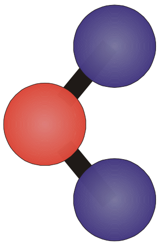
Total Hardness / Calcium / Magnesium / Carbonate hardness / buffer capacity / alkalinity

AquaCare GmbH & Co. KG
Am Wiesenbusch 11 - D-45966 Gladbeck - Germany
☏ +49 - 20 43 - 37 57 58-0 • 🖷: +49 - 20 43 – 37 57 58-90
www.aquacare.de • e-mail: info@aquacare.de

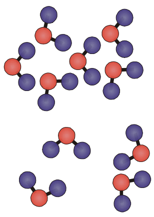
Natural lime deposit at a sinter terrace, Yellowstone National Park USA.

Water - a simple substance?

As simple the chemical structure of water is – one atom oxygen and two atoms hydrogen – as complicated are the characteristics of this fluid.



A water molecule consists of one oxygen and two hydrogen atoms.



Several water molecules are able to join loose to clusters.

In the water to be used for aquaristic purposes at lot of salts and gases are dissolved. These substances affect the biological usability crucially.

One of the main component is the system of hardness. Unfortunately this concept differs in theory and practice. If water technician or aquarist both mean different meaning. So it is important to define the following used concepts.

Total hardness - Sum of alkaline earth metals

The sum of alkaline earth metals – the old term is total hardness – is the concentration of a group of metal-ions: alkaline earth metals. Calcium and Magnesium are the most important an well known elements, further beryllium, strontium and barium. The last three are only important as a trace element – in higher concentrations they are toxic. The both major elements – magnesium and calcium – are building the total hardness. The German scale defines 1°dH with 10 mg (ppm) CaO (calcium oxide) or with 7,19 mg/l MgO (magnesium oxide). In other countries there are other scales:

France 1°fH = 5,6 mg/l CaO,
England 1°eH = 8,0 mg/l CaO,
USA 1°aH = 9,6 mg/l CaO,
Russia 1°H = 1,399 mg/l CaO.

This definition persuades that the measured calcium or magnesium is only bounded as calcium oxide respectively magnesium oxide. Normally these substances are not in the water and therefore only the electrical charge is measured. Therefore 1°dH correlates to a charge of 0,36 mval.

But this definition is not precise, too. At very high concentrations or in solutions with a high salt content, e.g. sea water, the calcium and magnesium compounds will not dissociate completely. Therefore some of the calcium and magnesium are present as ions (Ca^{2+} and Mg^{2+}) and some are present as uncharged compounds. So if you measure only the charge of calcium and magnesium you will forget some of them.

The latest definition is simply counting the magnesium and calcium atoms independent of the form (ion or compound). The new unit is the "mol" with its scale unit "mol". 1 mol is a very large number, because

	°dH	°fH	°eH	°aH	°H	mval/l	mmol/l	mg/l Ca	mg/l CaO	mg/l Mg	mg/l MgO
°dH (German hardness)	1	1,786	1,250	1,042	7,118	0,355	0,178	7,118	10,000	4,317	7,158
°fH (French hardness)	0,560	1	0,700	0,583	3,986	0,199	0,099	3,986	5,600	2,417	4,009
°eH (English hardness)	0,800	1,429	1	0,833	5,695	0,284	0,142	5,695	8,000	3,453	5,727
°aH (American hardness)	0,960	1,714	1,200	1	6,834	0,341	0,170	6,834	9,600	4,144	6,872
°H (Russian hardness)	0,140	0,251	0,176	0,146	1	0,050	0,025	1,000	1,399	0,606	1,006
mval/l	2,815	5,027	3,519	2,933	20,040	1	0,500	20,040	28,040	12,153	20,152
mmol/l or mol/m3	5,631	10,054	7,038	5,865	40,080	2,000	1	40,080	56,079	24,305	40,304
mg/l Ca	0,140	0,251	0,176	0,146	1,000	0,050	0,025	1	1,399	0,606	1,006
mg/l CaO	0,100	0,179	0,126	0,105	0,715	0,036	0,018	0,715	1	0,433	0,719
mg/l Mg	0,232	0,414	0,290	0,241	1,649	0,082	0,041	1,649	2,307	1	1,658
mg/l MgO	0,140	0,249	0,175	0,146	0,994	0,050	0,025	0,994	1,391	0,603	1

Conversion factors of some hardness units

the atoms or molecules are very, very small. 1 mol is 602.204.500.000.000.000.000.000 or $6{,}0*10^{23}$ particles.
With the new definition 1°dH is a concentration of 0.000,178 mol per liter or 0.178 mmol (millimol). It does not care if calcium or magnesium.

