CT 4471 Drinking water 1

Softening

Dr. ir. J. Q. J. C. Verberk
Room 2.98
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3. Hydraulics of fluidised bed
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Introduction
What is hard water?
What is hard water?

**total hardness:**  \([\text{Mg}^{2+}] + [\text{Ca}^{2+}] = 1.5 \text{ mmol/l}\)

<table>
<thead>
<tr>
<th></th>
<th>very soft</th>
<th>soft</th>
<th>fairly soft</th>
<th>fairly hard</th>
<th>hard</th>
<th>very hard</th>
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<tbody>
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<td>mmol/l</td>
<td>&lt; 0.5</td>
<td>0.5 - 1.0</td>
<td>1.0 - 1.8</td>
<td>1.8 - 2.5</td>
<td>2.5 - 5</td>
<td>&gt; 5</td>
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<tr>
<td>eq/m³</td>
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<td>1 - 2</td>
<td>2 - 3.5</td>
<td>3.5 - 5</td>
<td>5 - 10</td>
<td>&gt; 10</td>
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<tr>
<td>°D</td>
<td>&lt; 3</td>
<td>3 - 6</td>
<td>- 10</td>
<td>10 - 15</td>
<td>15 - 25</td>
<td>&gt; 25</td>
</tr>
</tbody>
</table>

1°D = 2.8 eq/m³; 1 mmol/l = 2.0 eq/m³

- **Limburg:** hard water
- **Veluwe:** soft water
- **Delft:** 1.5 – 1.7 mmol/l
How hard is your water?

See website of your water supply company
Examples of scaling from daily experience
Why softening?

Public health
• reduced uptake of heavy metals (Pb, Cu, Zn) from pipe material
• no domestic softeners

Environment
• heavy metals (Cu) in sludge of WWTP’s
• use of detergents and phosphate concentration in wastewater
• brine from domestic softeners

Economy
• detergent use
• scaling and corrosion of domestic devices
• energy consumption of heating devices
• destruction of clothing

Ethics
• prevention of stains
Softening methods

Formation of insoluble Ca- and Mg-ions:
- sludge process (USA)
- pellet softening

Exchange of Ca- (and Mg-)ions for Na-ions (ion exchange)

Removal of Ca- and Mg-ions by membrane filtration
Why pellet softening?

Waste product: production of a small amount of hard pellets

Water quality: effluent is almost at equilibrium pH value because of large specific surface area

Operation: minimal supervision, robust process

Costs: lower investment costs due to small volume
low chemical costs due to high efficiency
low costs for (carry-over) sludge treatment using Ca(OH)$_2$
no costs for sludge treatment using NaOH
Principle pellet softening

Fluidised bed
- large crystallisation surface
- rapid reaction
- compact installation
- high efficiency
- low costs
- no cementing of pellets

Crystallisation process
- pure, water free pellets
Water quality

pH \quad 8 < \text{pH} < 8.3
SI \quad -0.2 < SI < 0.3

\text{total hardness:} \quad [\text{Mg}^{2+}] + [\text{Ca}^{2+}] = 1.5 \text{ mmol/l} \ (\text{future 1.0 mmol/l})

\text{HCO}_3^- \text{ concentration:} \quad \text{minimum 1.0 mmol/l}
\quad \text{preferable 2.0 mmol/l}

\text{Na}^+ \text{ concentration:} \quad < 5.2 \text{ mmol/l}
**Water quality**

Cu- and Pb-solubility as low as possible

Cu\(^{2+}\) solubility: \[ 0.52 \cdot \text{TAC} - 1.37 \cdot \text{pH} + 2 \cdot [\text{SO}_4^{2-}] + 10.2 \]

Pb\(^{2+}\) solubility: \[ -141 \cdot \text{pH} + 12 \cdot T + 1135 \]

\[ \text{TAC} = \sum ([\text{CO}_3^{2-}] + [\text{HCO}_3^{-}] + [\text{CO}_2]) \]
Softening in groundwater treatment

