THE LINDE GROUP

When being green matters.

SOLVOCARB® neutralizes alkaline waters quickly and easily with CO_2.

For the environment's sake. Recently, the increased concern for environmental responsibility and sustainability has led to stricter regulations and frequent audits from various organizations. The pH value of wastewater, for instance, may only deviate minimally from the neutral point when discharged into a receiving watercourse (such as a river or a lake) or into a sewage system. Injecting carbon dioxide is the best way to neutralize alkalinity while also reducing environmental stress.

SOLVOCARB® is a registered trademark of the Linde Group.

No excessive acidification, less corrosion

Carbon dioxide is increasingly used to neutralize alkaline wastewater. When dissolved in water, carbon dioxide forms carbonic acid which has many advantages compared to mineral acids, such as:

- → preventing the excessive accumulation of salts such as chlorides and sulphates.
- → preventing the excessive acidification of wastewater due to the buffering capacity of carbon dioxide.
- → eliminating the safety risks of highly corrosive acids.

Safe supply

CO_2 is stored in pressure vessels as a liquid at 300 psig. It is converted to a gas at ambient temperatures before use. As CO_2 is a neutral gas until dissolved in water, this eliminates the requirements for eyewash stations and safety showers that are necessary with mineral acids. Furthermore, the application of CO_2 eliminates the risk of a harmful acid spill.

Multiple Applications

Additionally, carbon dioxide is so ecofriendly and safe that it even adjusts swimming pool water to the obligatory upper limit of pH 7.5. More commonly, however, carbon dioxide is used to neutralize alkaline process waters in many industries including:

- → Beverage
- → Dairies and butcheries
- → Bakery and confectionery
- → Electroplating
- → Cement and concrete
- → Paper and cellulose
- → Leather
- → Textile
- → Laundries and dye works
- → Photo-chemical

Dairies and butcheries

Dairies in particular, which generate a highly biodegradable effluent, produce alkaline and acidic wastewaters where the pH can vary between 4.5 and 10. They are pre-neutralized in buffer tanks and only then is SOLVOCARB® used to neutralize the excess alkalis.

Beverage industry

Cleaning returnable bottles produces wastewater with a high alkaline concentration. After the washing process, the wastewater pH value can reach up to 11. Before the filling process, the bottles must be rinsed. To avoid lime deposits accumulating on the bottle surface during this process, the pH value must be reduced.

Textile industry

In the textile industry, the mercerization process is used on cotton and sometimes on cotton blends to increase luster (thus also enhancing the appearance), to improve strength, and to improve their affinity for dyes. The process involves immersion under tension in a caustic soda (sodium hydroxide) solution, which is later neutralized using the SOLVOCARB® system.

Leather industry

The particular challenge consists in how to combine traditional leather production with a process not harmful to the environment while improving the hide quality. The solution is to apply SOLVOCARB® during the deliming process, eliminating acid shock risks, reducing nitrogenous discharge in the effluent and also reducing ammonia gas in the plant.

Pulp and paper industry

Whether deinking or bleaching or at the headbox – at every production step, the paper and pulp industries require exact pH values. Injecting carbon dioxide with SOLVOCARB® ensures precise results, due to a flat neutralization curve.

Concrete industry, cement works and construction sites

Concrete itself produces alkaline wastewaters. Carbon dioxide required for the neutralization of wastewaters from concrete production or construction sites ranges from 3–4.5 lbs/1000 gallons wastewater. In the concrete industry, further applications of carbon dioxide are possible to prevent lime scaling in the wastewater pumps or calcification on the concrete surface or mature concrete.

Laundries and dye works

The washing waters of laundries and the dyeing solutions of dye works are alkaline with pH values up to 12. Before discharge, the waters must be neutralized.

Electroplating

Most (metal) surface treatment and plating operations involve surface cleaning or preparation with solvents, alkaline cleaners, acid cleaners, abrasive materials and/or water. The used cleaning water can be neutralized with SOLVOCARB®.

