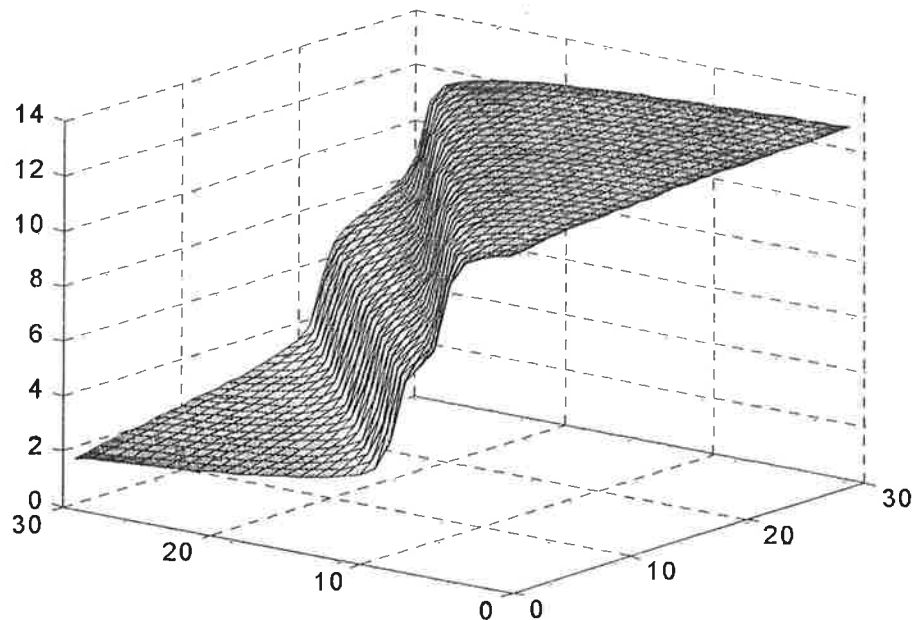


Dynamic Process Simulation of Wet Systems for Flue Gas Cleaning



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<i>Title and subtitle</i> Dynamic Process Simulation of Wet Systems for Flue Gas Cleaning		
<i>Abstract</i> <p>Combustion of waste produces large variations in flue gas composition due to the inhomogeneous composition of the fuel. These variations leads to dynamic effects in the emission control system which can be studied by the use of dynamic process simulation. The purpose of this work was to build a dynamic model with good agreement to operating data for a wet system for SO_2 removal. Consequences for plant design and improvements of the pH control system were also part of the purpose.</p> <p>A model was built using an existing plant in Hobro, Denmark as a model system. Experiments were carried out at the plant in Hobro in order to validate the model. During these experiments the pH controller tuning was improved. The model has a good agreement to operating data. There are however two important limitations to model performance. Neither the rate of oxidation of sulphites nor the absorption of HCl has been modeled and the experiments proved those to be important process characteristics. The model can still be used in plant and control system design.</p> <p>A linear analysis of the model shows that the process is approximately a first order system. Thus, pH control should be easy, having sensor and actuator dynamics as limits for how fast the control system can be. The process gain is however changing with changing chemical composition of the scrubber liquid. This must be considered in a robust control design.</p> <p>Considering plant design a few conclusions has been drawn. The recirculation tank should be kept small. The choice of pipes, pumps, valves and sensors should be given special attention. pH control in several tanks is advantageous.</p> <p>Considering future pH control systems, feedback control in one or two stages is likely to work well. Feed forward of pH should be avoided. Controllers should be designed with anti-windup and the sampling period remembered if implementing digital controllers.</p>		
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1 INTRODUCTION

Combustion of waste produces large variations in flue gas composition due to the inhomogeneous composition of the fuel. These variations leads to dynamic effects in the emission control system, effects unknown from combustion of homogeneous fuels such as oil, coal or black liquors. A typical effect is variations in scrubber liquid pH when the control system fails to respond in an appropriate way, variations that effects the absorption of pollutants.

One way to study dynamic properties and control strategies of a process is by the use of dynamic simulation. A model is developed and used to predict the dynamic response.

The main part of the report treats model development and dynamic simulation of the sulphur dioxide scrubber at I/S Fælles Forbrænding's waste incinerator plant in Hobro. One part describes experiments and model validation. The report also includes model analysis, control design and some aspects of plant design.

2 PURPOSE

The purpose of the dynamic simulation was to find out if and how it is possible to build a dynamic model with good agreement to operating data for a wet scrubber system for sulphur dioxide removal. An existing plant in Hobro, Denmark was used as model system.

Another purpose of this work was to investigate how knowledge of the dynamic properties can be implemented in plant design.

Different ways to improve the pH control system in the existing plant was a third purpose.

3 DYNAMIC PROCESS SIMULATION

With the increasing capacity of modern computers simulation has become an important tool in engineering [1,2]. In process engineering it has become possible to make detailed investigations of different process alternatives, to investigate the consequences of uncertainties in data etc. It has also become possible to study dynamic properties of a process. The purpose of dynamic process simulation can be to study for example:

- Transients in stationary processes
- Start up and shut down of a plant
- Impact of disturbances
- Control strategies
- Loss prevention.

The purpose can also be to get a deeper understanding of the process or to train operators. For processes with large and frequent changes in input, a dynamic study can also be an important tool for design.

A general approach to modeling and dynamic simulations is given in figure 1.

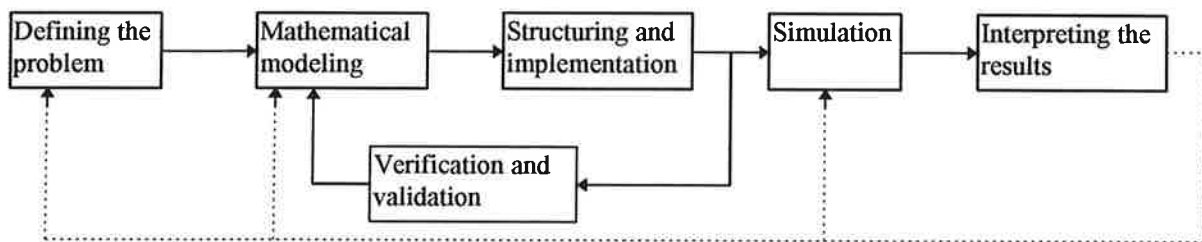


Figure 1. General approach to dynamic simulations.

Defining the problem and the object of the simulation is an important part of the procedure. For the following stages it is important to know what the desired result is, how much time is available etc.

Unless using a computer program for dynamic process simulation (such as SPEEDUP or DYNYSYS) a mathematical model describing the process is needed. Models for most processes can be found in the literature. The easiest approach is to reuse and adapt these models for the specific problem at hand. A correct use of a model still asks for a good understanding of its derivation. In any case it is important to use models that rests on a solid theoretical ground. For example, polynomials can fit most kinds of data but they often fail to describe the most characteristic properties of the phenomena. A theoretically derived model can describe such characteristics.

A dynamic model differs from stationary models in that an accumulation term is used in balance equations. A dynamic model normally include one or several differential equations as

well as several algebraic expressions. The mathematical model is derived using the laws of classical physics and chemistry. Those derivations are normally based on

- Balances on total mass
- Balances on component mass
- Balances on energy
- Balance on momentum
- Transport equations (e.g. the laws of Fick, Fourier and Newton)
- Equations of state (enthalpy, density ..)
- Equilibrium equations (phase equilibrium, chemical equilibrium)
- Rate equations for chemical reactions

Before proceeding to the next step it is important to decide which balances are important and which can be ignored. Can certain terms of an expression be ignored? Can parts of the process be described with stationary equations or must dynamics be included in every part?

The equations need a certain structure in order to be implemented in a computer. To write a computer program for solving the equations, decisions must be made in which order to solve the equations, which numerical method should be used etc. Commercial computer programs often demand a certain structure of the equations.

When implementing the model it is important to verify the model. Balances must fulfil stationary conditions and algebraic equations have known correct roots. If this is not the case there is something wrong either in the model or in the implementation. If parts of the model is unknown it is necessary to fit some parameters of the model by simulating and comparing with known process behaviour, in order to make it work as desired. Those parameters must then be measured or estimated to prove that the model is valid [3].

The procedure of modeling and validation can be seen as iterative. Start with a simple model. If it is not accurate enough increase the complexity of the model until the desired accuracy is obtained. The accuracy increases with increasing complexity only to a certain degree. When the model is too complex the accuracy decreases again [4].

The simulations are then carried out according to the purpose. If the study of different control strategies was the object of the simulations then different control system aspects are tested.

Last but not least, the results of the simulations must be interpreted. Are the results reliable and what are the consequences? In some cases the objectives of the simulations is fulfilled but maybe also new questions arise leading to new simulations. In other cases the interpretation can lead to the conclusion that the model must be improved or the problem definition changed etc.

4 PROPERTIES OF pH CONTROL

A good survey of properties of pH control is found in "*Fundamental Properties of Continuous pH Control*" by K.V Waller and T.K Gustafsson [5]. Most of the properties discussed below are treated in that article. Other aspects are found in [6] which also gives a thorough treatment of advanced pH control. Notice that the purpose in [5,6] is pH control in industrial waste water treatment plants, a very demanding task. Some problems can therefore be overestimated if comparing with another type of plant. Furthermore, the work is more than 10 years old.

pH control is a problem in many industrial plants with continuous oscillations, slow recovery from upsets etc. There are also systems that seem to perform well that in reality does not. The nice impression is just a lack of suitable measurements. The difficult problem in pH control is disturbances in feed composition. For example in commercial plants the process gain can change by orders of magnitude in few seconds. The specific problem is the very strong nonlinearity of the system in relation to linear control.

The conclusion of the nonlinearity of the system is that small dynamic effects can be expected to have a much stronger effect in pH control than in an ordinary linear composition control system. The S-shaped titration curve means that the process gain can vary a great deal, in practice frequently exceeding 1000:1. This variation is bound to create difficulties in pH control systems. If the controller gain is set low enough to ensure stability around the neutral point, then the controller becomes very inefficient and recovery from upsets very slow. A fixed gain controller efficient for large upsets will then probably cause continuous cycling around the neutral point. Thus a controller tuned for one situation may be of little value in another.

A number of conclusions can be drawn for the practical realization of a pH control system. Some actions is directed towards plant design, such as number and size of tanks, and some actions concerns the control philosophy used in control system.

4.1 Feedback control

The difficulties in coping with the disturbances by feedback control stem mainly from the nonlinearity of pH system in combination with the always occurring small dead times and time constants. The inclusion of large capacity in feedback loop to attenuate disturbances is questionable for pH control. Actually, increasing the capacity of the system by increasing tank size can be expected to decrease system performance if the capacity is included in a feedback loop. The reason is that an increased capacity usually also means increased secondary effects, such as mixing lags. It can also be expected that small dynamic effects in the measuring and actuator system can have strong bearing on the performance of continuous pH control systems.

The problem caused by the static nonlinearity is often overestimated. The reason for this is the titration curve for pure water. In this case the gain variation e.g. *in the interval* of pH 4 to 10 is about 200:1. These theoretical curves are however only relevant for solutions of strong acids and bases in distilled water. In other cases also small amounts of buffering agents change the pH-dependence of the process gain completely. In municipal water, buffered

mainly by small concentrations of carbonates, the gain variation can be as low as 2:1 in the considered pH interval. Thus the static nonlinearity is not such a difficult problem as may be believed when only the theoretical curve for pure water is considered.

The most typical pH control problem is the time-varying changes in the nonlinear characteristics. The reason is changing chemical composition of the solution in which pH is to be controlled. It is practically impossible to measure these variations in chemical composition because of the variety of possible variations. The measurement of pH is not enough because the state can not be determined by pH alone. Thus, process gain is not only varying with pH but also with time.

When choosing between various standard controllers, PID control should be chosen. Concerning the controller tuning, it may be advantageous to decrease the integrating action somewhat from standard recommendation. Changing the derivative action has, however, not been found to give any improvement.

A natural modification of the PID controller is a nonlinear controller having a lower gain near the control point and a higher gain at larger deviations. Other ways of using nonlinear controller gains is obtained for the system by modelling it through the concept of chemical reaction invariants. Another way to improve the performance is by the use of adaptive control. This means application of a controller which can extract information about the changing chemical composition and adapt its mechanism of feedback to the changing conditions.

4.2 Feed forward control

When trying to compensate for changes in feed composition by feed forward control a problem arise. The state of the feed is not determined by pH alone. The disturbance is known only if together with pH the total concentration of each acid base system present is known. A change in the pH value of the feed does not give information whether the disturbance will result in an increasing or decreasing pH value or any change at all. As a rule, linear feed forward from pH can not be used. Feed forward control is only applicable if the change of pH is always caused by the same type of disturbance.

4.3 Plant design

Concerning plant design, pH control can be performed advantageously in several steps, e.g. in stirred tanks in series. In the first tank a coarse control is made and in the following the accurate control is accomplished. By this arrangement each controller is allowed to work at less varying conditions.

Due to high sensitivity to small time constants and dead times the plant should be designed to minimize these effects. For example, in stirred tanks there is always a small effective dead time and a mixing lag, generally increasing with increasing tank size. Thus, increasing the tank size in order to increase attenuation also usually means increasing the corresponding mixing lag. The conclusion is that a smaller tank in the feedback loop is preferable. It may thus be advantageous to perform continuous pH control with quite small capacity (time constant) in the feedback loop. Special emphasis should be given to obtain fast and efficient

mixing in the tank. If large capacity is available it could preferably be placed before the feedback loop in order to smooth disturbances.

When designing a plant where pH is to be controlled there is also the problem of rangeability, i.e. the problem of the wide range of reagent flow which often must be provided, still with a high accuracy. The solution to this problem is two sequenced valves of different sizes or control in several steps, i.e. a tank series.

4.4 Measurements

As mentioned small dynamic effects are very important in pH control systems. This means that the measuring system should be carefully considered. Commercial measurement system, manufactured for control, are often dynamically unsuitably designed for pH control. The response of the pH electrode is strongly asymmetric, being slower going from high pH towards neutrality than going from low towards higher pH. A studied electrode had the time constants 7.2 and 32 s respectively.

4.5 Conclusions

The following concluding recommendations for pH control are given in order of importance:

1. Minimize the effective dead time, i.e. choose a small tank to ensure it is well mixed
2. Choose PID control and give special attention to tuning. Do not use feed forward control
3. Use a fast sensor system. Commercial pH measuring system may be unsuitable in this respect.
4. Use nonlinear controller gain.
5. Introduce adaptive control to automatically adjust controller gain to compensate for changing buffer capacities.

Items 1 to 3 should always be taken into account. The alternative to the last items is to perform the control in several steps.

5 THE HOBRO WASTE INCINERATOR PLANT

The five municipalities Hobro, Mariager, Nørager, Nørhald and Purhus on northern Jutland, Denmark have formed a common company, I/S Fælles Forbrænding to take care of their waste. In 1981 the Hobro incinerator was taken into operation with a capacity of 18 000 tons of waste a year. About 9600 tons of this refer to household waste and the remaining part is local industrial waste. About 85% of the energy needed in the district heating net in Hobro, about 110 TJ/year, is today supplied by the waste incinerator.

The original gas cleaning system with an electrostatic precipitator serving as the only emission control device was retrofitted with a two-stage wet scrubber delivered in 1992 by Fläkt Denmark A/S (presently ABB Energi A/S). The scrubber tower is an entire plastic construction where the flue gas, about 200 °C, first passes a quench cooler at the wet stage inlet section. Inside the tower the first stage nozzle bank is followed by a demister. This first stage is an acid stage to selectively remove HCl. The pH is about 0.5. The second stage is of the same construction but has a tray section in the bottom part allowing this liquid to be treated separately. In the upper stage a neutral absorption liquid based on sodium hydroxide is used to absorb SO₂. The pH is about 7. After the demisters the gases are passed to the stack without reheat.

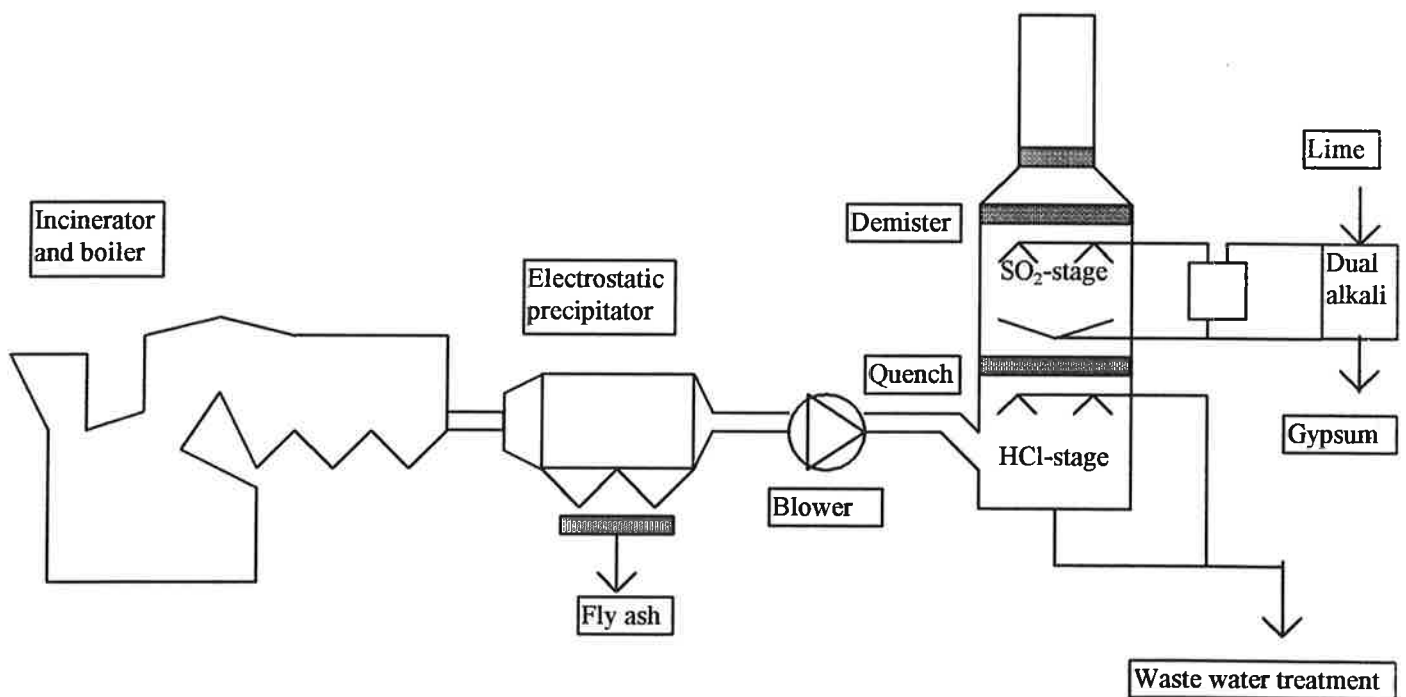


Figure 2. The Hobro plant.

The scrubber system is supervised and controlled by a process computer system. Measurements on gas concentrations, pH, levels and some flows are recorded and stored. Those measurements can be logged to a disc and analysed later. Some controllers are also implemented in the computer.

The use of sodium hydroxide instead of lime has several advantages. Most important is that all sodium salts are soluble thus avoiding the scaling problems associated with the lime based process. This means that less expensive materials can be used in the construction. It is also

possible to have scrubber stages on top of each other with intermediate tray sections since no solids are expected to precipitate and settle. This saves space and costs. The most important drawback is of course that NaOH is more expensive than lime. This drawback can be reduced if the NaOH is regenerated from the scrubber liquid using lime. This can be accomplished with the ABB Dual Alkali procedure. To find optimum operating parameters and study different operating situations for the ABB Dual Alkali process ABB Fläkt Industri AB financed a demo plant at Hobro.

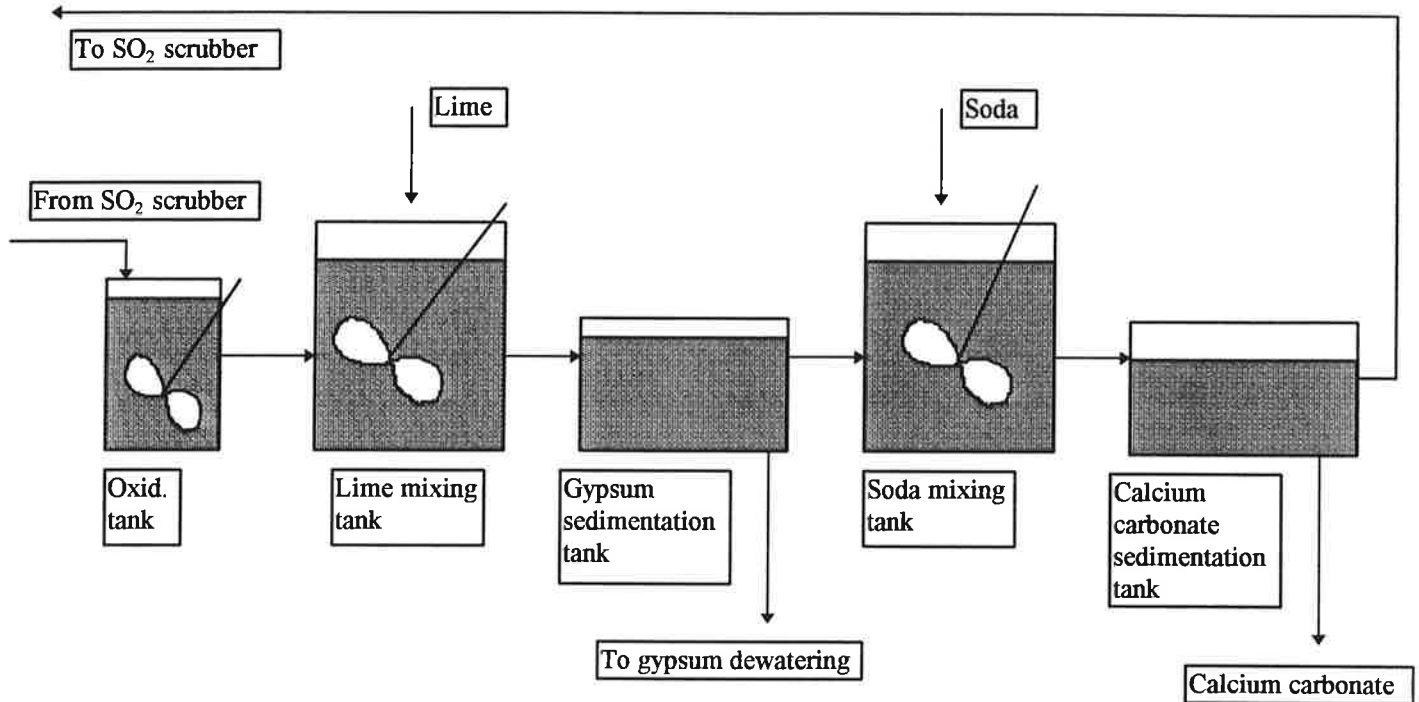
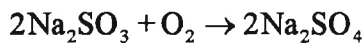
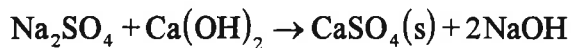


Figure 3. The ABB Dual Alkali process.

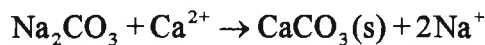
In principle, the ABB Dual Alkali process is quite simple. From the SO₂ scrubber stage a clear solution of sodium salts, mainly Na₂SO₄ and Na₂SO₃ is transferred to the ABB Dual Alkali plant for regeneration. First sulphite is oxidized to sulphate in an oxidation tank.



In a mixing tank the solution is mixed with lime and the following reaction take place.



The solids will settle in a following sedimentation tank. In a last stage a small amount of soda is added to precipitate excess of calcium and make up for losses in sodium.



This procedure further reduces the risk of scaling in the scrubber. The calcium carbonate settles in another sedimentation tank and the regenerated absorption liquid is pumped back to the scrubber controlled by pH in the scrubber loop.

6 MODELING

The process considered for dynamic studies is the second scrubber stage in Hobro. It works according to the principles in figure 4. Liquid is fed to the spray tower from a recirculation tank. After the spray tower part of the liquid bleeds off to the dual alkali system and most of it is returned to the tank. The bleed off is controlled by the level in the tank. In order to keep the scrubber liquid at a certain pH, NaOH is fed to the tank from the ABB Dual Alkali system. The feeding of alkali is controlled by a feed back loop using pH in the scrubber liquid and a feed forward loop using pH in the liquid coming from the spray tower. The actual flow of alkali is controlled using a secondary loop. At present all loops include PI-control.

