Softening

diameter 0.5 - 4 m

height +/- 6 meters

in progress

in rest

E

D

C

B

A

F

HCO_3 - raw water (mmol/l)

hardness reduction $[Ca^{2+}]$ (mmol/l)

$Ca(OH)_2$
NaOH
Na_2CO_3

NaOH
Na_2CO_3

Na_2CO_3

- groundwater NaOH
- surface water NaOH
- groundwater $Ca(OH)_2$
- surface water Na_2CO_3

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)

Framework

This module explains softening.

Contents

This module has the following contents:

1   Introduction

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, groundwater is in chemical equilibrium (i.e., calcium carbonate equilibrium).
Groundwater comes in contact with the atmosphere when it is pumped up or discharged into surface water. When carbon dioxide disappears from the water, it is not in calcium carbonate equilibrium anymore.
Also, when water is 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).
To prevent precipitation of calcium carbonate at the customers' taps, calcium ions are partially removed from the water by drinking water companies. This is called softening.

2   Principle

2.1   Why softening?
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.

In addition to decreasing the hardness of water, another important reason for softening is the

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

reduced release of heavy metals. Other reasons why softening is used are given in Table 1.

2.2   Water quality and softening
The hardness of water is classified from very soft to very hard (Table 2).

A number of water quality parameters are influenced as a result of the softening process. For these parameters, standards are included in the Dutch National Drinking Water Standards (Waterleidingbesluit). In addition to these standards, guideline values were developed by VEWIN.

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

Figure 1-   Scaled heating element

The produced water always needs to comply with the standards. The guideline is a target that the water companies set themselves.

The most important water quality parameters influenced by softening are acidity, hardness, bi carbonate, sodium, and the solubility potential for metals like copper and lead.

Acidity (pH)
-   standard = 7.0 < pH < 9.5
-   guideline = 8.0 < pH < 8.3

Directly after the softening process, acidity of the water is higher than the above-mentioned guideline. By means of pH-correction (acid dosing), pH is decreased to the desired value.

Hardness
-   standard = 1.5 mmol/l at the minimum
-   guideline = 1.5 < hardness < 2.5 mmol/l

Hardness is defined as the sum of the concentration of dissolved calcium and magnesium ions. The hardness is sometimes expressed in °D (German degrees), or equivalents, per m^3. Table 2 shows the conversion of mmol/l to German degrees and its equivalents per m^3.

Bicarbonate concentration
-   standard   = no standard
-   guideline   > 2 mmol/l

The bicarbonate concentration should be higher than 2.0 mmol/l, resulting in water with sufficient buffering capacity (pH stability);

Sodium concentration
-   standard   = 120 mg/l
-   guideline   = as low as possible

Because sodium influences blood pressure and therefore, indirectly, heart and vascular diseases, the concentration should not be higher than 120 mg/l.

Solubility potential
Softening also works to reduce the solubility of metals from pipe material. For drinking water the most important metals are lead (Pb) and copper (Cu), because these metals have a health impact.
-   standard $Cu^{2+} <$ 3 mg/l
-   guideline $Cu^{2+} <$ 2 mg/l
-   standard $Pb^{2+} <$ 0.2 μg/l
-   guideline $Pb^{2+} <$ 0.01 μg/l

The values for copper and lead solubility are determined by a pipe test. The pipe test is performed in stagnant water and takes 16 hours. Empirical relationships have been derived to give a rapid indication about the release:

$$Cu_{max} = 0.52 \cdot TAC - 1.37 \cdot pH + 2 \cdot \left[SO_4^{2-} \right] + 10.2$$

$$Pb_{max} = -141 \cdot pH + 12 \cdot T + 1135$$

Figure 2   - Pellet reactor used for softening of drinking water

in which:

Cu$_{max}$ = copper dissolving capacity   (mg/l)
TAC   = Total Anorganic Carbon   (mmol/l)
Pb$_{max}$ = lead dissolving capacity   (μg/l)
SO$_4^{2-}$ = sulfate concentration   (mmol/l)
T   = temperature   (^{o}C)

The TAC concentration can be influenced by the softening process (mainly caused by the decrease in HCO$_3^-$).

2.3   Softening processes
The hardness of raw water in the Netherlands varies between 0.5 and 5 mmol/l.
Groundwater extracted from calcareous subsoils, especially, can have a high degree of hardness. Water extracted from deep sand layers of the Veluwe is, on the other hand, fairly soft (approximately 0.5 mmol/l).
The hardness of surface water is normally from 2.0 to a maximum of 3.0 mmol/l.

The hardness of water can be decreased by means of different processes:
- dosing of a base
- ion exchange
- membrane filtration

Dosing of base (NaOH, Ca(OH)$_2$ or Na$_2$CO$_3$)
Because of a shift in the calcium carbonic acid equilibrium, spontaneous crystallization occurs.
By dosing the base in a reactor with seeding grains, crystallization will occur on the surface of the seeding grains, forming limestone pellets. This process is called softening in a pellet reactor and will be described further in section 2.4. The process of softening by means of a pellet reactor was developed in the early 70s by Amsterdam Water Supply.

Ion exchange
The ions (for this, calcium and/or magnesium) are exchanged with other ions (sodium is used the most).

Membrane filtration
Depending on the type of membrane, the hardness is partly (nanofiltration) or fully (reverse osmosis) removed.

2.4   Pellet reactor
The principle of the pellet reactor is shown in Figure 3.
The pellet reactor consists of a cylindrical vessel partially filled with seeding material. The diameter of the seeding material is approximately 0.2 - 0.6 mm and it has a large crystallized surface.
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.

