#### CT 4471 Drinking water 1

#### Softening



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#### Introduction





#### What is hard water?





#### What is hard water?

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

	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	> 5
eq/m <sup>3</sup>	< 1	1 - 2	2 – 3.5	3.5 – 5	5 - 10	>10
°D	< 3	3 - 6	- 10	10 - 15	15 - 25	>25

$$1^{\circ}D = 2.8 \text{ eq/m}^3$$
; 1 mmol/l = 2.0 eq/m<sup>3</sup>

Limburg:	
Veluwe:	
Delft:	

hard water soft water 1.5 – 1.7 mmol/l





kiwa

#### How hard is your water?

#### See website of you 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)<sub>2</sub> 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

рН	8 < pH < 8.3		
SI	-0.2 < SI < 0.3		

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

HCO<sub>3</sub><sup>-</sup> concentration: minimum 1.0 mmol/l preferable 2.0 mmol/l

Na<sup>+</sup> concentration: < 5.2 mmol/l



#### Water quality

#### Cu- and Pb-solubility as low as possible

Pb<sup>2+</sup> solubility: TAC

Cu<sup>2+</sup> solubility :  $0.52 \cdot TAC - 1.37 \cdot pH + 2 \cdot [SO_4^{2-}] + 10.2$ -141·pH + 12·T + 1135  $= \sum ([CO_3^{2}] + [HCO_3] + [CO_2])$ 



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## Softening in ground water treatment



#### Raw water

- + good removal of Fe and Mn
- high chemical consumption due to CO<sub>2</sub>
- chaotic pellet structure (PO<sub>4</sub>)

#### 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 :  $CO_2$  ,  $HCO_3^{-}$ ,  $CO_3^{2-}$ 

The following reactions are important:  $CO_2 + 2 \cdot H_2O < --> H_3O^+ + HCO_3^ K_1 = \frac{[H_3O^+] \cdot [HCO_3^-]}{[CO_2]}$   $K_1 (T=10^{\circ}C) = 3.44 \cdot 10^{-7}$ 

 $HCO_{3}^{-} + H_{2}O < --> H_{3}O^{+} + CO_{3}^{2-}$  $K_{2} = \frac{[H_{3}O^{+}] \cdot [CO_{3}^{2-}]}{[HCO_{3}^{-}]} K_{2} (T=10^{\circ}C) = 3.25 \cdot 10^{-11}$ 



#### % pH diagram for carbonic acid



pH for natural water is 7-8; thus mainly CO<sub>2</sub> en HCO<sub>3</sub><sup>-</sup>



#### Calcium - carbonic acid equilibrium

CaCO <sub>3</sub>	<>	$Ca^{2+} + CO_3^{2-}$	(K <sub>s</sub> )
$CO_2 + 2 \cdot H_2O$	<>	$HCO_{3}^{-} + H_{3}O^{+}$	(K <sub>1</sub> )
$CO_3^{2-} + H_3O^+$	<>	$HCO_{3}^{-} + H_{2}O$	(K <sub>2</sub> <sup>-1</sup> )
			+

 $CaCO_3 + CO_2 + H_2O$  <-->  $Ca^{2+} + 2 \cdot HCO_3^{-}$ 

$$K_{a} = \frac{[Ca^{2+}] \cdot [HCO_{3}^{-}]^{2}}{[CO_{2}]} = K_{s} \cdot K_{1} \cdot K_{2}^{-1}$$
$$K_{a} = \frac{3,89 \cdot 10^{-9} \cdot 3,44 \cdot 10^{-7}}{3,25 \cdot 10^{-11}} = 4,11 \cdot 10^{-5}$$



#### Tillmans

 $CaCO_{3} + CO_{2} + H_{2}O \qquad < --> \qquad Ca^{2+} + 2 \cdot HCO_{3}^{-} \qquad \frac{[Ca^{2+}] \cdot [HCO_{3}^{-}]^{2}}{[CO_{2}]} = K_{a}$ at 10°C -->  $K_{a} = 4.11 \cdot 10^{-5}$  $[HCO_{3}^{-}]^{3} = 2 \cdot K_{a} \cdot [CO_{2}]$  $[Ca^{2+}] = 1/2 \cdot [HCO_{3}^{-}]$ 