Raw water
- good removal of Fe and Mn
- high chemical consumption due to CO₂
- chaotic pellet structure (PO₄)

Aerated water
- reasonable removal of Fe and Mn
- coagulation of micro crystals by Fe
- increased dCa = super saturation

Clear water
- pure pellets
- no influence on existing treatment process
- filtration step needed for removal of micro crystals
Chemical aspects

See CT3011 and CT3420 for more information

Also chapters “Water quality” and “groundwater” of book “Drinking water - principles and practices”
Balance equations

Carbonic acid: \( \text{CO}_2, \text{HCO}_3^-, \text{CO}_3^{2-} \)

The following reactions are important:

\[
\text{CO}_2 + 2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_3^-
\]

\[
K_1 = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad K_1 (T=10^\circ\text{C}) = 3.44 \cdot 10^{-7}
\]

\[
\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CO}_3^{2-}
\]

\[
K_2 = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad K_2 (T=10^\circ\text{C}) = 3.25 \cdot 10^{-11}
\]
pH for natural water is 7-8; thus mainly CO₂ and HCO₃⁻.
Calcium - carbonic acid equilibrium

CaCO₃ ↔ Ca²⁺ + CO₃²⁻ (Kₛ)

CO₂ + 2·H₂O ↔ HCO₃⁻ + H₃O⁺ (K₁)

CO₃²⁻ + H₃O⁺ ↔ HCO₃⁻ + H₂O (K₂⁻¹)

---------- +

CaCO₃ + CO₂ + H₂O ↔ Ca²⁺ + 2·HCO₃⁻

Kₐ = \frac{[Ca^{2+}] \cdot [HCO_3^-]^2}{[CO_2]} = Kₛ \cdot K₁ \cdot K₂⁻¹

Kₐ = \frac{3,89 \cdot 10^{-9} \cdot 3,44 \cdot 10^{-7}}{3,25 \cdot 10^{-11}} = 4,11 \cdot 10^{-5}
\[
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad \leftrightarrow \quad \text{Ca}^{2+} + 2\cdot\text{HCO}_3^- \quad \frac{[\text{Ca}^{2+}] \cdot [\text{HCO}_3^-]^2}{[\text{CO}_2]} = K_a
\]

at 10°C \(\rightarrow K_a = 4.11 \cdot 10^{-5}\)

\[
[\text{Ca}^{2+}] = \frac{1}{2} \cdot [\text{HCO}_3^-]
\]

Above line: aggressive
Underneath line: scaling
Tillmans curve

At 10°C 0.7 g/m³ CO₂, equilibrium = 0.016 mmol/l

\[ [\text{HCO}_3^-] = (2 \cdot 4.11 \cdot 10^{-5} \cdot 1.6 \cdot 10^{-5})^{0.33} = 0.0011 \text{ mol/l} = 1.1 \text{ mmol/l} \]

\[ [\text{Ca}^{2+}] = 0.5 \cdot [\text{HCO}_3^-] = 0.55 \text{ mmol/l} \]

Due to sub-surface reduction processes, CO₂ concentration will increase to several tens of g/m³ --> higher hardness
Saturation index (SI)

Equilibrium equation calcium - carbonic acid

\[
[\text{Ca}^{2+}] = 0.5 \cdot [\text{HCO}_3^-]
\]

Tillmans

1st dissociation equation for carbon dioxide

\[
\frac{[\text{Ca}^{2+}] \cdot [\text{HCO}_3^-]^2}{[\text{CO}_2]} = K_a
\]

\[
\frac{[\text{H}_3\text{O}^+] \cdot [\text{HCO}_3^-]}{[\text{CO}_2]} = K_1
\]

