

Dynamic modelling for optimisation of pellet softening

K. M. van Schagen, L. C. Rietveld and R. Babuška

ABSTRACT

Mathematical models for the crystallisation process in pellet reactors have been developed during recent decades. In this paper, these models are extended with new insights in the pellet softening process. The diffusion of the supersaturated water to the pellet surface is included in the model and the fluidisation model of the bed is modified. The new model is calibrated in a pilot plant setup. Calibration results are validated in two different full-scale plants. The validation process shows that, even under basic process operation, the model can be used to identify a malfunctioning apparatus and identify undesired process conditions. For the normal situation the model gives satisfactory results in predicting fluidised bed porosity and water quality parameters such as calcium, pH, conductivity and m-alkalinity. The validated model is used to show that pellet size control in the reactor has significant influence on performance with respect to the water quality parameters. Maintaining the pellet size in the bottom of the reactor at 0.8 mm compared with 1.4 mm reduces the supersaturation of calcium carbonate in the water after the reactor by 50%, but increases the consumption of seeding material by 550%.

Key words | modelling, model validation, pellet softening, process optimisation

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LIST OF INDICES

c	CaCO ₃
p	pellets
w	water
g	garnet

LIST OF SYMBOLS

<i>A</i>	reactor area	m ²
<i>C</i>	crystallisation rate	mmol l ⁻¹ s ⁻¹
<i>C_{w2}</i>	drag coefficient Richardson-Zaki	-
<i>d</i>	average diameter	m
<i>D_f</i>	diffusivity coefficient	m ² s ⁻¹
<i>dP</i>	pressure drop	Pa
<i>F</i>	flow	m ³ s ⁻¹
<i>f</i>	activity	-
<i>g</i>	gravitational acceleration	ms ⁻²
<i>IS</i>	ionic strength	mmol l ⁻¹
<i>κ</i>	crystallisation kinetics	l ms ⁻¹ mmol ⁻¹
<i>K_{1,2}</i>	equilibrium constants	mmol l ⁻¹
<i>K_s</i>	solubility product	mmol ² l ⁻²

<i>k_T</i>	reaction rate	l ms ⁻¹ mmol ⁻¹
<i>K_w</i>	equilibrium constant	mmol ² l ⁻²
<i>k_f</i>	transport rate	l ms ⁻¹ mmol ⁻¹
<i>L</i>	bed height	m
<i>m</i>	mass	kg
<i>M</i>	m-alkalinity	mmol l ⁻¹
<i>M_c</i>	CaCO ₃ molecular weight	g mmol ⁻¹
<i>MSE</i>	mean squared error	-
<i>ν</i>	viscosity of water	m ² s ⁻¹
<i>p</i>	bed porosity	-
<i>P</i>	p-alkalinity	mmol l ⁻¹
<i>ρ</i>	density	kg m ⁻³
<i>Re_o</i>	terminal settling Reynolds number	-
<i>Re_h</i>	particle Reynolds number	-
<i>S</i>	crystallisation surface	m ² m ⁻³
<i>Sc</i>	Schmidt number	-
<i>Sh</i>	Sherwood number	-
<i>SI</i>	saturation index	-
<i>TCCP</i>	theoretical calcium carbonate crystallisation potential	mmol l ⁻¹
<i>v_o</i>	terminal settling velocity	ms ⁻¹

INTRODUCTION

In the Netherlands, central softening of drinking water is mainly carried out with fluidised pellet reactors. The pellet reactor consists of a cylindrical vessel that is partly filled with seeding material. The diameter of the seeding grain is small, between 0.2 and 0.4 mm, and consequently the crystallisation surface is large. The water is pumped through the reactor in an upward direction at high velocities, maintaining the seeding material in a fluidised condition. In the bottom of the reactor, chemicals are dosed (caustic soda, soda ash or lime). Calcium carbonate then becomes supersaturated and crystallises on the seeding material, resulting in the formation of pellets. At regular intervals, pellets at the bottom of the reactor are removed. These pellets can be re-used in industry.

Softening in a reactor is normally in excess of the required levels. Therefore, a part of the water can be bypassed and mixed with the effluent of the reactors. In general several identical parallel reactors are installed to increase the reliability of the system and the flexibility in operation. Reactors can be switched on and off in case of flow changes, maintaining water velocities between 60 and 100 m h^{-1} .

The mixture of the effluent of the reactors and the bypass water must be chemically stable to avoid crystallisation in the filters after the softening step. To optimise the operation of pellet softening reactors using caustic soda (NaOH), a mathematical model has been developed. The purpose of modelling is to simulate the softening process, in order to make decisions on operation, leading finally to model predictive control of the process. During operation, water quality and flow change frequently and manipulation of the process has influence on the behaviour of the softening process. The dynamics of the process are therefore taken into account.

MATHEMATICAL MODELLING OF THE SOFTENING PROCESS

The softening process consists of a number of fluidised bed reactors with one single bypass. The chemical reactions in the water take place in the reactor. The mixing process of reactor

effluents and bypass water is modelled as instantaneous mixing (taking the calcium carbonic equilibrium into account) without any reaction kinetics.

In the past, a number of models have been developed (van Dijk & Wilms 1991; ter Bogt *et al.* 1992). These models are steady-state models used for design purposes. In this article a dynamic model of the pellet softening process is described. This model takes diffusion in the fluidised bed and new insights in the fluidised bed behaviour of pellet softening reactors into account.

The model is deduced in three sections. In the first section, the calcium carbonic equilibrium, which determines the crystallisation in the reactor, is explained. The second section describes the fluidisation of the bed, which determines the available crystallisation surface in the reactor. And finally the crystallisation rate is modelled based on the crystallisation surface and the calcium carbonic equilibrium.