Above line: aggressive Underneath line: scaling



#### **Tillmans curve**

At 10°C 0.7 g/m<sup>3</sup> CO<sub>2,equilibrium</sub> = 0.016 mmol/l  $[HCO_3^-] = (2.4.11.10^{-5}.1.6.10^{-5})^{0.33} = 0.0011 \text{ mol/l} = 1.1 \text{ mmol/l}$  $[Ca^{2+}] = 0.5 \cdot [HCO_3^-] = 0.55 \text{ mmol/l}$ 



Due to sub surface reduction processes,  $CO_2$  concentration will increase to several tens of g/m<sup>3</sup> --> higher hardness

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## Saturation index (SI)

Equilibrium equation calcium - carbonic acid

Tillmans  $[Ca^{2+}] = 0.5 \cdot [HCO_3^{-}]$ 

1<sup>st</sup> dissociation equation for carbon dioxide

 $\frac{[\operatorname{Ca}^{2+}] \cdot [\operatorname{HCO}_3^{-}]^2}{[\operatorname{CO}_2]} = \mathrm{K}_a$ 

 $\frac{[H_3O^+]\cdot[HCO_3^-]}{[CO_2]} = K_1$ 

Combination of these equations results in  $[H_3O^+] = \frac{[HCO_3^-]^2 \cdot K_2}{2 \cdot K_s}$ or in p-values:

 $pH_{s} = -2 \cdot \log[HCO_{3}^{-}] - pK_{2} + pK_{s} + \log(2)$ 



#### Saturation index (SI)

 $SI = pH - pH_s$ 

if SI < 0 agressive SI > 0 scaling

When the water is in equilibrium, SI = 0, or

$$SI = pH - pH_S = 0 \Rightarrow$$

 $pH+ 2 \cdot log[HCO_3^{-}] + pK_2 - pK_s - log(2) = 0$ 



#### **Tillmans curve**



#### **Ca-pH relation in equilibrium** (Tillmans conditions, $Ca=0.5*HCO_3^{-}$ )



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#### Stable pH in distribution system



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#### Neutralisation reactions by dosing base

Dosing caustic soda NaOH NaOH +  $CO_2$ 

Dosing lime  $Ca(OH)_2$  $Ca(OH)_2 + 2 \cdot CO_2$ 

Dosing soda ash  $Na_2CO_3$  $Na_2CO_3 + CO_2 + H_2O$  --> Na<sup>+</sup> + HCO<sub>3</sub><sup>-</sup>

-->Ca<sup>2+</sup> + 2·HCO<sub>3</sub><sup>-</sup>

--> 2·Na<sup>+</sup> + 2·HCO<sub>3</sub><sup>-</sup>



#### Softening reactions by dosing base

Dosing caustic soda NaOH ---> Na+ + OH-NaOH  $OH^{-} + HCO_{2}^{-}$  $--> CO_3^{2-} + H_2O$  $CO_{2^{2-}} + Ca^{2+}$ --> CaCO<sub>3</sub> ↓  $NaOH + Ca^{2+} + HCO_3^{-}$  $--> CaCO_3 + H_2O + Na^+$ Dosing lime Ca(OH)<sub>2</sub>  $Ca(OH)_{2} + Ca^{2+} + 2 \cdot HCO_{3}^{-} = ->2 \cdot CaCO_{3} + 2 \cdot H_{2}O_{3}^{-}$ Dosing soda ash Na<sub>2</sub>CO<sub>3</sub>  $Na_{2}CO_{3} + Ca^{2+}$  $--> CaCO_3 + 2 \cdot Na^+$ 



#### Water composition change by dosing base

	NaOH	Ca(OH) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>
Neutralisation			
CO <sub>2</sub>	-1	-2	-1
HCO <sub>3</sub> -	1	2	2
Ca <sup>2+</sup>	0	1	0
Na+	1	0	2
Softening			
CO <sub>2</sub>	0	0	0
HCO <sub>3</sub> -	-1	-2	0
Ca <sup>2+</sup>	-1	-1	-1
Na <sup>+</sup>	1	0	2



#### Choice of chemicals, practice



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## Softening with Tillmans curve dosing chemical