Combining our technical know-how with standard technologies, Linde is able to provide tailored solutions to each customer:

- Static mixers
- Venturi systems
- Sintered matter
- Diffusers

Clever solution

The application of absorption varies depending on the properties of gas and liquid. The more soluble the gas, the less energy and equipment are required. As can be explained with the Henry-Dalton law and Fick's first law, dissolving gas in water is determined by five different parameters:

• Mass transfer coefficient, k	[m/s]
• Liquid saturation concentration of gas, $C^* \propto H \cdot p_i$	[mg/l]
• Actual concentration of gas in liquid, C	[mg/l]
• Interface between gas and liquid, A	[m2]
• Contact time between gas and liquid, t	[s]

Together these parameters describe the dissolution of gases in water as follows:

Absorbed gas $\propto k \cdot (C^* - C) \cdot A \cdot t$

Minor investment

Carbon dioxide dissolved in water forms carbonic acid. Due to the chemical properties of carbonic acid, carbon dioxide acts rapidly and effectively, without overshoot or localized areas of low pH. Excessive accumulation of salts and excessive acidification do not occur; neutralization to a target pH rapidly occurs with less hysteresis. Due to these well-balanced properties, neutralization with carbon dioxide maintains a consistent pH more easily, thus minimizing human intervention and reducing the costs of operation and maintenance while also increasing reliability.

Compared to other acids, carbon dioxide neutralizes waters at a very low consumption rate. In many cases, the amount of CO_2 required for neutralization is significantly less than the amount of a mineral acid required to perform the same neutralization. This is shown in Table 1. This is because waste-water usually contains buffer substances that make it necessary to use more acid.

This buffer capacity of a water is called alkalinity – it is defined as the capability of water to prevent a pH change when adding acid or a base. Alkalinity is equal to the concentration of bicarbonate HCO_3^-, carbonate CO_3^{2-} or hydroxyl OH^- ions (table 2). To define a water's phenolpthalein alkalinity, i.e. hydroxyl alkalinity, we use phenolphthalein as an indicator. Methyl orange is also used to define a water's carbonate alkalinity and bicarbonate alkalinity.

Process effluents with hydroxyl alkalinity can be neutralized with a standard recirculation system with pumps. If the effluent has carbonate alkalinity, or scale problems caused by high hardness, the carbon dioxide should be dissolved via bottom frames.

There are three ways of determining the CO_2 requirement:

- If data from a complete water analysis is available, we use a computer program to determine the exact requirement.
- Linde's North American Technical Center is equipped to perform CO_2 titrations. We also have simple sample mailing kits available.
- If there is a well-known mineral acid consumption, we can estimate the demand of carbon dioxide based on a stoichiometric conversion such as seen in table 1.

Table 1:
Relative usage of common acids (pound per pound)

Acid	MW	Equivalent Weight	Purity*	Pounds to = 1 pound CO_2
CO_2	44	44	99.98	1
H_2SO_4 Sulfuric Acid	98	48	93	1.18
HCl	36.5	36.5	35	2.37
HNO_3	63	63	90**	1.58

* Purity listed is most common US industrial grades.
Most mineral acids are sold as mixtures with water

** "Strong" nitric acid...Techncial grade (70%) is also widely sold.

Major balance

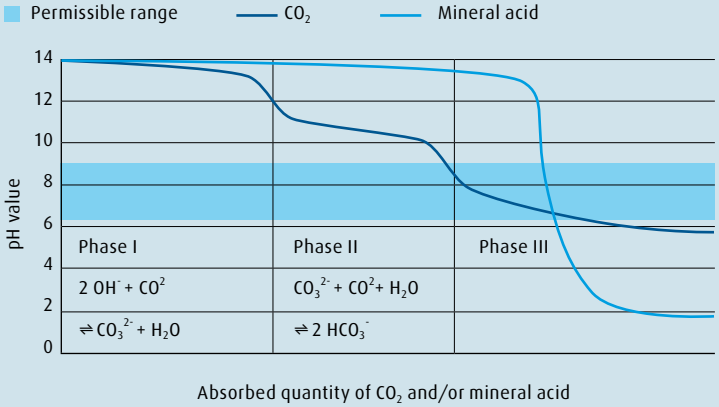
Most of the carbon dioxide in aqueous solutions takes the form of dissolved gas. A small proportion of the carbon dioxide is converted into carbonic acid by this reaction ($CO_2 + H_2O \rightleftharpoons H_2CO_3$). At high pH values, carbonic acid discharges two protons which then participate in the neutralization process. However, only one proton is discharged at pH values below 9. Although the neutralization process is continuous, there are three distinguishable chemical phases.