Modelling the calcium carbonic equilibrium

The crystallisation of calcium carbonate is a shift in the equilibrium between the solid and soluble state of calcium carbonate (Wiechers *et al.* 1975):



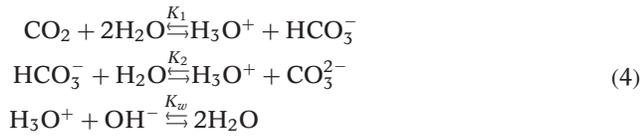
$$K_s = f^8 [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \quad (2)$$

where the equilibrium constant K_s is an experimentally determined constant depending on the water temperature. The activity factor f is based on the ionic strength (IS) of the water and is given by (Schock 1984):

$$\log(f) = \frac{-0.5\sqrt{\text{IS}}}{\sqrt{1000} + \sqrt{\text{IS}}} + 0.00015\text{IS} \quad (3)$$

To determine the carbonate concentration, the carbonic equilibrium must be taken into account. This is the balance between three carbonic fractions (CO_2 , HCO_3^- and CO_3^{2-}).

The ratio between the concentrations of these fractions has a strong relation to the pH. The following reactions describe the equilibrium:



The reaction rates of these equilibria are high, and it is therefore assumed that the carbonic fractions are always in equilibrium. The conservative parameters m-alkalinity (M) and p-alkalinity (P) are used to describe the equilibrium. The actual concentrations of the equilibrium can now be found by solving the following set of algebraic equations:

$$\begin{aligned} M &= 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}_3\text{O}^+] \\ P &= [\text{CO}_3^{2-}] - [\text{CO}_2] + [\text{OH}^-] - [\text{H}_3\text{O}^+] \\ K_1 &= f^2[\text{HCO}_3^-][\text{H}_3\text{O}^+][\text{CO}_2]^{-1} \\ K_2 &= f^4[\text{CO}_3^{2-}][\text{H}_3\text{O}^+][\text{HCO}_3^-]^{-1} \\ K_w &= f^2[\text{H}_3\text{O}^+][\text{OH}^-] \end{aligned} \quad (5)$$

where K_1 , K_2 and K_w are experimentally well-determined constants depending on the water temperature (Jacobsen & Langmuir 1974; Plummer & Busenberg 1982). Equation (5) is a set of five equations with seven unknown concentrations M , P , CO_2 , HCO_3^- , CO_3^{2-} , H_3O^+ and OH^- . Two concentrations must be known to determine the remaining ones. The H_3O^+ and the HCO_3^- are known concentrations in the raw water of the softening reactors. The H_3O^+ concentration is normally measured as pH:

$$\text{pH} = -\log(f[\text{H}_3\text{O}^+]) \quad (6)$$

It is now possible to determine the carbonate concentration throughout the crystallisation process. Based on the measured pH and HCO_3^- concentration, the m-alkalinity and the p-alkalinity are determined using Equations (5) and (6). The dosing of caustic soda causes an increase of the m-alkalinity and p-alkalinity due to the feed of OH^- . With the new m-alkalinity and p-alkalinity, the CO_3^{2-} concentration is determined. As soon as crystallisation takes place, carbonate (CO_3^{2-}) is removed from the water and m-alkalinity and p-alkalinity are accordingly lowered.

Based on the lowered m-alkalinity and p-alkalinity the new carbonate concentration is determined.

Two parameters describe the supersaturation of calcium carbonate in water. The Saturation Index (SI) is defined as the pH offset at which the actual calcium concentration is in equilibrium with the carbonate:

$$\text{SI} = \log\left(\frac{f^8[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_s}\right) \quad (7)$$

and is a measure for the driving force in the crystallisation process. The TCCP (theoretical calcium carbonate crystallisation potential) is the amount of calcium in mol m^{-3} that should crystallise to obtain water in chemical equilibrium. The TCCP is a measure for the amount of calcium carbonate that can be formed in consecutive process steps. The two indices are strongly related, but are both used separately to quantify the performance of the crystallisation process.

Modelling the fluidised bed

The aim of the fluidised bed model is to describe the fluidisation of the bed and the transportation of the pellets through the bed. The fluidisation model is necessary to determine bed properties such as bed height, pressure drop and porosity depending on pellet size, water flow, pellet discharge speed and temperature. The porosity is used to model the crystallisation rate in the next section.

The model is deduced by dividing the reactor into layers as shown in Figure 1. The water flow is schematised as a

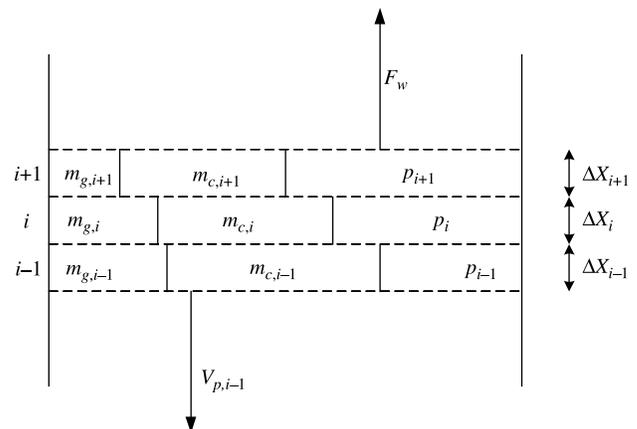


Figure 1 | Modelled layers in the reactor.

one – dimensional flow in an upward direction, keeping the bed of pellets fluidised. In the case of a pellet discharge the pellets are transported in a downward direction. The state variables of the fluidised bed model are the mass of the calcium carbonate m_c and the mass of the grains m_g .

