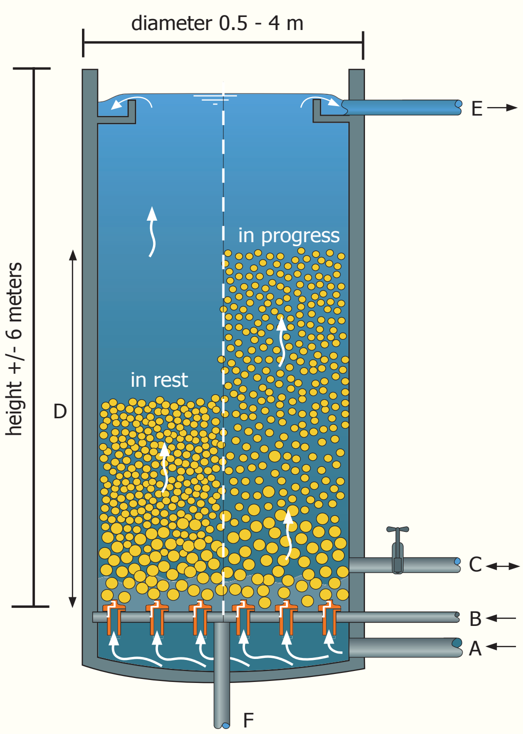
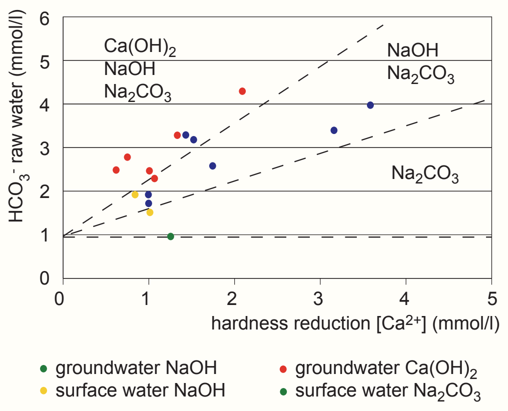
Softening



A supply of hard water
B supply of lye
C periodic dosing of sand grains (0.1-0.4 mm)
D forming pellets
E outlet for softened water
F periodic outlet of pellets (2 mm)



Contents

1. Introduction

Softening is the treatment process used to decrease the hardness of the water. Hardness is defined as the sum of the concentrations of Ca^{2+} and Mg^{2+} ions and its decrease prevents the precipitation of calcium carbonate at the customers' taps or water boilers. Other reasons to soften the water include the reduction of the use of detergents and the release of heavy metals, as indicated by Table 1.

Groundwater normally remains in the subsoil for many years before it is pumped up or flows out into the surface water. Due to the long residence time in the subsoil, the CO_2 of the groundwater can be in chemical equilibrium with the calcium carbonate of the soil, through the chemical equation of the calcium carbonate equilibrium, dissolving Calcium in the water:

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$$

Table 1- Reasons why softening is applied

Public health
- decreased release of heavy metals from distribution network - no use of household softening devices
Ethics
- prevention of stains - user's comfort
Environment
- reduction of heavy metals in sludge WWTP - reduction in use of detergent and decreased phosphate content in wastewater - reduction of concentrate discharge of household softening devices
Economy
- reduction in usage of detergent - reduction of scaling and corrosion of household equipment - reduction of energy consumption of heating devices - reduction in damage to clothes

When the water is used and heated the equilibrium is changing, the Ca^{2+} and HCO_3^- ions will precipitate in the form of calcium carbonate ($CaCO_3$). Especially high concentrations of Ca^{2+} and HCO_3^- ions will lead to inconveniences for the customers because of the calcium carbonate scaling (e.g., deposits in water boilers).
The hardness of water is classified from very soft to very hard (Table 2).

Groundwater extracted from calcareous subsoils, can have a high degree of hardness, groundwater extracted from deep sand layers is fairly soft (approximately 0.5 mmol/l) and Dutch surface water normally has a hardness from 2.0 to a maximum of 3.0 mmol/l.

The financial benefits of softening are greater than the costs. Amsterdam Water Supply calculated that the benefits of softened water for one single household comes to a saving of approximately 45 euros a year (mainly as a result of their decreased use of detergent, less maintenance on washing machines and boilers, and lower energy costs), whereas the softening costs for a household are approximately 10 euros a year.