First phase (pH > 11.8)
$H_2CO_3 + 2NaOH \rightleftharpoons Na_2CO_3 + 2\ H_2O$
Carbonate (CO_3^{2-}) ions predominate in this phase.

Second phase (8.3 < pH < 11.8)
$H_2CO_3 + Na_2CO_3 \rightleftharpoons 2NaHCO_3$
The percentage of hydrogen carbonate (HCO_3^-) increases as the pH value falls. The crucial advantage: bicarbonates are much more eco-compatible than the salts of stronger acids. Moreover, non-toxic carbon dioxide is non-inflammable, easy to handle, and safe to store. Thus, it is currently the most eco-friendly way of neutralizing alkaline wastewaters.

Third phase (pH < 8.3)
In the third phase, the percentage of free dissolved carbon dioxide continues to increase as the neutralization curve levels out. Below pH 5, almost all the carbon dioxide is in a physically dissolved state. The third phase is usually not reached because the pH value required by law is higher than this.

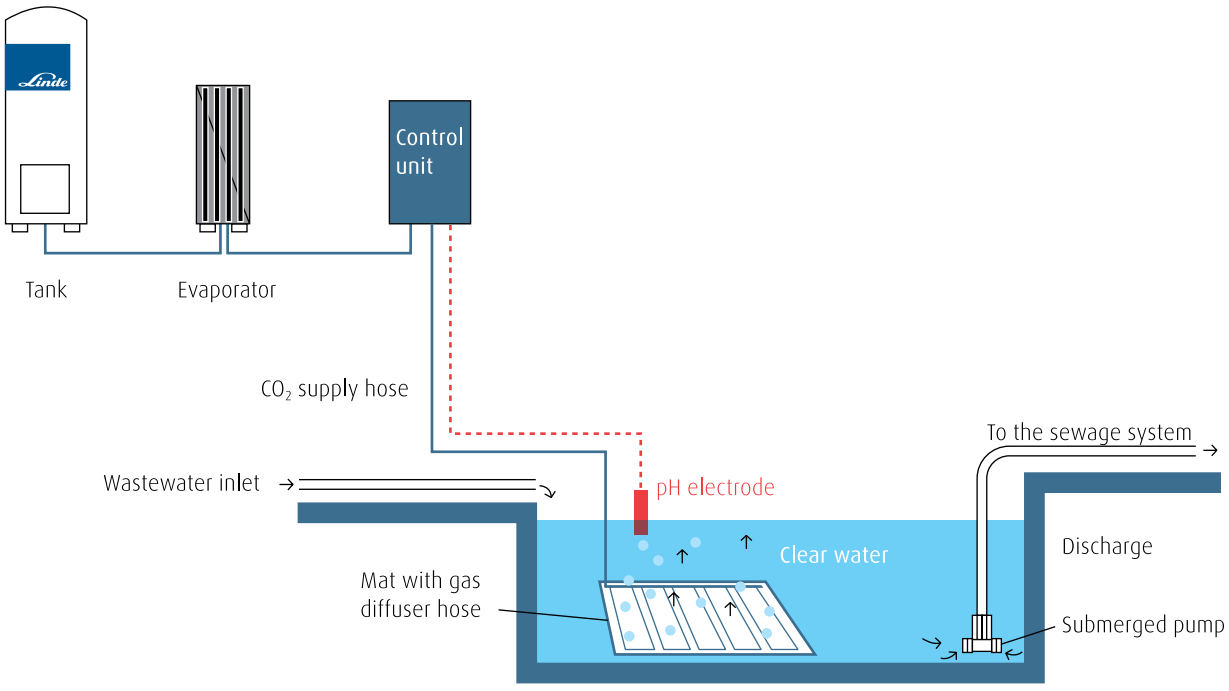
Table 2: Neutralization curves of caustic soda solution using carbon dioxide and a mineral acid



One technology, three options. SOLVOCARB® injects carbon dioxide either via hose, reactor, or nozzle. In each situation, this ensures the appropriate process for neutralizing alkaline wastewater and process waters – with mobile or stationary equipment, in industry or in wastewater treatment plants, in equalizing tanks or in pressure pipes.

