Gases improve drinking water quality

Water is the most important and the most strictly controlled foodstuff

The implementation of the European Council directive 98/83/EC in the national legislation of member states, is again invoking new or lower limit values for undesirable substances contained in the raw water, e. g. specific heavy metals or organic halogens.

Also, water suppliers have to make sure that drinking water complies to these limit values up to the tap (Figure 1).

This means that for example plumbosolvency in private household installations must be prevented by appropriately adjusted water chemistry.

Technical gases provide crucial contributions to technologies achieving this (Figure 2): as a natural component of healthy drinking water, they can be used as environmental friendly agents leaving no undesirable by-products or contamination and improving economics in water treatment. This paper presents the most important applications of gases in drinking water processing.

pH control is crucial in water treatment

A good quality drinking water should be neither corrosive nor scaling. To this end, the pH-value of the water has to be in balance with the degree of hardness (Figure 3).

Hardness is a natural property of water and is caused mainly by calcium and magnesium ions. While a certain degree of hardness is healthy and to some extent necessary for corrosion protection, a high calcium-hardness is inconvenient to all users. Hard tap water requires e.g. frequent descaling of all warm water equipment and water heaters in household equipment and also increases the usage of soaps and surfactants in washing and cleaning. Therefore, water with a middle hardness level is generally regarded as ideally suited for drinking water.

Figure 1: Highest standards apply for drinking water, our most important foodstuff. Gases help at achieving those.