Combination of these equations results in

\[
[\text{H}_3\text{O}^+] = \frac{[\text{HCO}_3^-]^2 \cdot K_2}{2 \cdot K_s}
\]

or in p-values:

\[
pH_s = -2 \cdot \log[\text{HCO}_3^-] - pK_2 + pK_s + \log(2)
\]
Saturation index (SI)

\[ SI = \text{pH} - \text{pH}_s \]

if \( SI < 0 \) aggressive
\( SI > 0 \) scaling

When the water is in equilibrium, \( SI = 0 \), or

\[ SI = \text{pH} - \text{pH}_s = 0 \implies \]
\[ \text{pH} + 2 \cdot \log[\text{HCO}_3^-] + pK_2 - pK_s - \log(2) = 0 \]
Tillmans curve

The graph shows the relationship between carbonate ions ($\text{HCO}_3^-$) and carbon dioxide ($\text{CO}_2$) concentrations in different pH conditions. The curves indicate how the concentration of carbon dioxide changes with increasing concentrations of carbonate ions at various pH levels. The graph includes lines representing different pH conditions: pH=6 (aggressive), pH=7 (scaling), and pH=8, each showing a distinct response pattern.
Ca-pH relation in equilibrium
(Tillmans conditions, Ca=0.5*HCO₃⁻)
Stable pH in distribution system

Optimal conditions: 
- SI > -0.2
- 7.8 < pH < 7.3
- TIC > 1.0 mmol/l

- Optimal conditions for public drinking water
- scaling
- CaCO₃ equilibrium: - 0.2 < SI < 0.3
- aggressive
Neutralisation reactions by dosing base

Dosing caustic soda NaOH
\[ \text{NaOH} + \text{CO}_2 \rightarrow \text{Na}^+ + \text{HCO}_3^- \]

Dosing lime Ca(OH)$_2$
\[ \text{Ca(OH)}_2 + 2 \cdot \text{CO}_2 \rightarrow \text{Ca}^{2+} + 2 \cdot \text{HCO}_3^- \]

Dosing soda ash Na$_2$CO$_3$
\[ \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2 \cdot \text{Na}^+ + 2 \cdot \text{HCO}_3^- \]
Softening reactions by dosing base

Dosing caustic soda NaOH

\[
\begin{align*}
NaOH & \quad \rightarrow Na^+ + OH^- \\
OH^- + HCO_3^- & \quad \rightarrow CO_3^{2-} + H_2O \\
CO_3^{2-} + Ca^{2+} & \quad \rightarrow CaCO_3 \\
NaOH + Ca^{2+} + HCO_3^- & \quad \rightarrow CaCO_3 + H_2O + Na^+
\end{align*}
\]

Dosing lime Ca(OH)\(_2\)

\[
\begin{align*}
Ca(OH)_2 + Ca^{2+} + 2\cdot HCO_3^- & \quad \rightarrow 2\cdot CaCO_3 + 2\cdot H_2O
\end{align*}
\]

Dosing soda ash Na\(_2\)CO\(_3\)

\[
\begin{align*}
Na_2CO_3 + Ca^{2+} & \quad \rightarrow CaCO_3 + 2\cdot Na^+
\end{align*}
\]
# Water composition change by dosing base

<table>
<thead>
<tr>
<th></th>
<th>NaOH</th>
<th>Ca(OH)$_2$</th>
<th>Na$_2$CO$_3$</th>
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<td>CO$_2$</td>
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<td>-2</td>
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</tr>
<tr>
<td>HCO$_3^-$</td>
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<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
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<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td><strong>Softening</strong></td>
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<tr>
<td>CO$_2$</td>
<td>0</td>
<td>0</td>
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<tr>
<td>HCO$_3^-$</td>
<td>-1</td>
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<tr>
<td>Ca$^{2+}$</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>
Choice of chemicals, practice

![Graph showing the relationship between hardness reduction and chemical usage](image)

- **Ca(OH)_2**
- **NaOH**
- **Na_2CO_3**

**HCO_3^-** raw water [mmol/l] vs. **hardness reduction** (Ca^{2+}) [mmol/l]

- **Groundwater NaOH**
- **Groundwater Ca(OH)_2**
- **Surface water NaOH**
- **Surface water Na_2CO_3**
Softening with Tillmans curve dosing chemical