2. Principle

2.1 Water quality parameters affected by softening

Several water quality parameters are affected by the softening process, including acidity, hardness, bicarbonate, sodium, and the solubility potential for metals like copper and lead.

The most relevant Dutch guideline values for each of the parameters, are presented below:

- Acidity (pH) must be between 8.0 and 8.3 to avoid scaling or corrosion. When after the softening process the pH is too high, it should be decreased through acid dosing.

Table 2 - Classification of hardness

unit	very soft	soft	fairly soft	fairly hard	hard	very hard
mmol/l	<0.5	0.5 - 1.0	1.0 - 1.8	1.8 - 2.5	2.5 - 5.0	> 5.0
eq/m^3	< 1	1 - 2	2 - 3.5	3.5 - 5	5 - 10	> 10
*D	< 3	3 - 6	6 -10	10 -15	15 - 25	> 25

- Hardness must be between 1.5 and 2.5 mmol/l to avoid excessive scaling.

- Bicarbonate concentration must be higher than 2 mmol/l to secure sufficient buffering capacity (pH stability) of the water.

2.2 Softening processes

The decrease of hardness can be achieved by dosing of a base, ion exchange or membrane filtration. Here we only focus on the first alternative.

Base dosing

Dosing a base in the water causes a shift in the calcium carbonic acid equilibrium, which results in a spontaneous crystallization .

The dosed base can be sodium hydroxide (NaOH) also known as caustic soda; calcium hydroxide ($Ca(OH)_2$), also known as lime, or sodium carbonate (Na_2CO_3), also known as soda.

In the Netherlands, the dosing of a base is usually done in combination with pellet reactors (Figure 1), developed in the early 70s by the Amsterdam Water Supply.

Pellet reactors

The principle of the pellet reactor is shown in Figure 2. The pellet reactor consists of a cylindrical vessel partially filled with seeding material, normally sand, with a diameter of 0.2 to 0.6 mm, where crystallization occurs, resulting in the formation of limestone ($CaCO_3$) pellets (Figure 3).

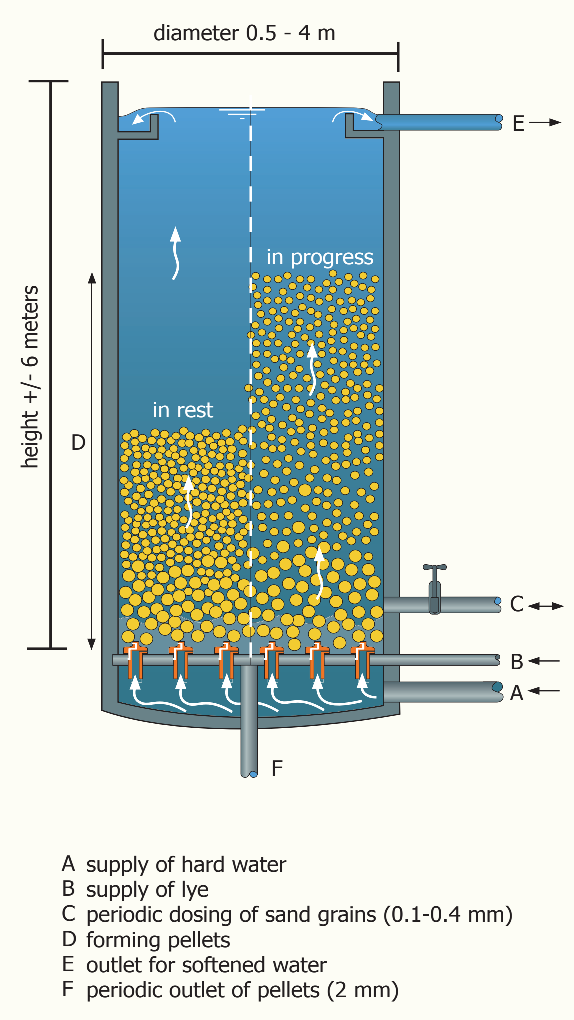
Water is pumped in an upward direction through the reactor at a velocity varying between 60 and 100 m/h. At these velocities the sand bed is in a fluidized condition.

The bed height at rest in a pellet reactor is about 2 m when sodium hydroxide is added, and about 4 m with lime. Depending on the upward water velocity and the pellet diameter, the expansion of the bed in operation is between 50 - 120% of the bed height at rest.

