



TECHNICAL NOTE



40 Choosing an acid pH correctant

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CHOOSING AN ACID PH CORRECTANT

This technical note reviews the various acid chemicals that may be used for pH correction – carbon dioxide, hydrochloric acid, sodium bisulphate and sulphuric acid. But first is the critical issue of safety.

RISK ASSESSMENT

Before settling on an acid, it is important you undertake a risk assessment in accordance with the Control of Substances Hazardous to Health Regulations 2002 (COSHH).

The Health & Safety Executive (HSE) gives guidance, which should be considered and taken into account.

Before you start the COSHH assessment, you need to think about:

- what do you do that involves hazardous substances?
- how can these cause harm?
- how can you reduce the risk of harm?

Always try to prevent exposure at source. For example:

- can you avoid using a hazardous substance or use a safer process?
- can you substitute the chemical for something safer?
- can you use a safer form, e.g., a solid rather than liquid to avoid splashes or a waxy solid instead of a dry powder to avoid dust?

If you can't prevent exposure, you need to control it adequately by applying the principles of **good control practice**. Control is adequate when the risk of harm is 'as low as is reasonably practicable'. This means:

- all control measures in good working order
- exposures are below the workplace exposure limit, where one exists
- exposure to substances that cause cancer, asthma or genetic damage is reduced to as low a level as possible.

The risk assessment should consider **control measures**, including:

- first, preventing exposure by substituting the hazardous substances or by using process design controls, if this is reasonably practicable
- if preventing exposure is not reasonably practicable, you should consider controlling exposure adequately by using a less hazardous substance or a less hazardous form of the substance.

The measures necessary to **control exposure adequately** could involve three approaches, to be used as appropriate and in accordance with the findings of the risk assessment, namely:

- controls in the exposure pathway between the source and the worker, such as containment with integrated local exhaust ventilation (LEV), using closed-loop transfer and sampling, fixed and portable LEV, or keeping a safe working distance

- worker-specific controls such as personal protection equipment (PPE) and limiting the time exposed through worker rotation
- administrative controls, such as supervision and training.

There are other important control measures.

- Apply the principles of good practice in controlling exposure outlined
- in COSHH Schedule 2A.
- Consider human factors, critical because they can affect the use of controls and lead to unnecessary exposures. These include awareness, work rate and interaction with controls, including how easy they are to use. Employers should consider the way workers use the controls when making decisions about the design, installation and use of controls.
- Review the reasons for the chosen methods of avoiding or minimising the foreseeable risks, e.g., why substitution is not practicable when a carcinogen is used, or why PPE is used rather than engineering controls like LEV.

Your risk assessment should also consider other requirements, including:

- correct use and efficient maintenance, examination and testing of control measures
- exposure monitoring, where required
- health surveillance, where required
- provision of information, instruction and training
- the ability to deal with accidents, incidents and emergencies
- ensuring employees or their representatives are informed about the outcome of the assessment.

CARBON DIOXIDE

CO₂ is a non-toxic and non-flammable gas, colourless and odourless but with a characteristic taste and pungency at higher concentrations.

The normal concentration of CO₂ in the air that we breathe is approximately 400 ppm (0.04% by volume). If its concentration in the ambient air is increased, the pulmonary gas exchange in the lungs is compromised. In simple terms, as its concentration in the ambient air increases, lower quantities of CO₂ leave the body and so there is less room for oxygen (O₂). Without sufficient O₂ one cannot live. This effect is called intoxication.

Such intoxication is independent of the effects of O₂ deficiency, so O₂ depletion monitors alone do not provide protection for monitoring atmospheres where CO₂ may be present. Separate gas detectors for CO₂ enrichment and O₂ depletion are required.

Gas detection – atmospheric monitoring

The requirement for gas detection equipment should be determined by the Premises Operator's risk assessment. 29 BCGA GN 30 – Revision 1

NOTE In addition to the gases being stored and in-use, there may be a variety of other gases, fumes and vapours, and the potential to produce these. These will all need to be considered as part of the risk assessment.

Where required, appropriate gas detectors should be fitted to detect any potentially hazardous and non-respirable atmospheres and to provide an alarm. The risk assessment should indicate the appropriate location(s) for the detector measurement head(s).

Separate gas sensors (and where necessary, systems) should be provided for the different foreseeable gas detection duties. For example, separate sensors are necessary for CO₂ enrichment and for O₂ deficiency.

Fixed gas detection equipment is preferable to personal mobile equipment. Fixed equipment has an improved ability to detect hazards before a person is exposed, whereas personal equipment generally confirms that the person is about to be or may already be exposed to the hazard (which may be too late). Fixed equipment also covers an area, rather than the spot location where an individual happens to be.