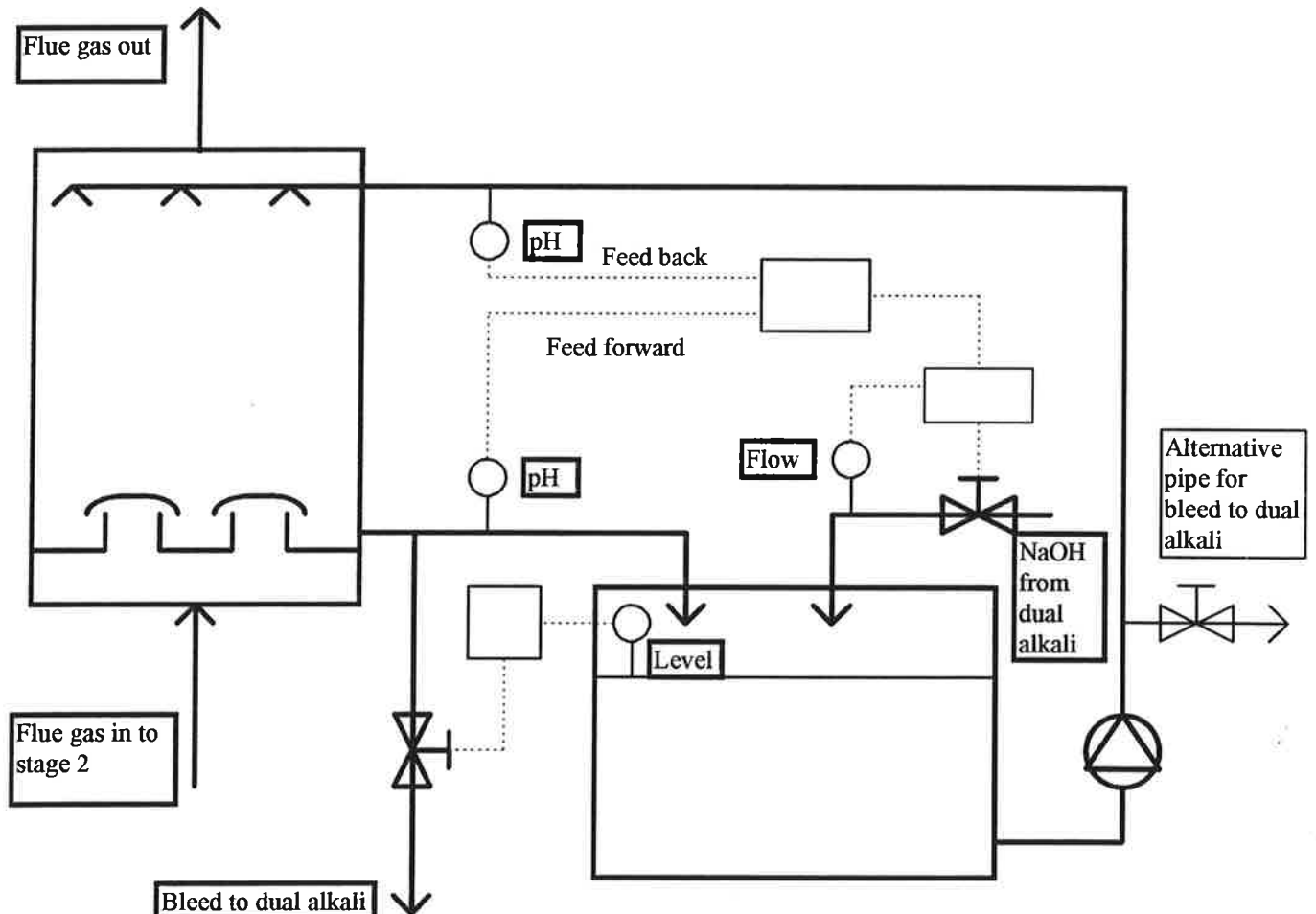


Figure 4. The model system.

The flue gas flow into this second scrubber stage has already passed an acidic stage and is free from most water soluble pollutants except for SO_2 . The gas is saturated with water and a small condensation occurs in this second stage. The temperature is almost constant at 60°C .

The flow of gas and liquid to the spray tower is relatively large and any changes will occur fast, in few seconds. On the other hand the tank is quite large in relation to the liquid flow and changes will take longer time, several minutes. Therefore the dynamics of the tower is very fast and of little interest when studying the tank and the control system. It is thus possible to create a dynamic model of the system that includes a stationary description of the spray tower.

6.1 Process chemistry

The process chemistry of wet scrubbing is very complicated. A large number of different ionic species are present [7] and many of them are a part of different equilibrium reactions. For modeling purpose it is almost impossible to include all knowledge on the process chemistry. Thus, only the most important reactions will be considered. Furthermore, concentrations will be used instead of activities.

There are two important phase equilibriums involved in sulphur dioxide scrubbing. These are:



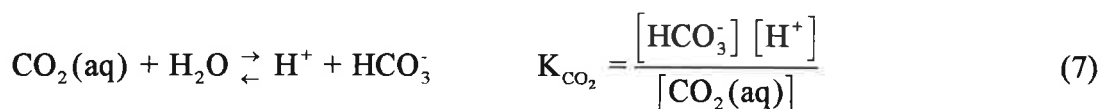
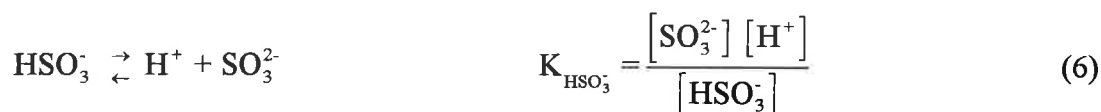
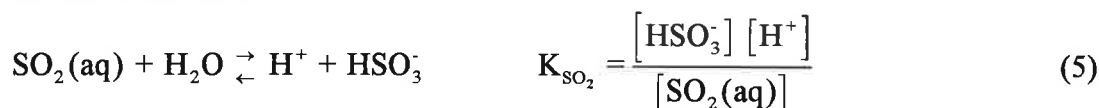
The equilibrium partial pressure over the solution is given by Henry's law, which applies well for low concentrations. Henry's constant for the equilibriums (1) and (2) are given as:

$$H_{\text{SO}_2} = \frac{P_{\text{SO}_2}}{[\text{SO}_2(\text{aq})]} \quad (3)$$

$$H_{\text{CO}_2} = \frac{P_{\text{CO}_2}}{[\text{CO}_2(\text{aq})]} \quad (4)$$

It is likely that rest of hydrogen halides from previous scrubber stages and small amounts of SO_3 will be absorbed in the SO_2 stage. All of these species are very soluble in water solutions and after the first scrubber stage the content in the gas should be very low.

The phase equilibriums above are strongly affected by the dissociation. When the concentrations of the non-dissociated species are decreased more will be absorbed from the gas. Sulphite and carbonate are dissociated in two steps. Given with the equilibrium constants we have:



As seen, a higher pH (lower $[H^+]$) in the liquid will strongly improve the conditions for both absorption processes.

A fraction of the sulphites is oxidized to sulphates. This is a well known phenomena causing scaling problems in calcium based scrubbers. This oxidation is known to be influenced by the pH of the liquid, fly ash removal efficiency, the ratio of oxygen to SO_2 and the content of nitrogen oxides in the flue gas. Presence of magnesium and chloride ions are also important [7].



The formed HSO_4^- is a rather strong acid



The scrubber liquid is neutralized using sodium hydroxide. The hydroxide ions react with the hydrogen ions



In calcium based scrubbers a number of different liquid solid equilibriums are important as well. In the sodium based scrubber the precipitation reactions are much less important and will be ignored.

As knowledge on the reaction rate of the oxidation reaction is lacking it can't be modeled in the normal way and a simplification is necessary. The oxidation will be considered happening in the moment of absorption and always to a certain degree. The oxidation level is defined:

$$\text{Ox. level} = \frac{\text{total sulfates}}{\text{total sulfates and sulfites}} \quad (12)$$

All the other reactions stated above are well known and the temperature dependence of equilibrium constants can be found in the literature. Inorganic acid-base reactions are very fast and can for any practical and most theoretical purposes be considered instantaneous, i.e. there are no dynamics in acid base reactions. Calculating the pH of the solution can be done in a beautiful and systematic way using chemical reaction invariance[6]. An easier approach is using some knowledge in general chemistry which of course will result in the same expression [8,9].

To get the correct proportion of all different ionic species a charge balance (electroneutrality condition) will be used

$$[HSO_3^-] + 2[SO_3^{2-}] + [HCO_3^-] + 2[CO_3^{2-}] + [HSO_4^-] + 2[SO_4^{2-}] + [OH^-] - [Na^+] - [H^+] = 0 \quad (13)$$

To be able to express the pH in terms of absorbed SO₂, CO₂, added sodium hydroxide and oxidation level the following relations are needed

$$s4 = [\text{SO}_2(\text{aq})] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}] \quad (14)$$

$$s6 = [\text{HSO}_4^-] + [\text{SO}_4^{2-}] \quad (15)$$

$$\text{Ctot} = [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (16)$$

$$\text{Na} = [\text{Na}^+] \quad (17)$$

s4 is simply the total concentration of sulphites, sulphur with the oxidation number 4. In the same way s6 is the total concentration sulphates and Ctot is the total concentration carbonates. Actually the expressions (13)-(17) are the chemical reaction invariants of the system. Using these relations and the equilibrium conditions the charge balance can be rewritten, see appendix 1, as:

$$\begin{aligned} & \frac{s4 \cdot K_{\text{SO}_2} \cdot [\text{H}^+]}{([\text{H}^+]^2 + K_{\text{SO}_2} \cdot [\text{H}^+] + K_{\text{SO}_2} \cdot K_{\text{HSO}_3^-})} + 2 \frac{s4 \cdot K_{\text{SO}_2} \cdot K_{\text{HSO}_3^-}}{([\text{H}^+]^2 + K_{\text{SO}_2} \cdot [\text{H}^+] + K_{\text{SO}_2} \cdot K_{\text{HSO}_3^-})} + \\ & \frac{s6 \cdot [\text{H}^+]}{(K_{\text{HSO}_4^-} + [\text{H}^+])} + 2 \frac{s6 \cdot K_{\text{HSO}_4^-}}{(K_{\text{HSO}_4^-} + [\text{H}^+])} + \frac{\text{Ctot} \cdot K_{\text{CO}_2} \cdot [\text{H}^+]}{([\text{H}^+]^2 + K_{\text{CO}_2} \cdot [\text{H}^+] + K_{\text{CO}_2} \cdot K_{\text{HCO}_3^-})} + \\ & 2 \frac{\text{Ctot} \cdot K_{\text{CO}_2} \cdot K_{\text{HCO}_3^-}}{([\text{H}^+]^2 + K_{\text{CO}_2} \cdot [\text{H}^+] + K_{\text{CO}_2} \cdot K_{\text{HCO}_3^-})} + \frac{K_w}{[\text{H}^+]} - \text{Na} \cdot [\text{H}^+] = 0 \end{aligned} \quad (18)$$

Knowing how much NaOH has been added, the absorption of SO₂ and CO₂ and the oxidation level this is an expression with only [H⁺] as unknown. Solving the equation for [H⁺] will then give pH using the definition, pH = -log([H⁺]). Solving the equation (18) is however not easy. It is impossible to find an analytical solution and using Newton-Raphsons method is not appealing. A better way is to rewrite the equation as a rational expression

$$\frac{A([\text{H}^+])}{B([\text{H}^+])} = 0 \quad (19)$$

This transformation is preferably done using a computer program handling symbolic mathematics, such as MathCad or Maple. Appendix 2 contains the result from this work in Maple. The polynomial A([H⁺]) is of 7th order in [H⁺] and can be solved using standard routines. The correct root is a positive, non-complex number.

Knowing the hydrogen ion concentration it is also possible to calculate the equilibrium partial pressure over the solution. Using Henry's law, the equilibrium constant for the dissociation of SO₂(aq) and information from (18) the partial pressure was found (see appendix 3) as

$$P_{SO_2} = H_{SO_2} \left(\frac{s_4}{1 + \frac{K_{SO_2}}{[H^+]} + \frac{K_{SO_2} \cdot K_{HSO_3}}{[H^+]^2}} \right) \quad (20)$$

This equation gives a quantitative relation for how the theoretical limit for the absorption process varies with pH. The equilibrium partial pressure of CO_2 can be found in the same way.

6.2 The absorption process

As concluded earlier a stationary model of the spray tower process is a reasonable simplification in this system. In the spray tower the flue gas is sprayed countercurrently with the scrubbing liquid. The gas enters the scrubber stage with a partial pressure of SO_2 , P_{in} , and leaves it with a lower partial pressure, P_{out} . The SO_2 removed from the gas leaves the spray tower with the liquid. The liquid enters the tower with equilibrium partial pressure $P_{SO_2,in}$ and leaves it with $P_{SO_2,out}$. The flow of gas and liquid is not affected by the absorption of some ppm SO_2 and the small condensation of water vapour can be ignored. Furthermore the temperature in the spray tower is almost constant, i.e. the process is isotherm and energy balances can be ignored.

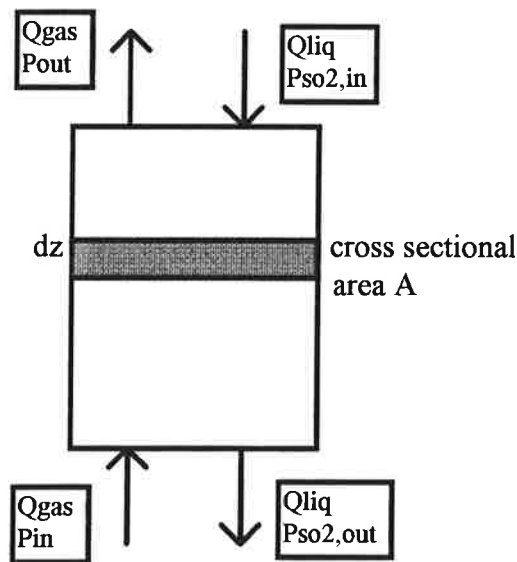


Figure 5. Spray tower with differential element dz .

The process includes diffusion of SO_2 from the gas bulk to the bulk of the droplets. Describing the mass transfer according to the film theory model [10,11], an overall mass transfer coefficient, $K_g a$, is defined:

$$\frac{1}{K_g a} = \frac{1}{k_g a} + \frac{H_A}{k_L a \cdot E} \quad (21)$$

where $k_g a$ is the mass transfer coefficient in the gasfilm, $k_L a$ is the mass transfer coefficient in the liquid film, H_A is Henry's constant for the gas in question and E is the enhancement factor due to chemical reaction. E is depending on the rate of the chemical reaction consuming the absorbed specie in the liquid. In the case of SO_2 , absorption the chemical reaction is the dissociation of SO_2 according to (5) and (6). The reaction is very fast and will take place if pH is high enough, i.e. E is very large and $\frac{1}{k_g a} \gg \frac{H_A}{k_L a \cdot E}$. This means that the overall mass transfer is controlled by the mass transfer in the gasfilm (as long as pH is high) and

$$K_g a \approx k_g a \quad (22)$$

$K_g a$ is depending on a lot of different physical parameters in the spray tower such as liquid load, nozzle efficiency, turbulence etc. Under best circumstances it can be considered constant for one spray tower at well defined flow rates. Under different conditions in another scrubber $K_g a$ will have a quite different value.

The content of SO_2 in the gas is low, normally given in ppm. At the same time the liquid flow is rather large. This means that the liquid doesn't change much in the scrubber and the equilibrium partial pressure is approximately constant. With this approximation a balance over a differential element dz with partial pressure P_{gas} of SO_2 in the gas can be written

$$Q_{gas} \cdot dP_{gas} = K_g a \cdot A \cdot dz \cdot R \cdot T \cdot (P_{gas} - P_{SO_2}) \quad (23)$$

where Q_{gas} is the gas flow, A is the cross-sectional area of the spray tower, R the ideal gas law constant, T the absolute temperature, z is the height of the spray tower and P_{SO_2} the equilibrium partial pressure over the scrubber liquid. The differential equation (23) can be integrated to give

$$\ln \left(\frac{P_{in} - P_{SO_2}}{P_{out} - P_{SO_2}} \right) = \frac{K_g a \cdot A \cdot R \cdot T}{Q_{gas}} z \quad (24)$$

Expression (24) can be solved for P_{out} which gives

$$P_{out} = P_{SO_2} + (P_{in} - P_{SO_2}) \cdot e^{-\left(\frac{K_g a \cdot A \cdot R \cdot T \cdot z}{Q_{gas}} \right)} \quad (25)$$

Expression (25) gives the partial pressure of SO_2 out from the scrubber if the partial pressure in, spray tower size, gas flow, mass transfer coefficient and equilibrium partial pressure are known. All partial pressures in (25) can be taken as a volume fraction in, e.g. ppm instead and n , the number of mol/s absorbed in the liquid will then be found as

$$n = \frac{P \cdot Q_{gas} \cdot (P_{in} - P_{out}) \cdot 10^{-6}}{R \cdot T} \quad (26)$$

where P is the absolute pressure in Pa. Using the oxidation level and the liquid flow will give the increase in sulphite and sulphate concentration in the liquid.

Since the measurement of SO₂ is done after cooling and condensing the gas at approximately 5 °C the concentration is obtained as ppm of dry gas at almost normal temperature and pressure. Thus, the flow of flue gas should be given as Nm³/h dry gas.

In principle, the absorption of CO₂ can be modelled the same way, but since no realistic data exist for the CO₂ content of the flue gas the liquid out of the spray tower will be given a constant concentration instead.

6.3 The recirculation tank

The recirculation tank has got two streams in, Q_{scr} from the spray tower and Q_{alk}, the alkaline stream from the dual alkali system. Only the stream Q_{out} leaves the tank and is sprayed into the spray tower. The liquid volume of the tank, V, can be described

$$\frac{dV}{dt} = Q_{scr} + Q_{alk} - Q_{out} \quad (27)$$

where t is time. To keep track of the chemical composition it is sufficient to model the total amount sulphite, sulphate, carbonate and sodium, i.e. s₄, s₆, C_{tot} and Na. The tank hasn't got any mixing device but there is a lot of turbulence due to the large flows. If the tank is considered completely mixed the component mass balances can be written in vector form

$$\frac{d}{dt}(V \cdot \bar{c}) = Q_{scr} \cdot \bar{c}_{scr} + Q_{alk} \cdot \bar{c}_{alk} - Q_{out} \cdot \bar{c} \quad (28)$$

where $\bar{c} = [s_4 \ s_6 \ Na \ C_{tot}]^T$ and the indexes designates the corresponding concentration vectors for the streams from the scrubber and from the dual alkali system.

6.4 Control system

The control system is modeled ideally, without sensor and actuator dynamics. The secondary loop in the pH control is considered as an actuator. The level in the tank is controlled measuring the level, h, in the tank and increasing or decreasing the bleed flow, Q_{bleed}, to the dual alkali system. Changing Q_{bleed} affects Q_{scr}.

$$Q_{bleed} = K(h - h_{ref}) + \frac{1}{T_i} \int_0^t (h - h_{ref}) d\tau \quad (29)$$

$$Q_{scr} = Q_{out} + \text{Condensing liquid} - Q_{bleed} \quad (30)$$

where K is proportional gain and T_i is integral time.

For the control of pH two measurements are used. The pH in the flow to the spray tower, pH_{in} and pH in the flow from the spray tower, pH_{out} are both affecting the flow Q_{alk}

$$Q_{alk} = K_{fb}(pH_{in} - pH_{in,ref}) + \frac{1}{T_{i,fb}} \int_0^t (pH_{in} - pH_{in,ref}) d\tau + K_{ff}(pH_{out} - pH_{out,ref}) + \frac{1}{T_{i,ff}} \int_0^t (pH_{out} - pH_{out,ref}) d\tau \quad (31)$$

The index fb designates the feed back loop parameters and ff the feed forward parameters. It must also be remembered that the feed forward controller never gives a negative output.

7 STRUCTURING AND IMPLEMENTATION

The model was implemented using MATLAB/SIMULINK. MATLAB is a computer program for numeric computations and visualization and can also be viewed as a high level programming language. SIMULINK is an extension of MATLAB, an interactive environment for simulating dynamic systems. In SIMULINK, dynamic systems are built as block diagrams in a hierarchical structure and it is possible to include parts written in MATLAB language (or C or Fortran)

Considering the mathematical model of the scrubber system it can be divided into one dynamic part and one stationary part. The dynamic part includes the differential equations for the recirculation tank and the control system. This part is ideal for the SIMULINK environment. The absorption process and the calculation of pH are static relations. The calculation of pH also includes a numeric problem. These parts are suited for the MATLAB language and numeric capabilities.

7.1 Calculating pH

Using MATLAB calculating the pH from the numerator polynomial in (19) is easy. The function that was written for this purpose is found in appendix 4. The function has a very simple structure. It calculates the polynomial coefficients, uses a MATLAB command to find the roots and then chooses the correct root. Input to the function is the four concentrations s_4 , s_6 , N_a and C_{tot} in mol/l and output is pH.

With this function it is possible to calculate the titration curve of a liquid. It is possible to investigate how changes in sulphur and carbonate concentration influence the titration curve. Figure 6 shows how the titration curve changes with the sulphur concentration if the carbonate concentration and oxidation level are constant.

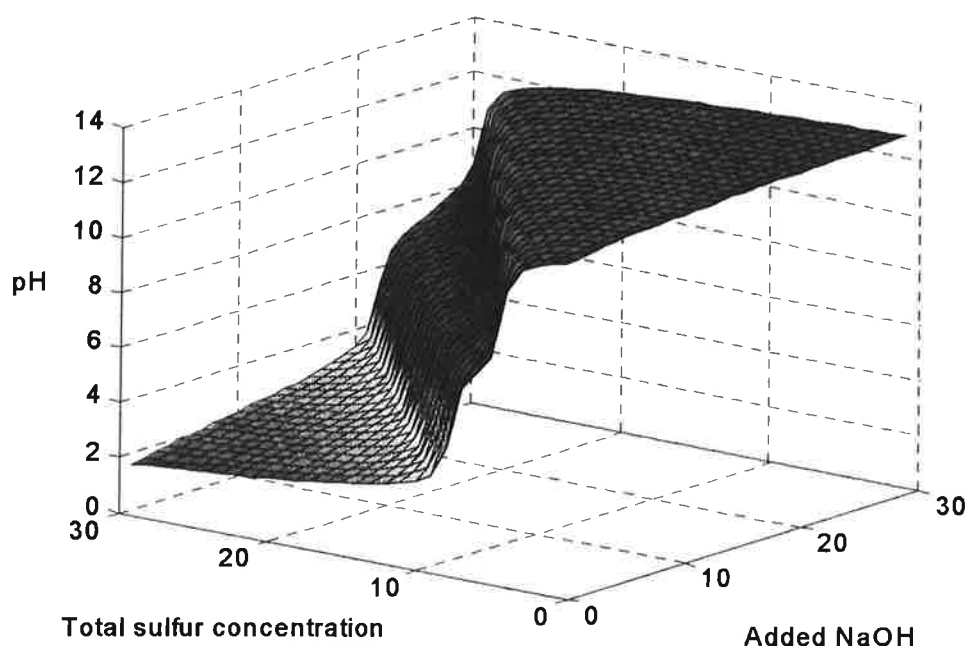


Figure 6. 3D-titration curve assuming a constant oxidation level.

7.2 The spray tower

A function was also written calculating the concentrations in streams out from the spray tower knowing the concentrations in. This function is found in appendix 5. Input to the function is the flow of dry gas in (Nm^3/h), concentration of SO_2 in the gas (ppm), liquid flow in (l/s), liquid concentration of s_4 , s_6 , Na and C_{tot} (mol/l) and liquid pH. Output are the same flows and concentrations out from the spray tower.

7.3 The tank

The tank model was built in SIMULINK. The five differential equations were grouped into separate units each representing a certain balance equation. The output from the mass balance is the tank volume and the level in the tank, calculated from the total volume and cross sectional area. Output from the component balances are the concentrations in the liquid of s_4 , s_6 , Na and C_{tot} . A transport delay of 10 s represents the pipe system before the pH measurement which is calculated using the MATLAB function. The block diagrams for the tank as a whole and the individual balances are found in appendix 6.

7.4 Control loops

A linear control system is easy to build in SIMULINK since there are available blocks for controllers. The level control is the simplest possible case using only a PID controller with no derivative action and a restriction on the flow. The pH control system is just slightly more complicated, having both feed back and feed forward loops. Wanting to use the controller parameters from the Hobro plant, both controller outputs are multiplied with a constant representing the actuator gain. The output, the flow from the dual alkali system, is also given a "start value" and a restriction. The controller block diagrams are found in appendix 7.

7.5 The scrubber system

In appendix 8 the block diagram for the whole process can be found. Efforts has been made to make it easy to understand, looking like a flowsheet for the process. The block "spray tower" simply contains the MATLAB function. The rest of the blocks are discussed above except for "SO₂in" and "Bleed". The "SO₂in" block gets operating data of the SO_2 concentration in the gas from the Hobro plant and passes it to the model. These data are obtained from the process computer and were logged 27/9 in 1994. The "Bleed" block only separates the bleed flow from the flow from the spray tower.

8 MODEL VALIDATION

The model is thus complete, using the SO_2 concentration in the gas in as the only input. The model was first compared to known data from the Hobro plant in order to verify a correct performance. Guided by the knowledge obtained from this first study experiments were planned and conducted at the Hobro plant in order to validate the model.

8.1 A first study

A lot of parameters in the model was unknown or only roughly known. The mass transfer coefficient, the actuator gain and all concentrations of sodium were completely unknown. For the gas and the liquid flow in the spray tower the design values were known. The initial concentrations in the tank were all unknown, but an old analysis provided some help with the magnitude. The concentration of sulphates and pH in the stream from the dual alkali plant are measured every day. The concentrations of carbonates and sulphites are not measured but are supposed to be zero.