Raw water and the dosing of a base (sodium hydroxide or lime) are injected into the bottom of the reactor by separate nozzles, promoting an even distribution over the cross-section of the reactor.

As a result of the base dosing the solubility product of calcium carbonate is exceeded, enhancing the crystallization onto the seeding material, making the pellets to grow.

Figure 1 - Pellet reactor used for softening of drinking water



A supply of hard water
B supply of lye
C periodic dosing of sand grains (0.1-0.4 mm)
D forming pellets
E outlet for softened water
F periodic outlet of pellets (2 mm)

Figure 2 - Schematic representation of a pellet reactor

The pellets will become heavier and settle to the bottom of the reactor. At the bottom, grown pellets (1.0 - 1.5 mm) are regularly drawn off and new sand grains (0.4 - 0.6 mm) are added.

With a pellet growth from 0.5 to 1.2 mm, the increase in volume is a factor of (1.2/0.5)3 = 13.8, so the use of seeding sand is about 8% of the $CaCO_3$ production.
The pellets can be reused in the industry, so there is no generation of waste products.

In the reactor chemical equilibrium is not totally reached because of the limited residence time. Usually, an effluent containing 0.05 - 0.15 mmol/l of super-saturated $CaCO_3$ is achievable. This could result in the precipitation of $CaCO_3$ in the post-filters when not enough acid is dosed, or when split-treatment is not applied.

Figure 3 - Limestone pellets

In a pellet reactor, calcium cannot be removed completely. For sufficient reaction rates, the effluent should contain $[Ca^{2+}] > 0.5$ mmol/l.

2.3 Softening configuration

To incorporate a softening installation into an existing groundwater treatment plant, the following possibilities are considered:
- softening as initial step
- softening after aeration
- softening after rapid filtration.

Softening of raw water is done directly after extraction. If iron and manganese are present in dissolved form in the water (anoxic water), these substances will be trapped in the $CaCO_3$ grains.
The advantage of this option is that the filters loading is reduced.
A disadvantage is that the $CaCO_3$ grains have a lower purity, affecting the growth of crystals and the commercialization of the pellets.
Another disadvantage is that the base dosage is high due to the reaction of the base with excess (aggressive) carbon dioxide .

In softening after aeration, a lower chemical dose is sufficient, because some of the carbon dioxide is removed during aeration.
An additional (possible) cost advantage of softening aerated raw water is that existing filters, that

have been used for iron and manganese removal, can also be applied as 'carry-over' filter .

In softening after filtration, the purest pellets are formed, because iron and manganese are already removed by the filters.
However, the disadvantage is that, after softening, a new rapid filtration step must be installed to remove the 'carry-over' from the pellet reactors

3. Theory

3.1 Equilibrium

The calcium carbonic acid equilibrium determines whether calcium carbonate precipitates. For an extensive explanation on this subject, read the chapter on water quality. Only the most important formulas are mentioned here (answers for T = 10 ºC) :

$$K_1 = \frac{\left[H_3O^+\right]\cdot\left[HCO_3^-\right]}{\left[CO_2\right]} = 3.44\cdot 10^{-7}$$

$$K_2 = \frac{\left[H_3O^+\right]\cdot\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]} = 3.25\cdot 10^{-11}$$

$$K_s = \left[Ca^{2+}\right]\cdot\left[CO_3^{2-}\right] = 4.4\cdot 10^{-9}$$

$$K_a = \frac{K_s\cdot K_1}{K_2} = 4.6\cdot 10^{-5}$$

$$\begin{aligned} SI &= pH - pH_s \\ &= -2\cdot\log\left[HCO_3^-\right] + pK_2 + pK_s + \log(2) \end{aligned}$$

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2\cdot HCO_3^-\left(K_a\right)$$

By softening through base dosing the pH of the water is increased and the carbonic acid equilibrium shifts to the left, forming calcium carbonate.