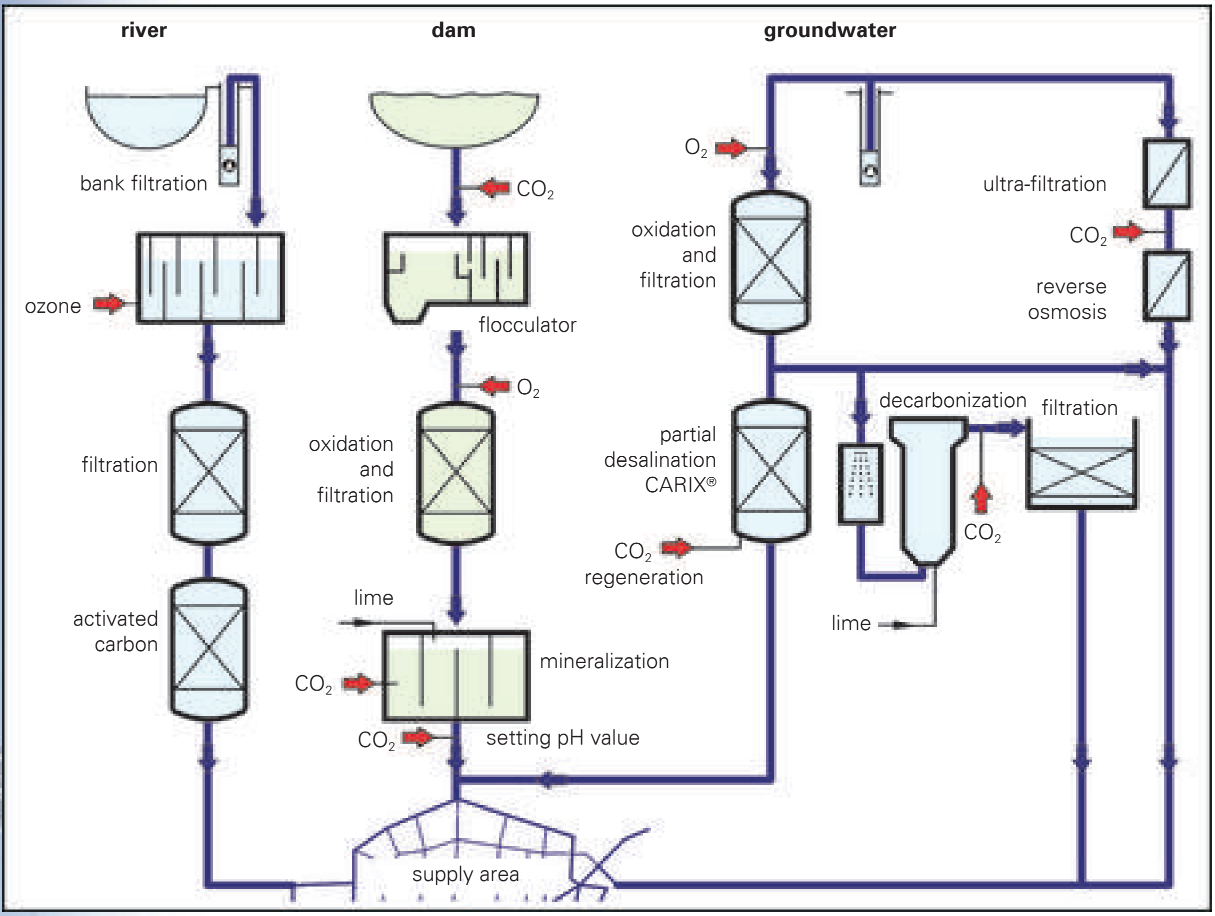

Figure 2: Gases are used in many processes for drinking water production

Many national recommendations contain a lower limit value for hardness. Soft water with lower hardness is always mineralized, to prevent corrosion in pipelines. However, an ever increasing number of water works also perform softening of hard and very hard raw waters in order to produce tap water that is ideally suited for all household uses.

Most softening is done by decarbonization in fluidized bed reactors.

At reactor entrance, lime or sodium hydroxide is injected into the water to increase the pH-value (Figure 4). As a result, dissolved calcium hardness is converted to insoluble hardness, which precipitates on the fluidized sand particles. These reactions also reverse the initial pH increase. Often, however, residual hardness and pH are not yet balanced at the reactor exit. Then calcium-carbonate precipitation can continue outside the reactor.

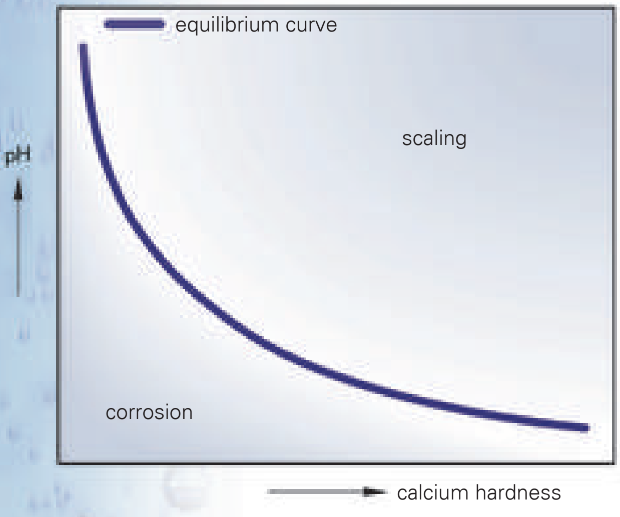

Figure 3: Influence of pH-value on drinking water quality

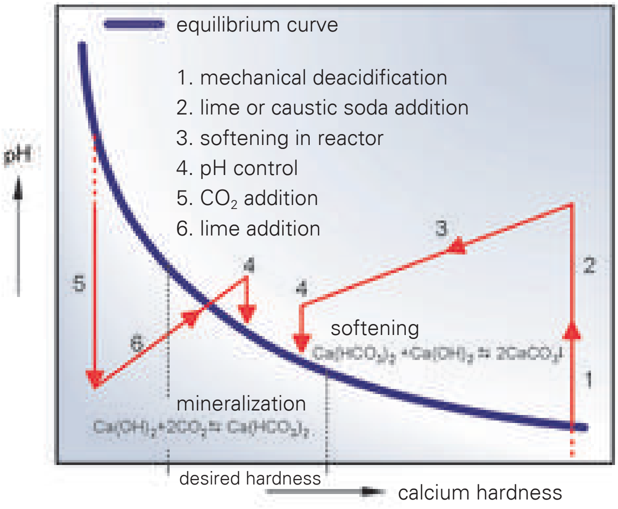

Figure 4: Softening and mineralization of drinking water with lime and carbon dioxide

Figure 5: Rapid decarbonization in a fluidized bed with carbon dioxide injection at reactor exit

This results in scaling of downstream pipelines and valves and shortened runtimes from downstream filters. To prevent this, pH control with acid is required. For this application the use of carbonic acid is advantageous. Carbonic acid is formed when carbon dioxide is introduced into water, where an equilibrium is reached between physically dissolved carbon dioxide and the products carbonic acid, hydrogen-carbonate and carbonate:

$$CO_2 + H_2O \longleftrightarrow [H_2CO_3] \longleftrightarrow H^+ + HCO_3^- \longleftrightarrow 2H^+ + CO_3^{2-}$$

All these forms of carbonic acid are natural components of water and do not change the quality of drinking water.