The terms “permanent hardness”, “non carbonate hardness”, “sulfate hardness” etc. induce big confusion. Please do not use these terms. For a hobby aquarists it is important to know the concentration of calcium and magnesium. It does not care if a calcium is a free ion or bounded together with sulfate or a complex.

Drop tests are a simple method to measure the total hardness or its components calcium and magnesium.

In the aquaristic branch drop tests (method: titration) are well known to measure the total hardness or better “sum of alkaline earth metals”. The accuracy is o.k. for this hobby. For sea water the sum of alkaline earth metals are not important: sea water has a total hardness of 370°dH. For sea water it is important to know the single ions calcium und magnesium, because both have very different tasks.

Carbonate hardness - alkalinity – buffer capacity

Another important attribute of water is the content of pH buffering substances or acid neutralizing capacity (ANC). If water has many buffering substances the pH will be nearly constant if acid or alkaline will reach the water (pH shows if water is acid, neutral or basic). The pH will go down if the water contains less buffer capacity and acid it added. If less alkalinity is in the water the pH will vary depending on the time: during the day photosynthesis takes place and take away a part of the carbonic acid – the pH goes up. During the night carbonic acid is produced by the fish and micro-organisms. Many fishes feel uneasy if the pH is fluctuating.

The old unit °KH (degree carbonate hardness) creates confusion. The definition: carbonate hardness is the part of calcium and magnesium that is that exists together with hydrogen carbonate. But the interesting component for the stability of the pH value is (nearly) only the hydrogen carbonate and carbonate – independent if they are together with calcium, magnesium of what else.

The aquarists use normally drop tests that determines the buffer capacity. The measured value estimates the capability of the water to hold the pH constant if acid or alcalines are added. The better term is “alkalinity”. The unit is mmol/l or mol/m³.

1°KH = 0,357 mmol/l HCO_3 (alkalinity)
1°KH = 21,78 mg/l HCO_3
1°KH = 17,86 mg/l $CaCO_3$

In west Europe normally the term Carbonate Hardness (KH) is used, although the alkalinity is meant.

The official definition of carbonate hardness is the part of magnesium and calcium compounds that is present as hydrogen carbonate (HCO_3^-). But if water contains only very less magnesium or calcium but high amounts of hydrogen carbonate or carbonate you will measure a high buffer capacity = alkalinity but the carbonate hardness is very low. All aquarists must know if they are measure the KH they will not get the carbonate hardness but the buffer capacity of the water – and this value is important (not the carbonate hardness). In this branch carbonate hardness is synonym to buffer capacity and alkalinity. If we are speaking about carbonate hardness or KH we mean the buffer capacity.

A typical soft water aquarium. Picture: Aqua-Care.

The soft water aquarium

You know al lot of fishes that are domiciled in soft water biotopes: the “king” of fish the discus, lots of tetras, barbels and many, many others. Conditions for keeping these group of fishes is a very low carbonate hardness (0…3°dH). The total hardness may be a little bit higher to have enough minerals in the water. The main factor is the pH. It should be about 4.5…6.5 – the water is slightly acid. For many species an addition of tannins (black water biotope) will rise the comfort. Tannins and other substances will lower the pH and inhibit a too much growing of bacteria. Many fish originated from black waters have a low defence capacity. – The discus has modified the skin to nourish the larvae and the capability to fight against bacteria is lowered.

Full automatically operating reverse osmosis unit with a downstream installed ultra pure water filters for producing soft and very clean water. Picture: AquaCare.

Normally the available water – tap water or well water – is not suitable for aquaristic purposes. The water is normally to hard and has a too high pH value. To blend this water with rainwater is one possibility to ensure the best water – but only if the rainwater is pure and does not comes from industrial zones. Other possibilities are ion exchange resins and reverse osmosis units (R.O.).

Too soft or too acid water may be treated with calcium carbonate gravels or with other chemical products (fluid or solid). For small tanks the addition of liquid or powdered hardness increasing substances is easy and cheap. For larger tanks a hardness producing filter behind the R.O. or ion exchanger is the better choice. The production is running automatically – only once or twice a year the filter filling should be changed.