Each layer is divided into three sections: the volume of grains, the volume of calcium carbonate and the water volume determined by the porosity. The height of each layer is given by the porosity of the bed and the mass of pellets, consisting of grains and calcium carbonate:

$$\Delta x_i = \left(\frac{m_{g,i}}{\rho_g} + \frac{m_{c,i}}{\rho_c} \right) (1 - p_i)^{-1} A^{-1} \quad (8)$$

The porosity p_i in the i th layer is based on temperature, pellet diameter and water velocity and is accurately described by the Richardson-Zaki expansion formula (Richardson & Zaki (1954)) (the indices i are dropped for readability):

$$p = \left(\frac{F_w}{A v_0} \right)^{\frac{1}{n}} \quad (9)$$

The terminal settling velocity v_0 and the exponent n are experimentally determined properties of a single particle. Richardson and Zaki found the following empirical relationship for the exponent n :

$$n = \begin{cases} 4.6 & \text{for } Re_0 < 0.2 \\ 4.4 Re_0^{-0.03} & \text{for } 0.2 \leq Re_0 < 1 \\ 4.4 Re_0^{-0.1} & \text{for } 1 \leq Re_0 < 500 \\ 2.4 & \text{for } Re \geq 500 \end{cases} \quad (10)$$

For perfectly round, smooth and uniform particles, v_0 can be determined using the Newton-Stokes equation (Bird *et al.* 1960):

$$v_0^2 = \frac{4 \bar{d}_p (\rho_p - \rho_w) g}{3 C_{w2} \rho_w} \quad (11)$$

The drag coefficient C_{w2} is experimentally determined. The following drag coefficient for calcium carbonate pellets with a garnet seeding material was found (van Schagen *et al.* 2007):

$$C_{w2} = \frac{24}{Re_0} (1 + 0.79 Re_0^{0.87}) \quad (12)$$

where the terminal settling Reynolds number is given by:

$$Re_0 = \frac{v_0 \bar{d}_p}{\nu} \quad (13)$$

The average pellet diameter is determined using the mass of crystallised material. Assuming an even distribution of the mass over the grains, in the layer under consideration, the pellet diameter is calculated as follows:

$$\bar{d}_p = \bar{d}_g \sqrt[3]{1 + \frac{m_c \rho_g}{m_g \rho_c}} \quad (14)$$

The pressure drop over each layer is given by the submerged weight of the fluidised pellets:

$$\Delta P = (\rho_p - \rho_w)(1 - p)g\Delta x \quad (15)$$

where the density of the pellets is a function of the accumulated mass of the crystallised material and the mass of the grains:

$$\rho_p = (m_c + m_g) \left(\frac{m_c}{\rho_c} + \frac{m_g}{\rho_g} \right)^{-1} \quad (16)$$

The transportation of pellets is modelled as a transportation of grain material with the calcium carbonate attached. The velocity of transportation $v_{p,i}$ is given in kilograms of grain material per second. The transportation of the calcium carbonate part of the pellet is given by the ratio of calcium carbonate mass and grain mass. Since grain material can be accumulated in the reactor, the transportation of grains into the layer is different from the transportation of grains out of the layer. The accumulation of calcium carbonate caused by pellet transportation through the reactor is given by:

$$\frac{dm_{c,i}}{dt} = v_{p,i+1} \frac{m_{c,i+1}}{m_{g,i+1}} - v_{p,i} \frac{m_{c,i}}{m_{g,i}} \quad (17)$$

The increase of calcium carbonate, due to the crystallisation process, is determined by the crystallisation reaction and is given at the end of the next section.

Modelling the crystallisation

The aim of the crystallisation model is to describe the crystallisation of calcium carbonate in the bed and the transportation of the dissolved components through the bed.

The crystallisation model is deduced using layers of the reactor as given in Figure 1. The m-alkalinity, p-alkalinity and ionic strength in a layer determine carbonic equilibrium as described by Equations (5) and (3). The crystallisation rate of the equilibrium in Equation (1) is determined by the crystallisation kinetics \mathcal{K} , the available crystallisation surface S and the supersaturation of calcium carbonate (Wiechers *et al.* 1975):

$$C = \mathcal{K} \cdot S \cdot \left([\text{Ca}^{2+}] [\text{CO}_3^{2-}] - \frac{K_s}{f_8} \right) \quad (18)$$

The specific surface of the pellets is determined by the porosity p of the layer from Equation (9) and the diameter of the pellet in the layer from Equation (14):

$$S = \frac{6(1-p)}{d_p} \quad (19)$$

The crystallisation kinetics are modelled as a two-stage crystallisation process (Karpinski 1980). The first stage is the transportation of supersaturated water to the pellet surface (k_f), which depends on water flow and temperature. The second stage is the crystallisation of the supersaturated water on the pellet (k_T), which only depends on temperature:

$$\mathcal{K} = \frac{k_T \cdot k_f}{k_T + k_f} \quad (20)$$

The transportation of the supersaturated water to the surface of the pellets depends on the flow pattern of the water between the pellets (Budz *et al.* 1984). Based on the Reynolds number of the water flow in the bed Re_h and the Schmidt number Sc the Sherwood number Sh is given by the Froessling equation:

$$Re_h = \frac{2}{3} \frac{v d_p}{(1-p)v} \quad (21)$$

$$Sc = \frac{D_f}{v} \quad (22)$$

$$Sh = 0.66 Re_h^{0.5} Sc^{0.35} \quad (23)$$

The transportation coefficient in Equation (20) is given by:

$$k_f = \frac{Sh \cdot D_f}{d_p} \quad (24)$$

The temperature dependency of k_T is found by Wiechers *et al.* (1975) as:

$$k_T = 1.053^{(T-20)} \cdot k_{T20} \quad (25)$$

The change of m-alkalinity, p-alkalinity and ionic strength and calcium over time in one layer is now given by the combination of water flow through the reactor and crystallisation of calcium carbonate. Based on the mass balance over the layer, this is given by:

$$p_i A \Delta x_i \frac{d[\text{Ca}^{2+}]_i}{dt} = F_w ([\text{Ca}^{2+}]_{i-1} - [\text{Ca}^{2+}]_i) - A \Delta x_i C \quad (26)$$

$$p_i A \Delta x_i \frac{dM_i}{dt} = F_w (M_{i-1} - M_i) - 2A \Delta x_i C \quad (27)$$

$$p_i A \Delta x_i \frac{dP_i}{dt} = F_w (P_{i-1} - P_i) - A \Delta x_i C \quad (28)$$

$$p_i A \Delta x_i \frac{dIS_i}{dt} = F_w (IS_{i-1} - IS_i) - 2A \Delta x_i C \quad (29)$$

