials contaminated with perchloric acid are extremely flammable and can ignite spontaneously or, if finely divided, explode on heating or slight friction. Solutions above 72% in concentration are unstable and may decompose explosively.

Perchloric acid solutions should be carefully stored in isolation from combustible materials. Clothing contaminated with perchloric acid should be remove at once and immediately washed with copious quantities of water.

Hydrofluoric acid

This is a colourless liquid which is highly corrosive and fumes strongly in moist air. Hydrofluoric acid dissolves glass and must therefore be stored in plastic vessels. For this reason hydrofluoric acid is used in the etching of glass and pottery products. It is used extensively in the manufacture of TV tubes.

Hydrofluoric acid has a particularly serious corrosive effect on skin and mucous membranes, resulting in deep-seated burns which are slow to heal.

If spilt on the skin, wash thoroughly under a stream of water for 15-60 minutes. Do not wait for symptoms before giving treatment. Coat contaminated skin with magnesium oxide made into a water paste with 20 percent glycerine.

Do not use oily ointments. Get medical attention as soon as possible.

Caustic soda

Caustic soda (sodium hydroxide) is a common alkali, extensively used in New Zealand industry. Typical uses include soap manufacture, the production of various industrial chemicals, oil refining, electroplating, and in particular as an industrial cleaning solution e.g. in the dairy industry.

Caustic soda is a white solid which absorbs moisture from the air and, as a result, slowly dissolves itself. The solid is usually purchased in the form of small hemispherical pieces called “pearls”. Caustic soda dissolves freely in water with the evolution of much heat. Special precautions are necessary when making up solutions and these are discussed in the following section.

Eye protection (either goggles or face shields) is essential when caustic soda is being used, and other protective equipment, such as gloves and an apron, is also important.

It is important for workers to appreciate that this chemical, which may be used in large quantities and with no apparent difficulties, still represents a serious hazard because of its corrosive nature.

Making up caustic soda solutions

Although caustic soda solutions are available commercially, it is often more practical to use pelletised solid caustic soda or “pearls” to make up solutions in convenient amounts and concentrations.

The danger with this operation arises from the considerable heat

generated when caustic soda is dissolved. This can cause the solution to froth and boil, splashing the worker, or even to erupt violently from the container. Plastic vessels may melt or distort.

The safe mixing steps are:

(a) Put on protective clothing, which should include a PVC suit or apron, face shield, gloves and boots.

(b) If the concentration of the solution required is known, prepare the appropriate weight of solid and volume of water.

(c) Select a suitable vessel for the mixing. This should have an adequate surface area so that the frothing and boiling will not cause the contents to erupt.

(d) Add the full volume of water to the mixing vessel. Always use *cold* water.

(e) Add the caustic soda gradually in small lumps, with frequent, thorough stirring.

Accident case histories

The following brief case histories are summaries of accidents involving corrosive chemicals notified to the Department of Labour in recent years.

These cases represent only a small proportion of all accidents reported and probably an even smaller proportion of all those occurring.

Although only two of these cases involved caustic soda, in reality caustic soda accounts for about 60% of all notified accidents involving corrosives. This probably reflects its widespread use in industry rather than any unique problem associated with this chemical.

This is how typical accidents with corrosives can occur:

Case 1

A caustic soda solution to be used for cleaning was being made up on a large scale by dissolving solid pearls of caustic in water with vigorous mechanical stirring.

This can be quite a slow process since, given the considerable heat generated, it is necessary to add the solid caustic at a moderate rate.

To speed things up, the worker added the pearls to hot water. The heat of the dissolution reaction, coupled with the fact that the water was already hot, resulted in the solution erupting.

The worker was wearing protective clothing, including gloves, face shield and overalls, but the eruption saturated him with the solution and he received serious burns to the shoulders and upper arms.

Clearly, this accident could have been avoided if the correct method for making up the solution had been fully adhered to.

Case 2

A worker in an electroplating firm was required to add a small quantity of concentrated nitric acid to a bath to bring it up to the necessary concentration. Because the amount being measured out was small the worker did not think it worth wearing the protective equipment supplied.

While pouring out the required amount from a plastic carboy he knocked the container against a bench. The embrittled plastic fractured, splashing acid onto his face.

The worker promptly grabbed a hose and washed his face under running water for some minutes. The burns he sustained were not serious and his sight was unaffected.

The lesson in this incident is that all relevant protective clothing must be worn, no matter how trivial the task may seem.

Case 3

A fault in a line which was part of an industrial process manufacturing oleum from sulphuric acid, require urgent remedial action when discovered by the night shift maintenance engineer. He took off his gloves and overalls while he went to the telephone to call the factory manager. On returning to the faulty line he started work without putting his protective equipment back on. Highly concentrated sulphuric acid splashed out and burnt his hands and chest.