Messer installs CO_2-dosing and injection equipments, which dissolve CO_2 shortly before or in the exit of the fluidized bed reactor. With this, further precipitation is stopped immediately which protects downstream equipment against scaling (Figure 5).

Carbon dioxide is the acid of choice

In drinking water processing, carbon dioxide is the acid of choice as it has many advantages over mineral acids:

- Salting up of water is prevented as sulfate and chloride concentrations are not increased. This is important for the corrosion-chemistry of the water
- Carbon dioxide is more economic than mineral acids in drinking water quality
- Storage and handling of carbon dioxide is simple and safe and causes no corrosion of nearby located equipment
- Carbon dioxide gives more precise pH control at less investment (Figure 6).

Figure 6 shows a schematic neutralization curve with the weak acid carbon dioxide, compared to that with a strong mineral acid.

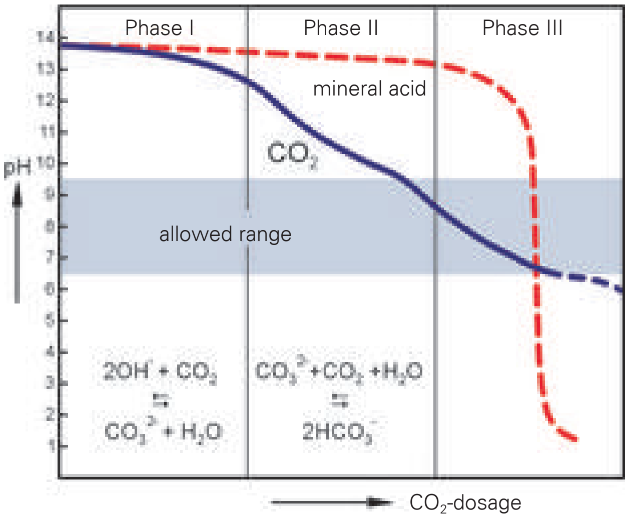

Figure 6: Comparison of neutralization curves with carbon dioxide and mineral acids

The flatter curve form with carbon dioxide shows, that also near to neutrality, carbon dioxide injection only results in small pH changes at a time, which practically excludes any over-acidification. Therefore, carbon dioxide does not require an elaborate control technique. Also, continuous dosing of small and varying amounts of acid is easier with a gas than with a liquid. This is particularly important when pH control is performed in a pipeline with plug flow characteristic.

Mineralization and remineralization: the classic carbon dioxide application

Raw water from dams or from wells in granite, sandstone or basalt areas can be very soft. Hardness below 0.5 mmol/l is not unknown. Also the steadily increasing amounts of drinking water desalinated by reverse osmosis or distillation are characterized by very low alkalinity, and therefore, without further treatment, they would be very aggressive. To prevent corrosion of pipelines and equipment, a mineralization step is required to achieve a hardness and buffer capacity of at least 0.5 mmol/l. As often drinking waters from more than one source enter a distribution network, hardness is generally set at values between 0.7 – 1.4 mmol/l. Also higher values occur.

The most economic process for mineralization is the dissolution of lime with the help of balanced amounts of carbon dioxide. Carbon dioxide assures that all of the added lime reacts to form the soluble calcium-bicarbonate (Figure 4).

Apart from softening, pH control with carbon dioxide is also advantageous in other treatment processes found in water works:

- In nano-filtration or reversed-osmosis with membranes, acidification of feed water with carbon dioxide prevents scaling of membranes – even for very hard raw waters with hardness of e.g. 7.5 mmol/l calcium – thereby maintaining constant productivity. As carbon dioxide permeates even reverse osmosis membranes, the treated water in the product stream already contains most of the carbon dioxide required for remineralization.
- pH control with carbon dioxide is also used at flocculation stages. Raw water from rivers and dams is often flocculated to remove small and colloidal particles before further treatment. In warm, southern countries, the pH of surface waters is sometimes observed to rise above a value of 9 during the summer, which is a result of algal growth. Addition of aluminate as a flocculant would then result in an undesirable, partial dissolution of aluminum into the water. Therefore, during these periods, pH control with carbon dioxide is used to prevent aluminium dissolution and to optimize flocculation.