Raw water and chemical (base) are injected into the bottom of the reactor by separate nozzles.
Water and chemicals are well-distributed over the cross-section of the reactor (plug flow) once sufficient flow resistance is realized over the nozzles.
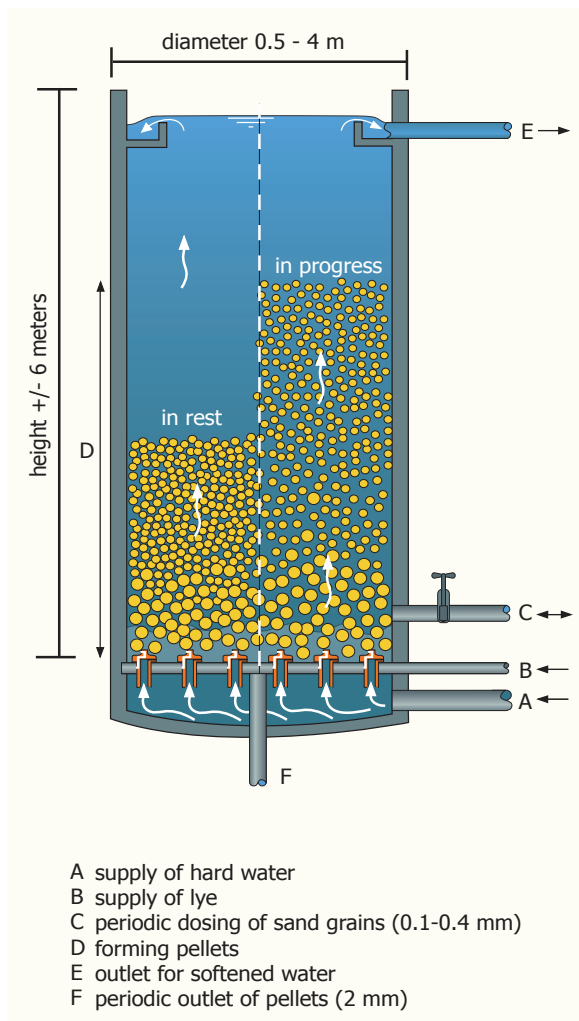
Figure 3   - Schematic representation of a pellet reactor

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)

The process conditions (such as chemical doses and flow velocity) need to be selected so that the solubility product of calcium carbonate is exceeded. As a result, calcium carbonate will be formed (quick reaction) and precipitate onto the seeding material.

Figure 4 - Limestone pellets

The seeding grains' diameter will increase as a result of the calcium carbonate deposit (formation of pellets). The pellets will become heavier and settle to the bottom of the reactor. Finally, the pellets (at a diameter of 1.0 - 1.2 mm) will be removed from the reactor and new seeding grains will be brought in.

The pellets can be reused in the industry.

Softening with a pellet reactor does not generate waste products.

2.5   Softening in a treatment plant

To incorporate a softening installation (including post treatment) into an existing groundwater treatment process, the following possibilities are considered:

- softening of raw water
- softening of aerated water
- softening after rapid filtration.

Softening of raw water is done directly after it is pumped up.

If iron and manganese are present in dissolved form in the water (anaerobic water), these substances will be trapped in the $CaCO_3$ grains.

The advantage of this is that the loading on the sand filters is reduced.

A disadvantage is that the $CaCO_3$ grains become less pure, affecting the growth of crystals, resulting in fluffy pellets.

Another disadvantage is that the base dosage is high due to the high concentration of carbon dioxide in raw water. Before the softening reaction starts, the carbon dioxide needs to be converted to HCO_3^- and CO_3^{2-} .

When softening takes place after an aeration phase, a lower chemical dose will be sufficient, because some of the carbon dioxide is removed during aeration.

An additional (possible) cost advantage of softening (aerated) raw water is that, in many cases, existing filters that have been used for iron and manganese removal uptill this point, can also be applied as 'carry-over' filters.

When softening after filtration is applied, the purest pellets are formed. Iron and manganese are removed by the filters.

A disadvantage is that after softening a new (expensive) rapid filtration step must be added to the process to remove the 'carry-over.'

3 Theory

3.1 Equilibrium

The calcium carbonic acid equilibrium determines whether calcium carbonate precipitates. For an extensive explanation on this subject, you are referred to lecture notes from the course 'Introduction in Sanitary Engineering (CT3420),' specifically the chapter on water quality. Only the most important formulas are mentioned here(answers for T = 10 ºC) :
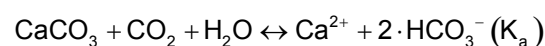
$$K_1 = \frac{[H_3O^+] \cdot [HCO_3^-]}{[CO_2]} = 3.44 \cdot 10^{-7}$$

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

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

$$K_a = \frac{K_s \cdot K_1}{K_2} = 4.6 \cdot 10^{-5}$$
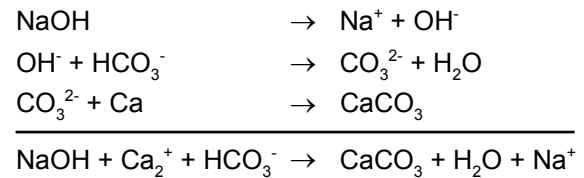
$$SI = pH - pH_s$$
$$= -2 \cdot \log[HCO_3^-] + pK_2 + pK_s + \log(2)$$

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

In groundwater abstracted in South Limburg, a high concentration of calcium ions is present. Given that there is no CO_3^{2-} in the water (pH is 6), calcium does not precipitate but remains in dissolved form in the water, resulting in water with a high degree of hardness.

By softening, the pH of the water is increased as a result of dosing a base. When caustic soda is used, the following reactions will occur:

NaOH	$\rightarrow$ Na$^+$ + OH$^-$
OH$^-$ + HCO$_3^-$	$\rightarrow$ CO$_3^{2-}$ + H$_2$O
CO$_3^{2-}$ + Ca	$\rightarrow$ CaCO$_3$

$$NaOH + Ca_2^+ + HCO_3^- \rightarrow CaCO_3 + H_2O + Na^+$$

The above-mentioned reactions are irreversible; in reality, equilibrium will be set.

Also for the bases $Ca(OH)_2$ and Na_2CO_3, similar reaction equations can be formulated.

By dosing a base, the carbonic acid equilibrium shifts to the left, forming calcium carbonate. The Saturation Index exceeds 1. At a similar SI, crystallization of calcium carbonate occurs, forming a deposit on the seeding grains present in the reactors.