By dosing sodium hydroxide (NaOH) the following reactions occur:

$NaOH + CO_2 \rightarrow HCO_3^- + Na^+$
$NaOH + HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + Na^+ + H_2O$

NaOH is consumed for the neutralizing reaction (removal of CO_2) and for the softening reaction (removal of Ca^{2+}).
For the softening reaction, as much NaOH is needed as the desired reduction of hardness (ΔCa^{2+}).
For neutralizing, almost all the CO_2 has to be removed if the final equilibrium pH is to be approximately 8. Per mmol/l reduction of hardness, the content of HCO_3^- drops with less than 1 mmol/l; 1 mmol/l $CaCO_3$ is formed and the content of Na^+ increases with more than 1 mmol/l.

By dosing lime the following reactions occur:

$Ca(OH)_2 + 2\ HCO_3^- + Ca^{2+} \rightarrow 2\ CaCO_3 + 2\ H_2O$
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

For the softening reaction, as much as $Ca(OH)_2$ is needed as the desired reduction of hardness (ΔCa^{2+}).
For neutralizing, almost all the CO_2 has to be removed.
When dosing lime, CO_2 is transformed into $CaCO_3$ and not into bicarbonate, as with sodium hydroxide. This is because the calcium in the lime also has to be removed to obtain a net softening.
Per mmol/l reduction of hardness, the content of HCO_3^- decreases by 2 mmol/l, and more than 2 mmol/l $CaCO_3$ is formed.

Compared to sodium hydroxide, the bicarbonate content is significantly lowered with lime. This demands that the raw water contains sufficient bicarbonate when applying lime to satisfy the quality requirements with the desired reduction of hardness. If this is the case, then lime is preferred over sodium hydroxide, because a higher pH is achieved.
Also the sodium content of the drinking water might require the use of lime instead of sodium hydroxide.

3.2 Kinetics

Experimental research shows that the kinetic equation for precipitation of calcium carbonate can be described with the following equation:

$$-\frac{d\left[Ca^{2+}\right]}{dt} = k_t \cdot S \cdot \left(\left[Ca^{2+}\right] \cdot \left[CO_3^{\,2-}\right] - K_s\right)$$

in which:

k_t = reaction constant(..)
S = specific area (..)
(…) = supersaturation or driving force

The reaction constant k_t is a function of temperature and is given by the next equation:

$K_t = 0.0255 \,.\, 1.053(T^{-20})$

The specific area in fluidized reactors is defined as:

$$S = 6 \cdot \frac{(1-p)}{d}$$

in which:

p = porosity (-)
d = diameter of the pellets (m)

A smaller diameter of pellets results in a larger specific area and, thus, a faster softening reaction. A smaller porosity results in a higher specific area and a faster reaction.

Super-saturation is the chemical driving force for the crystallization reaction. The higher this driving force, the faster the reaction proceeds.

3.3 Mass balance

In a pellet reactor calcium carbonate forms a deposit on the seeding grains added to the reactors. A decrease in calcium concentration results in an increase in pellet diameter. This increase is a function of the calcium concentration decrease:

$$\Delta d = f(\Delta c)$$

The total equation becomes:

$$N_k \cdot \frac{\pi}{6} \cdot \left(d_2^{\,3} - d_1^{\,3}\right) \cdot \rho_p = \left(\left[Ca\right]_1 - \left[Ca\right]_2\right) \cdot M \cdot Q$$

in which:

$[Ca]_1$ = calcium concentration before reaction (mol/m^3)
$[Ca]_2$ = calcium concentration after reaction (mol/m^3)
M = molecular weight of calcium carbonate (100 g/mol)
Q = flow (m^3/s)
N_k = number of pellets in the reactor per time unit (-)
d_1 = diameter of seeding material (m)
d_2 = diameter of pellets when they are removed from the reactor (m)
ρ_p = calcium carbonate density (=2840) (kg/m^3)

The seeding material with a small diameter will be located at the top of the reactor. Slowly, calcium carbonate starts to deposit on the seeding material, and the pellets grow and settle.
Eventually, the pellets are located at the bottom of the reactor and are discharged.

3.4 Hydraulics

With the hydraulic formulas, the porosity and height of the expanded (fluidized) bed can be determined.

The hydraulics of pellet reactors is the same as for rapid filters backwashing.

Water flows in an upward direction through the bottom of the reactor and, because of the high velocity, the bed fluidizes and expands. In sand filtration the expansion will extend a maximum of 20%; in the softening process the expansion can reach up to 200%.