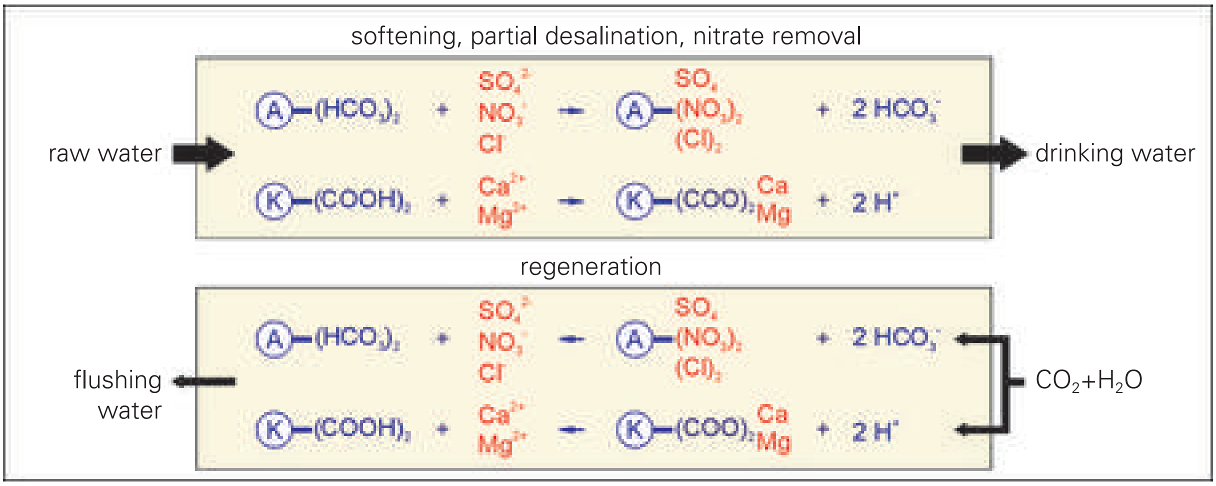

*Figure 7: Schematic representation of the Carix® process**

Partial desalination with carbon dioxide

A combination of elevated hardness, high nitrate content or high sulfate or chloride concentrations in raw water asks for treatment with the Carix®* process. The Carix®* process (Figure 7) is based on the combined use of a weak acid cation exchanger (adsorbing hardness) and an anion exchanger (adsorbing nitrate, chloride and sulfate). Both exchangers are applied together in one mixed bed. When both ion-exchangers are loaded they are regenerated jointly with carbon dioxide (Figure 8).

Favorable characteristics of the Carix®* process are:

- Regeneration of the flushing water only needs carbon dioxide and no additional salts. This means salting up is prevented and only those salts separated from the raw water are discharged. Most Carix® plants are allowed to discharge their back-flushing water to surface water.
- Hardness, sulfate, chloride and nitrate content are reduced to the desired levels in one single process step. This makes the process simple and economic.
- The bulk of carbon dioxide is recycled during the process, which improves economics of the process even more.
- Last but not least, partial desalination with Carix® is beneficial to corrosion index (Larson index), as not only bicarbonate is reduced (as in lime-decarbonisation) but also sulfate and chloride. Depending on the composition of the raw water, the ratio between anion exchanger and cation exchanger even can be set at such a level, that the emphasis is shifted from softening to anion removal.

Figure 8: Carix® plant with a capacity of 3000 m³/day

*Carix® is a registered trademark of VA TECH WABAG

Figure 9: Oxygen injection with an oxygenator for iron and manganese oxidation

Oxidation with oxygen

Oxidation reactions are used in several purification steps. The separation of iron and manganese certainly is the most widespread. Water works using groundwater mostly have to remove iron and manganese in order to prevent incrustation in distribution pipelines. As groundwater is oxygen depleted, it contains iron and manganese in a reduced, soluble form. After enrichment of groundwater with oxygen, iron(II) oxidizes very fast to iron(III)-oxide particles, which are held back on the filters. Under appropriate (chemical) conditions also oxidation of manganese and retention of manganese(IV)-oxide is performed in these filters.