A lot of process characteristics from the 27/9 were on the other hand known. The flow of alkali to the recirculation tank, pH in to and out from the spray tower and SO_2 concentrations in the gas in to and out from the spray tower. The SO_2 concentration in is used as input to the model, the rest of these data can be used to find the missing parameters comparing simulations with the measured data.

The simulations to verify the model were carried out in the following order:

1. The model pH controller was given the measured pH values as input and the output was compared with the measured flow from the dual alkali plant. At first it was impossible to find an actuator gain that gave the correct output. When turning off the integrating action of the feed forward controller the task was suddenly easy. In one way the result makes sense. A feed forward controller can not include integral action without yielding a very large signal. Probably the control system contains some algorithm to ignore too large outputs from the integral action.
2. Possible sulphites and carbonates in the flow from the dual alkali system was ignored. The sodium concentration was estimated from the pH and the sulphate concentration.
3. The mass transfer coefficient, $K_{g,a}$, was found in the following way. The scrubber liquid was given the rough values on the concentrations of s_4 and s_6 . The carbonate concentration was guessed as half the detection limit and Na was then estimated from the known pH. $K_{g,a}$ was then found comparing the simulated concentrations of SO_2 out with the measured.
4. The model gas flow was changed to give the measured consumption of alkali over a longer time. Every time the gas flow was changed, $K_{g,a}$, had to be changed as well.
5. Using the measured alkali consumption, the initial concentration in the tank were estimated comparing the response in pH with the measured response. Changing the sulphite concentration, the value of $K_{g,a}$ must be changed again. In trying to find the correct initial

chemical composition, 3D-titration curves such as figure 6 were a good help to understand how the behaviour of the solution would change if the composition changed in a certain way. Still, this was by far the most difficult step.

6. Having a correct gasflow, chemical composition and K_g the recirculation flow was estimated comparing pH out from the spray tower with the measured pH.

7. If the simulation of the whole model now didn't give a good agreement the procedure was repeated.

These simulations were very time consuming but gave a model with good agreement to the measured characteristics. The figures 7-9 show some of the results of the simulation together with measurements from the Hobro plant. The figures represent process behaviour during almost six hours.

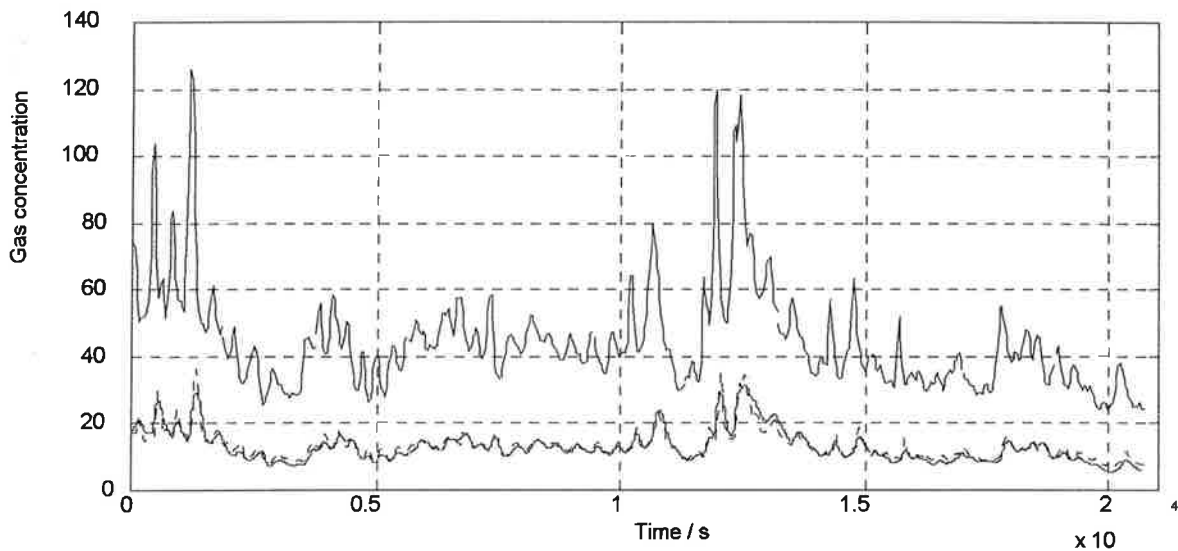


Figure 7. The gas concentration of SO_2 in to and out from the spray tower. Dotted line is simulated concentration out.

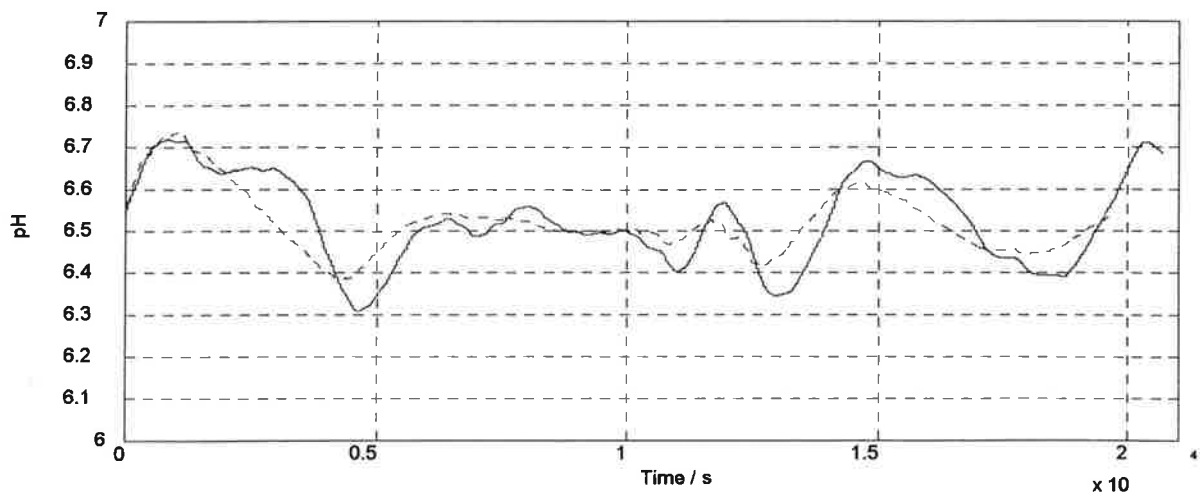


Figure 8. pH in to the spray tower. Dotted line is simulated. Setpoint pH is 6.5.

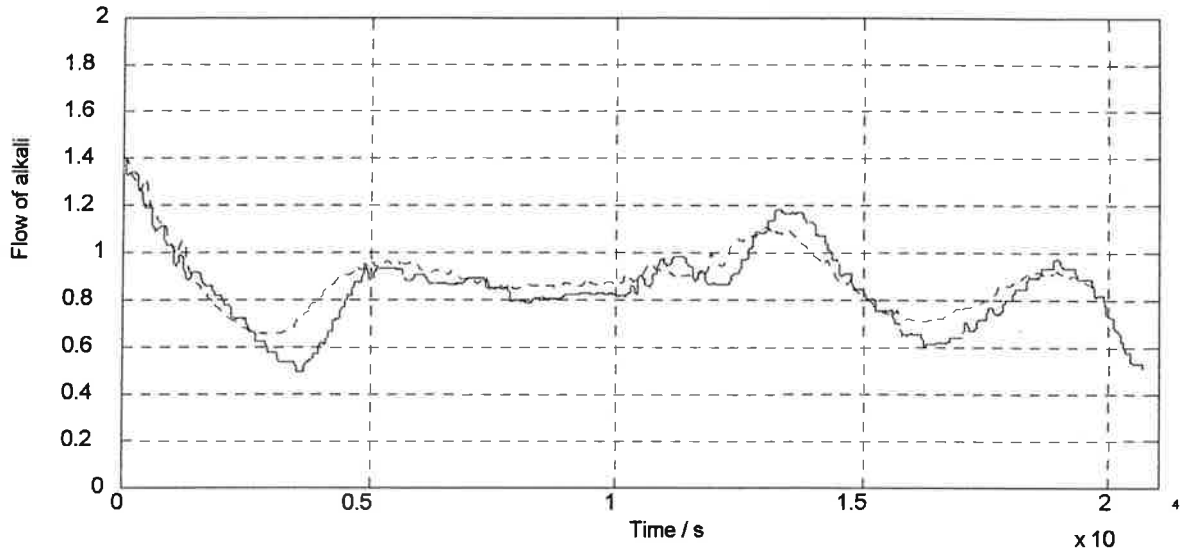


Figure 9. Flow of alkali to the tank (control signal). Dotted line is simulated.

From figures 7-9 it seems like the model has a potential to give a good agreement with operating data. However, this agreement is obtained after a lot of work fitting the model to operating data. All liquid chemistry is more or less unknown and has been manipulated to give the model the desired characteristics. The recirculation flow and the gas flow were also unknown. If the flows and the chemical composition of the liquid was known the simulation could be a way to determine the mass transfer coefficient, a method as good as any. With these parameters unknown the mass transfer coefficient adds up as another uncertain parameter. It must also be recognized that the changes in the SO_2 concentration in the gas here was rather small. There was no serious constraint on the model.

8.2 The Hobro experiments

In order to validate the model experiments were carried out at the plant in Hobro 941128 - 941130. The main intention was to create a large load disturbance on the process and observe the response. The experiments were planned based on simulations using the model.

8.2.1 The load disturbance

The load disturbance on the process was planned as a large, fast increase in the concentration of SO_2 in the flue gas. This increase was to take place after several hours of low concentration. This was accomplished avoiding gypsum paper waste and tires in the fuel during some hours and then using preferably these fuels. This experiment was carried out 941130 and figures 10-13 shows the behaviour recorded by the process computer during the hours 10.52 to 18.52.

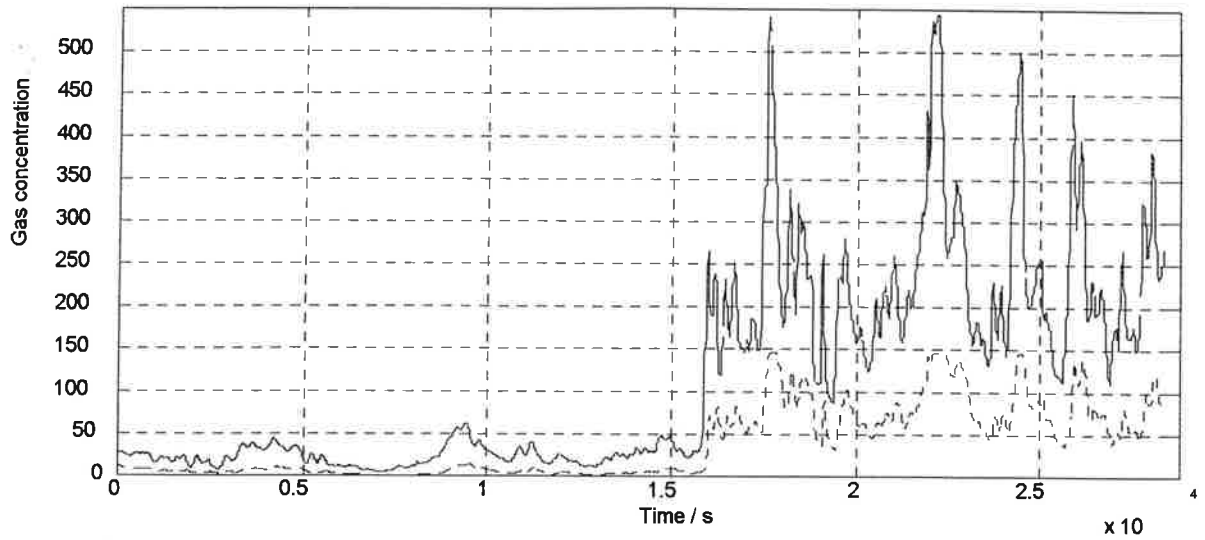


Figure 10. The gas concentration of SO_2 in to and out from the spray tower. Dotted line is the concentration out from the spray tower.

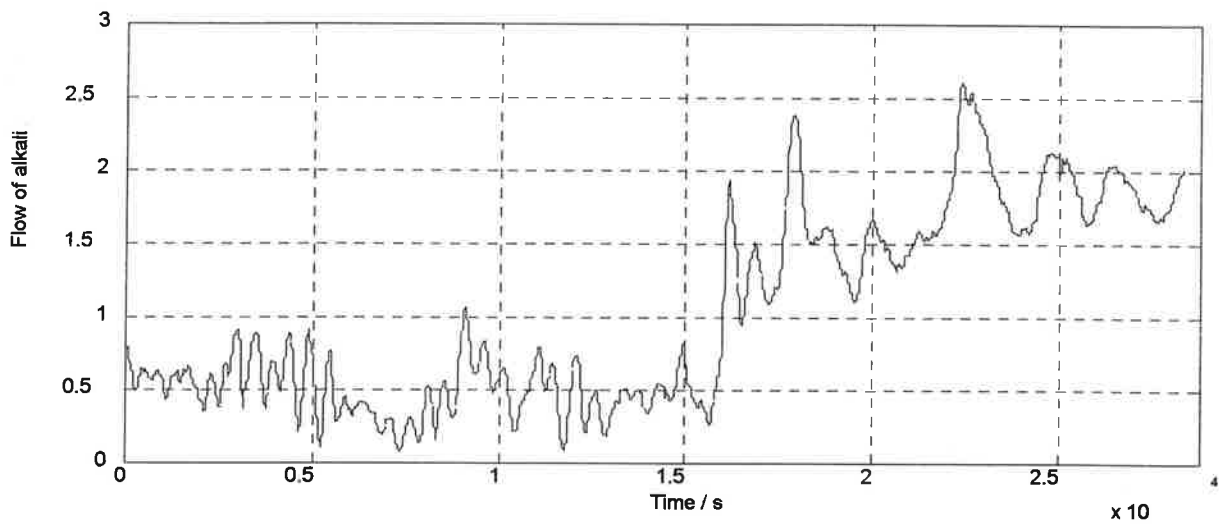


Figure 11. The flow of alkali to the recirculation tank

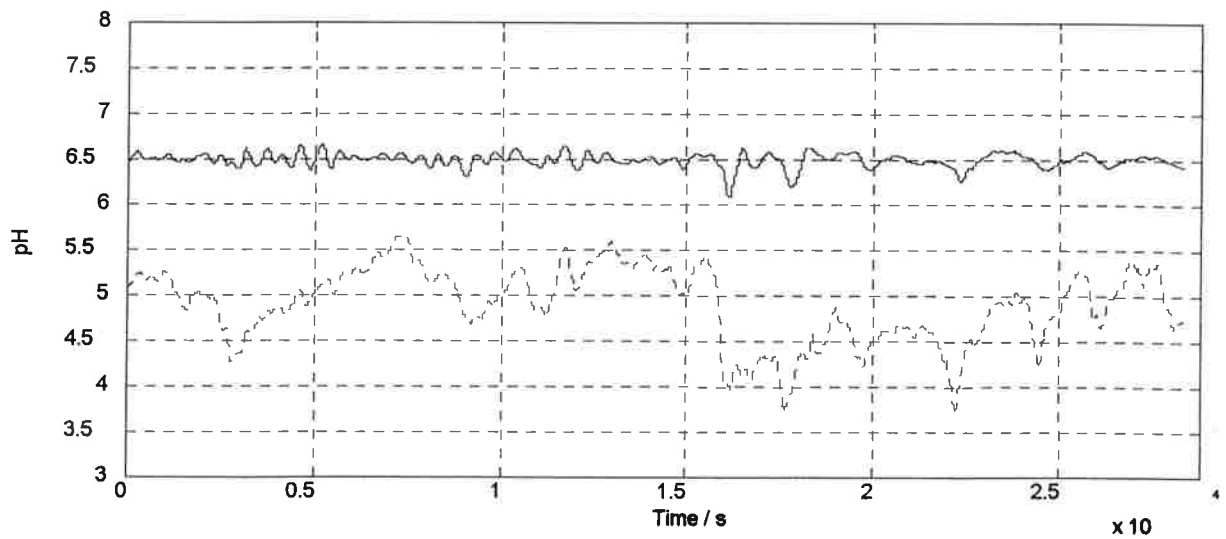


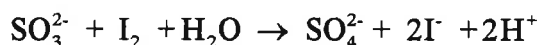
Figure 12. pH in to and out from (dotted) the spray tower. The setpoint for pH to the spray tower is 6.5. (Note that controller settings are different from figures 7-9)

Considering the profile of the SO₂ concentration only it seems like the experiment was very successful in this part. It must however be noted that there was a lack of waste to burn during the hours around noon and that this may have caused effects in parameters that were not recorded but assumed constant.

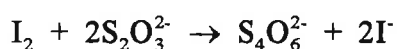
8.2.2 Chemical analysis

All species in the model was analysed in the stream to the spray tower just before increasing the SO₂ concentration. Calcium and chlorides were analysed in order to identify possible disturbances not included in the model. From simulations with the model it was recognized that sulphites would have the largest relative change in concentration due to a load disturbance. Actually, sulphites was the only specie that had a change in concentration large enough to be detectable with analytical methods. Sulphites were therefore analysed as often as possible during the increase of the SO₂ concentration and the following two hours. A full analysis was carried out again when ending the sulphite analysis. At the start and end point of the sulphite analysis a full analysis of the liquid from the spray tower was carried out as well. The true composition of the flow of alkali (from the dual alkali system) was also considered important and a full analysis was carried out at the same time as the analysis of the samples in the scrubber loop.

The sulphite concentrations were determined with iodometric back-titration, a well known method for sulphite analysis [9]. The sulphites in the sample react with an excess of iodine according to

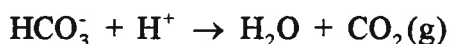


The excess of iodine is then determined by titration with thiosulphate

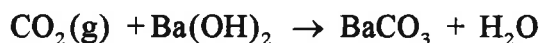


For this titration starch is used as indicator. It forms a dark blue colour if iodine is present. At the endpoint of the titration the colour disappears.

The concentration of carbonates were determined in principle by desorbing the carbonates from the sample by adding sulphuric acid, i.e.



The carbon dioxide was then absorbed in strong barium hydroxide



The consumption of barium hydroxide was then determined by backtitration with hydrochloric acid to a neutral point, indicated by phenolphthalein.

The analysis of sulphites and carbonates were carried out according to instructions from the analytical laboratory at ABB Fläkt Industri AB. The analysis of sodium, sulphates, calcium

and chlorides were carried out by the analytical laboratory. Sulphates and chlorides were analysed with a Dionex ionchromatograph. Sodium and calcium were analysed with a Varian atomic absorption spectrophotometer.

The results of the analysis of sulphites and carbonates are found in appendix 8. This appendix also includes some extra analyses on sulphite and carbonates that were made during the 28/11 and 29/11. They are included since they reveal some interesting facts about the process chemistry. The analysis report from the analytical laboratory is found in appendix 9.

8.2.3 Flow measurements

During the 22/11 and 23/11 -94 a lot of measurements on the gas flow in the Hobro plant were made. In appendix 10 a page from a preliminary report on those measurements are found. The gas flow is apparently varying at least between 18000 and 28000 Nm³/h dry gas.

There is no possibility in the plant to measure the flow of scrubber liquid to or from the spray tower direct. The electric current to the pump was measured however and from this the liquid flow was estimated.

During the experiments the bleed to the dual alkali plant was taken the alternative way according to figure 4.

8.3 The pH control system

During the experiments in Hobro an attempt was made to tune the controller. This will be discussed in detail in section 9. It was found that the controller works in a different way than assumed. For example the controller parameter was proportional band, P-band, not gain as the model assumed. Using some of the tuning experiments to do "open loop" simulations the actuator gain and control algorithm was investigated. "Open loop" simulations designates a procedure taking the controller model separately and feed it with measured pH and then compare the control signal obtained to the measured flow of alkali in the plant. Using data from P, PI, and PID control the action of each parameter could be compared. The result for the final PID controller is found in figure 13. It must be remembered that this is open loop simulations, that the model controller gets no feedback from its output. Large offsets between the measured and simulated signal would be no surprise. The signals should however have a similar behaviour.

The agreement in figure 13 is surprisingly good. The result is obtained using the following controller algorithm for both feedback and feed forward loops.

$$U = U_c + \frac{1}{\text{P-band}} \cdot e + \frac{1}{T_i} \int_0^t e d\tau + T_d \frac{de}{dt} \quad (32)$$

where U is the control signal, U_c is a bias term and e is the control error. The inverse P-band corresponds to controller gain.

Even though the result here looks satisfying the investigations was really not. The resulting controller algorithm did not always give the best agreement and it was always possible to find other controller tunings, that had nothing to do with the settings in Hobro, that had better agreement. Open loop simulation is a questionable method, but there is really no other way to find the controller algorithm.

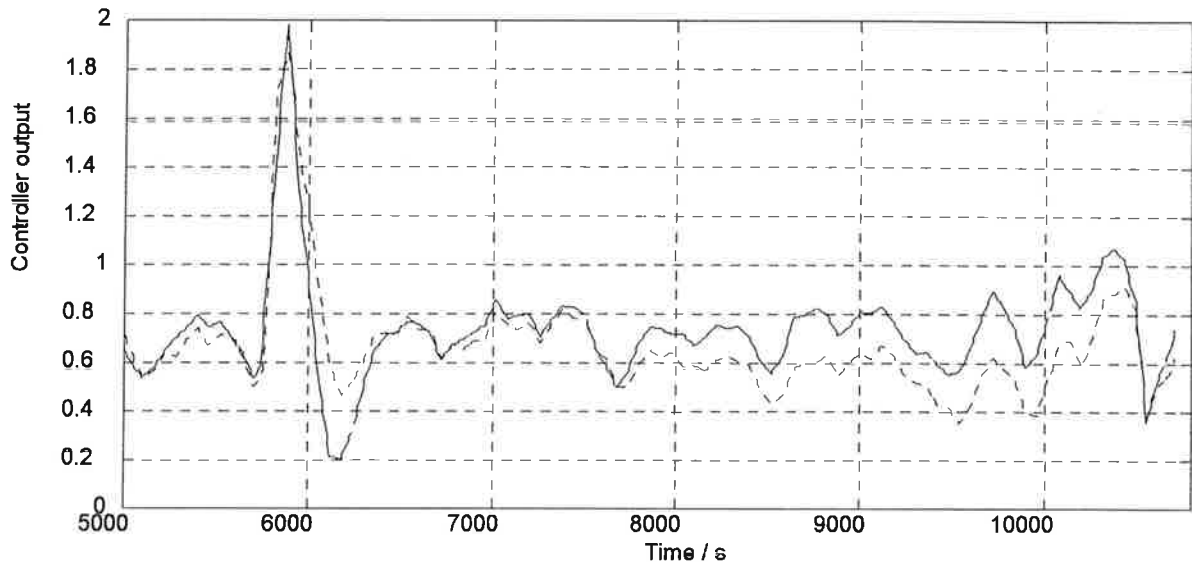


Figure 13. Result of open loop simulation. Full line is modeled PID controller and actuator output, dotted line is measured output in Hobro.

Studying the effects of setpoint changes on the flow of alkali it was also found that there is a maximum rate of change in the flow. This rate limit, which is an important feature of the actuator characteristics, was also used to get the result in figure 13.

8.4 Consequences for the model

The results from the experiments in Hobro have some minor consequences for the model. The smallest necessary change is that the input, the SO_2 concentration in the gas will be found in another file. This is just a new file name in the "SO2in" block in appendix 8. The change of pipe for the bleed to the dual alkali plant means connecting the "Bleed" block after the tank instead of before.

The results from the chemical analyses indicates several small but important assumptions in the model. The analysis of carbonates shows, considering the uncertainty in these measurements, that the concentration is almost constant in all parts of the process during several days. It is very clear that there is a relatively high concentration of carbonates in the stream leaving the dual alkali system. In fact, this concentration implies that the carbonates found in the scrubber loop originates from the alkali to a higher degree than from an absorption in the spray tower. The origin of these carbonates is likely to be the addition of soda in the dual alkali plant. As a consequence of this the model is changed. Carbonates are added with the alkali according to the measurements and the concentration out from the spray tower is the same as the concentration in to it. For the implementation this only means that one constant, the concentration of carbonates in the alkali, and one line in the function in appendix 5 are changed.

The model constant giving the sulphite concentration in the alkali is changed according to the measurements. The analysis for sulphites also indicates another interesting aspect. Two samples analysed for sulphite the 29/11 are only 1½ hour apart but have a large difference in sulphite concentration. The first sample was taken after a night with high SO₂ concentration in the flue gas. During the time between the samples the SO₂ content of the gas was very low. The large change in concentration can not be attributed to wash-out or any other physical process. It shows that the oxidation is a fast and important reaction in the scrubber loop. The approximation with a constant oxidation level in the moment of absorption is thus a serious error. Still lacking knowledge on reaction kinetics the assumption is unfortunately necessary. It must however be kept in mind.