3.2 Kinetics

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

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

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:

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

The specific area in fluidized reactors is defined as:

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

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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.

Supersaturation 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:

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

The total equation becomes:

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

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 re-
          moved 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

To design a pellet reactor, one must understand the hydraulics of a fluidized bed.

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

The hydraulics of pellet reactors are the same as backflushing rapid filters.

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 200%.

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

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

in which:
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:

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

in which:
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:

$$\frac{p_e^3}{\left(1-p_e^3\right)^{0.8}} = 130 \cdot \frac{v^{0.8}}{g} \cdot \frac{\rho_w}{\rho_p - \rho_w} \cdot \frac{v^{1.2}}{d^{1.8}}$$

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 5 through 7 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 5 implies that with an increasing upward velocity, porosity in the reactor increases.
Besides that, 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
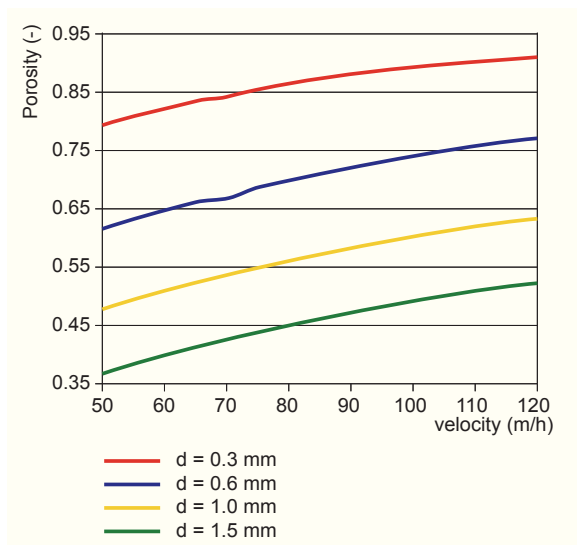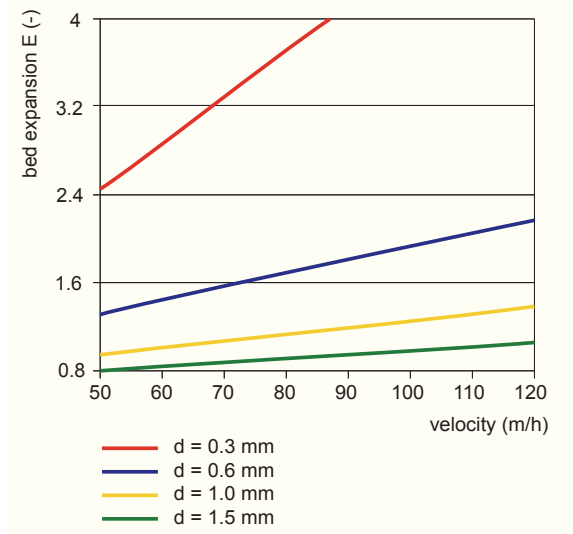

Figure 6   - Bed expansion as a function of pellet diameter and upward velocity

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.
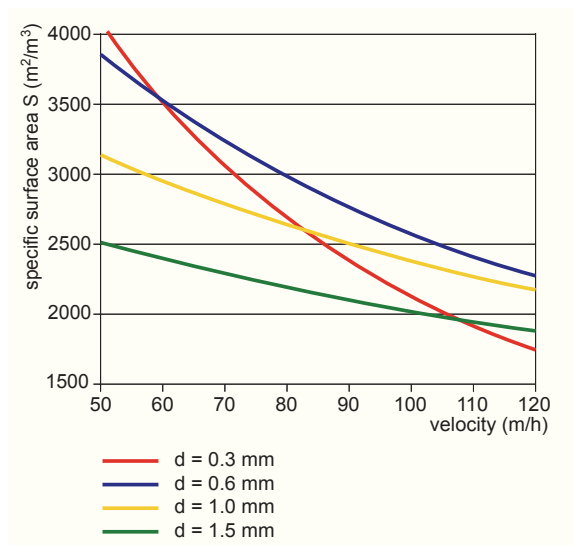These small particles can be flushed out.

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

Figure 7   - Specific area as a function of pellet diameter and upward velocity

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3.5   Influence of parameters

With the basic equations for softening reactions and the hydraulic equations for an expanded bed, it is possible to design a pellet reactor and show the values of some characteristic parameters as a function of height.

Because the solution of the equation is difficult (defining the reactor in terms of a number of discrete intervals, dx, and solving the equation per dx), computer programs are used to design installations.

Table 3 shows some input data of a reference calculation, Figure 8 shows the results of a calculation graphically.

The most important parameter for the design of a pellet reactor is the height of the expanded bed. This determines the height of the pellet reactor and the building where the pellet reactor will be placed.

Using the input data from Table 3 it follows that, after calculating, the height of the expanded bed is 5.43 m.

Table 4 shows the consequence of varying input parameters. The table still includes an unknown parameter, dCa. The computer program calculates a theoretical base dosage to reach the effluent concentration Ca_2. This value is only reached when the reactor is infinitely high, when the equilibrium is completely reached. However, an infinitely high reactor is neither practical nor feasible; therefore, a
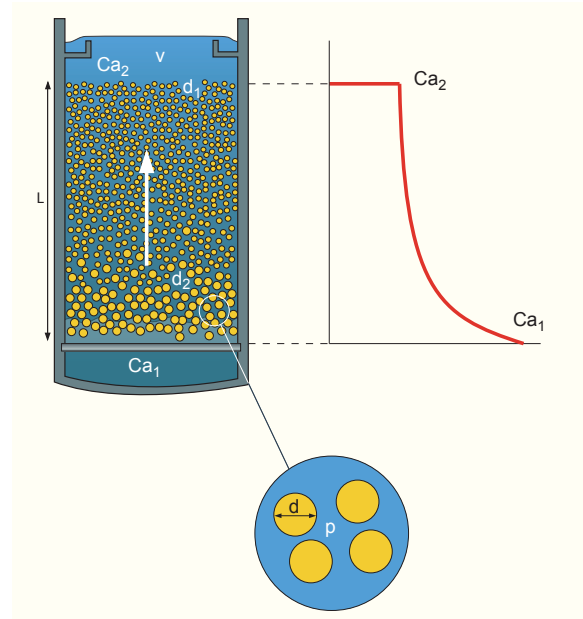

Figure 8   - Resistance as a function of upward velocity and grain diameter

supersaturation of calcium carbonate is accepted, and leads to a lower reactor. To reach the effluent concentration Ca_2, a higher dosing of a base should take place. In practice a value of dCa to 0.10 mmol/l is acceptable.