Gas detection equipment should be to a recognised national or international quality and performance standard. Gas detectors should be installed and maintained in line with the manufacturer's recommendations.

The gas detection system status should be checked for serviceability before entry to the protected area and during occupancy. Alarm warnings (flashing lights, audible alarms etc.) should be clearly visible and duplicated both outside (i.e., all access points) and inside the plant room. Appropriate, clear and legible warning signs should be provided and where beneficial repeated in several locations.

Personnel competence development programmes should include clear details of the gas monitoring system(s), and the actions to ensure safe entry to confined spaces, maintenance of the system, verifying status, how to respond to alarms etc.

Where mechanical ventilation systems are used, they should interconnect with the gas detection system to allow automatic operation. What 'automatic operation' precisely means will depend upon the details of the overall control system(s). An integrated control system should be provided, in line with the Confined Space Risk Assessment.



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Advantages of carbon dioxide

CO₂ is easier and safer to handle than other acids – no direct contact. It can be supplied in cylinders or bulk tank. Under COSHH regulations a pool operator must carry out a risk assessment in selecting the chemicals to use in a pool. The first step is to ascertain whether using an alternative process or chemical can eliminate a chemical risk: CO₂ scores on this count.

Unlike mineral acids, it is not possible to mix CO₂ with sodium or calcium hypochlorite (in liquid form) through spillage in bunds or operator error when acids are mixed in day or main tanks with hypochlorite. This means no possibility of accidental production of chlorine gas – a significant hazard in swimming pool installations.

Due to its natural buffering action, CO₂ provides improved process control. pH reduction is more gradual than with mineral acids, making accurate control inherently easier, but sometimes slower. CO₂ as a saturated solution has a pH of 5 while hydrochloric acid at 30% w/w has a pH of less than 1. Swimming pool water does not respond well to the sudden impact of chemicals. Some of the reactions taking place in pool water can take many hours, sometimes days, to complete. Gentle, gradual adjustment of chemicals is best practice.

There is no secondary pollution introduced into the treated water by salts such as chlorides (from hydrochloric acid) or sulphates (from sodium bisulphate). The introduction of CO₂ will contribute to the chemical equilibrium of water by forming carbonates and bicarbonates – contributing to total dissolved solids levels, but not to corrosion.

A study published in the scientific journal *Chemosphere* in 2010 suggested some further advantages of using CO₂. Its use slightly reduced the carbon footprint of a swimming pool, producing less greenhouse gas. It also found that three pools that changed from hydrochloric acid to CO₂ had lower chlorine consumption, lower levels of oxidants in the air above the swimming pool and of trihalomethanes in the pool water. Further research is needed to determine if the buffer effect of CO₂ is the main factor in this.

Disadvantages of CO₂

It acts as an asphyxiant when released in confined areas (see above).

It is not suitable for pools where the source water is high in alkalinity (over 150mg/l as CaCO₃) or calcium hardness (over 300mg/l as CaCO₃). It will react with alkaline materials to form carbonate and bicarbonate.

CO₂ is likely to be more expensive in terms of materials, but has less hidden costs. For example, a mineral acid dosing system is likely to require more staff time for the dosing procedures, and personal protection equipment. There are the costs associated with maintenance also with mineral acids. So there may be little to choose between the two. In any case, each pool can be individually assessed by a CO₂ supplier to provide an annual cost analysis for pH reduction.

HYDROCHLORIC ACID (HCl)

Hydrochloric acid is supplied in liquid form of varying

strengths. It is used for pH control when the pool water is treated with sodium or calcium hypochlorite.

Advantages of HCl

It is a colourless, odourless, non-fuming liquid when supplied as a 10 or 5% solution. It is a safer acid to handle than sulphuric acid. It can come in bulk and bulk storage is now available for 10% v/v acid strength.

It has less effect on alkalinity reduction than sulphuric acid or sodium bisulphate and contributes less to the total dissolved solids content.

Disadvantages of HCl

Stronger solutions (up to 35% concentration) are pungent and fuming and present a greater hazard during handling. Good seals are required when stronger acid strengths are utilised, to prevent the fumes escaping into the atmosphere. Fumes are a threat to the fabric of the building as well as people's health.

It is corrosive substance and can cause skin burns and eye damage on contact; ingestion can burn the mouth, throat and stomach. It is irritating to respiratory system and may cause respiratory failure at acute doses. Chronic exposure may cause irritant-induced asthma.