1 - 2 deacidifying
\[ \text{Ca(OH)}_2 + 2 \cdot \text{CO}_2 \rightarrow \text{Ca}^{2+} + 2 \cdot \text{HCO}_3^- \]

2 - 3 softening
\[ \text{Ca}^{2+} + 2 \cdot \text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]

T = 10°C, I = 5 mmol/l

\[ \begin{align*}
\text{pH} = 6 & \quad 1 \\
\text{pH} = 7 & \quad 2 \\
\text{pH} = 8 & \quad 3
\end{align*} \]
Example neutralisation and softening with lime

Raw water composition

\[
\begin{align*}
[\text{Ca}^{2+}] &= 3.0 \text{ mmol/l} \\
[\text{Mg}^{2+}] &= 0.5 \text{ mmol/l} \\
[\text{HCO}_3^-] &= 6 \text{ mmol/l} \\
[\text{CO}_2] &= 2 \text{ mmol/l} \\
[\text{Na}^+] &= 3 \text{ mmol/l} \\
\text{TH} &= 3.5 \text{ mmol/l}
\end{align*}
\]

Preferred TH = 1.5 mmol/l

dosing lime Ca(OH)\textsubscript{2}

neutralisation

\[2 \cdot \text{CO}_2 + \text{Ca(OH)}_2 \rightarrow 2 \cdot \text{HCO}_3^- + \text{Ca}^{2+}\]

needed: 1 mmol/l Ca(OH)\textsubscript{2}

result: \[\text{[HCO}_3^-\text{]} = 8 \text{ mmol/l} ; \text{[Ca}^{2+}\text{]} = 4.0 \text{ mmol/l}\]

softening

\[\text{Ca(OH)}_2 + \text{Ca}^{2+} + 2 \cdot \text{HCO}_3^- \rightarrow 2 \cdot \text{CaCO}_3 + 2 \cdot \text{H}_2\text{O}\]

needed: 3 mmol Ca(OH)\textsubscript{2}

result: \[\text{[HCO}_3^-\text{]} = 2 \text{ mmol/l} ; \text{[Ca}^{2+}\text{]} = 1.0 \text{ mmol/l} ; \text{[CaCO}_3\text{]} = 6 \text{ mmol/l}\]
Hydraulics of fluidised bed

- **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)
Hydraulics of fluidised bed

Head loss

\[
H = 130 \cdot \frac{v^{0.8}}{g} \cdot \frac{(1 - p)^{1.8}}{p^3} \cdot \frac{v^{1.2}}{d^{1.8}} \cdot L
\]

\[
H_{\text{max}} = (1 - p) \cdot L_0 \cdot \frac{\rho_p - \rho_w}{\rho_w}
\]

\[
p = \text{porosity} [-] \quad v = \text{upward velocity} [\text{m/s}]
\]

\[
d = \text{diameter pellet} [\text{m}] \quad L = \text{bed height} [\text{m}]
\]

\[
L_0 = \text{height fixed bed} [\text{m}]
\]

\[
\rho_w = \text{density water} [\text{kg/m}^3]
\]

\[
\rho_p = \text{density pellets} [\text{kg/m}^3]
\]

Porosity

\[
\frac{p}{(1 - p)^{0.8}} = 130 \cdot \frac{v^{0.8}}{g} \cdot \frac{\rho_w}{\rho_p - \rho_w} \cdot \frac{v^{1.2}}{d^{1.8}}
\]
Bed expansion

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

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

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

\[ L_e = \frac{1 - p_o}{1 - p_e} \cdot L_o \]
Porosity

![Graph showing porosity vs velocity for different diameters](image)

- Red line: $d = 0.3 \text{ mm}$
- Blue line: $d = 0.6 \text{ mm}$
- Yellow line: $d = 1.0 \text{ mm}$
- Green line: $d = 1.5 \text{ mm}$
Bed expansion