Not only the expanded bed height changes with changes in one of the input data, but other parameters also change.

Table 5 gives an overview of the influences of varying one input data point.

Figure 9 gives some parameters as a function of the level in the reactor.

Table 3   - Softening with caustic soda in pellet reactor

Raw water	Ca_1	(mmol/l)	3.5
composition	TAC	(mmol/l)	5.0
	HCO_3^-	(mmol/l)	4.25
	T	(°C)	10
Softened water	Ca_2	(mmol/l)	1.5
composition	dCa	(mmol/l)	0.06
Pellet reactor	v	(m/h)	80
characteristics	d_1	(mm)	0.3
	ρ_1	(kg/m³)	2650
	d_2	(mm)	1.0
	ρ_p	(kg/m³)	2840

Table 4   - Consequences of variation in input data on expanded bed height, dosing caustic soda

Reference conditions	Variable conditions	Expanded bed height L_e (m)
T = 10°C	T = 5 °C	6.73
v = 80 m/h	v = 120 m/h	10.9
d_2 = 1.0 mm	d_2 = 0.75 mm	5.39
d_1= 0.3 mm	d_1 = 0.2 mm	5.58
ρ_o = 2650 kg/m³	ρ_p =4200 kg/m³	4.55
dCa = 0.06 mmol/l	dCa = 0.10 mmol/l	2.78
Ca_2 = 1.50 mmol/l	Ca_2 = 1.0 mmol/l	3.12
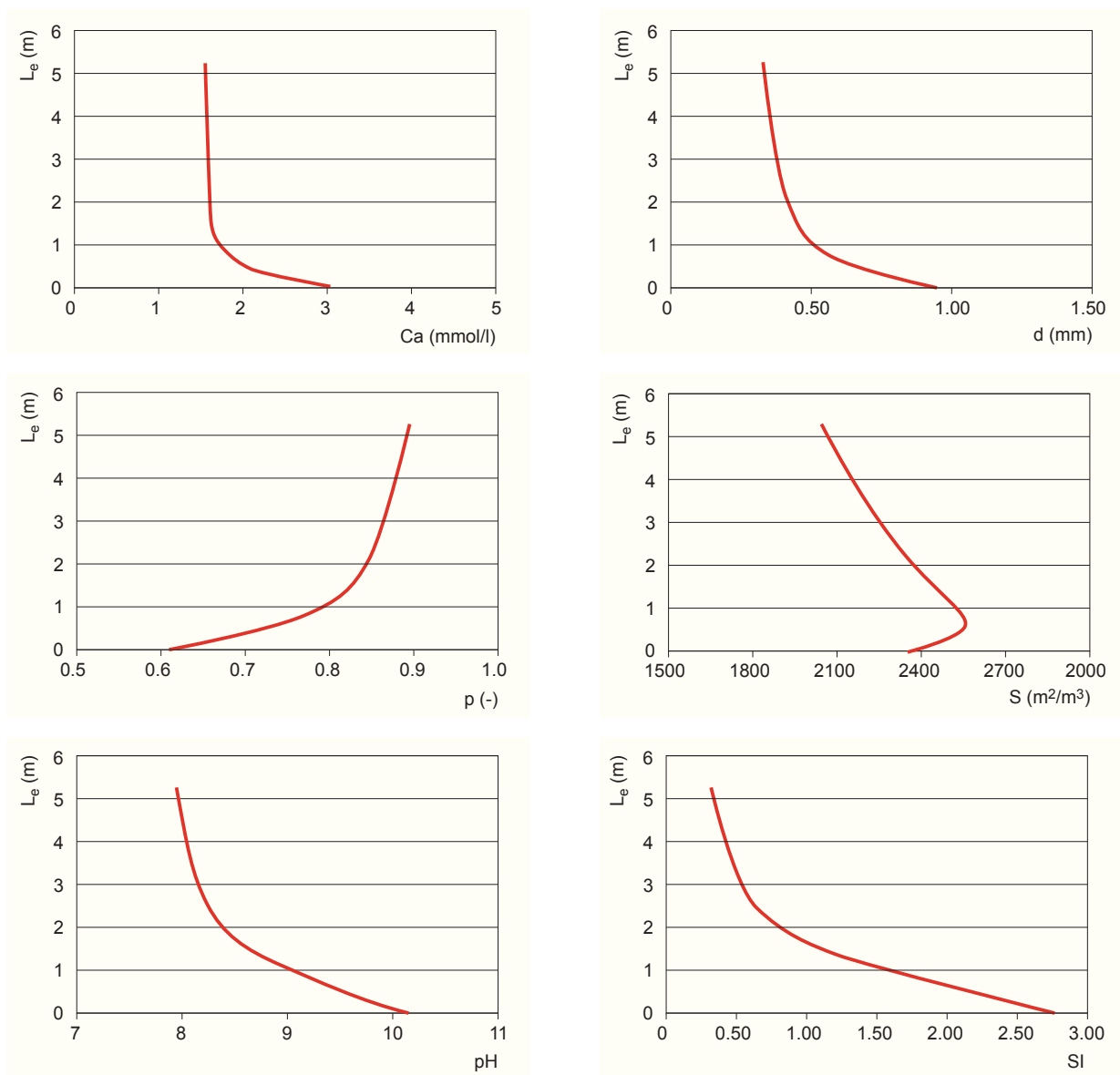
Ca : driving force calcium concentration = softening (supersaturation largest at the bottom of the reactor (see SI): thus most removal at the bottom of reactor);

d : as a result of the growing of pellets, stratification will take place, because the pellets with large diameters will settle to the bottom;

p : porosity increases because the diameter decreases in height (opposite of d);

S : specific area has a maximum at a certain height. Below this height S decreases because then the pellet diameter is decisive. Above this height S decreases because porosity is more decisive;

pH : highest at the bottom of the reactor due to chemical dosage at the bottom;

SI : see Ca (as a result of chemical dosage the supersaturation increases).

