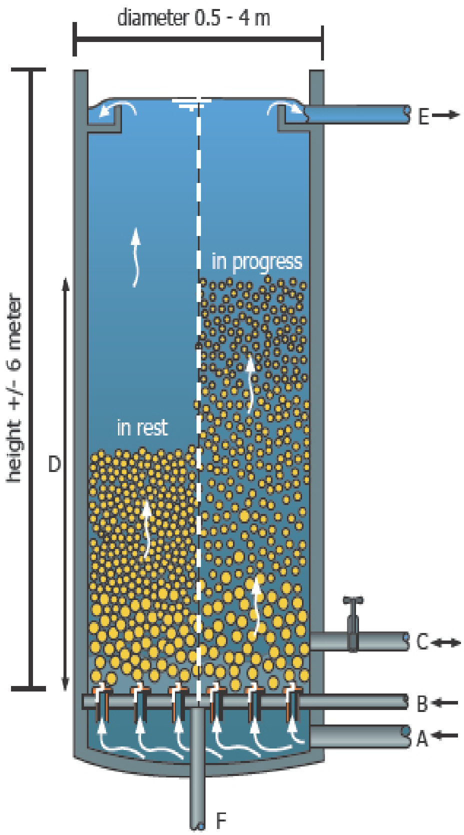
LAB EXPERIMENTS

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)

Framework
This module explains the lab experiment on softening.

Contents
This module has the following contents:

1. Objective

The hardness of tap water is defined as the sum of the calcium and magnesium concentration.
Hard water causes scaling, especially with high temperatures (boilers, cooling water, washing machines). Moreover hard water increases the consumption of detergents. On the other hand soft water can have a low pH-value, which can give corrosion. For those reasons the hardness is kept between certain limits. In the Netherlands softening is used at several plants. Mostly pellet reactors are used for softening processes.

Design parameters for pellet reactors are determined in a pilot plant. The objective of this experiment is to find the physical and chemical process parameters that characterize the softening process. The experiment will be evaluated with computer models on the website; www.stimela.com. These models are suited for chemical calculations of the calcium carbonic acid equilibrium and for reactor design.

A full-scale treatment plant has to be designed, using the results of laboratory experiments.

The objective is to determine the status of the process and to determine the best process conditions for operation of pellet reactors.

2. Theory

2.1 Chemical aspects

The total hardness of tap water (THH) is the sum of Ca^{2+} and Mg^{2+} concentration in mmol/l:

$$THH = [Ca^{2+}] + [Mg^{2+}] \qquad (mmol/l)$$

Softening of tap water removes Ca^{2+} by precipitation of calcium carbonate:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

This reaction only happens if sufficient CO_3^{2-} ions are present. To realize this the pH has to be increased. The equilibrium reactions of carbonic acid shift to the right and the CO_3^{2-} concentration increases (carbonic acid equilibrium):

$$CO_2 + 2\,H_2O \leftrightarrow H_3O^+ + HCO_3^-$$
$$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$$

The increase of pH is realized by adding a base solution that binds the H_3O^+ - ions. Sodiumhydroxide (NaOH) is used to achieve this. The more NaOH is added, the more the pH rises and the stronger the softening.

2.2 Physical aspects

The pellet reactor is filled with (garnet) sand and the feed flow is in upward direction. NaOH is added at the bottom of the reactor. The feed water is supersaturated with calcium carbonate that crystallizes on the grains in the fluidised bed. The grains serve as crystallisation surface. The reactions are fast and take place in the lower part of the column.

An important parameter is the contact surface of the sand bed which is determined by the diameter of the grains. Because higher flow velocities give a more expanded bed, the contact surface is also influenced by the water velocity (m/h).

The effluent is still supersaturated with calcium carbonate because of the short reaction time. The extent of this supersaturation is for the greater part dependent of the physical conditions in the reactor. The inlet construction, the upward flow velocities, the contact time, the chemical concentrations and the contact surface play an important role

2.3 Description of the installation

The softening process in the pilot plant installation of production location Weesperkarspel consists of two columns with a diameter of 31 cm and a height of 4.5m.
The flow is controlled by a regulated valve with a capacity between 4 m³/h and 7 m³/h.

In addition, the caustic soda flow and the pellet discharge can be automatically controlled. By-pass water can be mixed with the effluent of the two reactors.