The fresh water aquarium

The most common type of aquarium is the fresh water aquarium with fishes coming from soft and medium hard waters. Normally in these tanks are kept fishes from different continents and biotopes. The pH should be at around 7.0, hardness from 2 to about 8. At high alkalinity (carbonate hardness) a CO_2 dosing will help to kept down the pH and to supply the plants with enough CO_2. Without this CO_2-fertilization the pH will increase with the time over 9.0 – the plants will die and the fishes feel not well; lime crust are forming and the danger of an ammonia intoxication exists.

A typical hard coral tank with lots of small polyped scleractins SPS.

The East African cichlid aquarium (lake Malawi, Tanganyika, Victoria)

The East African lakes (lake Malawi, Tanganyika, Victoria, and others) are exceptional cases. The water has a high pH (about 8.5) and the total dissolved solids TDS are high. To create an acceptable water you take water with a high carbonate hardness (alkalinity) – the pH will be o.k. after a while.

If you only have soft water you can add hardness increasing reagents (for small tanks) or your filter with carbonate and/or magnesium containing materials. An CO_2 supply increases the total hardness and alkalinity.

The sea water aquarium without hard corals

A relative new part of the aquaristic is sea water. The requirements on filtration systems (LSS), water currents, lighting and not least on water treatment are high. The pH of sea water is about 8.1…8.4 with low oscillations of about 0.2 during the day. To keep the pH value constant the water must have a high amount of buffering substances (alkalinity, KH). – In a tank with mainly algae and not lime incrusting animals it is enough to add hard water (reverse osmosis water plus alkalinity) to adjust the water loss by evaporation. For the regular water change you may use a sea salt mixture with high buffer capacity. Fluid or powdery care products (e.g. AquaCare KH-plus, Ca-plus, Mg-plus, Triple Buffer) are suitable, too.

The same procedure is practical for

Type of aquarium / **Method**	soft water aquarium		normal fresh water tank		east African childs		sea water aquarium		reef aquarium	
	small	large	small	large	small	large	small	large	small	large
only rain water	+	+	+	+	-	-	-	-	-	-
only ion exchanger or reverse osmosis (R.O.)	+	+	+	+	-	-	-	-	-	-
ion exchanger or R.O. with mineral filter	-	-	+	+	-	-	-	-	-	-
ion exchanger or R.O. with mineral filter + CO2	-	-	±	±	+	+	+	+	+	±
additional lime reactor	-	-	-	-	-	-	-	+	+	+
chemical substances (hardness)	-	-	+	+	+	+	+	±	+	±
calcium carbonate gravels in biofilter	-	-	+	+	+	+	+	+	±	±

possibilities for water treatment: (+) well suitable, (-) not suitable, (±) partially suitable pure fish aquaria.

The reef tank

The typical reef aquarium was only feasible by constructing powerful lights and effective filtration technique especially skimmers. Consequence of the very bright lights is an increase of photosynthesis with its seasonable side effects of high oxygen concentration and good growth of all phototrophic organisms. But the needs of buffer capacity and calcium is high, especially with hard corals. If you do not refill the pools of both substances steadily the buffer capacity will fall below 5..7°dKH / 1.8…2.5 mmol/l. In natural surface sea water the alkalinity is about 2.15…2.50 mmol/l / 6…7°dKH. If the alkalinity is too low the pH will oscillate during the day too much and the lime needing animals will starve.

Growing invertebrates are nothing special in modern reef aquaristic.

The best method to supply calcium and alkalinity in form of hydrogen carbonate is the calcium-reactor or lime-reactor (e.g. AquaCare *Turbo* Chalk Reactor). Because of the high invest this unit makes only sense for large aquaria (about 400 liters / 100 US gal) or if the animals need high amounts of alkalinity and calcium.

Smaller tanks you may provide with fluid or powdery chemicals like AquaCare Ca-plus, Mg-plus, KH-plus (alkalinity-plus) and triple buffer.

With lime water („kalkwasser") only calcium is supplied. This method will not increase the alkalinity! It is very important to handle lime water very carefully. Otherwise high pH oscillations or a too high pH occur.