The quantities required for public pools may present a storage problem.

Chloride residue left in the water can attack metals if allowed to concentrate. As with any acidic liquid it produces chlorine gas when mixed with hypochlorites.

SODIUM BISULPHATE

Sodium bisulphate (NaHSO₄, sometimes termed dry acid) is supplied in crystal/powder form, generally white.

Advantages of sodium bisulphate

There is less atmospheric corrosion in the plant room than hydrochloric acid in its concentrated form. Diluted hydrochloric acid at strengths of 10% or less is unlikely to cause atmospheric corrosion but safeguards still need to be in place.

No additional chlorides are introduced into the pool water over and above that from a chlorinating disinfectant, therefore the risk of chloride corrosion of metallic parts that are in contact with the pool water may be less, depending on the water replacement regime.

A powder as opposed to liquid is thought to reduce mixing accidents.

Disadvantages of sodium bisulphate

It needs to be put into solution before use. As with any acidic liquid it produces chlorine gas when mixed with hypochlorites. Reaction can lead to exposure to a sulphuric acid mist, which over a long period of time is thought to be carcinogenic. It causes irritation on contact with skin. There is risk of damage to the eyes.

It reduces alkalinity much more rapidly than hydrochloric acid. It leaves a sulphate residue in the water requiring sulphate concentration to be monitored – and limited to 360mg/l – to minimise attack on cementitious grout and tile loss. (Sulphate resistant cements and epoxy grout may need to be used.)

SULPHURIC ACID

Sulphuric acid (H₂SO₄) is supplied as a liquid in various strengths. PWTAG has for some time been concerned about the use of concentrated sulphuric acid (48%) for pH correction in swimming and spa pool water.

Advantages of sulphuric acid

It produces less atmospheric corrosion in the plant room than hydrochloric acid – but only when the latter is in its concentrated form.

No additional chlorides are introduced into the pool water over and above that from a chlorinating disinfectant, therefore the risk of chloride corrosion of metallic parts that are in contact with the pool water may be less, depending on the water replacement regime.

H₂SO₄, when used undiluted direct from the delivered canister or drum, is of higher concentration compared with other acids and therefore very effective. Canisters can be fitted directly with suction lances, so only the canister needs to be handled, reducing exposure to the operator.

Disadvantages of sulphuric acid

It is a highly dangerous, corrosive acid; the greater the strength the greater the hazard. COSHH regulations place on employers the responsibility to use the 'least hazardous' chemical that gives satisfactory performance. As with any acidic liquid it produces chlorine gas when mixed with hypochlorites. Great care is required when handling.

Exposure to a sulphuric acid mist over a long period of time is thought to be carcinogenic. It causes serious skin burns and eye damage on contact with skin, damage to the gastrointestinal tract if ingested, and lung damage if inhaled.

When mixed with water, concentrated sulphuric acid has a vigorous exothermic reaction (i.e., producing heat) and produces significant fumes over and above the background fuming of hydrochloric acid. When dosed via a lance direct from the canister, a residue is left in the bottom of the drum which has to be removed prior to the return of the canister.

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Cautionary notes

If there is no bulk storage facility, H₂SO₄ should not be dosed via a day tank so that operators do not have to transfer the liquid from the drum that it is delivered



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in. All of the dosing equipment should be fitted with suction lances to fit the drum of which the acid is delivered. This means that, as with hydrochloric acid, exposure of this acid to the operator is minimised.

If it is used, it should not be as concentrated acid (48%), but diluted to 25% or lower by the supplier. Personal protection equipment should be worn when handling it.

Dosing needs to be monitored initially very carefully and dosed as required to adjust the pH slowly. Overdosing will reduce alkalinity. Therefore sizing the metering pump correctly is critical. Dosing should be undertaken only using an automatic dosing device (control of dosage and pH with pH electrode).

If pools are using a calcium hypochlorite circulation feeder whose nozzles need cleaning with acids, hydrochloric acid is the safer choice. In any case, the acid used must be stored appropriately, the manufacturers' instructions followed, and the acid flushed out to waste before any acid is fed again.

Dealing with spillages

Small spillages can be neutralised by containing the spill and using either a spill kit or sodium bicarbonate or carbonate to neutralise the acid. Larger spillages should be dealt with by calling the Fire & Rescue Service.

BULK DELIVERY WARNING

A key risk is the potential for mixing if the delivery person connects to the wrong bulk tank. Although different size nozzle adapters are installed at design, some delivery drivers carry delivery nozzle adaptors so that they can deliver into any tank, whatever the site tank connector size.