Figure 9   - Some characteristic softening parameters as a function of height

Table 5   - Influence of changes in input data on parameters

increase of	influence on					
	L_e	dos	N_k	S	G	SI_{max}
T	<<	<	-	>	>>	<
v	>>	-	-	<<	>>	-
d_2	>	-	<<	<<	>>	-
d_1	<>	-	>>	>	>	-
p_1	<	-	>>	>	>	-
Ca_1	<<	>	-	-	-	>
Ca_2	<>	<<	<<	-	-	<<
$Ca(OH)_2$	>>	-	-	-	-	<<

4   Practice

4.1   Split treatment

When only a part of the water flow is softened, it is called split treatment.
Figure 10 shows the principle. One part of the water passes through the softening installation (and obtains a lower hardness) and one part does not pass the softening installation (and has the same hardness as the raw water).
Afterwards, the two flows will 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 an amount of carbon dioxide exists which needs to be converted into carbonate.
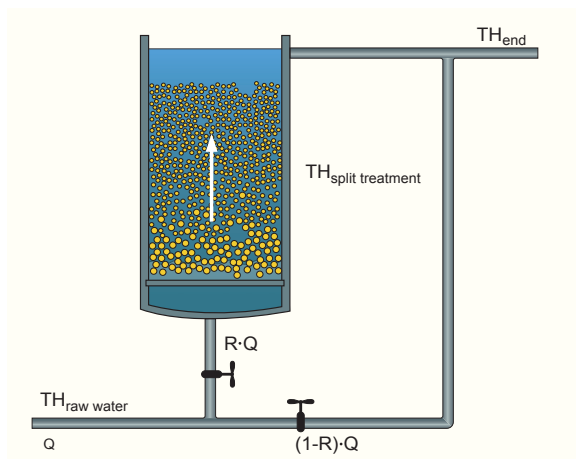

Figure 10 - Principle of split treatment

In the case of split treatment, only carbon dioxide needs to be converted in one part of the flow; in the by-pass, no dosage of chemicals takes place.

When softened water is mixed with raw water which bypassed the softening installation, the water has a lower supersaturation after mixing (principle of Tillmans curve).
Another advantage of split treatment is that the investment costs will be lower, because fewer reactors need to be built.
The choice for split treatment is significant for large design capacities (i.e., larger savings).

Split treatment will only be used when the concentration of magnesium in the raw water is not too high.
The maximum softening depth is down to a calcium concentration of 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

Selection of the proper chemical (caustic soda, lime or soda) is determined by the raw water composition and desired quality after softening. In case several chemicals are applicable, aspects of operational management will also become important.
Previous standards were given that must be complied with.
These standards determine, to a considerable extent, what base can be used for softening.
Table 6 shows the change in water quality for the most important parameters when bases are dosed to water (on the basis of irreversible reactions).

The water quality after softening can be easily determined and conclusions can be drawn as to whether the water meets the standards. In reality, equilibrium reactions occur but change the concentrations only slightly. However, for a first estimate, the values in Table 6 give an indication of the changes.

Table 6   - 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

It should be noted that with the above-mentioned reactions, the 'consumption' of bicarbonate (HCO$_3^-$) differs.

With the application of caustic soda (NaOH), 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$_2$CO$_3$), no HCO$_3^-$ is used.

The extent to which HCO$_3^-$ is still present in water, after removal of the desired concentration of calcium, is of importance regarding the buffering capacity of water and several other water quality parameters (copper resolution, corrosion index, etc.).

In addition, it should be mentioned that with the application of lime, twice the amount of calcium carbonate is formed than with the application of caustic soda or soda ash (thus more pellets).

When the sodium and calcium concentrations of raw water are high, it will not be possible to soften this water with caustic soda, because the sodium standard of 120 mg/l will be exceeded. When raw water has a low bicarbonate concentration, softening with lime will also not be possible.

In the Netherlands several softening installations have been built in which different bases are used for softening.

Figure 11 shows what base is used in Dutch practice. The figure uses lines to indicate the decrease in bicarbonate concentration in relation to hardness reduction.

With the application of caustic soda, for every mmol/l calcium reduction the hydrogen carbonate concentration decreases with 1 mmol/l (line 1:1). With lime per mmol/l hardness reduction, the hydrogen carbonate concentration decreases with 2 mmol/l (line 1:2).

Using the previously mentioned computer program, the exact water quality after softening with caustic soda or lime can be calculated. Figure 12 shows the progress for both the bases of some characteristic softening parameters as a function of height in the reactor. Distinct differences can be noticed. In case different chemicals can be used, a choice will need to be made that takes other quality parameters (such as Cu solubility, TAC) and operational management aspects into account.

Caustic soda

Caustic soda is provided as a 50% solution (= 50% caustic soda and 50% water) by a tanker truck.

Since a 50% caustic soda solution crystallizes at a temperature lower than 12°C, caustic soda is diluted to a 25% solution using demineralized water. This 25% solution only crystallizes at temperatures lower than -18°C.