The measurements of flows gives reason to change the constants representing these quantities. It is questionable if the gas flow can be represented by a constant but no correlation of the flow to measurements of e.g. the pressure drop over the spray tower exists so far. Therefore a constant is better than guessing a variation. The model was changed to a flue gas flow of 20000 Nm³/h. Since the gas flow is a part of the exponential expression in equation (25) there must be a corresponding change in K_ga, i.e. K_ga was changed so that the exponential expression did not change.

The recirculation flow is likely to be very constant but the estimation leaves a rather wide interval. The model was changed to a flow in the middle of that interval.

The controllers were changed according to the algorithm (32), the actuator gain was changed and the rate limit was implemented. The SIMULINK controller block has its own algorithm and the change here must be kept in mind so that the corresponding parameter is given to the controller. For example the controller proportional parameter must be given as the inverse P-band. Implementing the rate limit is just adding another SIMULINK block, a "rate limit" block.

8.5 Simulations

The model, with the changes according to section 8.3 was given the concentrations measured 15.05 the 30/11 as initial concentrations. Using the gas concentration of SO₂ logged from the process computer 15.05 to 18.52 as input the results below were obtained. In each figure the simulated result is compared to measured process behaviour.

The only extra adjustment in the model is the concentration of sodium in the scrubber liquid and from the dual alkali plant. The measurements are not accurate enough to give the correct, measured pH of the solution. The charge balance is only approximately fulfilled. Therefore, the concentration of sodium was adjusted to give the measured pH at the starting point. This could be done without violating the measurements since the changes needed were small.

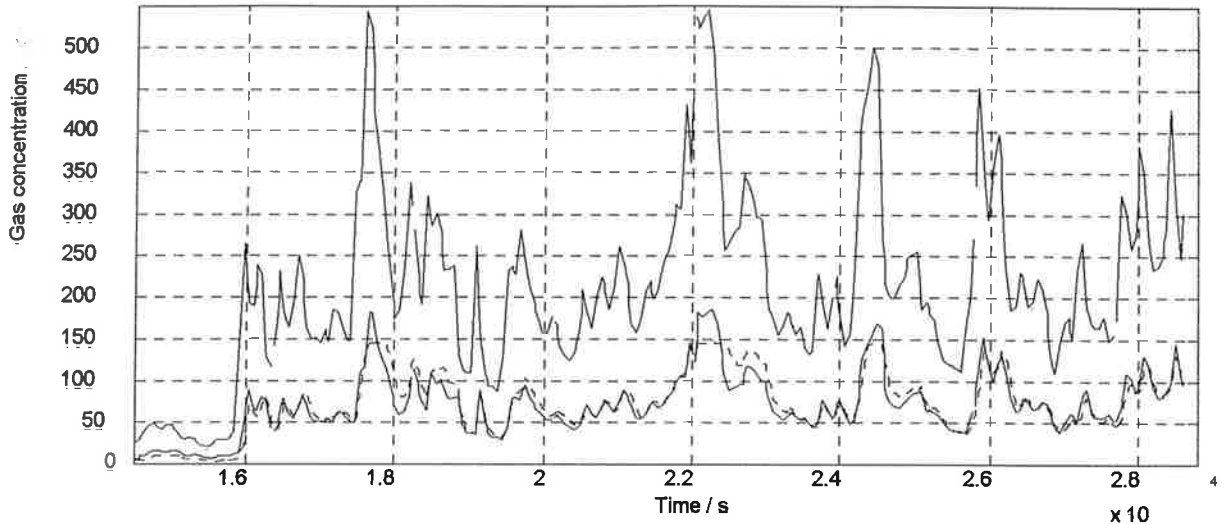


Figure 14. The gas concentration of SO₂ in to and out from the spray tower. Dotted line is measured concentration out.

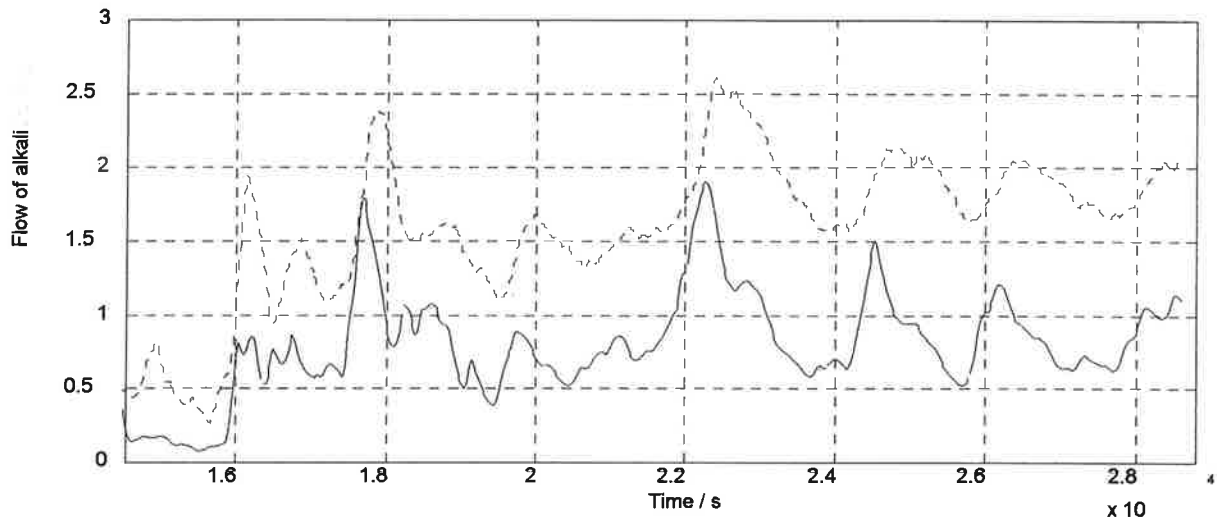


Figure 15. Flow of alkali to the recirculation tank. Dotted line is measured flow.

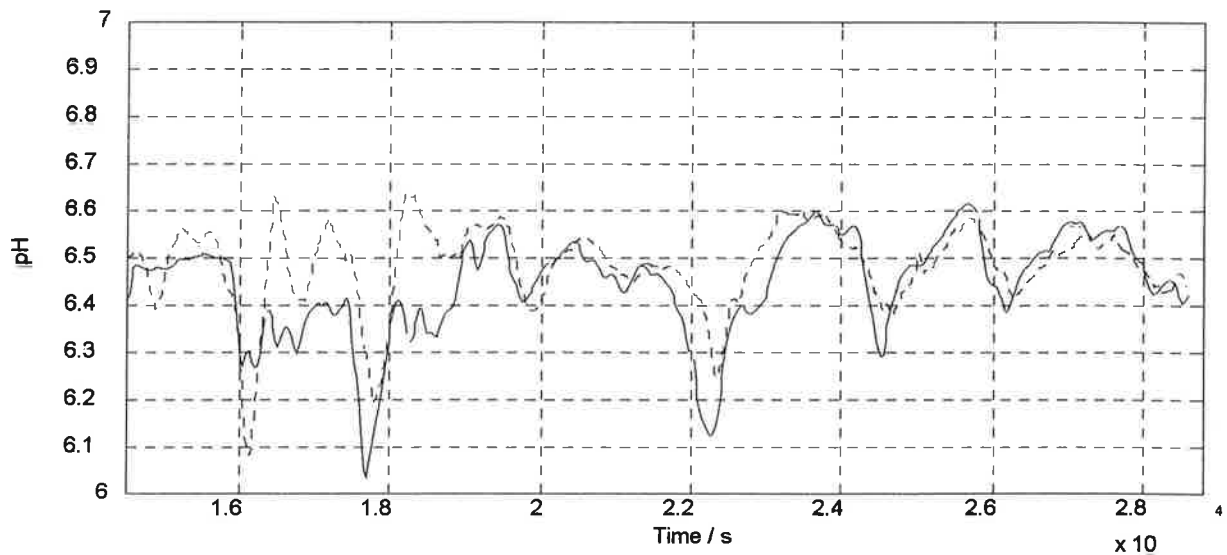


Figure 16. pH in to the spray tower. Dotted line is measured pH. Setpoint is pH 6.5

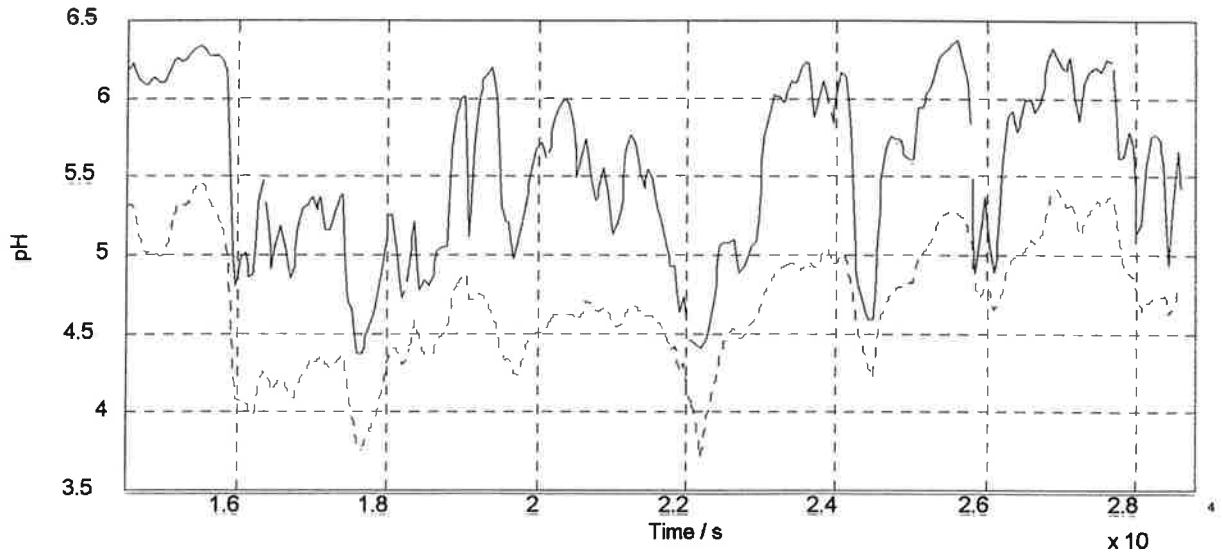


Figure 17. pH out from the spray tower. Dotted line is measured pH.

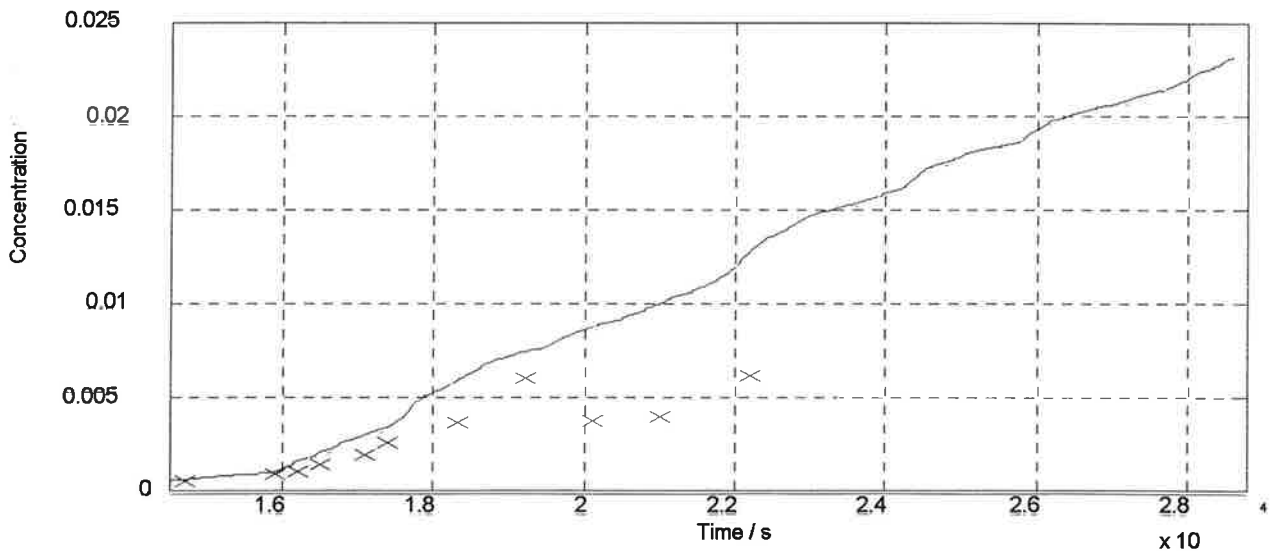


Figure 18. Concentration of sulphites in the liquid to the spray tower. x-marks represents the results of the chemical analysis.

8.6 Discussion

The agreement between measured and simulated outputs from the process are in some cases good in other cases there is an offset. A number of conclusions can be drawn comparing some of the results. Other results can only give rise to speculations.

In figure 14 it is hard to see any difference between measured and simulated concentration out from the scrubber. At occasions some simulated peaks is shown, but at these times the measurements show the maximum output for the sensor. Furthermore, sensor dynamics has not been modeled, the measurement is just given a time delay, which explains why the measurement sometimes changes a little bit slower. It must be concluded that the model describing the spray tower and the absorption is very good. All assumptions, stationarity, ignoring energy balances etc. are valid. The fact that the mass transfer coefficient didn't change when changing the chemistry according to the measurements indicate that the mass

transfer is the limit for the absorption and that the equilibrium partial pressure is of minor importance. In fact, other studies on this scrubber shows the same thing. There is something wrong with the nozzles which causes much less favourable conditions for the mass transfer.

The difference in the flow of alkali to the recirculation tank in figure 15 is noteworthy, but the trends are very similar. It can be seen in figure 11 that there is a consumption of approximately 0.5 units of alkali even when there is hardly any SO_2 in the gas at all. This difference is roughly equal to the difference between the simulated and measured flow of alkali. Could there be something else than SO_2 in the gas consuming alkali? If the first acidic scrubber stage doesn't remove all HCl then rests will be absorbed in this second stage and consume some amounts of alkali. As is seen in appendix 9 there are a rather high concentration of chlorides in the scrubber liquid. Since the dual alkali process doesn't remove chlorides at all this means that there is a build up in the entire process to a concentration allowing the bleed off to match the absorption. This explains why the concentration is so high but it also shows that there is an absorption of chlorides in the second scrubber stage. Rough estimations on the bleed from the dual alkali plant shows that approximately 0.5 units of alkali would be needed to neutralize the HCl absorbed in this stage[12]. The scrubber liquid is also known to have small concentrations of fluorides, indicating that other hydrogen halides are also absorbed in this scrubber stage.

If not all HCl is absorbed in the first scrubber stage it is reasonable to believe that rests of SO_3 passes as well and is absorbed in the second stage. High concentrations of SO_3 in the gas must coincide with high concentrations of SO_2 since they have the same origin, sulphur in the fuel. If this is the case there would be a slightly larger difference between simulated and measured consumption of alkali when there are high concentrations of SO_2 in the gas. There are such tendencies in figure 15. The importance of SO_3 for alkali consumption is however clearly much smaller than that of hydrogen halides discussed above.

Possible leakage of SO_3 and HCl is a reasonable explanation for the difference between simulated and measured flow of alkali. The phenomena can of course also be explained otherwise. A larger flue gas flow in the model will increase the need for alkali, and cause an increasing demand with higher SO_2 concentrations. If the pH in the alkali is lower than in the model there will also be an increased demand for alkali. To increase the flow of alkali enough for the difference between the simulations and the measurements to disappear would however mean very large changes. The increase in flue gas flow would be much larger than the measurements on the gas flow indicates is possible. The alkali would have to have a much lower pH than measured in order to make the difference disappear. Wrong flue gas flow and alkali concentration can not alone explain the difference, but are of course likely to be a part of it.

At a more careful examination of figure 15 it seems like the measured flow of alkali is drifting towards larger flows without any explanation in the gas concentration of SO_2 . The simulated flow shows no such tendency. This drift could be explained by a changing gas flow, changing alkali concentration but also e.g. by a possible oxidation of sulphites.

During the last three hours of simulation figure 16 shows a very good agreement between simulated pH and measured pH. During the first hour there are differences, sometimes as large as 0.2 in pH, which still must be considered as a very small difference. The large trends,

trends that can be attributed to changes in gas concentrations of SO₂, are the same in both simulated and measured pH. The measured pH has however a much faster and more unstable characteristic during this first hour. Reasons for this difference are hard to verify but there are several possible explanations. A weak buffering capacity of the liquid in combination with a fast change in the concentration of possible HCl would cause this behaviour. A sudden large change in gas flow could also be a reason. It is also a fact that the incinerator reached full capacity again, after the lack of fuel, less than an hour before the startpoint of simulations. This can be the origin of unknown dynamic effects. Another possibility is dynamic effects in the actuator system. The large load disturbance in the gas concentration leads to a very fast need for alkali. The change in setpoint for the secondary loop in the pH control is very fast and before reaching the setpoint it is changed again. This leads to effects in the secondary controller giving too large variations in the flow of alkali. This idea is supported by figure 15. It shows that during this first hour the measured flow of alkali varies more and faster than the simulated.

In figure 17 there is again an offset between the curves, in many ways similar to figure 15. The measured pH is always considerably lower than the simulated. Actually, this supports the theory that there is also an absorption of HCl and SO₃ in the spray tower. That would give exactly this kind of difference. In figure 12 there are large variations in pH out from the spray tower during the hours with low levels and no variations in SO₂. This is another support for the idea that there is a leakage of HCl from the first scrubber stage.

In figure 18 the simulated concentration of sulphites shows initially a decent agreement with the measurements but the difference gets bigger and bigger. The simulated concentration is always higher than the measured. It is also noteworthy that the final concentration of sulphite, measured after 4 hours of a high SO₂ level in the gas, is much higher than the measurement from the morning of 29/11. This measurement was made after a whole night of high SO₂ levels. All this is exactly what can be expected from a model that doesn't consider the oxidation reaction which is known to be important.

It is reasonable to believe that the liquid concentration of oxygen is important for the rate of oxidation. From figure 18 it also seems like the oxidation is faster at higher concentrations of sulphites, which is also very reasonable. Since the incinerator is controlled to have a certain amount of excess air the flue gas is likely to have an approximately constant concentration of oxygen. The scrubber liquid is constantly sprayed into the flue gas and the concentration in the liquid could therefore also be considered constant. At high concentrations of sulphite, oxygen is likely to limit the oxidation. This is however ignored here. A simple model for the rate of the oxidation, r_A , could look something like

$$r_A = k \cdot [s^4] \tag{33}$$

where the concentration of oxygen is contained in the constant. When implementing this model for the oxidation and adjusts the constant it is possible to obtain a much better agreement to the measured concentration, as is seen in figure 19.

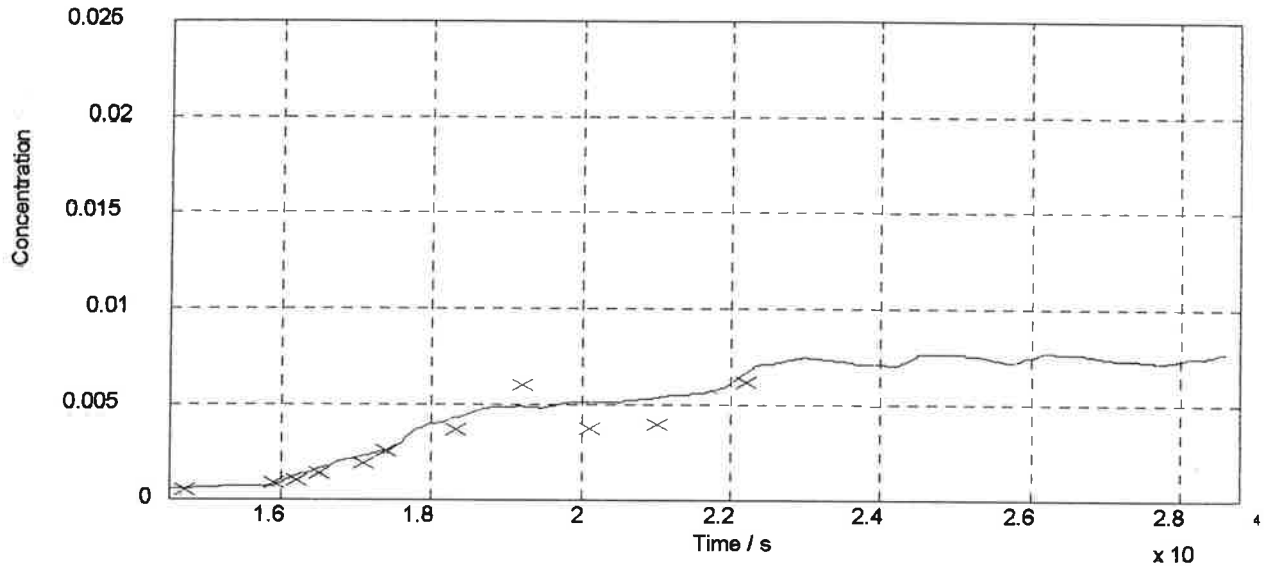


Figure 19. Concentration of sulphites in the liquid to the spray tower. Full line is simulated concentration with a model including oxidation. x-marks represents the results of the chemical analysis in Hobro.

This proves absolutely nothing about the reaction rate for the oxidation, but it proves that the difference between the simulated and measured concentration of sulphites according to figure 18 can be fully explained by the oxidation. It also implies that a good model for the scrubber system needs to include a model for the oxidation. This model must however be based on a theoretical and experimental study on the kinetics of the reaction. It can not be based on trial and error simulations.

Except for the features involving the oxidation the model seems to have a good agreement to operating data. The large difference between the simulated and measured characteristics, e.g. the flow of alkali, is not as serious or strange as it may seem at a first glance. There are quite easy explanations for all differences, explanations that has to do with the real world. There are always some things not included in a model that gives effects in reality. The important thing here is that the measured and simulated trends are more or less identical. The fact that the noise of a nasty reality sometimes causes an offset is less important.

9 pH CONTROL IN HOBRO

9.1 The controller

The pH control system has been discussed some times in sections 5-8. The main problem during the modeling and validation procedure has been the control system. There has been to little known about it. Actually, the only knowledge has been what is seen in figure 4, the controller parameters and that there is no anti-windup action in the controller. It is also known that the pH controller is implemented in the process computer, while the secondary controller is a standard digital controller. The controller parameters can only be set within restricted limits. The proportional band between 10 and 100 %, integral time between 0 (disconnected) and 1000 s and derivative time between 0 and 148 s. The meaning of the controller parameters, i.e. the controller algorithm, were however unknown.

The control and supervising system in the process computer is implemented in OMRON. The documentation on the pH controller is poor and consists of a large number of OMRON prints that are very hard to understand.

Section 8.2 describes in short some work done to investigate the controller algorithm. The result was the expression (32). This result was however not quite clear. The agreement between simulated and measured signals was sometimes better if using controller parameters that did not agree with those actually used. This was the case no matter what algorithm was used. This is probably an effect of the fact that the pH controller has got a very low priority in the real time processing. At the same time the process computer has been given more tasks than it can handle. Furthermore, it is not unusual that programmers implementing digital controllers doesn't know or forgets about the importance of the sampling period [3]. If this is forgotten the controller will work well but the parameters will be influenced by the sampling period. This could certainly be the case in Hobro and the simulations point in that direction. The expression (32) is thus not proved to be the correct algorithm. It will however be used during the rest of this work.

9.2 The sensor system

pH in to and out from the spray tower is measured with pH electrodes. These electrodes are from time to time calibrated in buffered solutions. At one such instant the 28/11 1994 the step response for these electrodes were studied. It was found that the electrode measuring pH out from the spray tower is slightly slower than the other electrode. In both cases the electrode response was slower going towards lower pH than towards higher. The time constant was however always very small. Less than two seconds for both electrodes going towards higher pH and 2-3 seconds going towards lower pH. This must be considered very fast. It is however likely that the response is slightly slower in the scrubber liquid than in the clean buffered solutions.

The time constant for the SO₂ measurement out from the spray tower was estimated to approximately 1 minute.

None of the sensors had a clearly noisy output. Furthermore, all signals are filtered before treated by the process computer. The noise level in input for the controllers are thus low.

9.3 Typical controller performance

From some data recorded on the process computer the 27/11 in 1994 the controller response to typical process disturbances can be studied. These data are shown in figures 20 to 22. Setpoint for pH was 7 and the P-band was 30%, the integral time 500 s in the feedback loop. The feed forward loop has setpoint pH 5.5, P-band 20% and no integral action. Neither feedback nor feed forward loops included derivative action at this time.

The pH control system is obviously very slow. There are large offsets from setpoint during hours. Ideally the alkali should be added to the process at the same time as SO₂ is absorbed. In figures 20 - 22 there is a time delay of approximately ½ to 1 hour between changes in gas concentration and changes in flow of alkali. Furthermore the flow is not able to respond to fast peaks in gas concentration. It seems like the controller works mainly on slow integral action.