At the bottom of the reactor, where caustic soda is dosed, the concentration of the water flowing into the first section is given as:

$$M_0 = \frac{(M_{raw} F_w + [\text{OH}^-] F_l)}{F_w + F_l} \quad (30)$$

$$P_0 = \frac{(P_{raw} F_w + [\text{OH}^-] F_l)}{F_w + F_l} \quad (31)$$

$$IS_0 = \frac{(IS_{raw} F_w + 0.5[\text{OH}^-] F_l)}{F_w + F_l} \quad (32)$$

Finally, the increase of crystallised material in the layer is equal to the crystallised mass of calcium in mol times the molecular weight of calcium carbonate (M_c):

$$\frac{dm_{c,i}}{dt} = A \Delta x_i M_c C \quad (33)$$

MATERIALS AND METHODS

To determine the parameters of the model, the model is calibrated at the pilot plant installation of the Weesperkarspel treatment plant of Waternet, the water cycle company of Amsterdam and surroundings. The calibrated model is validated using data from two full-scale installations. The first validation is performed with data from the full-scale installation of Weesperkarspel. The second validation is

performed with data from the full-scale installation of DZH at WTP Katwijk, the Netherlands.

Calibration

The aim is to calibrate the crystallisation constant k_T and diffusion constant D_f in the model. The model with the calibrated constants minimises the MSE (mean squared error) based on the measurements of total hardness, pH and m-alkalinity.

The model is calibrated with data from the Weesperkarspel pilot plant. The softening process in the pilot plant consists of two columns with a diameter of 31 cm and a height of 4.5 m. A regulated valve controls the flow between $4 \text{ m}^3 \text{ h}^{-1}$ and $7 \text{ m}^3 \text{ h}^{-1}$. Caustic soda dosage is controlled between 0 and 21 h^{-1} . To determine the fluidised bed status, the reactors are equipped with online measurements of water flow, water temperature, bed height, pressure drop over the total fluidised bed and pressure drop between 20 and 60 cm from the bottom of the reactor. To follow the crystallisation process, the turbidity pH, total hardness, m-alkalinity and the conductivity are automatically measured using an online titration unit (Applikon ADI 2040) every 15 minutes.

Before calibration one reactor was operated at constant flow ($6 \text{ m}^3 \text{ h}^{-1}$) and caustic soda dosage (11 h^{-1}) during one month (February 2005). In this period the discharge of pellets was controlled using the pressure drop measurement at the bottom of the reactor (set point of 3.5 kPa), resulting in a constant pellet size at the bottom of the reactor. The bed height was kept constant at a height of 4 m by dosing garnet sand as seeding material.

The composition of the bed was constant after this month. The state of the bed (described by m_{Cti} and m_{Sji}) is identified using manual pressure drop measurements at five heights in the bed and the online bed height measurement at three different flows. The identification was performed with a different number of layers, to determine the influence on the prediction of the pressure drop and level measurements. The best estimate minimises the MSE using a nonlinear optimisation technique. The MSE is used for all calibration and validation experiments and is generically given by:

$$MSE = \frac{1}{N} \sum_{j=1}^N \sqrt{\frac{1}{N_j} \sum_{i=1}^{N_j} \left(\frac{y_{model,j,i} - y_{data,j,i}}{y_{data,j,i}} \right)^2} \quad (34)$$

where y are the N outputs from the model and the measurement data and N_j are the number of samples for the j th output.

In the calibration experiment the water flow through the reactor and caustic soda flow were changed every 20 minutes. The water flow was varied between $4 \text{ m}^3 \text{ h}^{-1}$ and $7 \text{ m}^3 \text{ h}^{-1}$ and the caustic soda was varied between 0.5 and 1.51 h^{-1} . After 20 minutes the water quality parameters were measured automatically. In this manner 40 different combinations of water flow and caustic soda dosage settings were performed in a random order. This procedure was repeated three times.

Validation at Weesperkarspel full-scale plant

The model for the pellet softening process is first validated with data from the eight softening reactors of WTP Weesperkarspel of Waternet. The Weesperkarspel treatment plant uses lake water with relatively high organic concentrations as source water; before softening the water is treated with ozone.

The reactors operate at a variable flow velocity of $60\text{--}100 \text{ m h}^{-1}$ to keep the ratio between bypass and reactor flow constant for different total flows. The reactor height is 4.5 m, the seeding material is garnet sand and the dosage is caustic soda. The pellet discharge is based on the total pressure drop and the garnet sand dosage is based on the amount of discharged pellets.

The aim is to validate the dynamic output of the model. Therefore data from the full-scale plant is selected on relatively large variations in flow and caustic soda. For a five-day period (15–20 October 2005) the dynamic simulation is performed for all eight reactors. The inputs for the simulation model are the online measured temperature, water flow and caustic soda flow. The quality data (pH, bicarbonate, conductivity) are assumed constant based on laboratory values from that particular week. The state of the bed is deduced from the sieve analyses from the corresponding day.

The outputs of the model are compared with the online measured pH of the full-scale plant. The laboratory measurement of calcium is only performed once a day. This measurement is also compared with the simulated value.