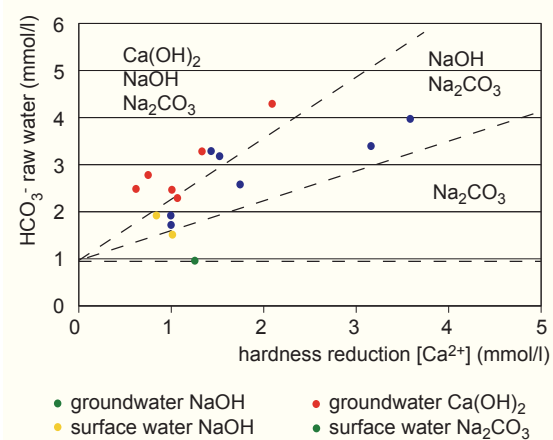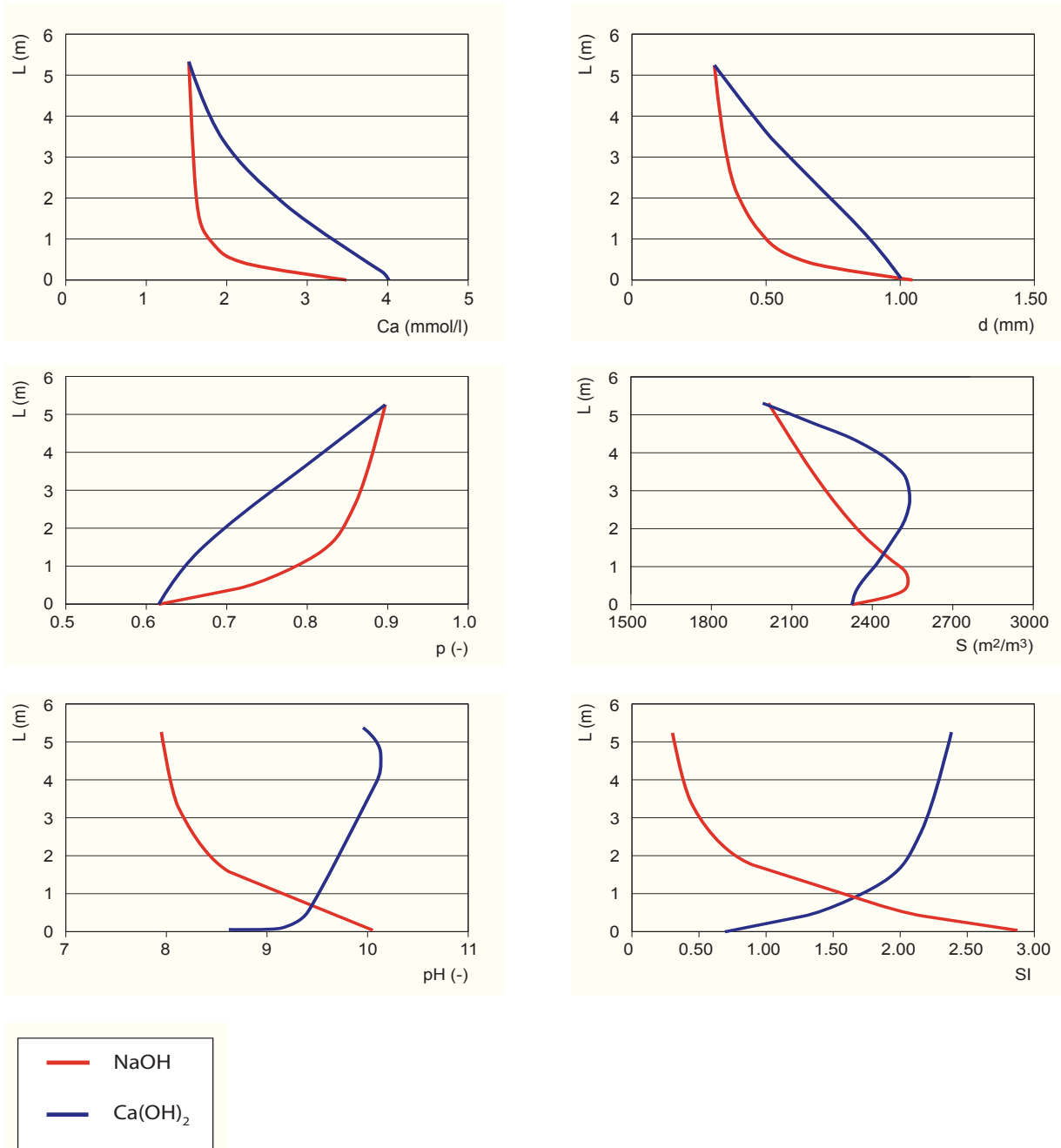The caustic soda is pumped out of the tanker in a storage tank truck.

Figure 11 - Application of base as a softening chemical in Dutch practice

Figure 12 - Softening with caustic soda (red) or lime (blue)

Ca : decrease in calcium concentration is slower with the application of lime than with caustic soda.

d : softening with lime is well-distributed over the reactor height.

p : porosity is directly dependent on the diameter of the particles.

S : specific area has a maximum at a certain height. With lime the maximum area is at a higher point.

pH : the pH of water increases initially with dosing lime as a result of dissolving the $Ca(OH)_2$ particles (lime dissolves faster than softening takes place).

SI : see Ca (as a result of chemical dosage, the supersaturation increases)

Often, more storage tanks are present.
Safety regulations prescribe that the storage tanks be placed apart from the softening installation in a reservoir with a volume of at least one storage tank plus 10% of the total storage capacity.
When caustic soda is diluted with partially softened water, calcium carbonate will be formed and needs to be removed from the storage tanks. Calcium carbonate will not precipitate in the storage tanks when demineralized water is used for dissolution. The demineralized water is prepared with ion exchangers.

From the storage tanks caustic soda is pumped into a dosing installation. This dosing installation can be one single dosing pump per pellet reactor or a caustic soda ring pipe. Caustic soda is injected using a nozzle at the bottom of the pellet reactor.