Blending with rainwater or other soft waters

If only very hard water is available there are some methods to reduce the hardness. In the past normally rain water or very soft well water was used to dilute the hard water and to decrease the hardness.

It is very important to have hard water as well diluting water without pollutants. Unwanted substances like nitrate or silicic acid have to removed with a strong acid ion exchanger – but the pH will change. Are there additional unwanted organic substances filter the water with a good activated carbon at very low flows (about 100 liter per day and liter activated carbon).

Block filter: activated carbon in a block is a very good tool remove sediments and organic substances.

Ion exchange resin for softening or demineralisation

Ion exchangers are able to change unwanted substances against harmless ions. An anion exchanger changes normally negative charged ions (anion) like nitrate (NO_3^-), sulphate (SO_4^{2-}), phosphate (PO_4^{3-}) or silicic acid (SiO) against chloride (Cl^-) or hydroxyl ions (OH^-). A cation resin changes positive ions like calcium (Ca^{2+}), Magnesium (Mg^{2+}) against sodium (Na^+) or proton (H^+). If both resins (H^+-form and OH^--form) are used simultaneously or sequentially anions will be kept by the anion exchanger and cations are kept by the cation changer. The emitted H^+ and OH^- will generate H_2O = water. So all salt are removed.

With weak resins you will produce water with conductivities about 10 µS/cm with strong resins (high performance resins) you will generate waters with conductivities below 0.1 µS/cm.

Reverse osmosis for eliminating hardness and other harmful substances

Reverse osmosis (R.O.) is a very simple and safe method for water treatment. Apart from demineralisation and particle removal other substances like residues of pesticides, medicine and others are rejected.

With the help of the water pressure of the water line (about 3...5 bar / 40...70 psi) the water is pressed through a semi permeable membrane. Pollutants, bacteria, viruses, algae and ions (salts) are rejected about 98% - sea water desalination with more than 99.5%.

It is important that the membrane is made of plastic (TFC) to prevent biological degradation. The R.O. unit discharges the rejected substance with the brine (waste water outlet). To ensure a long life time the membrane should be flushed regularly and the unit should have an activated carbon filter against chlorine and for adsorbing gaseous substances and a particle filter (sediment filter).

Powdery or fluid additives for increasing the hardness

If the tap water has too less hardness or alkalinity or if only some special substances are missing and the water quality is otherwise o.k. it is helpful to use fluid or powdery additives. The common method to increase total hardness and carbonate hardness (alkalinity) are calcium chloride, magnesium chloride and sodium hydrogen carbonate.

But with every adding of chemical you will not get only calcium resp. magnesium and alkalinity but other ions like sodium and chloride, too. It is very important to make a regular water change. Otherwise by and by the consistence of the water will change and the animals will get problems. You should change minimum 1% per months in sea water tanks and 10-20% in fresh water aquaria.

It is possible to prevent approximately the change of the consistence by adding mineral salts.

Fresh water plants need absolutely a regular addition of trace elements especially iron. In tap water or reverse osmosis water these essential substances are missing almost completely.

In sea water it depends on the quality of the sea salt and the amount of monthly water change. Normally it makes sense to use trace elements. With iron you must take care, because green algae are loving iron, too.

Calcium carbonate gravels: mineralising filter – bio-filter – calcium reactor

The calcium carbonate granules is a pure natural product (purity more than 99.5%, the rest is harmless and is needed in every aquarium), that was created several millions years ago. A special procedure has transformed the hard calcium carbonate gravels to round and very porous granules with an extremely high solubility.

At pH values below 8.2 the insoluble calcium carbonate reacts with acids to calcium and hydrogen carbonate (alkalinity):

$$CaCO_3 + 2\ H^+ \Rightarrow Ca^{2+} + 2\ HCO_3^-$$

So this material have ideal buffering qualities for sea water and East African cichlid tanks. Reverse osmosis or other soft waters are enriched with essential calcium and alkalinity.

The AquaCare calcium carbonate granules are porous and highly soluble.

Mineralising filter

The pure water of a reverse osmosis unit or ion exchanger is for many purposes too soft for direct use.