1 - 2 deacidifying
 2 - 3 softening

 $\begin{array}{c} Ca(OH)_2 + 2 \cdot CO_2 \xrightarrow{\phantom{a}} Ca^{2+} + 2 \cdot HCO_3^{-} \\ Ca^{2+} + 2 \cdot HCO_3^{-} \xrightarrow{\phantom{a}} CaCO_3 + CO_2 + H_2O \end{array}$ 





# Example neutralisation and softening with lime

Raw water composition  $[Ca^{2+}] = 3,0 \text{ mmol/l}$   $[Mg^{2+}] = 0,5 \text{ mmol/l}$  TH = 3,5 mmol/l $[HCO_3^{-1}] = 6 \text{ mmol/l}$   $[CO_2] = 2 \text{ mmol/l}$   $[Na^+] = 3 \text{ mmol/l}$ preferred TH = 1,5 mmol/ldosing lime Ca(OH)<sub>2</sub> neutralisation  $2 \cdot CO_2 + Ca(OH)_2 -> 2 \cdot HCO_3 + Ca^{2+}$ needed: 1 mmol/l Ca(OH)<sub>2</sub> result:  $[HCO_3^{-}] = 8 \text{ mmol/l}; [Ca^{2+}] = 4.0 \text{ mmol/l}$  $Ca(OH_{2}) + Ca^{2+} + 2 \cdot HCO_{3}^{-} - > 2 \cdot CaCO_{3} + 2 \cdot H_{2}O$ softening needed: 3 mmol Ca(OH)<sub>2</sub>

result:  $[HCO_3^-]=2 \text{ mmol/l}; [Ca^{2+}]=1.0 \text{ mmol/l}; [CaCO_3]=6 \text{ mmol/l}$ 



#### Hydraulics of fluidised bed





#### Hydraulics of fluidised bed

Head loss

$$H = 130 \cdot \frac{v^{0.8}}{g} \cdot \frac{(1-p)^{1.8}}{p^3} \cdot \frac{v^{1.2}}{d^{1.8}} \cdot L$$
$$H_{max} = (1-p) \cdot L_0 \cdot \frac{\rho_p - \rho_w}{\rho_w}$$

p = porosity [-]d = diameter pellet [m] L<sub>0</sub> = height fixed bed [m]  $\rho_w$  = density water [kg/m<sup>3</sup>] v = upward velocity [m/s]

 $\rho_p$  = density pellets [kg/m<sup>3</sup>]

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**



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#### **Porosity**





#### **Bed expansion**





#### **Specific surface**



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#### **Kinetics and mass balance**





## **Crystallisation kinetics**

Kinetic equilibrium

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

Parameters1. Super saturation $[Ca^{2+}] \cdot [CO_3^{2-}] - K_s = K_s \cdot (10^{-SI} - 1)$ 2. Specific surface $\mathbf{S} = \mathbf{6} \cdot \frac{(1-p)}{d}$ 3. Reaction constantk = f(T)



#### **Mass balance**



$$\begin{split} \Delta \mathbf{d} &= \mathbf{f}(\Delta \mathbf{C}) \\ \mathbf{N}_{k} \cdot \frac{\pi}{6} \cdot \left( \mathbf{d}_{2}^{3} - \mathbf{d}_{1}^{3} \right) \cdot \mathbf{\rho}_{p} = \left( \left[ \mathbf{Ca} \right]_{1} - \left[ \mathbf{Ca} \right]_{2} \right) \cdot \mathbf{M} \cdot \mathbf{Q} \end{split}$$

- 1. Equilibrium
- 2. Kinetics
- 3. Mass balance

$$Ca^{2+} = c_{s} = \frac{K_{s}}{[CO_{3}^{2-}]}$$
$$-\frac{dc}{dt} = k \cdot S \cdot \left\{ \begin{bmatrix} CO_{3}^{2-} \end{bmatrix} \cdot \begin{bmatrix} CO_{3}^{2-} \end{bmatrix} - K_{s} \right\}$$
$$\Delta d = f(\Delta c)$$



#### **Model calculations and softening**







#### **Reference calculation**

Raw water composition:

Softened water composition:

Reactor settings:

$Ca_1 =$ TAC =	3.5 mmol/l 5.0 mmol/l
пс0 <sub>3</sub> =	
1 =	
1 =	12.1 mmol/
$Ca_2 =$	1.5 mmol/l
dCa =	0.06 mmol/
V =	80 m/h
d <sub>1</sub> =	0.3 mm
$\rho_1 =$	2650 kg/m <sup>3</sup>
$d_2 =$	1.0 mm
$\rho_{p} =$	2840 kg/m <sup>3</sup>