Case 4

A worker was overhauling a sulphuric acid supply line at a fertiliser works. When he overtightened a number of nuts on a valve flange the line fractured and he was sprayed with acid.

The worker ran to an emergency shower but in his panic he turned the lever the wrong way and sheared it off. He had to run to the next available shower, some distance away, with the result that the burns he received were more extensive than they would otherwise have been. He suffered serious burns to the side of his face and his upper body. The worker was not wearing protective clothing because he thought he was in a safe situation.

This accident illustrates that the most effective emergency showers are those which are operated by stepping on a pressure plate. Also, the worker should have been wearing adequate protective clothing when working on equipment holding concentrated sulphuric acid.

Case 5

A hot caustic soda solution was being used to dissolve aluminium from the inner surfaces of steel extrusion dies. The worker inadvertently dropped several dies when loading the bath and received splashes of hot caustic solution in his face and eyes. He was not wearing eye protection. As a result he was permanently blinded in the right eye.

Case 6

A worker was unloading 20 litre carboys of nitric acid (weighing 32 kg) from a truck tray about 1.2 m above the ground. These containers were obviously rather awkward to handle and one was dropped; the bottom fractured and acid splashed over the worker. He was not wearing any protective clothing because he did not anticipate a problem. He suffered serious leg burns and small splash burns on his face.

Clearly, the handling method was a poor one. A better method would have been to use a forklift to transfer a complete pallet load of carboys down to ground level and then carry them into the store.

Case 7

A worker slipped on a wet floor and knocked over an unstoppered container full of concentrated acetic acid. The liquid splashed over his

ungloved hands, and even though he rinsed them for some time under running water he still suffered extensive burns to the hands and wrists.

The container should have been stoppered while not being used and gloves should have been worn.

Legislative requirements

(a) Factories and Commercial Premises Act 1981

The following provisions of the Factories and Commercial Premises Act 1981 are pertinent to the safe storage, handling and use of corrosive chemicals:

Section 18: Safety generally

This provision sets out a general safety duty to be observed by occupiers, workers and other persons lawfully on the premises. It also incorporates duties to be observed by employees in respect of safety and health matters.

Section 20: Training and supervision

Occupiers must ensure either that all workers have sufficient knowledge and experience to perform the work safely or that they are adequately trained or supervised.

Section 21: Protective clothing and equipment

Obviously such a section is particularly pertinent to work with corrosive chemicals. The provision requires that employers supply such protective clothing and a equipment as may be necessary to afford protection against a particular risk or danger. In the case of protection against corrosives this equipment would include suitable clothing, face or eye protection, gloves and boots.

There is a further duty placed on the occupier to ensure that the protective clothing and equipment supplied is in fact worn whenever necessary.

Section 22: Storage of dangerous substances

Corrosives are specifically mentioned in this provision, which requires that these materials (among others) are safely and securely stored, and clearly labelled.

Section 23: Storage of materials generally

This section extends the scope of section 22 above to provide for the full instruction of workers in safe handling and storage of materials, including corrosives.

Section 36: Removal of steam, fumes and dust

This provision requires the occupier to protect workers against the inhalation of any impurity (including, among other things, fumes which could arise from corrosive chemicals). The means of protection can include mechanical extraction ventilation at the point of or' in of the fumes. Section 35, which discusses general ventilation of work rooms, is also relevant.

Section 53: Record of accidents

Under this provision the occupier

must keep a register in which are recorded details of accidents which occur on the premises.

Section 54: Notification of serious accidents

Serious injury or illness is defined as an injury or illness of such a nature as to be likely to render a person incapable of working for 48 hours or more. When such an injury or illness occurs, the occupier must notify the Department of Labour in writing, within 48 hours of the incident, giving full details of the person injured and the circumstances.

While other sections of the Factories and Commercial Premises Act may have some relevance to work with corrosives, the above notes summarise the sections of particular importance.

(b) Toxic Substances Act 1979

The following provisions of the Toxic Substances Act 1979 apply to corrosives.

Part III. This includes provisions covering sales, packing and safe storage of corrosives.

Part V. This contains provisions covering importation procedures and makes it an offence to send, carry or import any corrosive under a false description.

The Toxic Substances Regulations 1983, Part V, set out more detailed requirements for transporting corrosives, including the need for emergency information on vehicles and drivers' responsibilities during loading, unloading, and in the event of a spillage.

The regulations require that NZS 1983, 1st Amendment 1986 (363) is 5433:1983 *Code of Practice for the* particularly relevant as it sets out *Transport of Hazardous Substances* requirements for bulk tankers, bulk *on Land* be followed.

The Toxic Substances Regulations 1983, 1st amendment 1986 (363) is particularly relevant as it sets out requirements for bulk tankers, bulk tank trailers, and bulk storage vessels for corrosives.