The maximum resistance is given by the weight of the grains under water, or:

$$H_{max} = (1-p) \cdot L \cdot \frac{\rho_p - \rho_w}{\rho_w}$$

where:
H_{max} = maximum resistance (m)
ρ_w = density water (kg/m^3)
ρ_p = density pellets (kg/m^3)

The velocity at maximum resistance is called v_{min}. At a higher velocity than v_{min}, the resistance remains constant and the bed expands.

The expansion can be calculated with the equation:

$$E = \frac{L_e}{L_o} = \frac{1-p_o}{1-p_e}$$

where:
L_e = height of expanded bed(m)
L_o = height of fixed bed (m)
p_e = porosity of expanded bed (-)
p_o = porosity of fixed bed (-)

The porosity of an expanded bed at a certain upward velocity is calculated using:

$$p_e^3/(1-p_e)^{0.8} = 130 \cdot (\nu^{0.8}/g) \cdot (\rho_w/p_p-\rho_w) \cdot (v^{1.2}/d^{1.8})$$

The height of the expanded bed can be calculated when the upward velocity and the porosity are known:

$$L_e = \frac{1-p_o}{1-p_e} \cdot L_o$$

In Figures 4 through 6 the influence of some hydraulic parameters as a function of upward velocity is given.
A particle with a diameter of 0.3 mm is seeding material; a particle with a diameter of 1.5 mm is the discharged pellet.
Figure 4 implies that with an increasing upward velocity, porosity in the reactor increases.

Besides, it is obvious that with a larger diameter (for example, caused by deposits of calcium carbonate on seeding material forming pellets), the porosity decreases.

The specific surface area for crystallization decreases in the reactor from top to bottom. A direct consequence of the increase in porosity at a higher upward velocity is the greater bed expansion.

The specific area decreases at a higher upward velocity due to higher porosity.
For particles with a diameter of 0.3 mm, the increase in the expansion at higher upward velocities is relatively large.
These small particles can be flushed out.

4. Practice of pellet softening

4.1 Split treatment

Split treatment is the process in which only part of the water flow is softened.
Figure 7 shows the principle. Part of the water passes through the softening installation, (and obtains a lower hardness) and the other part does not pass the softening installation, keeping the same hardness as the raw water.