The AquaCare mineralising filter is connected after an R.O. unit or ion exchanger. The pure water is flowing through the filter. The carbon dioxide CO_2 – it is not rejected by an R.O. unit or ion exchanger – and acidifies the water to following equation:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3$$

carbon dioxide + water ⇔ carbonic acid

Because the pure water has a very low alkalinity – it is rejected by the R.O. membrane – the water gets acid, the pH is far below 7. If this acid water reaches the calcium carbonate material it dissolves the surface:

$$H_2CO_3 + CaCO_3 \Leftrightarrow Ca^{2+} + 2\ HCO_3^-$$

carbonic acid + calcium carbonate ⇔ calcium + hydrogen carbonate (alkalinity)

This process the better reacts the warmer the water, the slower the water runs through the filter, the larger the surface (the smaller the granules), the higher the carbon dioxide concentration of the R.O. water (the higher the alkalinity of the feed water of the R.O. unit).

The temperature is given by the place of installation of the R.O. and mineralising filter. It makes normally no sense to warm up the water – the control of the temperature is to complicated.

The water flow is defined by the daily performance of the R.O. unit; look at the technical data. If your R.O. produces more than about 120 litres per day (50 GPD) you must install two 10” mineralising filter in sequence or you must use a larger type – especially if you use a CO_2 connection.

To realize a large surface AquaCare uses a fine round and porous calcium carbonate (*Turbo*-Ca-Granules) with a diameter of 3…5 mm.

The most important factor is the concentration of carbon dioxide respectively carbonic acid. If you use the AquaCare mineralising filter without CO_2 – only the CO_2 of the CO_2 – only the CO_2 of the tap water - you will get a carbonate hardness (KH) or 2…4°dKH / 0.7…1.4 mval alkalinity. The harder the tap water the more CO_2 in the water and the more hardness with the mineralising filter.

To realise larger amounts of hydrogen carbonate you need a CO_2 connection before the filter. The more CO_2 will bubble into the filter the higher the alkalinity and calcium concentration of the outgoing water.

For a better control the CO_2 should be monitored by a bubble counter. If you use too less CO_2 the concentration of calcium and hardness is too low. If you use to much CO_2 not all bubbles will dissolve and you loose them – the outgoing water has a too low pH. Per 1000 litres water and 1°dH you need theoretically 7.0 grams (179 mmol) CO_2. In practice you need slightly more.

We recommend a very good check valve to prevent damages at the pressure relief valve and the CO_2 pressure tank.

Substrate or filter material for East African biotope

In the aquarium some bio-chemically reactions are producing acid that consumes hydrogen carbonate / alkalinity. For example: the first step of the nitrification (ammonia oxidation) releases acid:

$$NH_4^+ + 1½\ O_2 \Rightarrow NO_2^- + H_2O + 2\ H^+$$

ammonium + oxygen ⇒ nitrite + water + acid

Some degradation reactions of organic substances are producing acids, too.

To inhibit the slowly disappearing of the alkalinity and the decreasing pH value it is very important to buffer the uprising acid. Otherwise the falling pH will cause damages on fishes.

In the graphic below a calcium carbonate gravel of a bio-filter or from the substrate is sketched. Bacteria are growing at its surface and producing acid. The acid will not diffuse into the open water but is bounded directly at the surface of the gravel. The originate calcium diffuses into the open water and the hydrogen carbonate ion is used by e.g. nitrification bacteria and by plants as a carbon source (autotrophic organisms). The calcium carbonate gravel complies three important tasks:

1. Bacteria are well growing on the rough surface and do their biochemical reactions.
2. Produced acid will be buffered and prevents the falling of the pH value and the carbonate hardness. Chemical and biological sequences are more stable.
3. During the neutralization process the generated hydrogen carbonate that is use by autotrophic organisms (special bacteria, algae, plants) and benefits their growth.

The Calcium Reactor / Lime Reactor

In sea water aquaria – especially in reef or hard coral tanks – a lot of calcium and hydrogen carbonate is needed by lime incorporating organisms. These organisms – e.g. hard corals, feather worms, coralline algae – are using hydrogen carbonate and calcium to form their calciferous skeletons and tubes.

In a well growing sea water aquarium it may happen that the concentration of calcium and hydrogen carbonate will fall down in a short time below a critical limit. This implicates an unstable pH value (pH oscillations during the day) and the lime depending animals are not able to grow further more. Algae will overgrow them. This is normally the death for the animals. It is important that the calcium concentration is above 400 mg/l and hydrogen carbonate concentration above 150 mg/l (= 7°dH = 2,5 mval).