In the influent and the effluent the following water quality parameters are measured on-line:
- pH
- alkalinity
- temperature
- conductivity
- calcium concentration

In addition, measurements are carried out to determine the state of the fluidised bed:
- bed height
- head loss over the fluidised bed.

2.4 Dosing quantity of NaOH

Dosing of NaOH is calculated by the following equation (in mmol/l):

$$NaOH = \frac{q_{NaOH}}{Q_w + q_{NaOH}} \frac{\varphi_{NaOH} \cdot \rho_{NaOH}}{M_{NaOH}}$$

in which:

φ_{NaOH} = Strength of caustic soda solution (25%)
ρ_{NaOH} = Density of caustic soda solution (=1270 kg/m^3)
M_{NaOH} = Molar mass of caustic soda (g/mol)
q_{NaOH} = Density of caustic soda solution (kg/m^3)

2.5 Determination of the reactor state

The height of the fluidised pellet bed is determined by the water velocity through the reactor, the diameter of the pellets in the bed and the water temperature. These parameters also influence the specific crystallisation surface of the fluidised bed and with the crystallisation coefficient the super-saturated calcium carbonate concentration in the effluent of the reactor.

The pellet size distribution in the bed can be determined by sampling the bed and sieving the sample, but this is time consuming. Therefore a derived parameter is used: the pressure drop measurement.

The relation between pressure drop, temperature, water flow and grain size can be determined by the following equations.

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

and

$$p = \left(\frac{v}{v_0}\right)^{\frac{1}{n}}$$

Considering that

$$\rho_p = \frac{\rho_g \frac{1}{6}\pi d^3{}_0 + \rho_s \frac{1}{6}\pi (d^3{}_p - d^3{}_0)}{\frac{1}{6}\pi d^3{}_p}$$

in which:

v_0 = terminal settling velocity
p = porosity
ρ_p = density pellets
ρ_w = density water
v = velocity
n = exponent

The terminal settling velocity and the exponent (n) represent the proporties of a single particle and are determined experimentally (see http://dx.doi.org/10.1016/j.watres.2007.07.019), paragraph about Richardson-Zaki approach for all formulas.

The measurements that are carried out are not always reliable and therefore verification should taken place. One of the verification is that a fixed relation exists between incoming and outgoing alkalinity and calcium concentration and caustic soda dosing.

$$m_{out} = m_{in} + NaOH - 2(Ca_{out} - Ca_{in})$$

3. Method

Test one of the following process conditions:
- flow: 5 and 6 m^3/h
- caustic soda dosing: 1 l/h

Read from the equipment the measured data:
- pressure drop (20-60 cm, 20-150 cm, 20-height cm)
- pH
- alkalinity (m-value)
- temperature
- conductivity
- calcium concentration

4. Elaboration

The measurements can be checked with the model for the pellet reactor. For calculations log in at the site www.stimela.com and download the excel sheet 'Calculations Pellet Softening.xls'.

Because the pellets do not grow fast, the pellet discharge speed can be neglected in this experiment.

Execute the following steps:
- Calculate the porosity and pellet size over the reactor assuming the density of the garnet sand to be 4100 kg/m^3 and the density of calcium carbonate to be 2660 kg/m^3
- Put the values of the influent quality in the model and calculate the water quality, Compare the results of the model with the measured effluent quality. Give your comments.
- Assume the testwater in practice will be softened in a partial flow. The required total hardness (Mg+Ca), after mixing the treated and non-treated flow, is 1.5 mmol/l. Assume Mg-conc. = 0.27 mmol/l (will not be removed). Calculate for this situation the required partial flow for a Ca-conc. of 0.5 mmol/l after treatment in the partial flow. Use the model for pellet softening to determine the required NaOH dosing. Calculate with the model for Calcium Carbonic Acid equilibrium the composition of the final product after mixing: pH, Ca, p- and m-number, supersaturated $CaCO_3$ and Saturation index). Keep in mind that Ca, m- and p-number and ionic strength are conservative (summable) parameters.

Data form

Group number: Date:

Flow through reactor (m^3/h)	
Caustic soda flow (l/h)	
Dosing of NaOH (mmol/l)	
Fluidised bed height	

	Pressure drop	Amount of grains	Diameter of grains
H=			
H=			
H=			

Water quality	Influent	Effluent
pH		
m-number		
Conductivity		
Ca concentration		
Temperature		