A nozzle is a specially designed dosing element for the equal distribution of the chemical. Figure 13 shows the Amsterdam nozzle, Figure 14 shows the working mechanism.
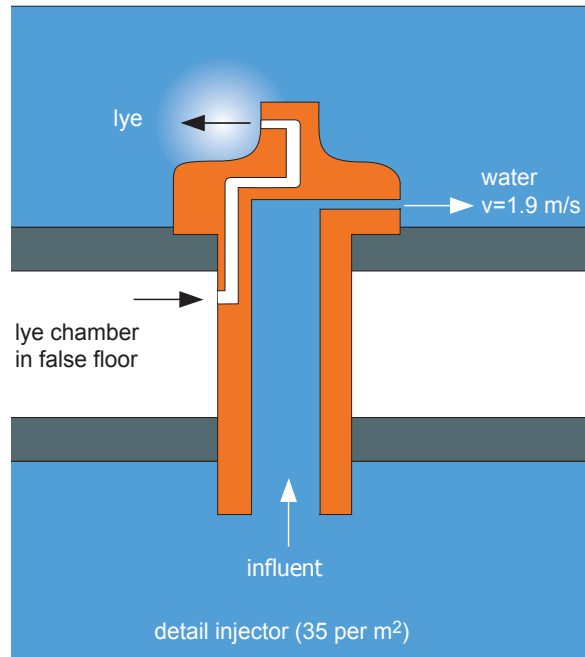

Figure 14 - Schematic representation of an Amsterdam nozzle

Because water and caustic soda flow through the Amsterdam nozzle, a false bottom design is utilized in the reactor. Under this bottom, the water is present. Between the bottom plates caustic soda is present, and above the bottom plates the actual reactor starts.
Water to be softened flows through the nozzle into the reactor. At the same time, but through another channel, a concentration of caustic soda flows through the same nozzle into the reactor. When the outflow velocity of the water is sufficient (1-9 m/h), a good mixing of the chemical and water takes place.

Figure 13 - The Amsterdam nozzle

Figure 15 - Dosing system with separate caustic soda and water dosing nozzles in the bottom

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Figure 16 - Dosing system with separate caustic soda and water dosing nozzles in the bottom

In addition to the Amsterdam nozzle, many more dosing systems exist. There are systems with separate dosing points in the bottom of the reactor, with an inflow of water by separate water nozzles.

An equal distribution of chemical (calcium or caustic soda) and water over the bottom should be taken into account in the design.

Especially for dosing caustic soda, sufficient dosing points need to be realized. For every m^2 of reactor bottom, 30-40 nozzles need to be present.

Dosing on one point in the reactor, like a tangential inlet, is exclusively possible with lime, because the softening reaction is much slower.

Lime

Dosage of lime is, as far as operational management is concerned (necessary installation + maintenance activities), more complicated than dosing caustic soda.

Lime is a suspension that is less soluble than caustic soda (solubility 1.7 g/l) and it needs to be produced on location.

There are several options for the production of lime:

- quick lime (installation: dosing + hydration installation, dosing + solution installation, dosing installation)
- hydrated lime (installation: dosing + solution installation, dosing installation)
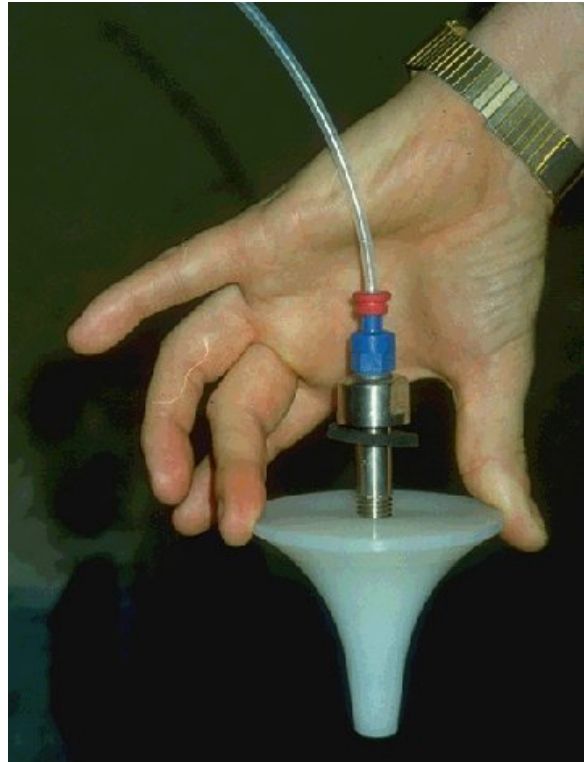- stable lime water (installation: dosing installation).

Figure 17 - Lime water dosing nozzle

The flow of lime water can be up to 10% of the total flow through the reactor.

Lime water in powdered form is supplied by tanker trucks and stored in silos. From the lime silos, powdered lime is transported to a production tank (underneath the silo). In the production tank, lime water is produced in the desired concentration. Lime water dosage can take place with one dosing pump per reactor or by using a ring pipe.

In Figure 17 a lime water dosing nozzle is shown, and in Figure 18 the supply pipes of the lime dosing nozzles are represented.

Equal resistance in every pipe is important. If that is not the case an unequal distribution of chemicals
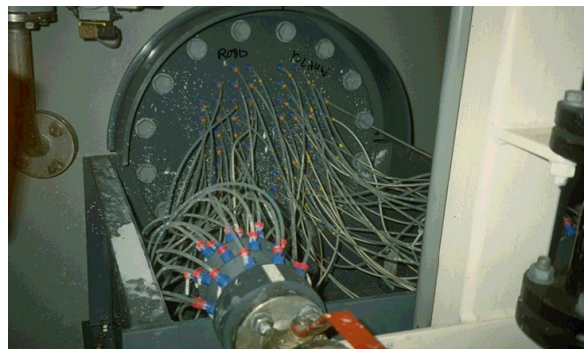

Figure 18 - Supply pipes of the lime dosing nozzles

takes place at the bottom of the pellet reactor and the softening process will be affected.

Another aspect of lime as a chemical is that water, after leaving the softening reactor, has an increased suspended matter concentration. The deposit content is called carry-over and is a result of:

- contamination of calcium hydroxide
- $CaCO_3$ from calcium hydroxide preparation
- undissolved calcium hydroxide particles
- homogeneous nucleation (spontaneous precipitation not on seeding material) and pellet erosion.