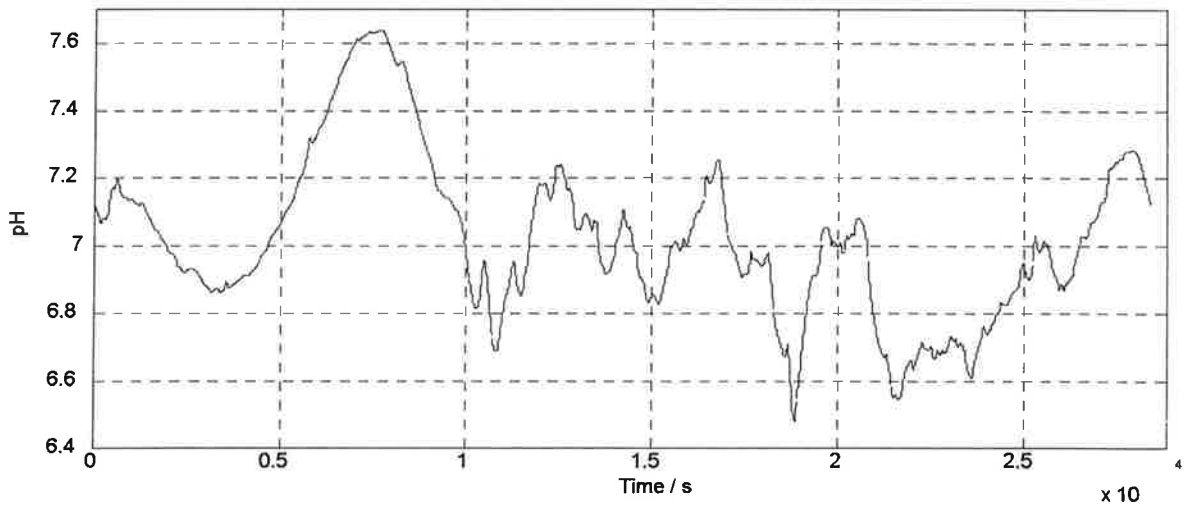


Figure 20. pH in to the spray tower. Note that the scaling is different from earlier figures.

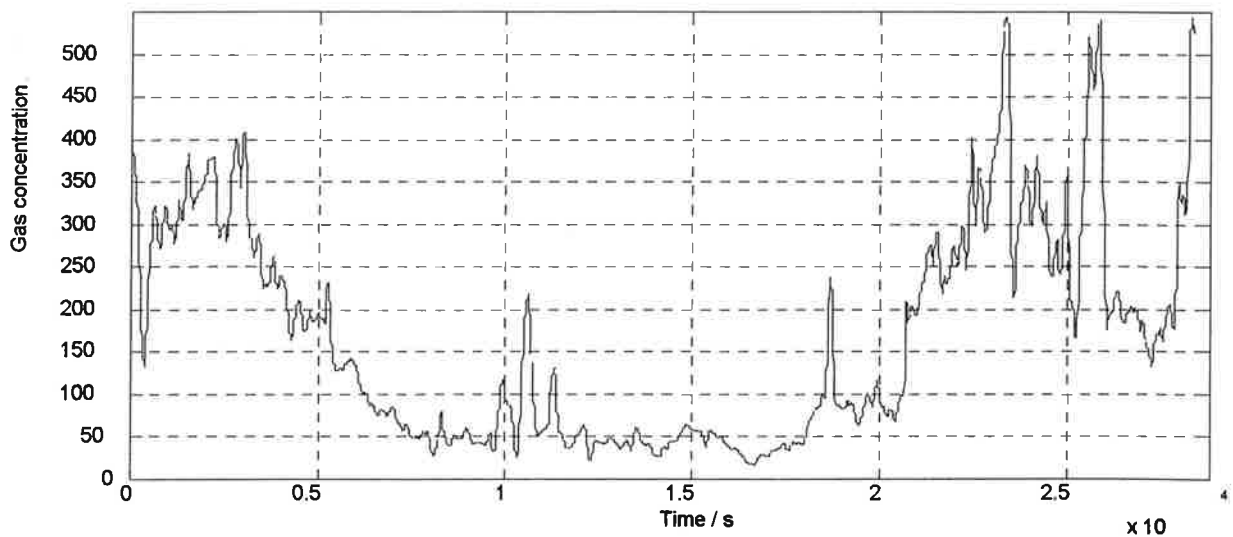


Figure 21. Gas concentration of SO₂ in to the spray tower.

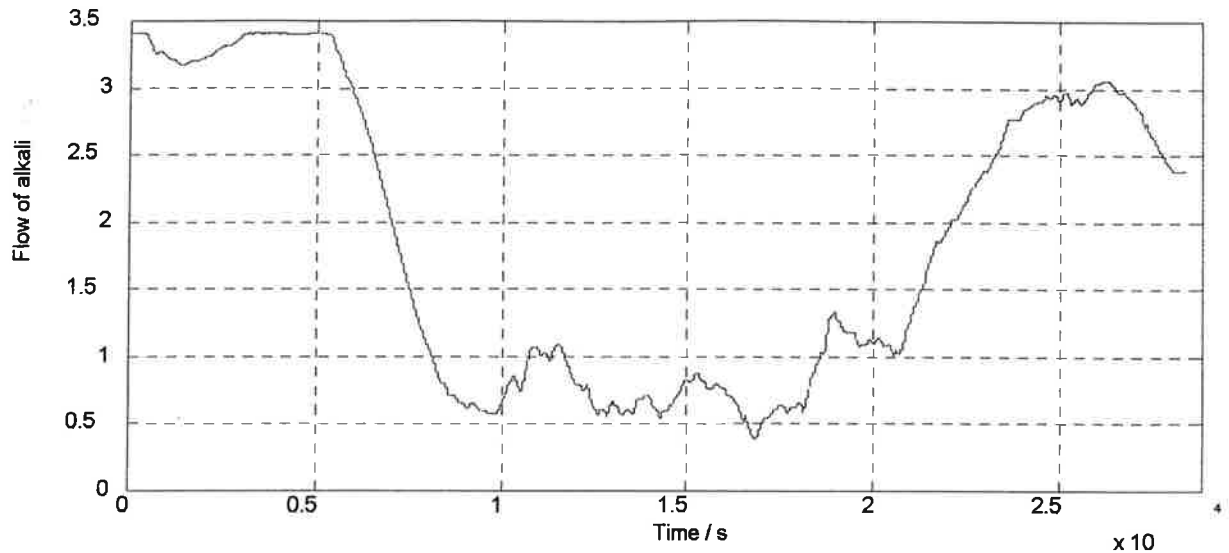


Figure 22. Flow of alkali to the recirculation tank.

9.4 Manual tuning of the controller

During the Hobro experiments the 28/11 to the 30/11 1994 the slow controller response was considered as a problem. The object was to study process characteristics, not the result of a much too slow controller. Thus some effort was made to improve the tuning of the controller. This was made using manual tuning based on the knowledge discussed in section 4, some experience from simulations with the first model and ordinary rules of thumb for manual tuning.

Rules of thumb for tuning controllers are well known and has been developed from knowledge of how controller parameters influence the control performance and a lot of experience [13]. These simplified rules have limitations but are very useful. These rules are of the type:

+Increasing the gain decreases steady state error.

-Increasing the gain decreases stability.

+Increasing T_i improves stability.

-Increasing T_i gives a slower control performance.

+Increasing T_d improves stability

-Increasing T_d increases noise sensitivity

In section 9.3 it was concluded that the control system is too slow and have large offsets from setpoint during long time. Using the rules of thumb above it would be improved by higher gain and shorter integral time, T_i . Simulations with the first model showed that this was true. Controller gain could be increased several times and integral time decreased considerably. Good controller parameters were found but since the algorithm was wrong these parameters

were useless. The simulations still showed in which direction the controller parameters should be changed.

From the sources referred to in section 4 a great deal is known about the problems in pH control. For example it is known that feed forward of pH can not be used to improve control performance. Tuning of a feedback controller can be hard and should be given special attention. PID control is recommended.

The tuning of the controller was started at 14.00 the 29/11 1994. The feed forward action was disconnected by setting the setpoint for pH out from the spray tower to 4 (since the feed forward loop only can give a positive contribution and pH out from the spray tower is more or less always higher than 4, this means disconnection of the feed forward loop). Integral action was then disconnected and the P-band was set to 10%, giving maximum possible gain. The setpoint for pH was kept at 7. The result is shown in figure 23 during the first 1700 seconds. Those first changes were made at a time corresponding to 300 s in the figure.

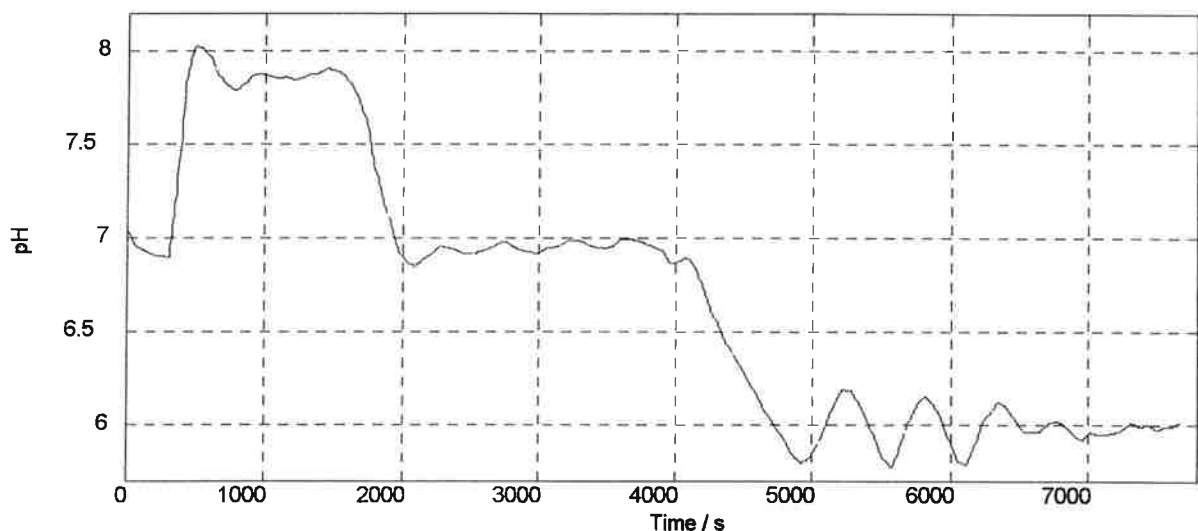


Figure 23. pH in the liquid in to the spray tower from 13.55 to 16.05 the 29/11.

The result is a rather stable control with a large offset, 0.8-0.9 in pH, from setpoint. To investigate if this large offset really was just the steady state error the setpoint was change after half an hour (1700 s in figure 23) to pH 6. In figure 23 it is shown that pH changes very smoothly to about pH 7 (1800 to 2000 s). This shows that at maximum controller gain the steady state error is almost 1.0 in pH! The control is however very stable.

In order to eliminate the control error integral action was connected again and the integral time, T_i , set to 140 s. The result is shown in figure 23 (4000 s to 6500 s). The control error disappeared but instead there was a continuous cycling around the setpoint. After another half hour T_i was increased to 300 s in order to improve the stability. The cycling disappeared (figure 23 after 6500 s).

In order to study the response to a change in setpoint the setpoint was changed to pH 6.5. The result is shown in figure 24 (7800 s to 10 000 s). The change is fast and rather stable. Trying to improve the stability T_i was increased to 600 s and then the setpoint was changed to pH 7

in order to study the response. As seen in figure 24 (10 000 s to 13 000 s) the result was not satisfying. The result was a less stable response to a setpoint change.

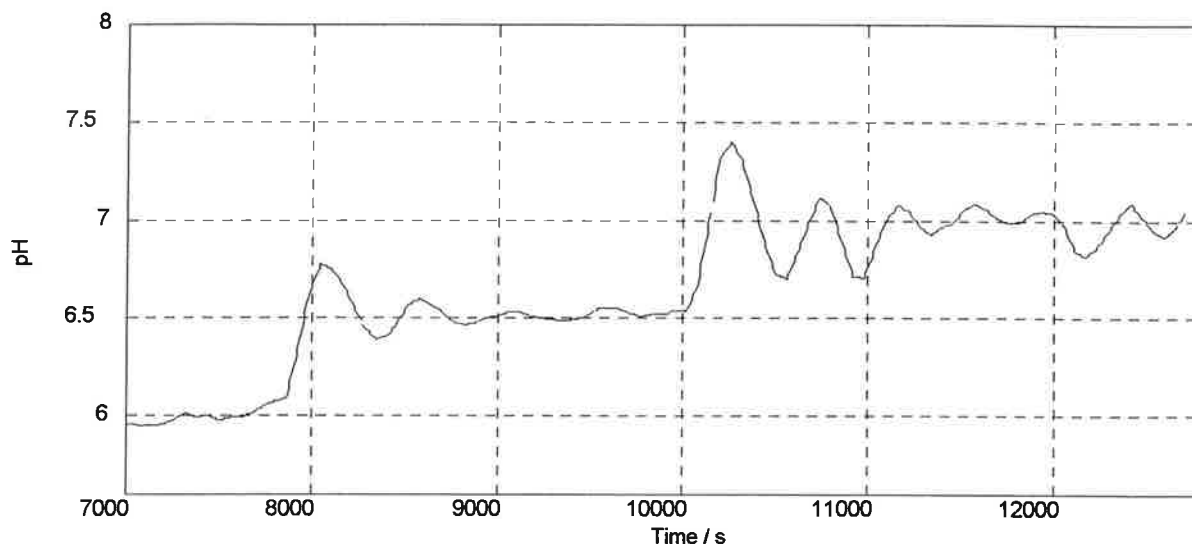


Figure 24. pH in the liquid in to the spray tower from 16.00 to 17.30 the 29/11.

Another attempt to improve stability was made decreasing the gain. The P-band was set to 15% and T_i again to 140 s. The setpoint was changed to pH 6. The result is seen in figure 25 (13 000 s to 15 000 s). Again there was a cycling around the setpoint, a cycling much like last time T_i was 140 s, se figure 23. It was hard to see any improvement in stability. The P-band was not decreased further since speed was considered an important characteristic of an improved controller. Instead T_i was again set to 300 s. The setpoint was changed to pH 6.5 and then to pH 7. The result of these changes are shown in figure 25. The controller performance was considered promising and it was left to work overnight.

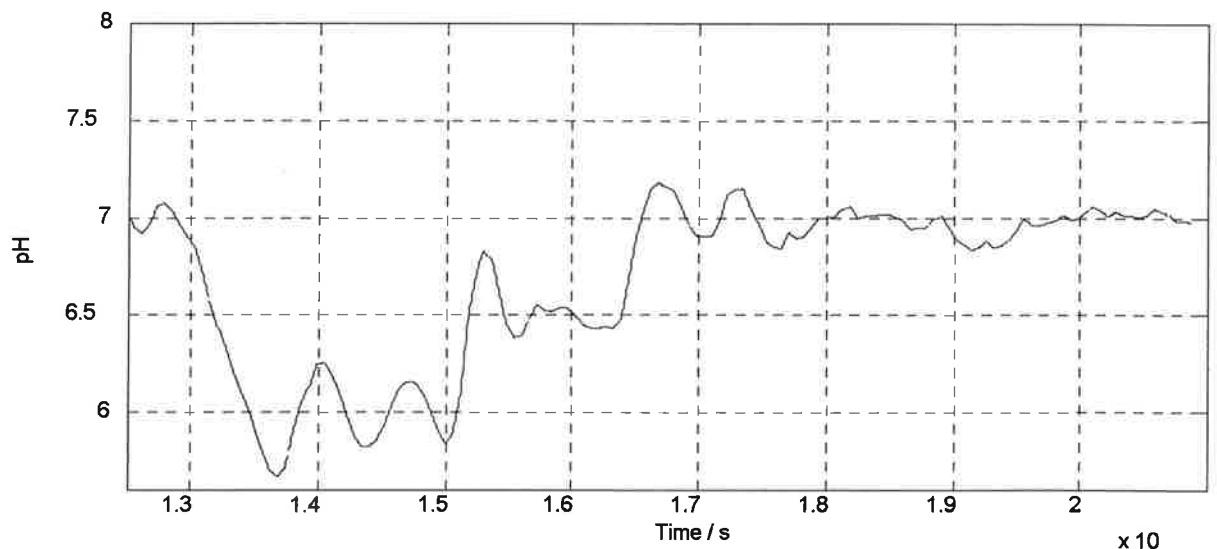


Figure 25. pH in the liquid in to the spray tower from 17.30 to 19.50 the 29/11.

The following morning pH during the night was studied and the result was considered very satisfying. Still, it was attempted to further smooth the performance by introducing derivative action. This is shown in figure 26. At 08.15 (66 000 s in figure 26) the derivative time, T_d , was set to 40 s. The change is hardly noticeable in figure 26. At the plant however it was

noticed that the flow of alkali was changing very fast and frequently in a more or less random way. A look at the secondary controller showed that it received larger and faster changes in setpoint than it could handle. It was obvious that the noise of process and sensors now was giving immediate response in the control signal, the derivative action was too high. Therefore, T_d was decreased to 10 s (at 68 600 s in figure 26). The secondary controller now received much more reasonable signals and the changes in flow of alkali became more smooth.

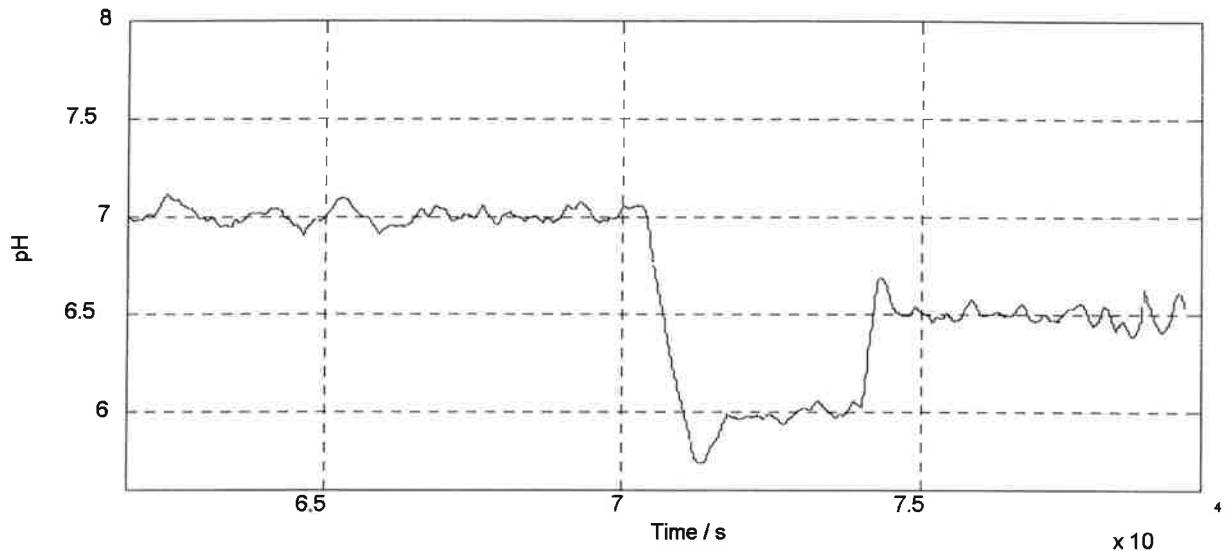


Figure 26. pH in the liquid in to the spray tower 07.00 to 12.00 the 30/11.

The setpoint was then changed to pH 6 in order to investigate if the derivative action really was doing any good. In figure 26, at 70 000 s to 74 000 s, the result looks quite good. The secondary loop had however again had some problems and in order to ease the stress on the actuators T_d was decreased again to 5 s. In order to increase the speed the gain was again set to its maximum value, i.e. the P-band was set to 10% (at 73 000 s in figure 26) The setpoint was then changed again to 6.5 (at 74 000 s in figure 26). In less than 10 minutes the controller reached a stable point at pH 6.5. At this point the work tuning the controller was stopped.

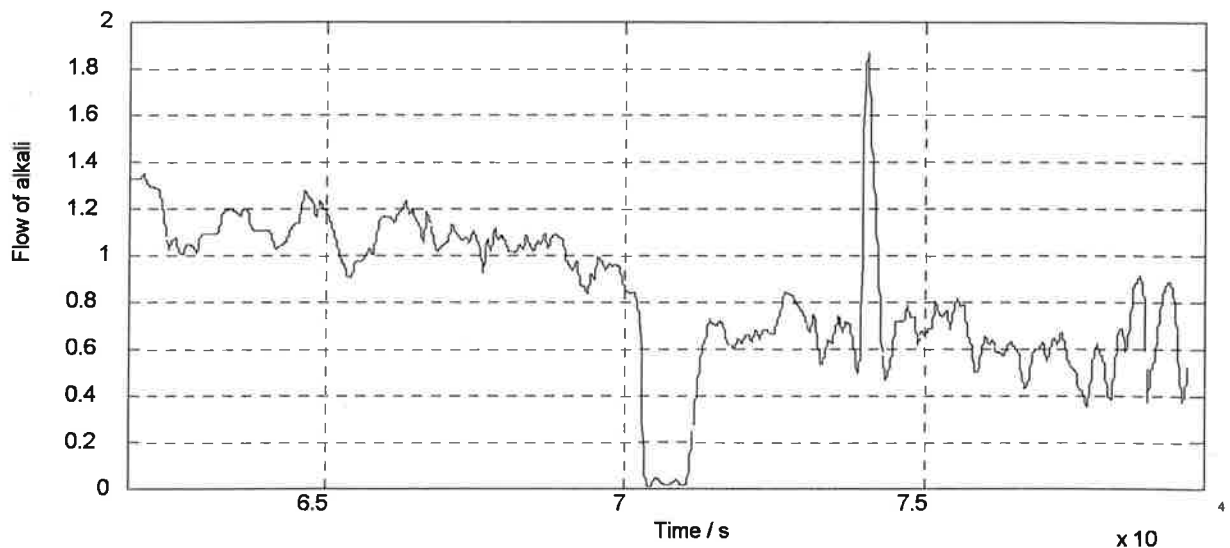


Figure 27. The flow of alkali 07.00 to 12.00 the 30/11.

In figure 26 another aspect becomes very clear. At both setpoint changes, pH first passes the setpoint and then comes back. In both occasions this feature has a sharp V-shape. This indicates integrator windup which is an effect of saturating actuators in combination with a controller with integral action. In figure 27 the flow of alkali during the same time is seen. The actuator saturation at setpoint changes is obvious. At both occasions the flow is changing with maximum rate, i.e. the pH controller output is likely to be at maximum or minimum values respectively. During the first change, there is no flow of alkali at all for some time, a typical actuator saturation.

9.5 Discussion

Section 9.4 can be viewed as an example of manual tuning using the rules of thumb. The experience from simulations and the knowledge from section 4 was however more important than is clear from that section. The controller can of course be improved further but the work already done means a significant improvement of the controller performance.

In figure 20 pH in to the spray tower varies between 6.5 and 7.65 when setpoint is pH 7. This was before tuning the controller. In figure 16 the measured pH in to the spray tower, with similar changes in gas concentration, varies between 6.1 and 6.6 when setpoint is 6.5. Furthermore there are no large offsets during long time. The improvement is even more clear when comparing addition of alkali with gas concentration of SO₂. In figures 21 and 22 there is a large time delay, ½-1 hour, between SO₂ peaks and peaks in the flow of alkali. There are no real peaks in the flow of alkali before tuning the controller, but rather slow trends. In figures 14 and 15 the time delay is much shorter, maybe 2 minutes. The curves of SO₂ and flow of alkali could with different scaling be made to coincide. Peaks in SO₂ corresponds almost immediately to peaks in the flow of alkali. This is the desired performance.

The scrubber process is a process that in practice never reaches a steady state. The complicated interaction between scrubber liquid chemistry, gas concentration of SO₂ and the addition of alkali is by itself a reason for this. Furthermore, there is never a constant concentration of SO₂ in the flue gas when burning waste. This process is constantly changing and is always a subject to different disturbances. This makes tuning more difficult than it may seem. The evaluation of a parameter change or a change of setpoint must always consider at least process disturbances. This is for example the reason why the controller in figure 25, coinciding with SO₂ peaks, was considered more promising than the controllers in figure 24.

There is also a problem with the unknown disturbances, e.g. the possible leakage of HCl discussed in section 8.5. Such leakage could for example explain why the increase of T_i from 300 s to 600 s in figure 24 led to a *less* stable setpoint change. There was no SO₂ peak at that time.

The introduction of derivative action in figure 26 looks promising but some things must be kept in mind. All experiments with P and PI control were conducted an afternoon with low buffering capacity in the scrubber liquid. Low buffering means a higher process gain and a larger change in process gain with pH. Thus the process is harder to control with low buffering capacity. The derivative action was introduced on an occasion with a high buffering capacity. Changes would have been more stable at that time in any case. During the following hours the buffering capacity decreases. It can be seen how the pH is getting more and more

unstable while the buffering capacity decreases. Just before noon pH does not look better with PID control than it did with PI control the day before. It is thus hard to make any conclusions whether the derivative action is an improvement or not. No simulation has showed any improvement by derivative action, but the simulations are of course based on a simplified model and is no proof either.

The controller clearly has windup problems. This can be avoided if the controller knows about the saturation limit. This knowledge can be introduced in the control algorithm, a technique called anti-windup. If using a controller with anti-windup, the "V-turns" would not appear.

It is hard to decide which controller tuning is best, the very last or the controller used during the night and morning hours the 30/11. Both has a good performance. The last one has a higher gain and is a bit faster but at lower buffering capacity it seems a bit "nervous". The difference between the two controllers is very small and a good tuning is definitely something like this.