A very efficient method is a calcium reactor or lime reactor, e.g. AquaCare *Turbo* Chalk Reactor. In a calcium reactor calcium carbonate gravels are dissolved with the help of carbonic acid (please look at chapter mineralising filter). But it is important that the added CO_2 is very well mixed and dissolved to get high dissolving rates of the calcium carbonate and the flow through the system is very low. Otherwise the low pH of about 6.0 (AquaCare Turbo Chalk Reactor > 7.0) will decrease the pH of the aquarium water. Additional at that low pH value a lot of free CO_2 is still in the water and will enhance green algae growth.

A CO_2 driven calcium reactor is also suitable to regulate the pH value of an aquarium. Therefore the pH probe has to be mounted in the aquarium water and a CO_2 solenoid in the CO_2 inlet tube. If the control read out a too low pH (e.g. 8.0) the CO_2 supply for the calcium reactor stops. So the pH will never fall below 8.0.

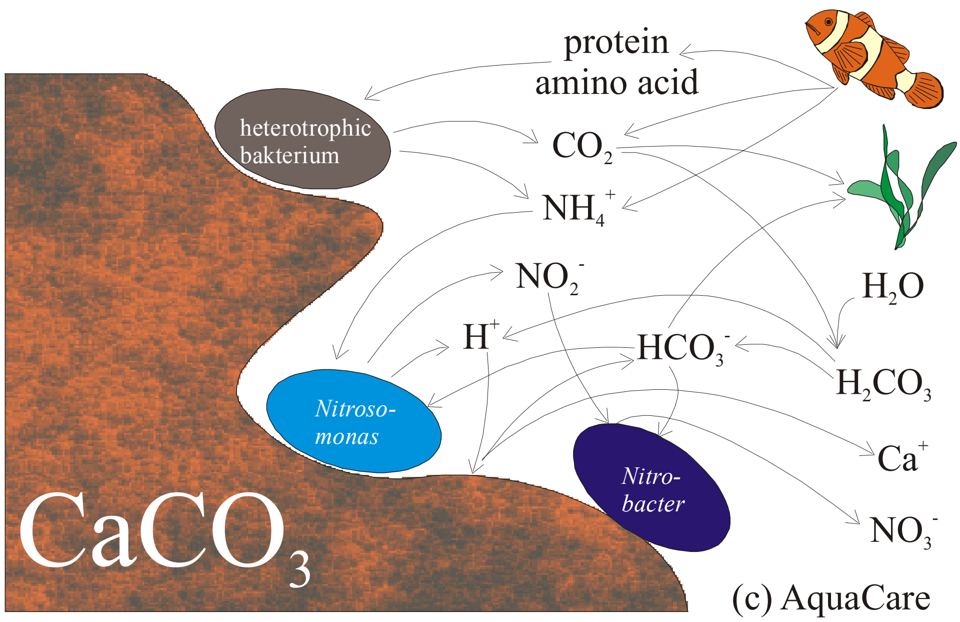
A second internal pH control will avoid that too much CO_2 will flow into the reactor. A too much CO_2 will go out with the outlet water and will reduce the pH in the aquarium dramatically. Some calcium reactors will stop their internal water cycling if too much CO_2 is bubbled in.

With an automatically driven calcium reactor it is possible to realise higher calcium concentrations and higher alkalinity compared with the system of dosing CO_2 directly into the sea water aquarium and its neutralization with calcium carbonate containing substrates. The free CO_2 concentration in the water is low and the danger of a rapid algae growth is lower, too.

To regulate the pH value is especially necessary at systems with less water volume but very strong lights. In those systems the daily pH oscillations are high even with 7…8°dKH / 2.5…3.0 mval alkalinity.

Another way to stabilize the pH value is to higher the buffer capacity. But values over 12°dKH / 4.3 mval alkalinity are not advisable, because at high hydrogen carbonate concentrations especially at high pH may cause an uncontrolled precipitation. Some aquarists have got a white reef landscape triggered by calcium carbonate precipitation.

But the performance of each calcium reactor has un upper limit. It is not possible to enlarge the power by raising the input water flow. The effect of the too much free CO_2 will destroy the complete water chemistry and algae and other unwanted organisms will proliferate. – The AquaCare calcium reactor has solved this problem, by neutralising the too low pH of the out coming water.



Some biological and chemical processes at the surface of calcium carbonate gravels.