4.3 Construction alternatives for reactors

Different types of reactors can be used for softening. There are cylindrical reactors and reactors with varying diameters over height. In the Netherlands ,mainly cylindrical reactors are used. Two Dutch versions are briefly discussed:

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

Due to the cylindrical form of the Amsterdam reactor, homogeneous fluidization occurs; mixing in horizontal directions hardly occurs.

Pellet reactors are discharged several times a day. To remove limestone grains several discharge points are installed in the bottom. The discharge of grains cannot take place in one central place, otherwise a cone shape occurs in the reactor. During the discharge the dosing of caustic soda is stopped to prevent loss of caustic soda in the reactor.
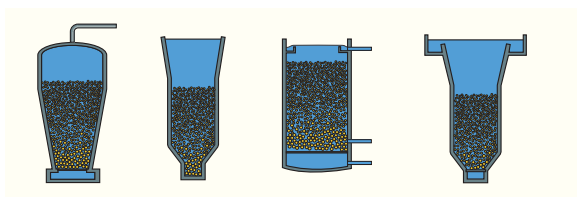

Figure 19 - Different types of reactors

Figure 20 - Tangential flow of raw water

Seeding material is brought in at about 1 m above the bottom of the pellet reactor.

In the cylindrical reactor with a 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.

Softened water leaves the pellet reactor through an overflow weir.

The function of the overflow weir is to provide a uniform abstraction of softened water from the reactor by avoiding preferential flow paths. For a uniform abstraction, a notched weir can be used (Figure 22).

To prevent seeding material from flushing out, the pellet reactor can have a widened upper part. In this widened upper part, the upward velocity

Figure 21 - Several pipes at the bottom of a pellet reactor

will decrease and the seeding material will settle back.

Several pipes are present at the bottom of the reactor:
- a supply pipe for raw, not softened, water
- a supply pipe for dosing the chemical
- a supply pipe for seeding material
- a drain pipe for pellets.

All these pipes need to be well arranged in the treatment building. Typically, pipes of different colors are chosen to prevent mistakes.

The upper part of the softening installation needs to be constructed in such a manner that, with a possible unequal inflow of water, the water will leave the softening reactor equally. Therefore, a notched weir construction can be used as shown in Figure 22.
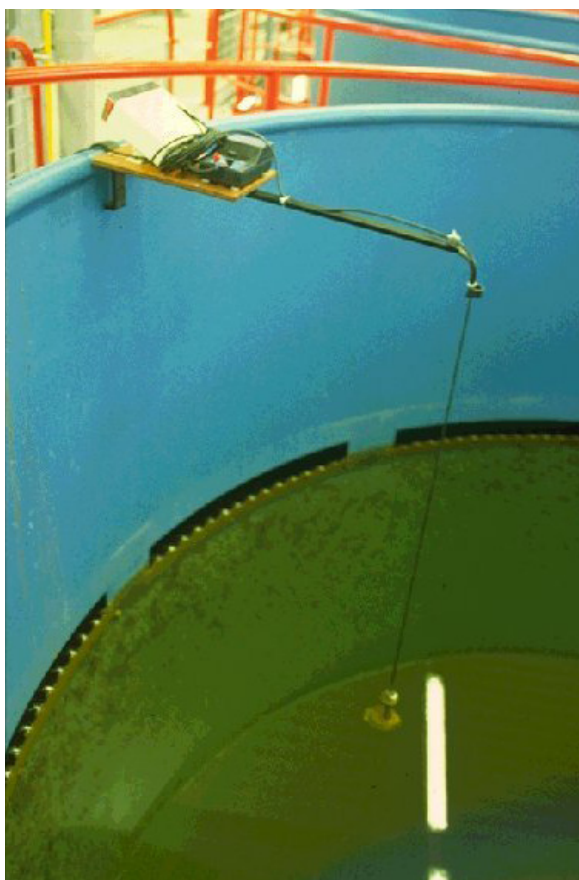
4.4   Seeding material

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

The seeding material is usually disinfected to be sure no bacteriological contamination of water will occur. This disinfection of seeding material takes place with caustic soda or chlorine bleaching lye.

To prevent seeding material from washing out of the reactor and affecting the next treatment processes with a fine fraction of seeding material, the seeding material is washed before it enters the reactor. Here, seeding material is brought into a silo with a washing velocity higher than the velocity in the pellet reactor. In this way, the finest fraction of seeding material is removed.

Figure 22 - Notched water weir

Figure 23 - Seeding sand storage silo with sand washer underneath

The use of seeding sand is minimal.
The storage capacity is usually sufficient for a number of months.

4.5   Pellet storage

Pellet storage can be managed in silos and containers.
The size of the pellet storage is dependent on the pellet production and frequency of pellet collection.
With the application of lime, twice the amount of pellets are produced than are produced with caustic soda.
The volume of a pellet silo is usually equal to the amount of pellets produced in one week.

The pellet silos are equipped with a drainage system to drain water that comes with the pellet discharge.

The pellets shown in Figure 24 consist of 99.5% calcium carbonate. These pellets are brown in color. The reason for this brown coloring is the presence of only 0.5% iron in the pellets.
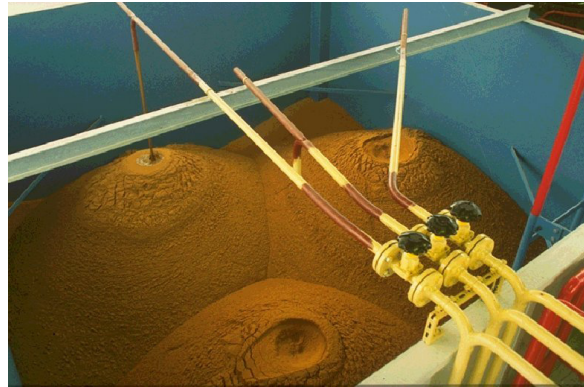

Figure 24 - Pellet storage silo

Further reading

*   Unit processes in drinking water treatment, W. Masschelein (1992), (ISBN 0 8247 8678 5) (635 pgs)

*   Het kalkkoolzuurevenwicht opnieuw bezien DHV (1983), (118 pgs)