Validation at Katwijk full-scale plant

A second validation is performed at WTP Katwijk of DZH. The Katwijk treatment plant treats dune water. At WTP Katwijk there are four softening reactors with a height of 6 m. The seeding material is garnet sand and caustic soda is dosed. The reactors operate at a constant flow velocity of 90 m h^{-1} . The dosage and bypass are varied to get the desired effluent concentration for different water flows. The pellet discharge is based on the total pressure drop and the garnet sand dosage is based on measured bed height.

The validation is performed with five datasets recorded under the typical constant operation conditions. The datasets are given in Table 1 with the typical values. The last three datasets are randomly chosen from all available data.

The validation of the model consists of two steps. The first is the validation of the pressure drop of the total bed. Based on the sieve analysis at different heights in the bed and the total bed height, the bed composition is determined. The reactor is divided in as many layers as there are sieve analyses (6 to 8). The theoretical porosity of the layer is calculated using the fluidisation theory (Equation (9)) based on the measured pellet diameter and water velocity. The volume and mass of pellets (garnet and calcium carbonate) in each layer is found using the calculated porosity. The mass in each layer contributes to the total pressure drop. The measured total pressure drop is then compared with the calculated pressure drop from the model.

Table 1 | Datasets for the validation experiments

No.	Incoming calcium (mg l^{-1})	Temperature ($^{\circ}\text{C}$)	Description
A	69	10	Average conditions
B	67	11	Low calcium concentration
C	80	9	High calcium concentration
D	75	9	Low temperature
E	71	16	High temperature
F	75	12	Random set 1
G	79	9	Random set 2
H	67	11	Random set 3

The second validation is of the crystallisation model in the reactor. The model is verified for calcium, pH, conductivity and m-alkalinity. Using the estimated bed composition, the effluent water quality parameters are calculated by integrating Equations (26) to (29) over the height of the reactor. Since the caustic soda dosage in Equations (30) to (32) is not measured regularly, this dosage is calculated using the available $[\text{Na}^+]$ measurement from the laboratory data. The increase in sodium concentration in the reactor is caused by the caustic soda (NaOH) dosage.

Optimisation of pellet size in a reactor

Using the validated model of a single reactor at WTP Weesperkarspel, the pellet size in the reactor is studied in a simulation. The main difference between the summer and winter situation is the temperature of the water. The other water quality parameters of the water before the softening process show insignificant variation.

In this model, the pellet diameter at the bottom of the reactor is directly controlled at different values for each run. The bed height is kept constant at 4.5 m by dosing garnet material. The pellet discharge and seeding material dosage is modelled as a direct control loop. In practice direct control of diameter is not possible, but it can be achieved by using a soft sensor, based on pressure drop in the bottom of the reactor.

The goal of the simulation is to investigate the super-saturation of calcium carbonate in the effluent water for different pellet sizes. The diameter of the pellet is varied from 0.8 mm, which is the smallest diameter permitted for a calcium carbonate percentage of 95% in the discharged pellets, to 1.2 mm, which is the maximum pellet diameter to maintain fluidisation in winter and in summer. The water velocity in the reactor is simulated at a constant velocity of 67 m h^{-1} .

The influent water quality is based on real-time measurement data from 2003 and 2004 from the treatment plant. The influent water quality is practically constant for pH, calcium and bicarbonate, but the temperature varies between 5 and 25°C for winter and summer. Due to the temperature variation, the influent saturation index varies during the year between 0.1 (in winter) and 0.2 (in summer).

RESULTS AND DISCUSSION

Calibration

After one month of constant operation at the pilot plant, the total pressure drop in the bed is at a constant level of 29 kPa. The bed is at the desired height of 4 m and the pressure drop between 20 and 60 cm above the bottom of the reactor is 3.5 kPa. The temperature of the water is 11 °C.

From the pressure drop measurements, the state of the bed is identified. For a water flow of $6.5 \text{ m}^3\text{h}^{-1}$ the estimated pellet diameters are plotted in Figure 2 (left). In the graph, the estimated pellet diameter is plotted against the modelled height in the reactor. As expected, the bottom part of the reactor is filled with large pellets, while the top part is filled with small pellets. The resulting MSE, based on pressure drop and bed height, for the different number of layers is shown in Figure 2 (right). The MSE decreases for an increasing number of layers and becomes practically constant after five layers.

The parameters for the crystallisation (k_{T20} and D_f) are calibrated using the estimated bed compositions. During model calibration, it turned out that the pH measurement of

the experimental setup had a slow drift over time (see Figure 3). This caused a large offset at the time of this experiment, therefore a pH offset (Δ_{pH}) was calibrated. The results from the calibration are given in Table 2, where the MSE calculation is based on the calcium concentration, pH and the m-alkalinity in the effluent of the reactor. It must be noted that the performance (MSE) of the estimate does not improve if the number of layers is increased. The MSE is almost constant at about 0.022. But the calibrated diffusion constant decreases as the number of layers increases and becomes constant at about seven modelled layers. The transportation model (Equations (21)–(24)) is independent of the number of modelled layers if the reactor is modeled with a minimal seven layers. The calibrated crystallisation constant k_T is close to the crystallisation constant of 0.0255 found in batch experiments for conditions without diffusion (Wiechers *et al.* 1975).

Validation at Weesperkarspel full-scale plant

The results of the validation are shown in Table 3. The first column shows the MSE for the simulated and measured pH.