It is also hard to define an objectively best tuning. A weighting of the importance of stability and how fast the controller should be must ultimately be made.

10 LINEAR ANALYSIS

The developed model is complex and nonlinear. That makes it hard to analyse the model. Most mathematical methods for analysis of models works for linear models only. Those methods are however available if the model is linearized.

10.1 Linearization

The model consists of several more or less individual parts. The block diagram in figure 28 describes the most essential flow of information in the system, ignoring e.g. level control and feed forward of pH.

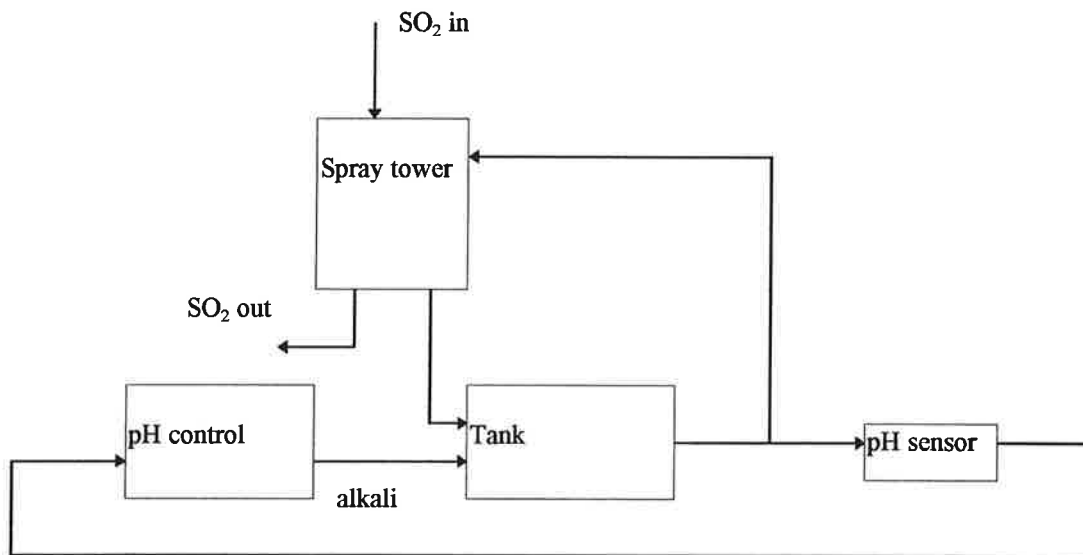


Figure 28. Simplified block diagram representation of the scrubber process.

The blocks in figure 28 are more or less identical to the structural parts used in the implementation (section 7). The spray tower and pH sensor system are both described by nonlinear algebraic expressions. The tank is described by a nonlinear system of differential equations. These models can be linearized using Taylor series expansion of the nonlinear functions around a steady state solution. A steady state solution was found simulating with constant flue gas concentration of SO₂ and a pH setpoint at 6.5 for a long time. The result was proved fulfilling a mass balance on sulphur. The buffering capacity was rather high.

In appendix 11 the model is linearized. Ignoring changing concentration of SO₂ results in a state space description of the process.

$$\begin{aligned} \dot{x} &= Ax + Bu \\ y &= Cx \end{aligned} \tag{33}$$

where x designates deviations in the concentration vector \bar{c} , u deviations in the flow of alkali Q_{alk} and y deviations in pH.

The matrices A, B and C are approximately

$$A = \begin{bmatrix} -1.437 \cdot 10^{-4} & -2.826 \cdot 10^{-5} & 1.248 \cdot 10^{-5} & -8.189 \cdot 10^{-6} \\ -1.518 \cdot 10^{-5} & -1.517 \cdot 10^{-4} & 1.108 \cdot 10^{-5} & -7.262 \cdot 10^{-6} \\ 0 & 0 & -1.266 \cdot 10^{-4} & 0 \\ 0 & 0 & 0 & -1.219 \cdot 10^{-4} \end{bmatrix}$$

$$B = \begin{bmatrix} 3.677 \cdot 10^{-7} \\ 5.806 \cdot 10^{-5} \\ .419 \cdot 10^{-4} \\ 2.581 \cdot 10^{-7} \end{bmatrix}$$

$$C = [-296.5 \quad -544.3 \quad 264.5 \quad -165.0]$$

MATLAB contains routines for linearizing a nonlinear SIMULINK model. However, these routines couldn't cope with the extreme nonlinearity in the model for the scrubber process. The results from the linearizing routines, in the cases results were obtained at all, were all absurd.

10.2 Eigenvalues

The state space model (33) has a general analytical solution

$$\begin{aligned} x(t) &= e^{At} \cdot x(0) + \int_0^t e^{A(t-\tau)} Bu(\tau) d\tau \\ y(t) &= C \cdot x(t) \end{aligned} \quad (34)$$

where $x(0)$ is the initial condition. The exponential matrix e^{At} is an essential part of this solution. The characteristics of the solution is determined by the matrix A. The influence of the B matrix is essentially a weighting of the input signals [13].

The eigenvalues, λ_i , of the matrix A play an important role for the solution of (33). The solution is a sum of exponential functions $P_{k_i-1}(t) \cdot e^{\lambda_i t}$. k_i is the multiplicity of eigenvalue λ_i and $P_{k_i-1}(t)$ is a polynomial of t with a maximum degree of k_i-1 . The eigenvalues will determine the time functions that build up the solution. Eigenvalues with positive real part give solutions that increase with time, while eigenvalues with negative real part gives solutions that decay with time. Real eigenvalues corresponds to real exponential functions. Complex eigenvalues, $\lambda = \sigma + i\omega$, corresponds to a solution $e^{\lambda t} = e^{(\sigma+i\omega)t} = e^{\sigma t} (\cos \omega t + i \sin \omega t)$. Thus complex eigenvalues gives an oscillatory solution. If all eigenvalues of matrix A have negative real parts then all the components of the state vector, x, will approach zero independent of the initial value, when the input is zero. The system is stable. If any

eigenvalue has a positive real part the system is unstable, since at least one exponential will increase without bounds.

The transients of a system is dominated by the eigenvalue with the smallest absolute value. The inverse of the eigenvalues being the time constant of the system thus gives a feel for the time scale of the process.

The eigenvalues of the A matrix in the linearized model (33) are approximately

$$\lambda_1 = -1.266 \cdot 10^{-4}$$

$$\lambda_2 = -1.688 \cdot 10^{-4}$$

$$\lambda_3 = -1.266 \cdot 10^{-4}$$

$$\lambda_4 = -1.219 \cdot 10^{-4}$$

All eigenvalues are negative and real. Thus the system is stable and non oscillatory, i.e. the process does not give rise to oscillations. All eigenvalues are in the same range and the time constant of the process is approximately $T_c = \frac{1}{\lambda_4} \approx 8200$ s, i.e. a bit more than two hours.

10.3 Controllability and observability

If it is possible to determine a control signal such that any state of the system can be passed, the system is said to be controllable [13]. The controllability depends on the internal coupling between the states, x , and how the control signal influences the states, i.e. the A and B matrices. The matrix

$$W_c = [B \quad AB \quad A^2B \quad \dots \quad A^{n-1}B] \quad (35)$$

is called the controllability matrix of the system and n is the order of the system,. If the matrix W_c has rank n , the system is controllable.

A system is observable if it is possible to reconstruct the states of the system given only the input and output signals [13,14]. The states of an observable system can be estimated using an estimator model. The system is observable if the observability matrix

$$W_o = [C \quad CA \quad CA^2 \quad \dots \quad CA^{n-1}]^T$$

has rank n .

The linearized model is a 4th order system and rank $W_c = 3$,i.e. three states in the system is controllable. Since rank $W_o = 3$ only three states in the model are observable.

10.4 The transfer function

Assuming that $x(0)=0$ in (33), i.e. the system is at steady state at time $t=0$, the Laplace transform of the output can be found as

$$Y(s) = C \cdot (sI - A)^{-1} \cdot B \cdot U(s) = G(s) \cdot U(s) \quad (36)$$

where $Y(s)$ and $U(s)$ are the Laplace transform of y and u respectively. $G(s)$ is the transfer function of the system.

$$G(s) = C(sI - A)^{-1} B = \frac{B(s)}{A(s)} \quad (37)$$

where $B(s)$ and $A(s)$ are polynomials in the Laplace variable s . The transfer function for the system (33) is

$$G(s) = \frac{B(s)}{A(s)} = \frac{5.783 \cdot 10^{-3} s^3 + 2.318 \cdot 10^{-6} s^2 + 3.081 \cdot 10^{-10} s + 1.359 \cdot 10^{-14}}{s^4 + 5.439 \cdot 10^{-4} s^3 + 1.102 \cdot 10^{-7} s^2 + 9.870 \cdot 10^{-12} s + 3.299 \cdot 10^{-16}} \quad (38)$$

The roots of the denominator polynomial $A(s)$ are the poles of the system. Notice that the poles are the same as the eigenvalues of the matrix A . Thus they have the same interpretation. The poles closest to the origin gives the time scale of the process, poles with positive real parts makes the system unstable and complex parts makes the system oscillatory. Poles far from the origin makes the system sensitive to noise.

The roots of the numerator $B(s)$ are the zeros of the process. The zeros are a measure of the weight of the different poles but the influence is much more difficult to determine [13]. The zeros weights how the control signal will affect the system. A zero in the origin is an extreme where a constant input gives no output at all. Zeros with positive real parts gives rise to a nonminimum phase system. Many nonminimum phase system are inverse response system, i.e. the step response starts in the wrong direction. Zeros far from the origin are normally uninteresting having no effect on the system at all.

Both poles and zeros are important to determine the time response of a system. It is common to represent a process graphically by its singularity diagram. In such a diagram the poles are represented by crosses and the zeros by circles in the complex s -plane. The singularity diagram for the linearized model is found in figure 29.

If a pole and a zero coincides the effect of both is cancelled. As is seen in figure 29 the system has got a least two pole-zero cancellations and all poles and zeros are quite close. Using the roots of the $A(s)$ and $B(s)$ polynomials the transfer function can be rewritten

$$G(s) = \frac{5.783 \cdot 10^{-3} (s + 1.523 \cdot 10^{-4})(s + 1.266 \cdot 10^{-4})(s + 1.219 \cdot 10^{-4})}{(s + 1.689 \cdot 10^{-4})(s + 1.266 \cdot 10^{-4})(s + 1.266 \cdot 10^{-4})(s + 1.219 \cdot 10^{-4})} = \quad (39)$$

$$= \frac{5.783 \cdot 10^{-3} (s + 1.523 \cdot 10^{-4})}{(s + 1.689 \cdot 10^{-4})(s + 1.266 \cdot 10^{-4})} \quad \left(\approx \frac{5.783 \cdot 10^{-3}}{(s + 1.266 \cdot 10^{-4})} \right)$$

The three parantheses $(s + 1.266 \cdot 10^{-4})$ are mathematically identical. The two parantheses $(s + 1.219 \cdot 10^{-4})$ are identical to the sixth digit.

As seen from (39) the system is not as complicated as it seemed from (38). It is actually a second order system with a zero and approximately a first order system. Such a system will respond immediately to change without delay.

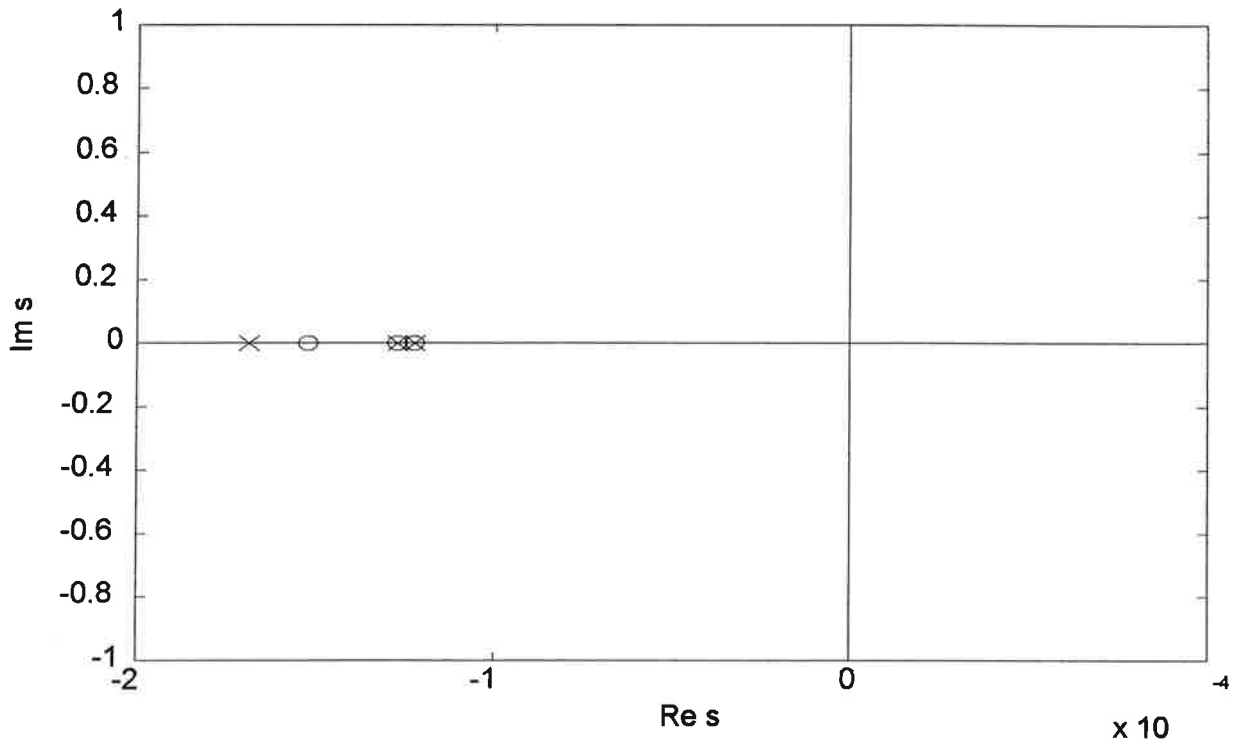


Figure 29. Singularity diagram for the linearized model.

10.5 Discussion

From the linearized version of the model a number of conclusions have been drawn. The validity of those conclusions is dependent on how good the linearization is. The model was linearized about pH 6.5 and a rather high buffering capacity. Considering the extreme nonlinearity of the system the linearized version can only be valid in a very restricted surrounding to that state. On the other hand, the majority of the conclusions comes from information in the A matrix. This matrix describes the process including the tank and the spray tower. The tank and the spray tower are nonlinear, but not extremely so. The large nonlinearity is found in the calculation of pH. This calculation is linearized into the vector C. From the size of the elements in C it is obvious that small changes in concentration will lead to large changes in pH. Furthermore, the C vector would change radically if linearizing about another pH or a state with another buffering capacity. But since the C vector is less important for the analysis, the linear approach can be useful.

The knowledge from section 10.2 and 10.4 can be used to predict a step response of the process. A first order system will respond immediately to a step and the largest slope of the output signal will occur at once. After one time constant the process will have reached 63% of its new steady stationary state. The response will not be oscillatory but quite smooth. Using the full nonlinear model to simulate a step response from the stationary state gives the result in figure 30. The step was an increase in the flow of alkali introduced after 200 s. As seen the

process response was immediate and quite smooth. 63% of the new steady state was reached after about 10 000 s, i.e. almost 3 hours. The simulated time constant is slightly larger than was indicated by the eigenvalues but absolutely in the same range. The gross features of the prediction seems to be correct.

A time constant of two or three hours may seem strange. The mean residence time for the recirculating liquid in the tank is 7 minutes and the mean residence time for the liquid in the scrubber system is 7 hours. This kind of reasoning does however not consider the complicated interaction between scrubber liquid and the flue gases in the spray tower. This interaction must have effects on the process. Therefore the time constant is somewhere in between of the two extreme reasoning results. The time constant is still clearly dependent on the residence time for the liquid in the scrubber loop. This time is dependent on the flow of alkali and the tank volume. Simulations has showed that a larger step in the flow of alkali gives a smaller time constant.

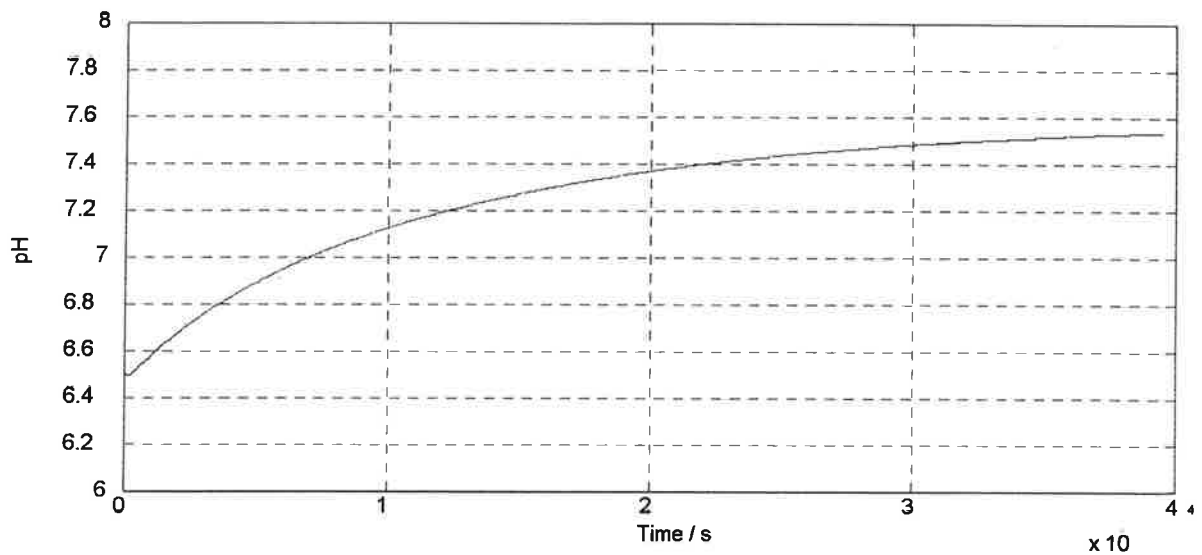


Figure 30. Step response

The fact that the process is approximately of first order explains why the proportional control in section 9.4 was so stable. A proportional controller introduces no extra poles to the system. Integral and derivative action introduces new poles and thus a risk for oscillations. In fact all oscillations observed in this process are due to the controller, not to the process.

It can also be noted that the system has four states but a second order (approximately first order) transfer function. Both controllability and observability are three. If it was one concentration being neither observable nor controllable, then the transfer function should have been of third order. A second order means that there is one concentration that is not controllable and another concentration that is not observable.

The fact that the controllability of the system was less than 4 does not mean that it is impossible to control pH. It simply means that it is impossible to control all four concentrations in the model. Only sodium has an exclusive origin in the alkali according to the model. Thus at least the concentration of sodium can definitely be controlled. This is however enough. pH depends on all four concentrations and changing the concentration of

sodium alone can give the whole range of different pH values. The importance of sodium hydroxide is the physical interpretation of the system being approximately first order

An observability less than 4 just means that the concentrations can not be estimated using an estimator model. Both observability and controllability excludes the use of an advanced type of controller called state space controllers.

11 CONTROLLER DESIGN

Several methods exist for finding a good controller tuning, a good controller design. One way, manual tuning, has already been discussed in section 9.4. Another way is to use empirical methods, such as the well known Ziegler and Nichols step response and ultimate period methods. A third way is different model based design techniques such as pole placement or phase compensation.

11.1 The KT-method

The KT-method (or the $\kappa\tau$ -method) is an empirical method recently developed at the Department of Automatic Control, Lund Institute of Technology [15]. The method can be regarded as an extension of the Ziegler-Nichols method. The main difference is that three parameters is used instead of two parameters used by Ziegler and Nichols. All three parameters can be determined from the conventional Ziegler-Nichols experiment. Just as Ziegler-Nichols the KT method includes tuning rules based on step response data as well as frequency response data. The additional parameters are dimension free, relative dead time τ for the step response method and relative gain κ for the frequency response method. The method and its derivation is described in [15].

11.1.1 The step response method

This method uses a step response, such as the one in figure 29, to determine the static gain K_p , the apparent dead time L and the time constant T . Just as in the Ziegler-Nichols method the parameter

$$a = K_p \frac{L}{T} \quad (40)$$

is used. The relative dead time

$$\tau = \frac{L}{L+T} \quad (41)$$

is introduced as the new parameter.

The step response in figure 30 was used to determine the parameters K_p , L and T . It was found that $K_p \approx 52$, $L \approx 28$ s and $T \approx 10\ 500$ s. This gives according to (40) and (41) $a \approx 0.14$ and $\tau \approx 0.0027$.

Controller parameters were found using tables in [15]. The tables permits the estimation of parameters for both PI and PID controllers with either robust or fast design. Those parameters were then converted to be in agreement with the controller algorithm(32). For a PI controller with robust design the parameters found were

P-band :48 %
 T_i :4020 s

The fast PI controller design resulted in

P-band :18 %
 T_i :4020 s

The PID design recommendation for a robust controller resulted in

P-band :4 %
 T_i :185 s
 T_d :31 s

The faster design gives the same T_i and T_d but a P-band of 1.7 %.

11.1.2 The frequency response method

This method is based on the parameters ultimate gain K_u and ultimate period T_u just as the Ziegler and Nichols frequency response method. The third parameter is gain ratio

$$\kappa = \frac{1}{K_p \cdot K_u}$$

These parameters are to be obtained from a Ziegler and Nichols experiment or a relay experiment. When simulating with a relay instead of the controller the result in figure 31 was obtained. As seen there are no oscillations but rather a saw-tooth response. The period of the "saw-tooth" are identical with twice the step size in the numerical integration. It doesn't matter what step size is chosen, it just produces a new saw-tooth response with the same connection to the step size. Thus the model gives no oscillations at all and the frequency response method can not be used.

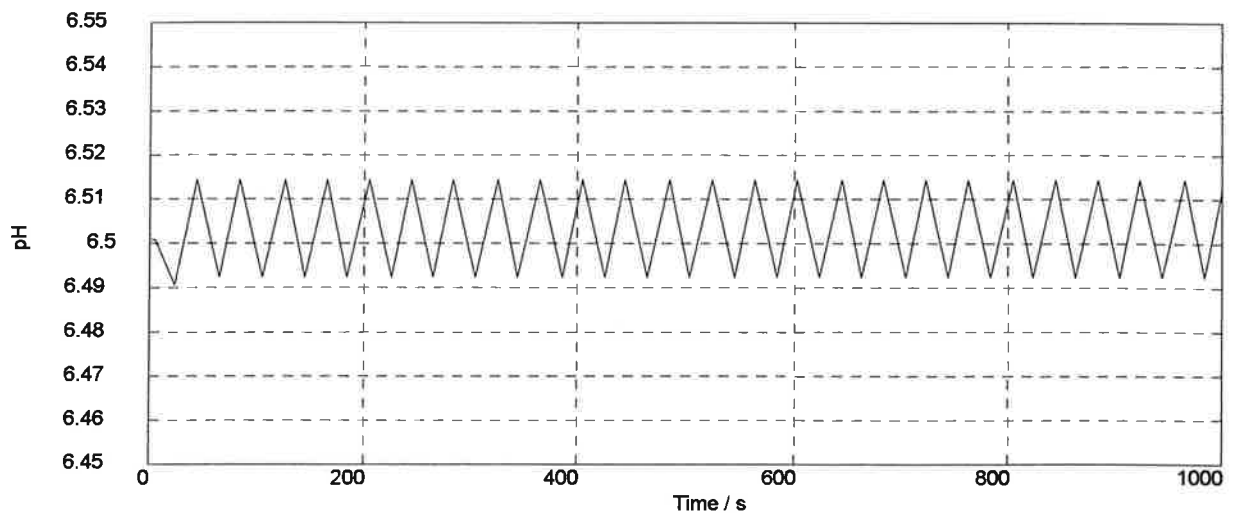


Figure 31. pH during simulated relay experiment.

11.1.3 Discussion

The controller parameters found in section 11.1.1 are not very useful. Often they are outside the range for what is possible in Hobro (P-band 10-100%, T_i 0-1000s and T_d 0-148 s). The

experience from tuning in Hobro, section 9.4, also shows that the parameters found here would not be good. The PI controller settings would yield a very slow controller. Both P -band and T_i are too large. The PID controller demands an extremely narrow proportional band *and* a shorter integral time than what experience proved to be good. Furthermore the derivative time would make the controller very sensitive to noise.

The step response method was not good and the frequency response method didn't work at all. The reason for this can be found in section 10 combined with the derivation of the KT method. The process is approximately a first order system. Such systems are not included in the derivation of the KT method [15]. An important property of a first order system is that there is no dead time. This means that all tuning methods that use dead time as a parameter is useless for this system, e.g. the Ziegler-Nichols method would not have worked either. From section 10 it is also known that the system in itself does not oscillate. The relay does not introduce oscillations and therefore there are no oscillations in the response.

The Ziegler-Nichols method is known to demand a certain ratio of dead time and time constant [13]. For the KT method this is not explicitly pointed out, though the derivation does not at all consider systems with extremely small values of τ . Since the method is quite new a warning should be made.