SOLVOCARB®-B

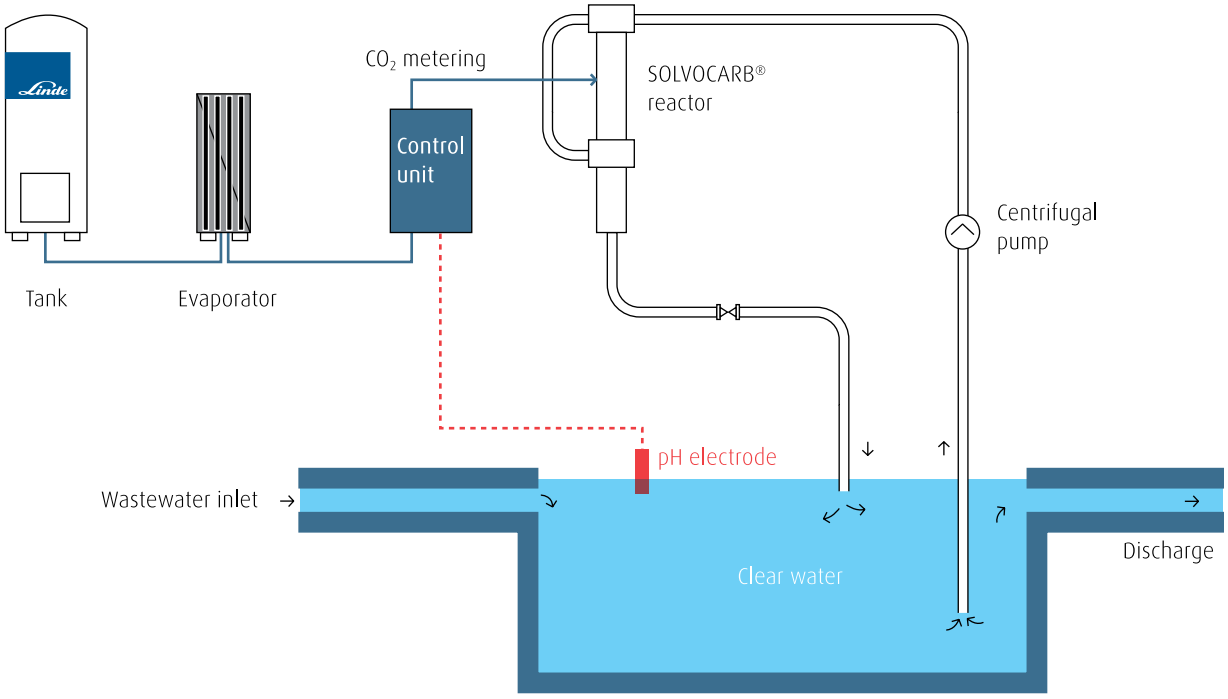
The SOLVOCARB®-B process neutralizes alkaline waters in lagoons or buffer tanks. The gas diffuser hoses inject carbon dioxide uniformly into the water, thereby ensuring optimum utilization. Fixed at the bottom of the neutralizing tank, the perforated hoses are made of resistant elastomer. When the carbon dioxide is switched on, the pores open and small bubbles of gas are emitted. The carbon dioxide is injected without requiring an additional energy source, and is controlled by a pH measurement.



SOLVOCARB®-B process.