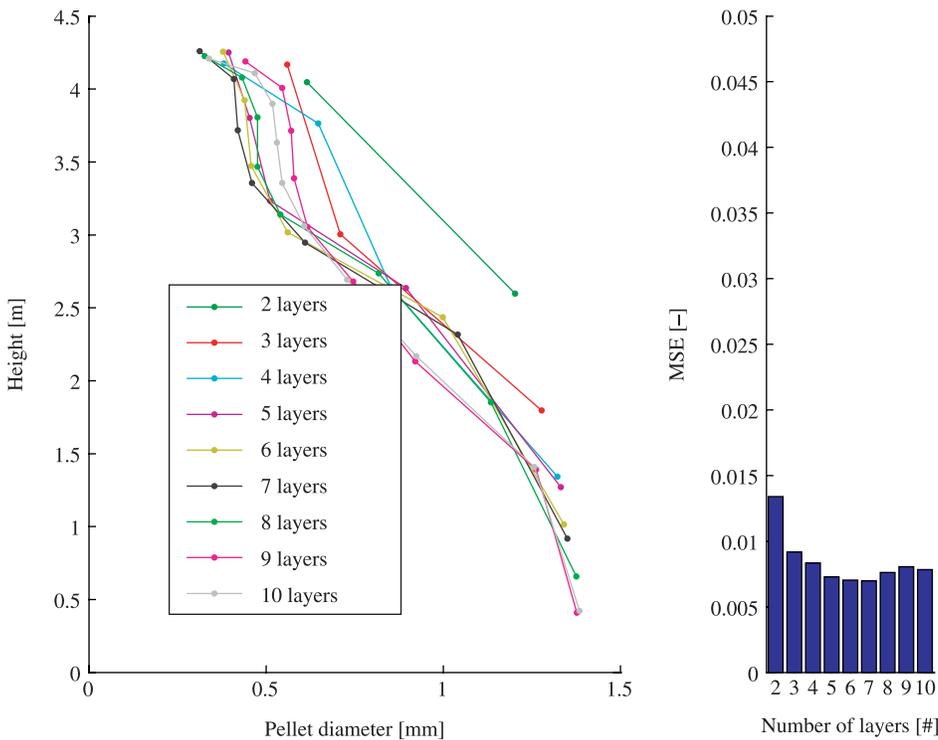


Figure 2 | Estimated state of the bed (left) and MSE (right) for different number of modelled layers.

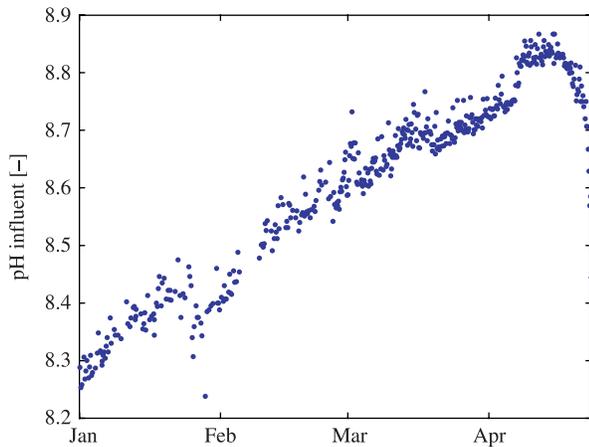


Figure 3 | pH measurement of the pilot plant influent water.

This value is calculated using the 7200 online pH measurements. The accuracy of the model varies between 7% and 0.8%. This is larger than the absolute measurement error of pH (2%). The online pH measurement suffers from static offset due to drift of the measurement device. For reactor 6 the pH measurement was recalibrated on 18 October, after which the pH measurement is close to the simulated value (Figure 4). If the offset of the pH measurement is corrected, the MSE gets smaller than the measurement error except for reactor 2. Reactor 2 was in a fresh startup in that period (2 days in operation), which may have caused the difference.

The laboratory data for calcium concentration for reactors 1, 2, 3 and 5 are missing, but the simulation results for the other reactors are at about 10% accuracy. This is probably caused by the moment of sampling of the water, because the exact sampling moment is not known and the selected period is chosen for the instable process conditions.

Table 2 | Calibration results

No. layers	k_r	D_f	Δ_{pH}	MSE
2	0.0308	$1.33e - 010$	-1.00	0.022
3	0.0237	$6.89e - 011$	-1.00	0.023
4	0.0267	$4.55e - 011$	-0.98	0.022
5	0.0195	$3.54e - 011$	-0.96	0.023
6	0.0221	$3.07e - 011$	-0.98	0.023
7	0.0254	$2.67e - 011$	-0.99	0.022
8	0.0219	$3.05e - 011$	-0.98	0.023
9	0.0406	$2.86e - 011$	-1.00	0.022
10	0.0218	$3.08e - 011$	-0.98	0.023

Table 3 | Validation data WTP Weesperkarspel

Reactor	MSE pH	MSE corr. pH	(correction)	MSE Calcium
1	0.015	0.006	(-0.1)	-
2	0.069	0.058	(0.3)	-
3	0.010	0.005	(0.1)	-
4	0.022	0.006	(-0.2)	0.12
5	0.018	0.006	(0.1)	-
6	0.024	0.013	(0.2)	0.13
7	0.008	0.006	(0.0)	0.11
8	0.049	0.009	(-0.4)	0.07

Validation at Katwijk full-scale plant

The validation of the fluidised bed model gives the results shown in Table 4. The pressure drop of the model is within 0.3 kPa for five datasets. There are three datasets which show larger deviations. For datasets D and G the diameter of the pellets in the bottom of the reactor turned out to be large. In these cases the bed is not fluidised, therefore the measured pressure drop is lower than the modelled pressure drop. For dataset C the pressure drop over the reactor nozzles (27 kPa) is larger than the normal pressure drop over these nozzles (13–14 kPa). This indicates that some of the nozzles in the bottom of the reactor are clogged and only a part of the reactor surface is effectively used for fluidisation, causing higher water flows and thus a leaner bed.

For data sets A, B, E, F and H, the resulting bed composition is simulated with the given influent quality of the water. Based on the modelled and measured values of calcium, pH, conductivity and m-alkalinity the relative error $((model - data)/data)$ and the MSE is determined and listed in Table 5.