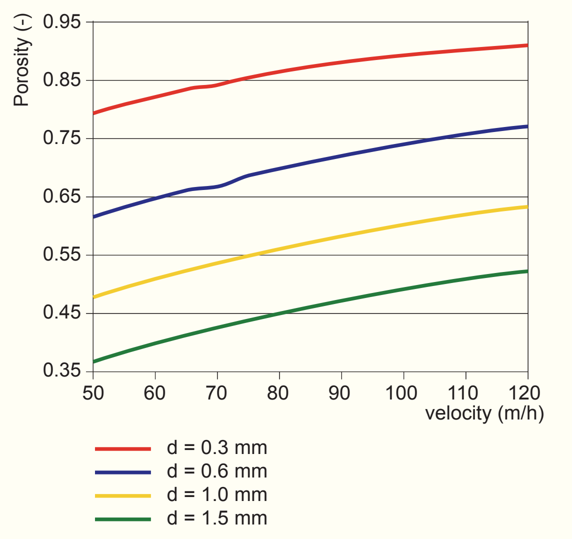


Figure 4 - Porosity as a function of pellet diameter and upward velocity

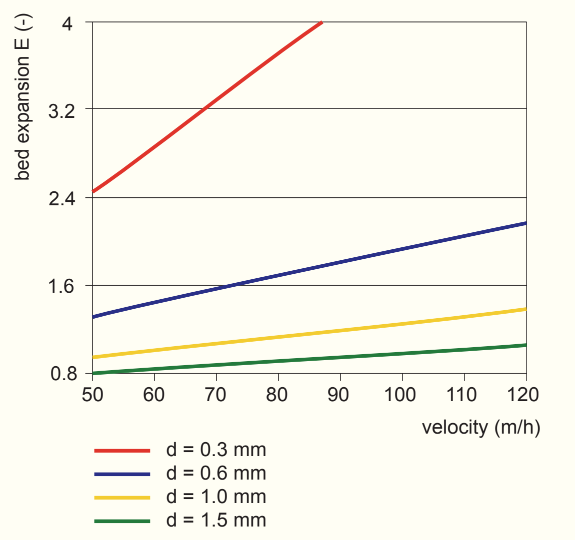


Figure 5 - Bed expansion as a function of pellet diameter and upward velocity

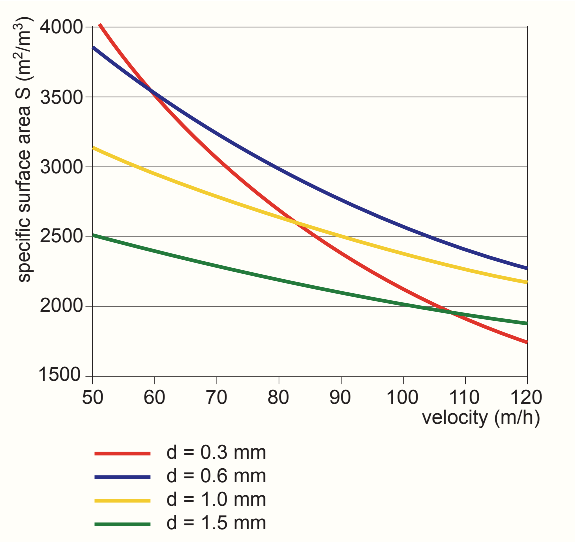


Figure 6 - Specific area as a function of pellet diameter and upward velocity

Afterwards, the two flows mix, resulting in an overall hardness of 1.5 mmol/l.

Split treatment has a number of advantages. One is that the consumption of chemicals is lower. In raw water there is an amount of carbon dioxide that needs to be converted into carbonate.
When split treatment is applied, carbon dioxide needs to be converted in only one part of the flow .

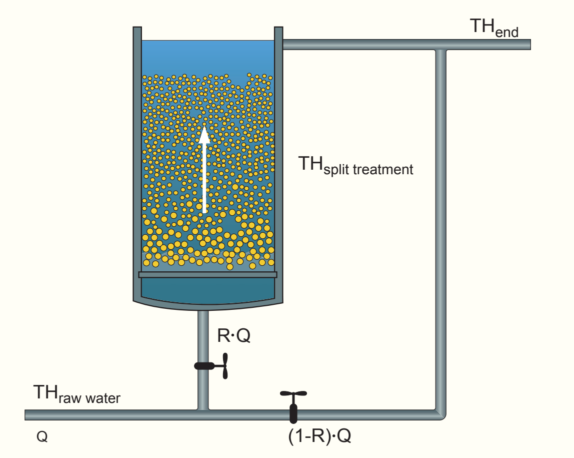


Figure 7 - Principle of split treatment

When softened water is mixed with raw water which bypassed the softening installation, a lower super-saturation of calcium carbonate is obtained than in full treatment, reducing the acid dosing for pH neutralization (principle of Tillmans' curve). Another advantage of split treatment is that the investment costs are lower, because fewer reactors need to be built.
Split treatment is only used when the concentration of magnesium in the raw water is not too high. The effluent calcium concentration from the reactor (after softening) has a minimum 0.5 mmol/l. When the magnesium concentration is high (about 1 mmol/l), the bypass percentage approaches 0% to reach a total hardness of 1.5 mmol/l.

4.2. Choice of chemicals

The selection of the proper chemical, caustic soda (NaOH), lime ($Ca(OH)_2$) or soda (Na_2CO_3), is determined by the raw water composition and the desired quality after softening. In case that several chemicals are applicable, operational aspects should be considered, as well as other parameters such as Cu and Pb solubility. Table 3 shows the changes in water quality for the most important parameters when the bases are dosed to water.

With the application of caustic soda (NaOH), about 1 mmol/l HCO_3^- is used for the removal of 1 mmol/l calcium.
With lime ($Ca(OH)_2$) that is 2 mmol/l and a dosing of soda ash (Na_2CO_3), no HCO_3^- is used.
With the application of lime, twice the amount of calcium carbonate is formed than with the appli-

cation of caustic soda or soda ash (thus more pellets production).
When the sodium and calcium concentrations of raw water are high, it will not be possible to soften this water with caustic soda, to avoid too high sodium concentrations (above the guidelines). When raw water has a low bicarbonate concentration, softening with lime is not possible.

In the Netherlands several softening installations have been built using different bases for softening, see Figure 8.