- d = 0.3 mm
- d = 0.6 mm
- d = 1.0 mm
- d = 1.5 mm

Velocity [m/h] vs. bed expansion E [-]
Specific surface

![Graph showing specific surface area vs. velocity for different particle diameters.](image)
Kinetics and mass balance
Crystallisation kinetics

Kinetic equilibrium

\[ -\frac{dCa^{2+}}{dt} = k \cdot S \cdot \left\{ [Ca^{2+}] \cdot [CO_3^{2-}] - K_s \right\} \]

Parameters

1. Super saturation \([Ca^{2+}] \cdot [CO_3^{2-}] - K_s = K_s \cdot (10^{-SI} - 1)\)
2. Specific surface \(S = 6 \cdot \frac{(1-p)}{d}\)
3. Reaction constant \(k = f(T)\)
1. Equilibrium
   \[ \text{Ca}^{2+} = c_S = \frac{K_s}{[\text{CO}_3^{2-}]} \]

2. Kinetics
   \[ -\frac{dc}{dt} = k \cdot S \cdot \left\{ \left[ \text{Ca}^{2+} \right] \cdot [\text{CO}_3^{2-}] - K_s \right\} \]

3. Mass balance
   \[ \Delta d = f(\Delta c) \]

\[ \Delta d = f(\Delta c) \]

\[ N_k \cdot \frac{\pi}{6} \cdot (d_2^3 - d_1^3) \cdot \rho_p = ([\text{Ca}]_1 - [\text{Ca}]_2) \cdot M \cdot Q \]
Model calculations and softening

\[ \frac{\partial c_{Ca}}{\partial t} = \frac{Q}{A_f \varepsilon_e} \frac{\partial c_{Ca}}{\partial x} - k_f a(c_{Ca} c_{CO3} - \frac{K_{L}}{f^k}) \]

\[ \frac{\partial m}{\partial t} = \frac{Q}{A_f \varepsilon_e} \frac{\partial m}{\partial x} - 2k_f a(c_{Ca} c_{CO3} - \frac{K_{L}}{f^k}) \]

\[ \frac{\partial p}{\partial t} = \frac{Q}{A_f \varepsilon_e} \frac{\partial p}{\partial x} - k_f a(c_{Ca} c_{CO3} - \frac{K_{L}}{f^k}) \]

\[ \frac{\partial BIS}{\partial t} = \frac{Q}{A_f \varepsilon_e} \frac{\partial BIS}{\partial x} - 2k_f a(c_{Ca} c_{CO3} - \frac{K_{L}}{f^k}) \]

\[ \frac{\partial c_{Ca(CO3)}}{\partial t} = \frac{Q}{A_f} \frac{\partial c_{Ca(CO3)}}{\partial x} + \varepsilon_f k_f a(c_{Ca} c_{CO3} - \frac{K_{L}}{f^k}) \]
Reference calculation

Raw water composition:
- Ca$_1$ = 3.5 mmol/l
- TAC = 5.0 mmol/l
- HCO$_3$- = 4.25 mmol/l
- T = 10°C
- I = 12.1 mmol/l

Softened water composition:
- Ca$_2$ = 1.5 mmol/l
- dCa = 0.06 mmol/l

Reactor settings:
- v = 80 m/h
- d$_1$ = 0.3 mm
- $\rho_1$ = 2650 kg/m$^3$
- d$_2$ = 1.0 mm
- $\rho_p$ = 2840 kg/m$^3$
Reference calculation
## Influence variables on reactor height