To analyse accuracy of the quality data, a balance over the reactor is made. The only reaction taking place in the reactor is the crystallisation of calcium carbonate (Equation (1)). The removal of calcium in a reactor must therefore be equal to twice the reduction of m-alkalinity in the reactor. The relative error in the data is given by:

$$error_{data} = \frac{2([Ca^{2+}]_{raw} - [Ca^{2+}]_{reactor}) - (M_{raw} + [OH^-]_{dos} - M_{reactor})}{2([Ca^{2+}]_{raw} - [Ca^{2+}]_{reactor})} \quad (35)$$

This relative error is given in the last column of Table 5. Only for dataset H is the relative error in the data smaller than

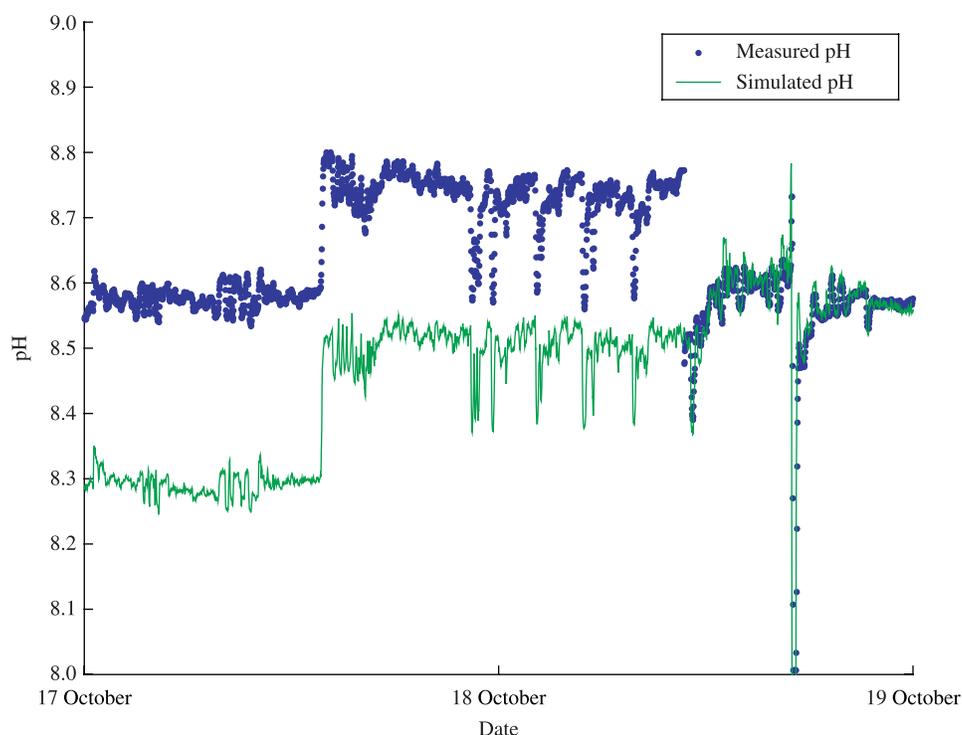


Figure 4 | Measured and simulated pH for reactor 6.

the measurement error of 2% of the individual measurement devices. For these data sets the model predicts the effluent quality parameters almost perfectly, with a MSE of only 1.8%. The datasets A, B, E and F all have higher relative errors in the measurement data. Especially in dataset F the reduction of calcium in comparison to the reduction in m-alkalinity is 66% off. From the data it cannot be deduced which of the measurements is erroneous, but if the model is correct, it can be concluded that the calcium measurement of the reactor effluent is probably incorrect, since this measurement has the biggest relative error between data and model.

Taking the quality of the measurement data into account, the model gives a good estimate if the data is good and if the fluidised bed is operated in completely fluidised state. As soon as the fluidisation is disturbed the model of the reactor is inaccurate.

Optimisation of pellet size in a reactor

The resulting variation in saturation index in the effluent of the reactor for different pellet sizes is shown in Figure 5.

The supersaturation after the reactor is higher in the winter than in the summer. This is caused by the temperature dependency of the reaction kinetics (Equations (18) – (25)) in three ways. The specific surface (for constant pellet size and water velocity) is lower, due to the increased porosity at lower temperatures. The crystallisation rate k_T is lower for lower temperatures and the transportation to the crystallisation surface k_f is lower due to lower Reynolds numbers in winter.

Table 4 | Fluidised bed data WTP Katwijk

	Pressure drop			Max pellet diameter [mm]	Nozzle drop [kPa]
	Measured [kPa]	Model [kPa]	MSE		
A	2.24	2.23	0.004	1.4	15.6
B	2.42	2.53	0.046	1.9	12.5
C	2.40	2.83	0.178	1.8	27.1
D	2.44	2.92	0.198	2.0	14.2
E	2.41	2.18	0.094	1.7	12.7
F	2.61	2.66	0.019	1.8	12.9
G	2.29	3.03	0.321	2.0	14.7
H	2.53	2.43	0.039	1.6	13.0