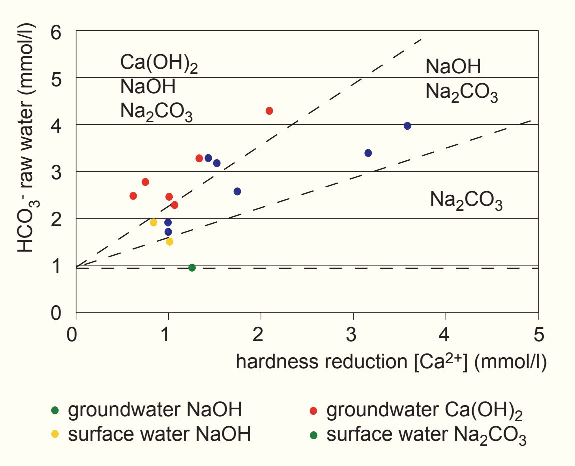


Figure 8 - Application of base as a softening chemical in Dutch practice

4.3 Construction alternatives for reactors

Different types of reactors can be used for softening (Figure 9). There are cylindrical reactors and reactors with varying diameters over height. In the Netherlands, mainly cylindrical reactors are used:

- cylindrical reactor with flat bottom (Amsterdam reactor)
- cylindrical reactor with conical bottom and tangential inlet.

Due to the cylindrical form of the Amsterdam reactor, homogeneous fluidization occurs; mixing in horizontal directions hardly occurs.
To remove limestone grains several discharge points are installed in the bottom.

In the cylindrical reactor with conical bottom and tangential inlet, water is brought in at the bottom of the reactor (mixing compartment) using a baffle to direct the water flow. In the mixing compartment, the chemical is dosed and mixing takes place.
Limestone grains are discharged through a point in the mixing compartment. At about 1 m above the mixing compartment, seeding material is brought into the pellet reactor.

Table 3 - Change in water composition (mmol/l) per mmol/l dosage of chemicals

	NaOH	Ca(OH)$_2$	Na$_2$CO$_3$
neutralization			
CO$_2$	-1	-2	-1
HCO_3^-	1	2	2
Ca^{2+}	0	1	0
Na$^+$	1	0	2
softening			
CO$_2$	0	0	0
HCO_3^-	-1	-2	0
Ca^{2+}	-1	-1	-1
Na$^+$	1	0	2

In both types of reactor, softened water leaves the pellet reactor through an overflow weir.

To prevent seeding material from flushing out, the pellet reactor can have a widened upper part, where the upward velocity decreases and the seeding material settles back into the reactor.

4.4 Seeding material and pellet storage

Seeding sand storage takes place in a silo (Figure 10) and it is dosed from the silo (by a vibrating gully, for example) into a washer, where small particles can be washed out.
For the purpose of disinfection, it is also possible to dose caustic soda or chlorine into the washed seeding sand.

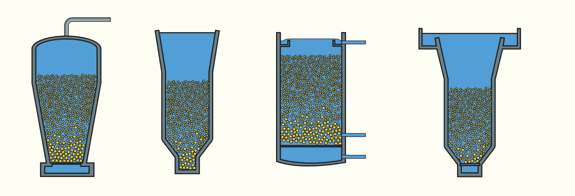


Figure 9 - Different types of reactors

Pellet storage is done in silos and containers too. The size of the storage depends on the pellet production and collection frequency. The pellet silos are equipped with a drainage system to drain water that comes with the pellet discharge.

The pellets shown in Figure 11 consist of 99.5% calcium carbonate. These pellets are brown in colour. due to the presence of 0.5% iron.

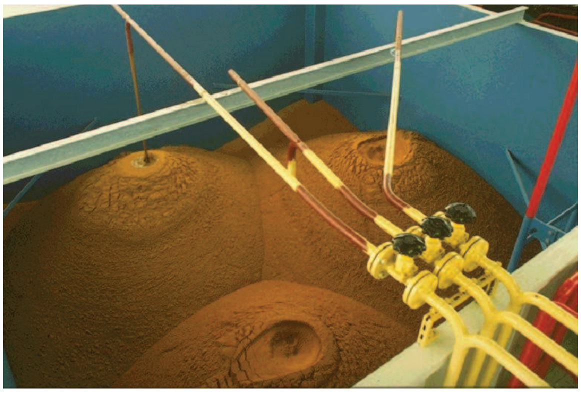


Figure 11 - Pellet storage silo

Figure 10 - Seeding sand storage silo with sand washer underneath