The main conclusion of section 11.1 must be that neither the KT nor the Ziegler-Nichols methods can be used to tune the pH controller in this process.

11.2 Pole placement

The linear model derived in section 10.1 can be used for controller design purposes. The pole placement technique uses the controller parameters to place the poles of the system that includes both process and controller.

A further simplification of the block diagram in figure 28 results in a scheme according to figure 32.

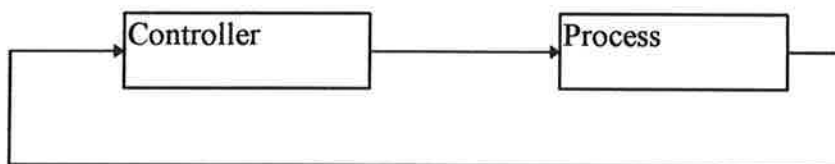


Figure 32. Block diagram representation of controller and process.

The linear model describes the process and the controller can be described with the algorithm (32). The transfer function for the closed loop system in figure 31, G_{cl} , is found as

$$G_{cl}(s) = \frac{G(s) \cdot G_{PID}(s)}{1 + G(s) \cdot G_{PID}(s)}$$

where G_{PID} is the transfer function for the controller. The properties of the closed loop system will be determined by its poles and these poles are dependent on the controller parameters.

Approximating the transfer function of the process with a first order system gives

$$G(s) = \frac{5.783 \cdot 10^{-3}}{(s + 1.266 \cdot 10^{-4})} = \frac{b}{(s + a)}$$

The transfer function for a PI controller according to (32) including the actuator gain, g , is

$$G_{PI}(s) = \left(K + \frac{1}{s \cdot T_i}\right) \cdot g = \frac{\left(K \cdot s + \frac{1}{T_i}\right) \cdot g}{s}$$

where $K = \frac{1}{P\text{-band}}$. The closed loop transfer function is then

$$G_{cl}(s) = \frac{G(s) \cdot G_{PI}(s)}{1 + G(s) \cdot G_{PI}(s)} = \frac{gbKs + \frac{gb}{T_i}}{s^2 + (a + gbK)s + \frac{gb}{T_i}}$$

The poles of the closed loop transfer function is given by the characteristic equation

$$s^2 + (a + gbK)s + \frac{gb}{T_i} = 0 \quad (42)$$

The closed loop system is thus of second order. By choosing the controller parameters any characteristic equation can be obtained. If the characteristic equation is written

$$s^2 + 2\zeta\omega s + \omega^2 = 0 \quad (43)$$

ω is called the natural frequency of the system and ζ is called the relative damping. In a singularity diagram, ω is the distance from the origin to the pole and $\zeta\omega$ is the real part of the pole. Standard recommendations are that the damping should be $\zeta \approx 0.7$ and the natural frequency should be in the same range as the time constant for the system. For a first order process however ω can be chosen as ten times the time constant, in this case as 0.00127.

Identification of the coefficients of equal powers of s in (42) and (43) gives

$$a + gbK = 2\zeta\omega$$

$$\frac{gb}{T_i} = \omega^2$$

Solving for the controller parameters gives $K = 3.4$ i.e. P-band = 29 % and $T_i = 299$ s.

Comparing this with the tuning experiences in Hobro, section 9.4, shows that this is a reasonable design. This is actually not far from the original parameter setting used at the plant which was stable but slow, only the integral time is somewhat shorter. This would give a faster recovery from the long time upsets but the proportional band is too broad and would not give a fast response to disturbances. This could however be a good start for manual fine tuning.

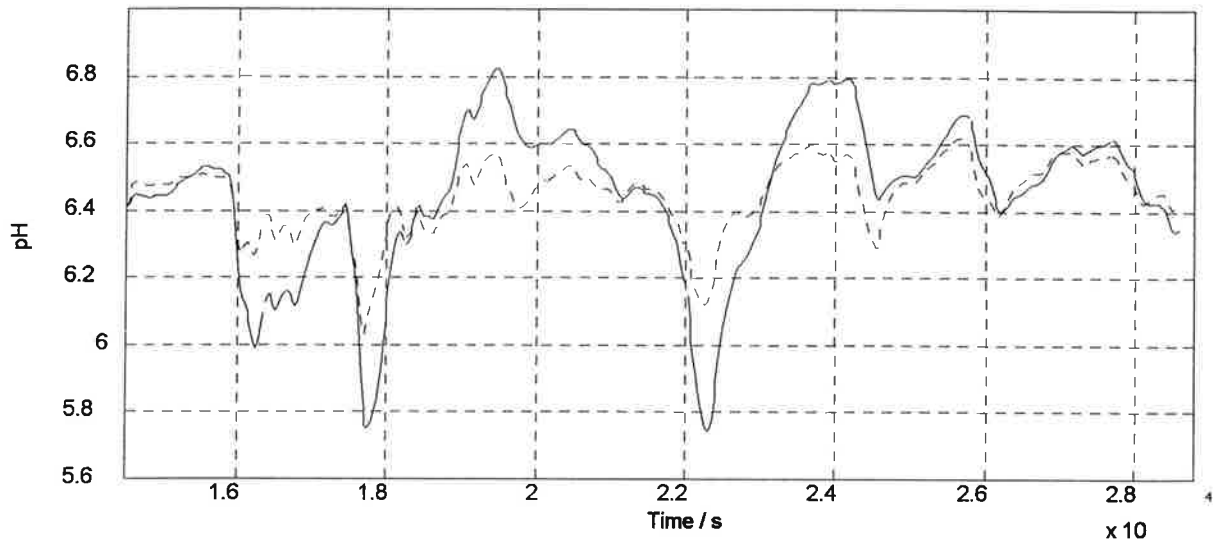


Figure 33. Simulated pH during the experimental load disturbance. Dotted line is the used controller, full line is controller according to pole placement design.

Figure 33 gives a simulated comparison of the controller used during the experimental load disturbance in Hobro and the controller design obtained with pole placement. As seen the controller has got difficulties coping with fast disturbances.

It must of course be noted that pole placement is not a real design method. It just changes the choice of parameters to a choice of ω and ζ . The choice of ω and ζ is however easier to understand and give a direct interpretation. This is why the controller found here was not perfect. The choice of ω and ζ was not perfect.

11.3 Bode analysis

The linearized model can also be used in a frequency domain approach to analysis and controller design. This approach uses Bode diagrams (or Nyquist diagrams). The method makes it possible to determine which frequencies that will be amplified or attenuated by the system. The response of a system to a sinusoidal input can be characterized as changes in phase and amplitude. The amplitude and phase changes can be determined with the transfer function. They can be interpreted as a frequency dependent gain of the process. Based on the response of an open loop system it is easy to determine if a system is stable or not. It is also possible to determine suitable controllers.

The Bode diagram is a way to graphically display the frequency response. The amplitude and the phase are drawn separately as functions of the frequency using logarithmic diagrams. The

amplitude (or magnitude) is $\log|G(i\omega)|$ and the phase is $\arg G(i\omega)$. $G(i\omega)$ is the transfer function of the open loop evaluated along the positive imaginary axis, i.e. for $s=i\omega$. The open loop transfer function, $G_o(s)$, in figure 31 is

$$G_o = G(s) \cdot G_{\text{PID}}(s)$$

Nyquist's theorem of stability can be given a simple explanation in the Bode diagram. The system is stable if the phase is above -180° when the magnitude is equal to one. The degree of stability is measured by amplitude margin, A_m , and phase margin ϕ_m . The amplitude margin is the inverse magnitude at the lowest frequency such that the phase is -180° and decreasing. The phase margin is how much the phase is above -180° at the cross over frequency, i.e. the smallest frequency where the magnitude is one. The system is unstable if $A_m < 1$. Amplitude margin and phase margin is used for design recommendations. Typical recommended values are $A_m=2-6$ and $\phi_m=30-60^\circ$ [13].

A MATLAB function was written that plots the Bode diagram using the state space matrices and the controller parameters. The function is found in appendix 12.

Figure 34 shows the Bode diagram for the system using a controller with P-band=30% and $T_i=50$ s. This controller setting was used some days during the autumn of 94 and resulted in large continuous oscillations with an approximate period of 20 minutes.

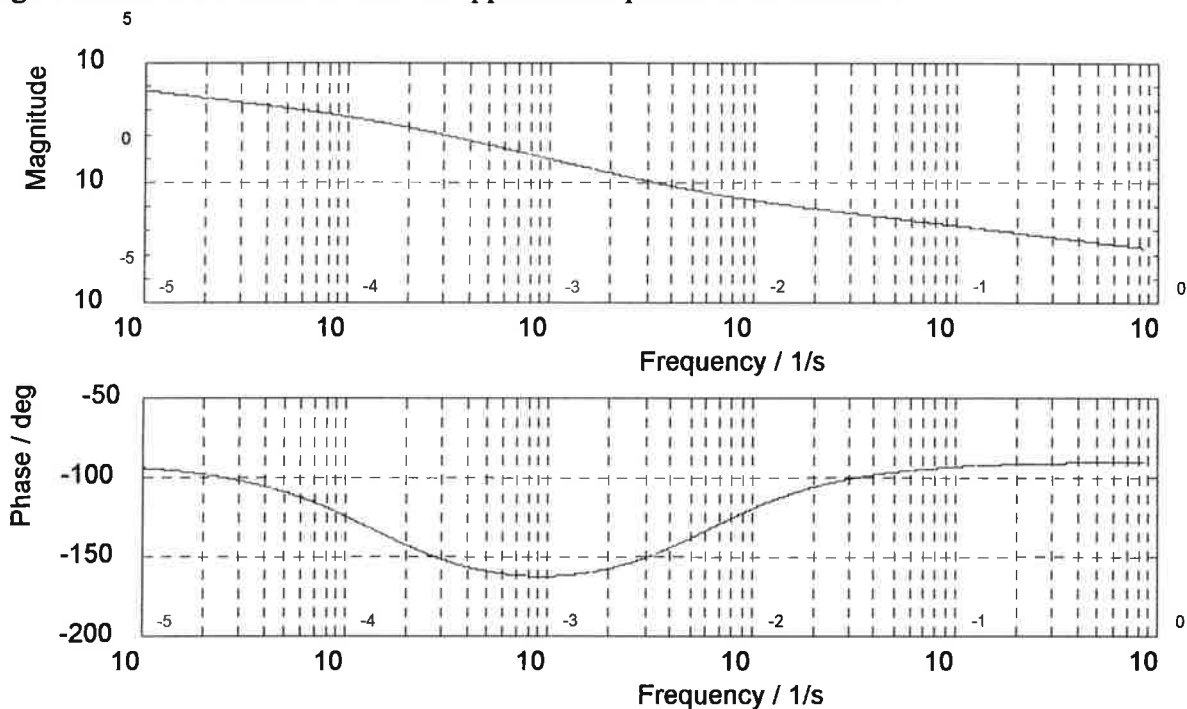


Figure 34. Bode diagram for process and controller with P-band=30% and $T_i=50$ s.

Studying figure 34 it is hard to see instability. The phase curve never crosses -180° . Keeping in mind that the diagram was made from a linearized version of a simplified model it is not strange that the curve can't be interpreted exactly as usual. The phase curve starts and ends at -90° with a minimum at -160° . This minimum occurs at frequencies in the interval of $0.0008-0.001 \text{ s}^{-1}$. This corresponds to a period time of 17-21 minutes, which was the approximate period of the observed oscillations.

The fact that the period of the observed oscillations coincide with the frequency where the phase curve is closest to -180° means that there still is a strong connection between the phase curve and the real process. This means that the linearization is good. The fact that the system oscillates even though the phase curve does not cross -180° is probably caused by nonlinear effects. Investigating this connection between the Bode diagram and the real process further could give new design criterions using the Bode diagram.

Figure 35 shows the Bode diagram for the system with different proportional band. A smaller P-band increases the cross over frequency and the magnitude at higher frequencies and decreases the minimum of the phase curve. The increasing cross-over frequency means a higher amplification of higher frequencies, e.g. fast pH changes but also process and sensor noise.

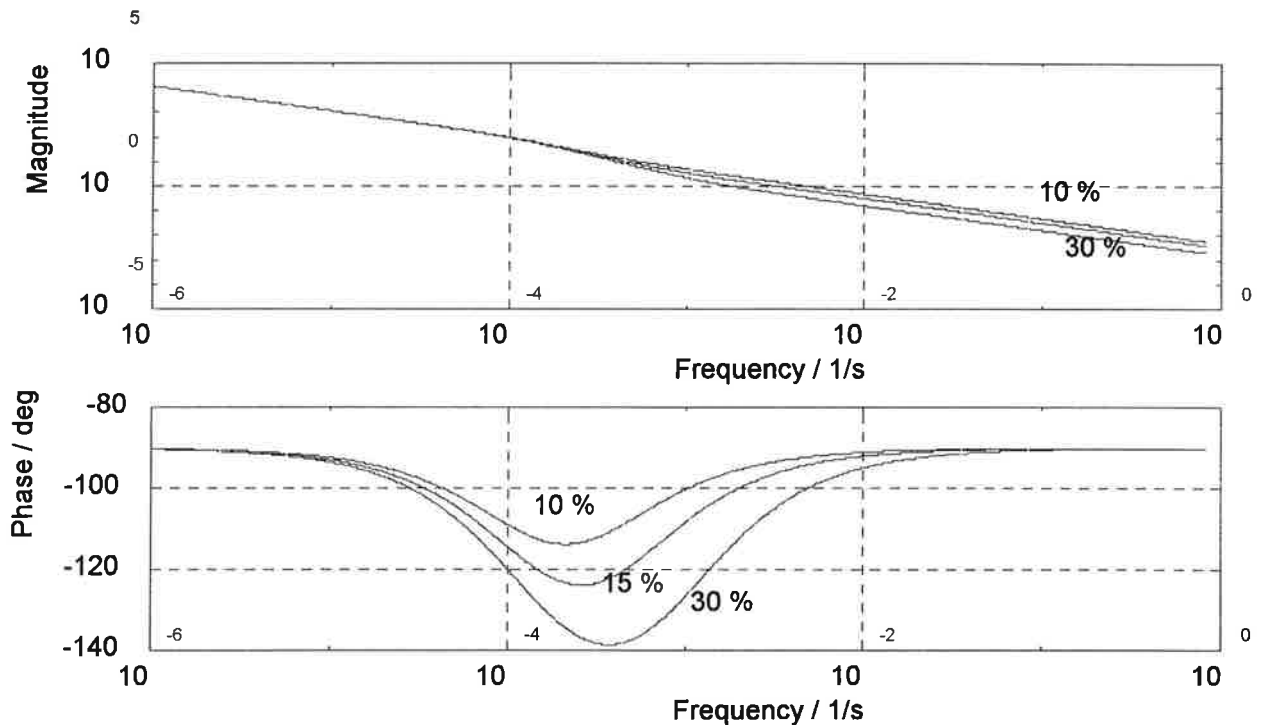


Figure 35. Bode diagram for different proportional band. $T_i=300$ s and $T_d=0$ s.

Both 10 and 15 % P-band has been used with the integrating time in figure 35 during the tuning experiments in Hobro. None of them were sensitive to noise. Since this is the minimum bandwidth in Hobro there is no point in further investigating the relation of P-band, cross over frequency and noise sensitivity.

Figure 36 shows the Bode diagram with different integral time. A short T_i increases the magnitude at low frequencies but have no effect on the cross-over frequency. A shorter T_i also means a larger negative value on the minimum of the phase curve. In Hobro it was found that with this P-band $T_i=140$ s gave an oscillatory response to setpoint changes. $T_i=300$ s was however stable. Thus the phase curve minimum limit should be between -140° ($T_i=140$ s) and -120° ($T_i=300$ s). A short integral time is desired since it avoids long time offsets. Stability is the limit for how short it should be. A desired controller should thus have a phase curve minimum of about -120° .

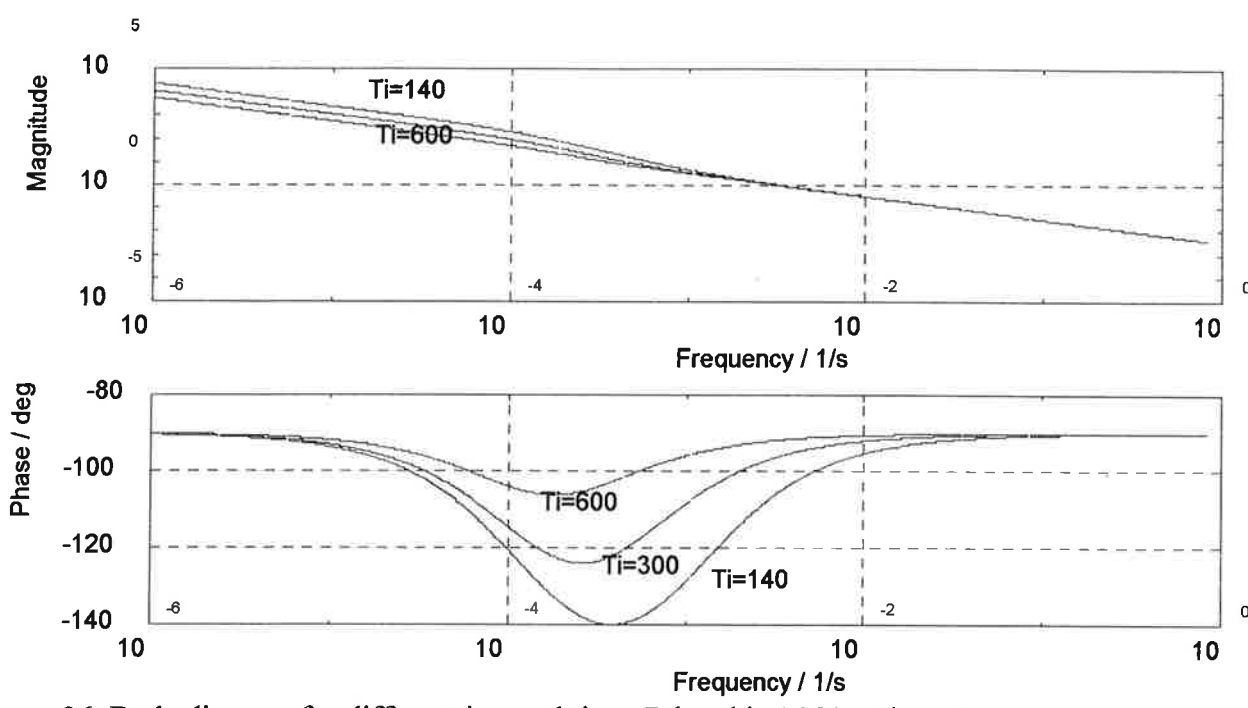


Figure 36. Bode diagram for different integral time. P-band is 15 % and $T_d=0$ s.

Figure 37 shows the Bode diagram with different derivative time. An increased derivative time increases the magnitude at high frequencies, i.e. the noise sensitivity. In this case it doesn't change the cross-over frequency. It also creates a maximum in the phase curve. This maximum is however not at the same frequency as the phase minimum and will thus not improve stability. From figure 37 derivative action doesn't seem to improve stability but it does improve the sensitivity to noise.

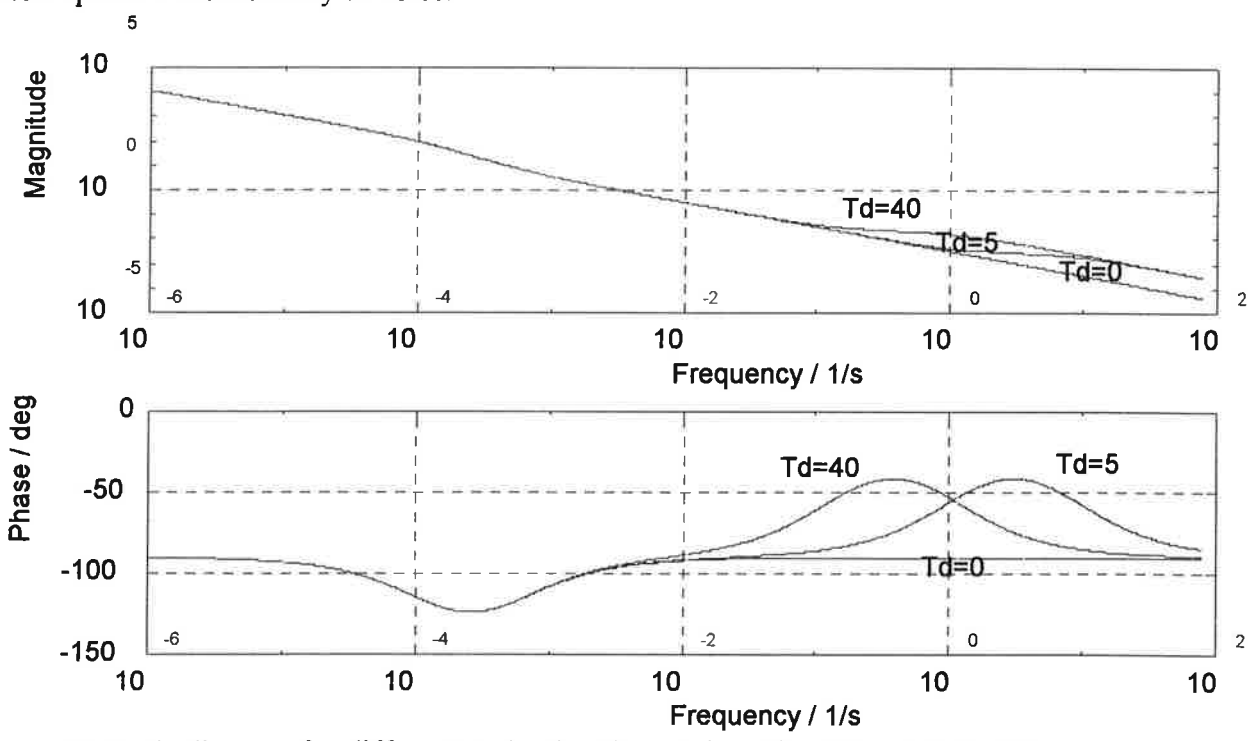


Figure 37. Bode diagram for different derivative time. P-band is 15% and T_i is 300 s.

The design conclusions are that the phase curve minimum should be close to -120° . Derivative action does only increase the noise sensitivity and should be avoided. The cross

over frequency is not a problem since the maximum proportional action has been used without difficulties. Using these design criteria it was easy to find a controller tuning P -band=10%, $T_i=225$ s and $T_d=0$ to fulfil them. Figure 38 gives a simulated comparison of the controller used during the experimental load disturbance in Hobro and this controller design. The performance is very hard to tell apart from that of the controller used. It must thus be concluded that the developed design criterions gives a good controller tuning. It also shows that the manual tuning done in Hobro resulted in a controller with good performance.

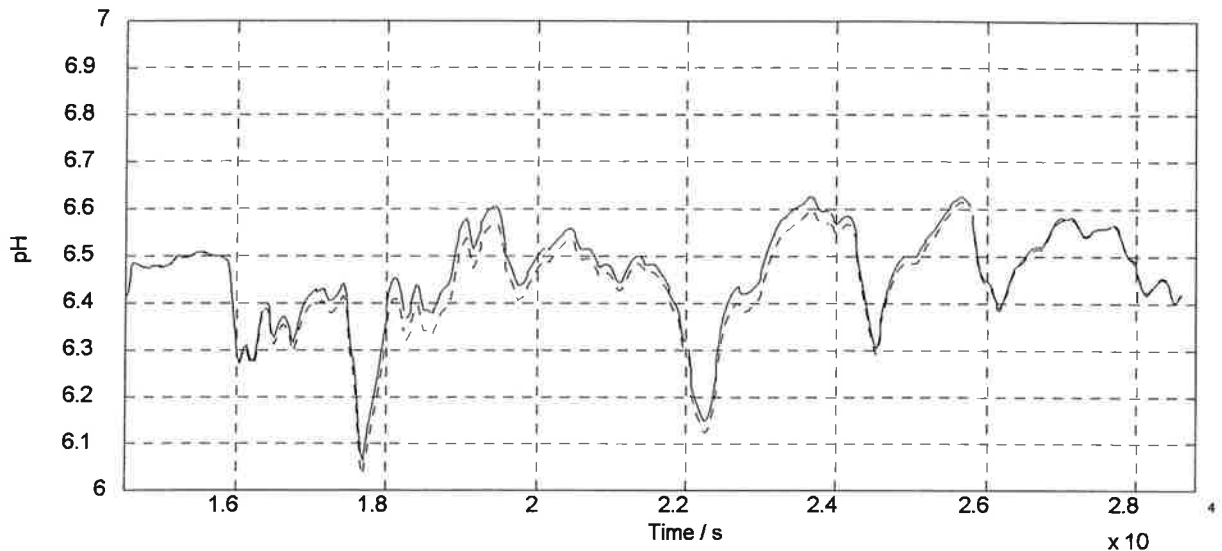


Figure 38. Simulated pH during the experimental load disturbance. Dotted line is the used controller, full line is the controller according to Bode analysis.

11.4 Discussion

Some different methods of controller design has been tried. It was concluded that empirical methods such as Ziegler-Nichols and the KT method can not be used to tune the pH controller in the process in question. A pole placement design based on a linearized model gave a much better result. The resulting controller design can however not be considered as an optimal design. The Bode analysis used both the linearized model and process experience to create design criterions. This gave the best result.