From a stoichiometric point of view, oxidation of iron and manganese requires only small amounts of oxygen. Therefore, the required oxygen enrichment could be performed with air, but the use of Messer's Oxysolv® process with pure oxygen is more economic and has many advantages:

- Use of oxygen instead of air often leads to a distinct increase in filter throughput between back-flushing cycles. This minimizes water loss in back-flushing and also reduces costs for treatment or discharge of back-flushing water. Aeration often implies an oversaturation of the water with nitrogen, especially when pressure aeration is applied. During operation, the pressure drop in the filters causes degassing of nitrogen, which accumulates in the filter bed as micro-bubbles. The accumulated micro-bubbles block the filter so that early back-flushing is required. Operation with pure oxygen instead of air avoids this and achieves longer filter runtimes.
- Oxygen avoids "white water" at the tap. With intense aeration, nitrogen also degasses in the distribution system and at the tap. The customer observes this as so-called white water.
- With pure oxygen, oxygen concentrations of 20 mg/l and more are easily attained. This is important when raw water also contains ammonia, methane and hydrogen sulfide, as oxidation of these compounds requires much more oxygen, by comparison.
- Oxygen is a clean, hygienic and good quality ingredient. The use of oxygen prevents hygienic or sensory (e. g. odor) problems.
- Loss of carbon dioxide from soft water is prevented as only the exact oxygen requirement is injected and stripping of carbon dioxide by larger air volumes does not occur. In this way, the carbon dioxide content of raw water remains available for subsequent mineralization.

Thus, use of pure oxygen often is more economic than pressure aeration. Low investment and operational costs and omission of, or considerably lower, maintenance and cleaning expenditure for compressors and vent valves are in favor of oxygen. These advantages have led to oxygen applications in many German water works, where it is regarded as state of the art technology (Figure 9).

Ozone, the universal remedy

When traditional purification steps such as flocculation, filtration and/or chlorination are insufficient to ensure the quality and safety of drinking water, advanced oxidation with the strong oxidizing agent ozone is used as an environmental friendly and effective remedy. Next to fluorine, ozone is the strongest oxidizing agent available. It reacts, however, to relatively harmless oxidation products and oxygen and leaves no undesirable by-products or taste in the water.

Figure 10: Modern ozone generators like this 3 kg/h installation use pure oxygen as feed

Ozone treatment can contribute to drinking water processing in many ways:

- Ozone is used for disinfection, often in combination with UV. Compared to chlorine compounds, ozone acts faster on bacteria (e.g. legionella), cysts, spores, fungi, parasites, cryptosporidium (types of monads which cause diarrhoea) and is more effective against viruses. Also, use of ozone prevents the formation of chloramines and other chlorhydrocarbons, connected with chlorination.
- Ozone is used for oxidation of iron and manganese when these are complexed by organics such as humic acids and cannot be oxidized by oxygen.
- Ozone inhibits algal growth and prevents formation of biological slimes on surfaces.
- Ozone is used for oxidation of (persistent) organics, thereby improving color, turbidity, odor, and taste. It is often used in combination with granular activated carbon (GAC) filters for pesticide control. Ozone also cracks precursors for haloforms (CHX3). This is important when subsequent chlorination at entrance of the distribution network is performed.
- Ozone improves flocculation.

Ozone, the tri-atomic form of oxygen, is not stable and has to be produced on-site (Figure 10). Especially for medium and large size plants, oxygen as feed gas is more economic than air: oxygen does not require a high capital cost preparation plant to remove any moisture, trace compounds and particulates which would affect the lifetime of the ozone generators. Furthermore, oxygen allows for much higher ozone concentrations in the product gas (10 – 15 % by weight). Therefore ozone generators and ozone injectors are more compact, less expensive and require less energy. As a result, all modern ozone installations in e.g. Germany or UK use pure oxygen. Also many old ozone generators using air are refitted for pure oxygen to save high costs for monitoring and maintenance of the air preparation unit.

Conclusion

From well to tap, carbon dioxide (for pH control, softening, mineralization, partial desalination and so on), oxygen or ozone (oxidations and disinfections) are used in the total process chain for drinking water production. Messer's team of qualified scientists, engineers and technicians have extensive experience with the applications described in this paper and the know-how to use the gases efficiently in these processes. They consult on location and offer solutions comprising engineering, hardware and gas supply. As a results, more than 200 reference installations have been commissioned at waterworks all over Europe in recent years.

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