#### **Reference calculation**



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#### Influence variables on reactor height

Reference conditions Variable conditions

 $T = 10^{\circ}C$ v = 80 m/h $d_2 = 1.0 \text{ mm}$  $d_1 = 0.3 \text{ mm}$  $\rho_{\rm p} = 2,650 \text{ kg/m}^3$ dCa = 0.06 mmol/l $Ca_2 = 1.50 \text{ mmol/l}$ 

 $T = 5^{\circ}C$ v = 120 m/h $d_2 = 0.75 \text{ mm}$  $d_1 = 0.2 \text{ mm}$  $\rho_{\rm p} = 4,200 \text{ kg/m}^3$ dCa = 0.10 mmol/l $Ca_2 = 1.00 \text{ mmol/l}$ 

 $L_{o} = 6.73 \text{ m}$  $L_{o} = 10.9 \text{ m}$  $L_{a} = 5.39 \text{ m}$  $L_{p} = 5.58 \text{ m}$  $L_{e} = 4.55 \text{ m}$  $L_{e} = 2.78 \text{ m}$  $L_{e} = 3.12 \text{ m}$ 

 $L_{e} = 5.43 \text{ m}$ 



#### Influence variables

increase	influence on				
of	L <sub>e</sub>	dos	N <sub>k</sub>	S	Si <sub>max</sub>
Т	<<	<	-	>	<
V	>>	-	-	<<	-
$d_2$	>	-	<<	<<	-
d <sub>1</sub>	<>	-	>>	<	-
ρ <sub>1</sub>	<	-	>>	>	-
Ca <sub>1</sub>	<<	>	-	-	>
Ca <sub>2</sub>	<>	<<	<<	-	<<
Size of					
Ca(OH) <sub>2</sub>	>>	-	-	-	<<



#### **Split treatment**

Advantages:
1. lower chemical consumption

dCa is less
no chemicals in split treatment flow (CO<sub>2</sub>)

2. mixed water approaches equilibrium
3. lower loading on filters
4. Lower cost due to less reactors/reactor area

 $Mg^{2+}$  concentration no too high Max depth of Ca<sup>2+</sup> softening = 0.5 mmol/l





#### **Selection of chemical**





#### **Choice of chemicals**

Chemicals: NaOH = caustic soda  $Ca(OH)_2 = lime$   $NA_2CO_3 = soda ash$ Water quality total hardness:  $HCO_3^{-}$ -concentration:

Na<sup>+</sup>-concentration: < 5.2 m Copper and lead solubility as low as possible Operation



1.5 mmol/l minimum 1.0 mmol/l preferred 2.0 mmol/l < 5.2 mmol/l

## **Dosing of lime**

Causes of carry-over (presence of sludge particles in effluent of reactor) Contamination of lime 1. CaCO<sub>3</sub> of lime preparation 2. - CO<sub>2</sub>-assimilation of air - HCO<sub>3</sub><sup>-</sup> of lime make-up water Non-dissolved lime parts 3. - hydrated lime 10 mm? - quick lime 5 mm? - SST 2 mm? Homogenous nucleation (spontaneous precipitation, not on 4. 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)









softening with NaOH and Ca(OH)<sub>2</sub>





### **Other aspects**





#### **Dutch practice**

installation	chemical	velocity	Lo	dTH
		(m/h)	(m)	(mmol/l)
Scheveningen	Ca(OH) <sub>2</sub>	100	3.0	1.0 - 1.5
Seppe	Ca(OH) <sub>2</sub>	80	3.5	1.0
Wijk aan Zee	NaOH	90	2.0	0.9
Hendrik Ido A.	NaOH	100	2.0	0.9
Leiduin	NaOH	100	2.0	0.85 - 1.1
Noord Bergum	Ca(OH) <sub>2</sub>	100	3.5	1.0

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



#### **Reactors design**



#### **Amsterdam reactor**





#### **Bottom Amsterdam reactor**





#### **Top view of Amsterdam reactor**





### Seeding grain storage







### **Pellet storage**





#### **Tangential inlet at Woerden reactor**