<table>
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<tr>
<th>Reference conditions</th>
<th>Variable conditions</th>
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<td>( T = 10^\circ C )</td>
<td>( T = 5^\circ C )</td>
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<tr>
<td>( v = 80 \text{ m/h} )</td>
<td>( v = 120 \text{ m/h} )</td>
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<tr>
<td>( d_2 = 1.0 \text{ mm} )</td>
<td>( d_2 = 0.75 \text{ mm} )</td>
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<tr>
<td>( d_1 = 0.3 \text{ mm} )</td>
<td>( d_1 = 0.2 \text{ mm} )</td>
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<tr>
<td>( \rho_p = 2,650 \text{ kg/m}^3 )</td>
<td>( \rho_p = 4,200 \text{ kg/m}^3 )</td>
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<td>( \text{dCa} = 0.06 \text{ mmol/l} )</td>
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## Influence variables

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<td>Ca(OH)$_2$</td>
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<td>-</td>
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Split treatment

Advantages:
1. lower chemical consumption
   - dCa is less
   - no chemicals in split treatment flow (CO₂)
2. mixed water approaches equilibrium
3. lower loading on filters
4. Lower cost due to less reactors/reactor area

Mg²⁺ concentration no too high
Max depth of Ca²⁺ softening = 0.5 mmol/l
Selection of chemical
Choice of chemicals

Chemicals:
- NaOH = caustic soda
- Ca(OH)$_2$ = lime
- NA$_2$CO$_3$ = soda ash

Water quality
- total hardness: 1.5 mmol/l
- HCO$_3^-$-concentration: minimum 1.0 mmol/l, preferred 2.0 mmol/l
- Na$^+$-concentration: < 5.2 mmol/l
- Copper and lead solubility as low as possible

Operation
Dosing of lime

Causes of carry-over (presence of sludge particles in effluent of reactor)

1. Contamination of lime
2. CaCO₃ of lime preparation
   - CO₂-assimilation of air
   - HCO₃⁻ of lime make-up water
3. Non-dissolved lime parts
   - hydrated lime 10 mm?
   - quick lime 5 mm?
   - SST 2 mm?
4. Homogenous nucleation (spontaneous precipitation, not on seeding grains) and pellet erosion
Dosing of lime
Dosing of caustic soda

- wide range of use
- low production of pellets
- simple operation, simple dosing
  (50% solution in tanker, 25% solution in storage)
Dosing of caustic soda

- Lye
- Water $v=1.9 \text{ m/s}$
- Lye chamber in false floor
- Influent
- Detail injector (35 per m$^2$)
Selection of chemical softening with \( \text{NaOH} \) and \( \text{Ca(OH)}_2 \)
Other aspects
## Dutch practice

<table>
<thead>
<tr>
<th>Installation</th>
<th>Chemical</th>
<th>Velocity (m/h)</th>
<th>$L_0$ (m)</th>
<th>dTH (mmol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheveningen</td>
<td>Ca(OH)$_2$</td>
<td>100</td>
<td>3.0</td>
<td>1.0 - 1.5</td>
</tr>
<tr>
<td>Seppe</td>
<td>Ca(OH)$_2$</td>
<td>80</td>
<td>3.5</td>
<td>1.0</td>
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<tr>
<td>Wijk aan Zee</td>
<td>NaOH</td>
<td>90</td>
<td>2.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Hendrik Ido A.</td>
<td>NaOH</td>
<td>100</td>
<td>2.0</td>
<td>0.9</td>
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<tr>
<td>Leiduin</td>
<td>NaOH</td>
<td>100</td>
<td>2.0</td>
<td>0.85 - 1.1</td>
</tr>
<tr>
<td>Noord Bergum</td>
<td>Ca(OH)$_2$</td>
<td>100</td>
<td>3.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Bed height = 2.0 - 3.5 m
Expanded bed height = 6 - 8 m
Reactors design

- Spiractor reactor
- Blackpool reactor
- Amsterdam reactor
- Woerden reactor

- dosing seeding grains
- discharge of pellets
- influent
- effluent
- chemicals
Amsterdam reactor
Bottom Amsterdam reactor
Top view of Amsterdam reactor
Seeding grain storage
Pellet storage
Tangential inlet at Woerden reactor
Oops!!