SOLVOCARB®-R

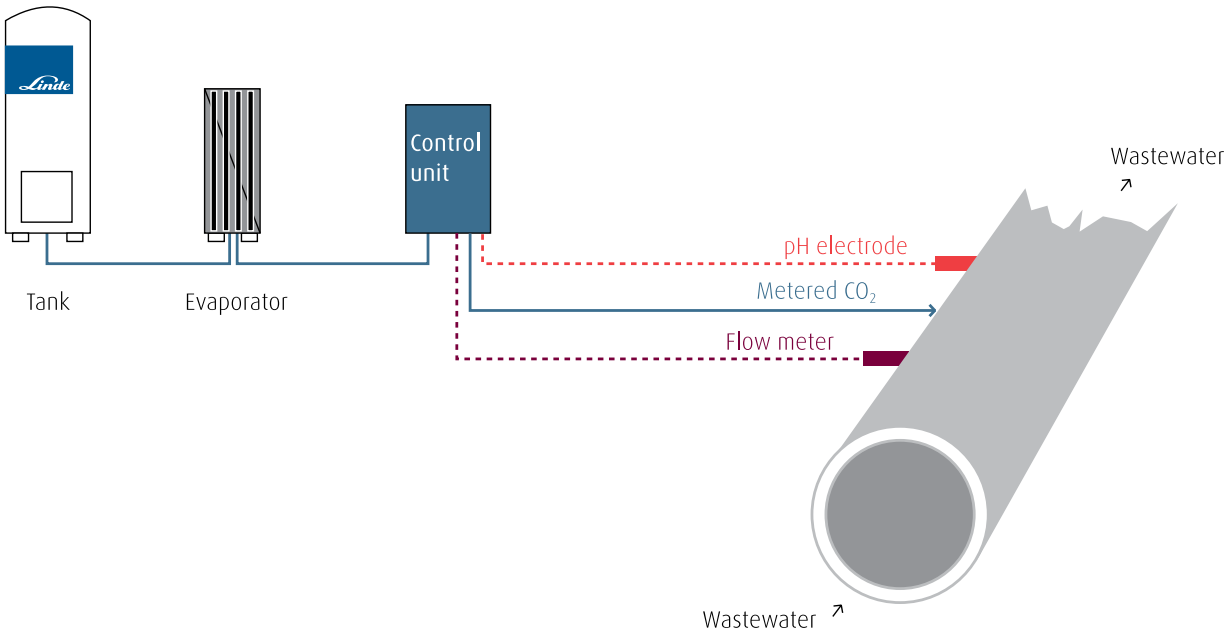
In the SOLVOCARB®-R process, carbon dioxide dissolves in the wastewater by means of a reactor and can be inserted in the main flow or in a bypass flow. Made of plastic, these reactors are usually operated at a pressure up to 90 psig gauge. The maximum operating temperature is 110°F. Stainless steel reactors can be used for higher temperatures or pressures.



SOLVOCARB®-R process.

SOLVOCARB®-D

The SOLVOCARB®-D process uses a nozzle to inject carbon dioxide into a pipeline. However, when dissolving in wastewater, carbon dioxide requires a certain reaction distance after the supply point. This reaction distance can be significantly reduced by installing a static mixer.



SOLVOCARB®-D process.

Success through diversity. Each facility is unique – SOLVOCARB® is uniquely flexible. The neutralization of alkaline wastewater and process waters plays a major role in many industrial sectors. Therefore, SOLVOCARB® systems are applicable in many different industries: from the food to the clothing industry, from electroplating to photochemistry, from the construction to the printing industry, and so many more ...

Getting ahead through innovation.

With its innovative concepts, Linde is playing a pioneering role in the global market. As a technology leader, it is our task to constantly raise the bar. Traditionally driven by entrepreneurship, we are working steadily on new high-quality products and innovative processes.

Linde offers more. We create added value, clearly discernible competitive advantages, and greater profitability. Each concept is tailored specifically to meet our customers' requirements – offering standardized as well as customized solutions. This applies to all industries and all companies regardless of their size.

If you want to keep pace with tomorrow's competition, you need a partner by your side for whom top quality, process optimization, and enhanced productivity are part of daily business. However, we define partnership not merely as being there for you but being with you. After all, joint activities form the core of commercial success.

Linde – ideas become solutions.

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