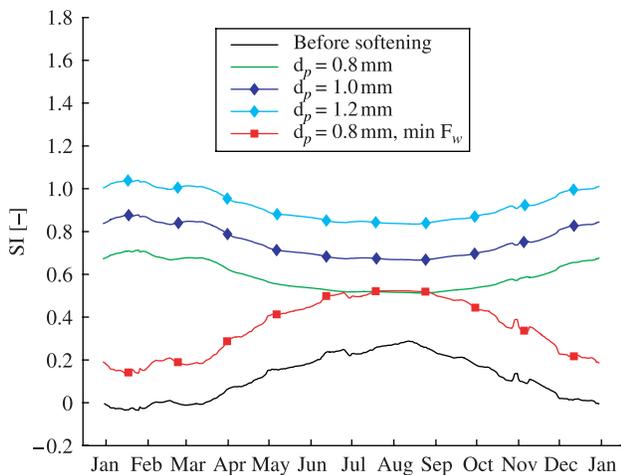
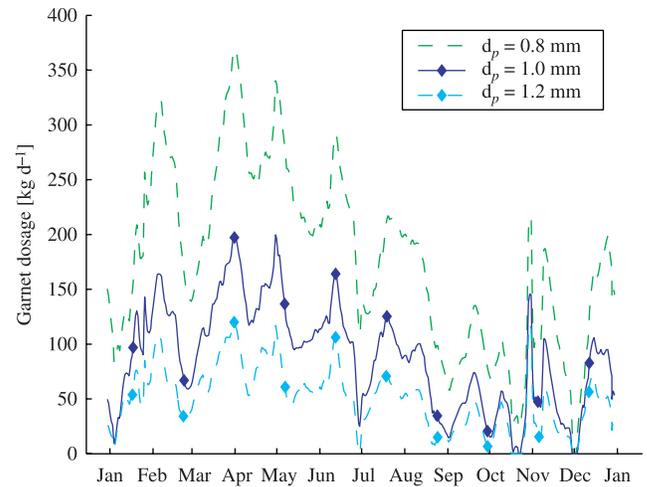
Table 5 | Results and data accuracy for WTP Katwijk

	Calcium	pH	EGV	m-alkalinity	MSE	Data
A	-0.12	-0.01	-0.04	-0.07	0.074	-0.101
B	0.06	0.01	-0.02	0.01	0.030	-0.034
E	-0.12	0.00	-0.05	-0.05	0.072	-0.058
F	-0.19	0.02	-0.05	-0.06	0.103	0.668
H	0.00	0.01	-0.03	-0.02	0.018	-0.001

There is a significant difference in the chemical performance for different pellet sizes. Small pellets in the reactor cause lower supersaturation of calcium carbonate at the effluent of the reactor. But in the simulated situation the supersaturation never drops below 0.6. Therefore acid has to be dosed all year, if bypass flows are not applied. A final simulation with a pellet size of 0.8 mm and a minimal flow through the reactor to keep the bed fluidised shows that bypassing a reactor gives an improvement of the SI, especially in the winter period.

The garnet dosage shows a correlation with temperature (Figure 6). The garnet dosage is higher if the temperature rises. Due to the increase of temperature the porosity decreases. To maintain the same bed height the garnet dosage must be increased. In case of decreasing temperatures the garnet dosage almost stops.

There is a significant difference in garnet use for different pellet sizes. Since the amount of calcium carbonate that has to be removed is the same in all cases, the pellet size is directly

**Figure 5** | SI before and after the softening process step for different pellet diameters.**Figure 6** | Garnet dosage during the year to maintain a bed height of 4.5 m and a desired pellet diameter.

related to garnet sand usage. The average use of garnet sand for 1 mm pellets is about 51% of the garnet sand use for pellets of 0.8 mm and for 1.2 mm this is about 29%.

These are significant reductions and must be compensated by the quality improvement mentioned above.

CONCLUSIONS

The model of the pellet softening reactor can not only be used to evaluate the current performance of the pellet softening process, but also be used to optimise the operation of the softening reactor.

During the calibration and validation procedure the measurement data taken from the pilot plant process and full-scale process showed unexpected deviations from the process model. It turned out that most of these errors were not caused by modelling errors, but by measurement errors or unexpected process conditions.

The first application of the model is the evaluation of the current process operation and the detection of undesired process conditions. Using the available data and the validated model, data and model can be compared and process abnormalities can be identified. This can be used in the basic day-to-day process operation. As soon as process data and laboratory results are available, these data can be checked with the model. Model and data mismatch is caused by process abnormalities, which can be tackled with operator action.

In this way the process is kept at normal process conditions, even without advanced control implementation.

At regular intervals, sieve analyses are performed over the height of the bed. Using these sieve analyses, the theoretical pressure drop over the bed can be calculated using the model. As soon as theoretical pressure drop and measured pressure drop differ the process is no longer in a stable operation. In the case that the pressure drop measurement is malfunctioning this has direct impact on the process operation. In the current operation the pressure drop measurement is used for pellet discharge and seeding material dosage. In the case that the theoretical pressure drop is offset, the bed is no longer in a completely in fluidised state or disturbances in the fluidised bed exist.

The applied dosage of caustic soda is an important parameter in process operation, but the online determination of this parameter is inaccurate due to measurement errors in flow and concentration. The measurement of the caustic soda flow is unreliable; due to the chemical properties of caustic soda, the flow measurement drifts after a certain period of time. Using the identified bed model the chemical model of the bed can be used and compared with the real-time data. The m-alkalinity and calcium measurements of influent and reactor effluent can be used to determine caustic soda dosage mismatch. If m-alkalinity and calcium concentration are in correct correlation with the caustic soda dosage, but the level of calcium, m-alkalinity and pH are incorrect, there is a process disruption or measurement error. In the case of measurement error this can be estimated as shown in the calibration of the model.

Finally the model can be used to optimise the operation of the pellet reactor. Simulations show that the pellet size in the reactor must be as small as possible to minimise supersaturation of calcium carbonate in the water and reduce acid dosage after the reactor. Nevertheless decreasing the pellet size in the reactor increases the use of garnet seeding material significantly. Increasing the bypass to a maximum reduces the supersaturation of the mixed effluent

even further. This bypass is limited by the minimal flow through the reactor to keep the bed fluidised.

ACKNOWLEDGEMENTS

This research is part of the PROMICIT project of Waternet, Delft University of Technology, DHV B.V. and ABB B.V. The project is sponsored by SenterNovem, Ministry of Economic Affairs of the Netherlands.

The authors are grateful to the water-companies Waternet and DZH for providing the data from their full-scale plants.

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First received 15 December 2006; accepted in revised form 8 June 2007