There is however several uncertainties. The most important is that the algorithm used in this work might be incorrect. If the sampling period was forgotten when implementing the controller in Hobro all analysis will be in vain. Manual tuning will then be the only way to find good controller parameters for this controller. The nonlinear model can of course also be used to do manual tuning but the result is also dependent on the algorithm.

The conclusion that derivative action is not desired contradicts the recommendations in section 4. It is possible that this is an erroneous result caused by the linearization or other approximations done. Simulations have however not shown improvements using derivative action. It is also possible that the oxidation reaction, not included in the model, introduces dynamics that makes derivative action an improvement. Other aspects not included in the model can of course also have that effect. As discussed in section 9.5, the tuning experience in Hobro is not a proof for derivative action being an improvement either. It can be noted that

the recommendation comes from a work dealing mainly with adaptive control and not PID control. The experience that pH control is a difficult problem may be the reason for the recommendation rather than analysis.

Thus it seems like a fast PI controller would be the best controller for this process, maybe with some derivative action. The linearization is done about a steady state with high buffering capacity. A high buffering means a lower process gain. At higher process gain the controller gain should be reduced. The experiments in Hobro showed that a P-band of 10 % was not sensitive to noise but it was a bit "nervous" at low buffering. The conclusion for the Hobro plant is thus that the P-band should possibly be reduced to 12-15 % to get a more robust controller. The integral time works well at 300 s and should not be decreased, especially not if increasing the proportional band. The derivative time can be kept at 5 s. This derivative time does no harm even if it is unclear whether derivative action is an improvement or not.

In section 10 it is found that the process is approximately a first order system. Such processes are normally very easy to control and they have no stability problems. The control design can be based on noise sensitivity and how fast sensors and actuators are instead of stability. This is likely to be true in this process but here is another problem as well. The nonlinear, varying process gain makes it hard to find a robust design.

12 CONCLUSIONS

Sections 4-11 has provided a lot of information about the process and the developed model. A number of conclusions can be drawn about the model, plant design and control system design.

12.1 The model

12.1.1 Model performance

The developed model has a good agreement to operating data. It catches the most important features of the process and describes the absorption process specifically well. There are however two important limitations to the model performance. Most important is that the rate of sulphite oxidation is not modeled and thus the model has no capability to predict such property. Furthermore, the model does not include absorption of hydrochloric acid and other hydrogen halides which according to measurements are important. This has a significantly negative effect on the agreement to operating consumption of alkali. It should however be remembered that the scrubber used in the validation has a very poor absorption in both the acidic and the neutral stage due to neglected maintenance of the nozzles.

12.1.2 Possible model improvements

The model can of course be improved in several aspects. The process chemistry could be described using activities instead of concentrations and partial pressures. The model could be extended to include the absorption of carbon dioxide. This absorption is however less important as long as the main source of carbonates is in the alkali.

A more urgent improvement would be to include the absorption of HCl. This would however demand knowledge of the flue gas concentration of HCl in to and out from the neutral scrubber stage. A larger extension of the model would be to include the first acidic scrubber as well. It would then not only give the HCl concentration entering the neutral stage but in fact make it possible to simulate the whole scrubber system.

If it is possible to find the programmer that implemented the controller in Hobro it would of course be interesting to find what algorithm he actually used and if the sampling period was included in the algorithm. This is of course less important if studying another plant.

12.1.3 Possible use of the model

It is possible to use the developed model for several different purposes. The SIMULINK environment makes model reuse very simple, i.e. the basic blocks that are developed can be copied and connected in new ways in a very simple manner. Thus, without further modeling, it is possible to investigate the use of e.g. several spray towers in sequence, several tanks, different sizes of tanks etc. If the model is extended with the acidic scrubber stage it would be possible to investigate dynamic properties of entire scrubber systems.

In any case dynamic studies must be considered as an important tool for design of scrubbers for waste incineration plants. The model can be used to investigate the dynamic properties of different design alternatives as described above. Sensitivity of the absorption process to liquid

concentration of sulphites and pH can be studied to give specifications for process and control system design. Improving the model with the kinetics of sulphite oxidation would make it possible to investigate tank design in this respect. The consumption of alkali due to the absorption of SO_2 can be estimated with real logged flue gas data and gives knowledge for design of pipes and valves for the flow of alkali.

The model is of course also useful in control system design. It can be used to investigate different control strategies. It can also be used to provide a good tuning of controllers, even for a plant not built. A desired control signal is found and the actuator system is then simply designed with the desired characteristics. The model limitations discussed above are of little or no importance for control system design.

Simulations can of course also be used to get experience and understanding of how the process works, how different parameters influences the performance etc. Such understanding would be valuable in plant design, control system design and work with for example start up or controller tuning in a plant.

12.2 Plant design

Plant design can be considered from both a process engineering and a control engineering point of view. This is however just different sides of the same coin. A good control is necessary for good process performance. To achieve a good control it is important to include control aspects in plant design and process knowledge in control system design. Plant and control system design are far too often treated separately.

12.2.1 Tank design

Wanting a fast control the recirculation tank should be kept small. A smaller tank gives a shorter time constant for the process and thus possibilities for a faster control. The limit for how small the tank can be is how fast sensors and actuators are. The dynamics of sensors and actuators, e.g. control valves, must always be considerably faster than the controlled system.

The buffering capacity of the scrubber liquid is an important feature of the process. A high buffering means a lower process gain and smaller pH dependent variations in process gain. Thus it will be easier to control the process with a high buffering capacity. A high buffering capacity is thus a desired property considering control. The buffering capacity will also influence the absorption process.

From a process engineering point of view it is obvious that a small tank will be advantageous for the buffering capacity. There are of course several other aspects of tank design, but the overall conclusion is that the tank should be kept rather small.

The use of a small tank would give a faster control but probably not better than can be attributed to the improved buffering. If a better control is desired it can be carried out in several tanks in series as discussed in section 4. This is likely to be a simple and very efficient way to improve the stability of pH in to the spray tower.

12.2.2 Pipes, pumps and valves

The design of pipes, pumps, nozzles and valves for the recirculation flow is not a dynamic problem. This flow should be kept constant at a level giving optimum mass transfer condition. The flow of alkali to the recirculation tank is however a more difficult problem. A fast control demands fast, frequent and often large changes in the flow of alkali. For a plant larger than Hobro the problem of rangeability is likely to be important. Pipes and pumps must of course be designed to meet a maximum case. The solution to the problem of rangeability is, as mentioned in section 4, two valves of different size in sequence or performing the control in several steps. Thus, there are at least two reasons to use a tank series instead of a single tank. If using valves they must have fast and good control characteristics. If using the pump to control the flow it must meet high demands for flexibility and accuracy.

12.2.3 Sensors

When designing a process it is important to place sensors and actuators so that the dead time is minimized [16]. The control of flow is normally free from dead time since a change of a valve immediately changes the flow in the entire pipe. For the scrubber process it is thus only the pH electrode that needs consideration. It should be placed as close to the tank as possible but *not* in the tank. A measurement in the tank would be dependent on how well the liquid is mixed. Placing the electrode immediately after the tank gives a measurement in a well mixed liquid and practically no dead time at all.

12.3 Control

After tuning the controller in Hobro the system seems to work rather well. pH control is generally a difficult problem but a scrubber loop is probably one of the easiest cases. The disturbances are low concentrations of pollutants in a flue gas and thus the disturbances are much smaller than for example in an industrial waste water treatment plant. Furthermore there is a considerable buffering capacity in the liquid. The problem can be solved using linear feedback in one or two stages.

Concerning the Hobro plant the feed forward action of the pH control should be kept "disconnected". The controller parameters can be according to the manual tuning in section 9.4 ($P\text{-band}=10\%$, $T_i=300\text{ s}$ and $T_d=5\text{ s}$), maybe with a slightly increased proportional band, 12-15%.

For new plants and control systems a few things can be concluded and some ideas added.

- Feed forward of pH can not be used. A pH measurement provides no information about the change of states. Integral action must never be used in a feed forward loop.

- A more flexible parameter setting than in Hobro is advisable, at least a higher possible maximum gain.

- Anti-windup should be used in the controller.

-Take the time necessary to get a good controller tuning. Simulations can be used to get good parameters but manual fine tuning can provide improvements. Using the rules of thumb, section 9.4, it is not that hard. It must however be remembered that Ziegler-Nichols method or the new KT-method can not be used to tune the pH controllers.

-If implementing digital controllers, make sure that the controller algorithm includes the sampling period in a proper way. If this is not the case, simulations and control analysis can not be used to find a good controller tuning.

-The level control in the recirculation tank could be improved by using feed forward from the flow of alkali, the main disturbance.

pH control can be improved by performing the control in several steps but there are of course also more sophisticated ways. In section 4 there are some recommendations, the use of nonlinear controllers and adaptive control.

Using a nonlinear controller with different gain dependent on the pH is a technique called gain scheduling. Gain scheduling is a well known technique in pH control when having a low or constant buffering capacity. It would probably work well in the acidic scrubber stage. The technique is however questionable in this case. The controller works in a rather restricted range of pH and the large variation in process gain is due to changes in chemical composition, not changes in pH.

It would be desirable to have a controller with a gain dependent on buffering capacity instead of pH. At least a high gain when high buffering capacity and a lower gain when a low buffering capacity. The problem is to estimate the change.

These changes in process gain could be estimated and used in an adaptive controller that changed the controller gain according to the changes in process gain. This would probably work very well but is maybe more sophisticated than needed. Furthermore, adaptive controllers are not as simple as may be believed. They demand a very competent operating personnel.

An intermediate technique would be using a state space controller. This is however not possible since it is impossible both to observe and control all states with only one sensor. To use a controller like this demands more measurements.

Feed forward of the concentration of SO_2 in the flue gas to the flow of alkali is a possible idea. A good early measurement of SO_2 would be crucial to operate such system. Feed forward demands a certain dead time between measurement and impact of the disturbance [16]. In the combustion of waste the variation in SO_2 concentration is very large and very fast, several hundred ppm in few minutes. This would demand a very good SO_2 sensor with short time constant and a fast actuator system. To get a proper response to such fast changes would be hard and there is a risk that it would only result in extra process noise.

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Appendix 1.

$$[\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{HSO}_4^-] + 2[\text{SO}_4^{2-}] + [\text{OH}^-] - [\text{Na}^+] - [\text{H}^+] = 0$$

This charge balance is to be expressed using only s4, s6, Ctot and Na defined

$$s4 = [\text{SO}_2(\text{aq})] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]$$

$$s6 = [\text{HSO}_4^-] + [\text{SO}_4^{2-}]$$

$$\text{Ctot} = [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$\text{Na} = [\text{Na}^+]$$

and the hydrogen ion concentration $[\text{H}^+]$. The following equilibrium relations are needed.

$$K_{\text{SO}_2} = \frac{[\text{HSO}_3^-] [\text{H}^+]}{[\text{SO}_2(\text{aq})]} \quad K_{\text{HSO}_3^-} = \frac{[\text{SO}_3^{2-}] [\text{H}^+]}{[\text{HSO}_3^-]}$$

$$K_{\text{CO}_2} = \frac{[\text{HCO}_3^-] [\text{H}^+]}{[\text{CO}_2(\text{aq})]} \quad K_{\text{HCO}_3^-} = \frac{[\text{CO}_3^{2-}] [\text{H}^+]}{[\text{HCO}_3^-]}$$

$$K_{\text{HSO}_4^-} = \frac{[\text{SO}_4^{2-}] [\text{H}^+]}{[\text{HSO}_4^-]} \quad K_w = [\text{OH}^-] [\text{H}^+]$$

The terms in the charge balance will be replaced one by one. Starting with $[\text{HSO}_3^-]$ we have

$$s4 = [\text{SO}_2(\text{aq})] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]$$

The equilibrium gives

$$[\text{HSO}_3^-] = \frac{K_{\text{SO}_2} [\text{SO}_2(\text{aq})]}{[\text{H}^+]}$$

Expressing $[\text{HSO}_3^-]$ using s4 we have

$$[\text{HSO}_3^-] = \frac{K_{\text{SO}_2} \cdot s4}{[\text{H}^+]} - \frac{K_{\text{SO}_2} [\text{HSO}_3^-]}{[\text{H}^+]} - \frac{K_{\text{SO}_2} [\text{SO}_3^{2-}]}{[\text{H}^+]}$$

Inserting the equilibrium for $[\text{SO}_3^{2-}]$ gives

$$[\text{HSO}_3^-] = \frac{K_{\text{SO}_2} \cdot s_4}{[\text{H}^+]} - \frac{K_{\text{SO}_2} [\text{HSO}_3^-]}{[\text{H}^+]} - \frac{K_{\text{SO}_2} \cdot K_{\text{HSO}_3} [\text{HSO}_3^-]}{[\text{H}^+]^2}$$

Solving the equation for $[\text{HSO}_3^-]$ gives

$$[\text{HSO}_3^-] = \frac{s_4 \cdot K_{\text{SO}_2}}{\left([\text{H}^+] + K_{\text{SO}_2} + \frac{K_{\text{SO}_2} \cdot K_{\text{HSO}_3}}{[\text{H}^+]} \right)}$$

This is the desired expression for the first term of the charge balance only using constants, s_4 and the hydrogen ion concentration.

The same method is used for $[\text{SO}_3^{2-}]$. Using the equilibria the concentration can be given as

$$[\text{SO}_3^{2-}] = \frac{K_{\text{HSO}_3} [\text{HSO}_3^-]}{[\text{H}^+]} = \frac{K_{\text{SO}_2} \cdot K_{\text{HSO}_3} [\text{SO}_2(\text{aq})]}{[\text{H}^+]^2}$$

Writing the same concentration using s_4

$$[\text{SO}_3^{2-}] = \frac{K_{\text{SO}_2} \cdot K_{\text{HSO}_3} \cdot s_4}{[\text{H}^+]^2} - \frac{K_{\text{SO}_2} \cdot K_{\text{HSO}_3} [\text{HSO}_3^-]}{[\text{H}^+]^2} - \frac{K_{\text{SO}_2} \cdot K_{\text{HSO}_3} [\text{SO}_3^{2-}]}{[\text{H}^+]^2}$$

Replacing $[\text{HSO}_3^-]$ using the equilibrium expression

$$[\text{SO}_3^{2-}] = \frac{K_{\text{SO}_2} \cdot K_{\text{HSO}_3} \cdot s_4}{[\text{H}^+]^2} - \frac{K_{\text{SO}_2} [\text{SO}_3^{2-}]}{[\text{H}^+]} - \frac{K_{\text{SO}_2} \cdot K_{\text{HSO}_3} [\text{SO}_3^{2-}]}{[\text{H}^+]^2}$$

Solving for $[\text{SO}_3^{2-}]$ gives

$$[\text{SO}_3^{2-}] = \frac{K_{\text{SO}_2} \cdot s_4}{\left(\frac{[\text{H}^+]^2}{K_{\text{HSO}_3}} + \frac{[\text{H}^+] K_{\text{SO}_2}}{K_{\text{HSO}_3}} + K_{\text{SO}_2} \right)}$$

This is the desired expression for $[\text{SO}_3^{2-}]$. Deriving the same expressions for the carbonates is quite analogous to the sulfites, the only difference is using C_{tot} and the equilibria for carbonates instead. The same derivation gives

$$[\text{HCO}_3^-] = \frac{C_{\text{tot}} \cdot K_{\text{CO}_2}}{\left([\text{H}^+] + K_{\text{CO}_2} + \frac{K_{\text{CO}_2} \cdot K_{\text{HCO}_3}}{[\text{H}^+]} \right)}$$

and

$$[\text{CO}_3^{2-}] = \frac{K_{\text{CO}_2} \cdot \text{C}_{\text{tot}}}{\left(\frac{[\text{H}^+]^2}{K_{\text{HCO}_3^-}} + \frac{[\text{H}^+]}{K_{\text{HCO}_3^-}} + K_{\text{CO}_2} \right)}$$

The relation for s6 only contain two terms which makes the derivation of $[\text{HSO}_4^-]$ and $[\text{SO}_4^{2-}]$ easier than the derivations above. Using the same method gives

$$[\text{HSO}_4^-] = \frac{s6 \cdot [\text{H}^+]}{([\text{H}^+] + K_{\text{HSO}_4^-})}$$

and

$$[\text{SO}_4^{2-}] = \frac{s6 \cdot K_{\text{HSO}_4^-}}{([\text{H}^+] + K_{\text{HSO}_4^-})}$$

The hydroxide ion concentration is obtained direct from the equilibrium

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

Substituting all concentration in the charge balance with these expression gives

$$\begin{aligned} & \frac{s4 \cdot K_{\text{SO}_2} \cdot [\text{H}^+]}{([\text{H}^+]^2 + K_{\text{SO}_2} \cdot [\text{H}^+] + K_{\text{SO}_2} \cdot K_{\text{HSO}_3^-})} + 2 \frac{s4 \cdot K_{\text{SO}_2} \cdot K_{\text{HSO}_3^-}}{([\text{H}^+]^2 + K_{\text{SO}_2} \cdot [\text{H}^+] + K_{\text{SO}_2} \cdot K_{\text{HSO}_3^-})} + \\ & \frac{s6 \cdot [\text{H}^+]}{(K_{\text{HSO}_4^-} + [\text{H}^+])} + 2 \frac{s6 \cdot K_{\text{HSO}_4^-}}{(K_{\text{HSO}_4^-} + [\text{H}^+])} + \frac{\text{C}_{\text{tot}} \cdot K_{\text{CO}_2} \cdot [\text{H}^+]}{([\text{H}^+]^2 + K_{\text{CO}_2} \cdot [\text{H}^+] + K_{\text{CO}_2} \cdot K_{\text{HCO}_3^-})} + \\ & 2 \frac{\text{C}_{\text{tot}} \cdot K_{\text{CO}_2} \cdot K_{\text{HCO}_3^-}}{([\text{H}^+]^2 + K_{\text{CO}_2} \cdot [\text{H}^+] + K_{\text{CO}_2} \cdot K_{\text{HCO}_3^-})} + \frac{K_w}{[\text{H}^+]} - \text{Na}^+ - [\text{H}^+] = 0 \end{aligned}$$

Appendix 2.

> charge:=s4*kso2*x/(x^2+kso2*x+kso2*khso3)+2*(s4*kso2*khso3)/(x^2+kso2*x+kso2*khso3)+s6*x/(x+khso4)+2*(khso4*s6)/(x+khso4)+kco2*ctot*x/(x^2+kco2*x+kco2*khco3)+2*(kco2*ctot*khco3)/(x^2+kco2*x+kco2*khco3)+kw/x-na-x;

$$\begin{aligned}
 \text{charge} := & \frac{s4 \text{ kso2 } x}{x^2 + \text{kso2 } x + \text{kso2 } \text{khso3}} \\
 & + 2 \frac{s4 \text{ kso2 } \text{khso3}}{x^2 + \text{kso2 } x + \text{kso2 } \text{khso3}} + \frac{s6 \text{ } x}{x + \text{khso4}} + 2 \frac{\text{khso4 } s6}{x + \text{khso4}} \\
 & + \frac{\text{kco2 } \text{ctot } x}{x^2 + \text{kco2 } x + \text{kco2 } \text{khco3}} + 2 \frac{\text{kco2 } \text{ctot } \text{khco3}}{x^2 + \text{kco2 } x + \text{kco2 } \text{khco3}} \\
 & + \frac{\text{kw}}{x} - \text{na} - x
 \end{aligned}$$

> collnum:=collect(numerator,x); The numerator polynomial

$$\begin{aligned}
 \text{collnum} := & -x^7 + (-\text{na} + s6 - \text{kso2} - \text{kco2} - \text{khso4}) x^6 + (s6 \text{ kso2} \\
 & - \text{na } \text{khso4} + \text{kw} - \text{kso2 } \text{khso3} - \text{na } \text{kco2} + \text{kco2 } \text{ctot} \\
 & - \text{na } \text{kso2} - \text{kso2 } \text{khso4} + 2 \text{ khso4 } s6 + s4 \text{ kso2} \\
 & - \text{khso4 } \text{kco2} - \text{kco2 } \text{khco3} - \text{kso2 } \text{kco2} + s6 \text{ kco2}) x^5 + (\\
 & \text{kw } \text{kso2} - \text{kso2 } \text{kco2 } \text{khco3} + \text{kco2 } \text{ctot } \text{khso4} \\
 & + \text{kco2 } \text{ctot } \text{kso2} - \text{na } \text{khso4 } \text{kco2} - \text{kso2 } \text{khso4 } \text{kco2} \\
 & - \text{na } \text{kso2 } \text{khso4} + 2 \text{ kco2 } \text{ctot } \text{khco3} - \text{khso4 } \text{kco2 } \text{khco3} \\
 & + \text{kw } \text{khso4} - \text{na } \text{kco2 } \text{khco3} + \text{kw } \text{kco2} + s6 \text{ kso2 } \text{khso3} \\
 & + s6 \text{ kco2 } \text{khco3} - \text{na } \text{kso2 } \text{kco2} - \text{kso2 } \text{khso3 } \text{khso4} \\
 & - \text{na } \text{kso2 } \text{khso3} + 2 s4 \text{ kso2 } \text{khso3} + s6 \text{ kso2 } \text{kco2} \\
 & + 2 \text{ khso4 } s6 \text{ kco2} + s4 \text{ kso2 } \text{khso4} + 2 \text{ khso4 } s6 \text{ kso2} \\
 & + s4 \text{ kso2 } \text{kco2} - \text{kso2 } \text{khso3 } \text{kco2}) x^4 + (
 \end{aligned}$$

$$\begin{aligned}
& -k_{so2} k_{hso3} k_{co2} k_{hco3} + k_w k_{co2} k_{hco3} + k_w k_{hso4} k_{co2} \\
& + k_w k_{so2} k_{co2} + k_w k_{so2} k_{hso4} + k_w k_{so2} k_{hso3} \\
& + s_4 k_{so2} k_{co2} k_{hco3} + s_4 k_{so2} k_{hso4} k_{co2} \\
& + 2 s_4 k_{so2} k_{hso3} k_{co2} + s_6 k_{so2} k_{co2} k_{hco3} \\
& + 2 s_4 k_{so2} k_{hso3} k_{hso4} + 2 k_{hso4} s_6 k_{co2} k_{hco3} \\
& + 2 k_{hso4} s_6 k_{so2} k_{co2} + 2 k_{hso4} s_6 k_{so2} k_{hso3} \\
& + s_6 k_{so2} k_{hso3} k_{co2} + k_{co2} c_{tot} k_{so2} k_{hso4} \\
& + k_{co2} c_{tot} k_{so2} k_{hso3} + 2 k_{co2} c_{tot} k_{hco3} k_{hso4} \\
& + 2 k_{co2} c_{tot} k_{hco3} k_{so2} - n_a k_{so2} k_{hso3} k_{co2} \\
& - n_a k_{so2} k_{hso3} k_{hso4} - k_{so2} k_{hso4} k_{co2} k_{hco3} \\
& - n_a k_{hso4} k_{co2} k_{hco3} - n_a k_{so2} k_{co2} k_{hco3} \\
& - n_a k_{so2} k_{hso4} k_{co2} - k_{so2} k_{hso3} k_{hso4} k_{co2}) x^3 + (\\
& 2 s_4 k_{so2} k_{hso3} k_{co2} k_{hco3} + k_w k_{so2} k_{co2} k_{hco3} \\
& + 2 s_4 k_{so2} k_{hso3} k_{hso4} k_{co2} + k_w k_{hso4} k_{co2} k_{hco3} \\
& + 2 k_{co2} c_{tot} k_{hco3} k_{so2} k_{hso3} \\
& - n_a k_{so2} k_{hso4} k_{co2} k_{hco3} + k_w k_{so2} k_{hso3} k_{co2} \\
& - k_{so2} k_{hso3} k_{hso4} k_{co2} k_{hco3} \\
& + k_{co2} c_{tot} k_{so2} k_{hso3} k_{hso4} + k_w k_{so2} k_{hso4} k_{co2} \\
& - n_a k_{so2} k_{hso3} k_{hso4} k_{co2} + s_4 k_{so2} k_{hso4} k_{co2} k_{hco3} \\
& + 2 k_{co2} c_{tot} k_{hco3} k_{so2} k_{hso4} + k_w k_{so2} k_{hso3} k_{hso4} \\
& - n_a k_{so2} k_{hso3} k_{co2} k_{hco3} + 2 k_{hso4} s_6 k_{so2} k_{co2} k_{hco3} \\
& + 2 k_{hso4} s_6 k_{so2} k_{hso3} k_{co2} + s_6 k_{so2} k_{hso3} k_{co2} k_{hco3}
\end{aligned}$$

$$\begin{aligned}
&) x^2 + (2 k_{CO2} c_{TOT} k_{HCO3} k_{SO2} k_{HSO3} k_{HSO4} \\
& + 2 k_{HSO4} s_6 k_{SO2} k_{HSO3} k_{CO2} k_{HCO3} \\
& + 2 s_4 k_{SO2} k_{HSO3} k_{HSO4} k_{CO2} k_{HCO3} \\
& + k_w k_{SO2} k_{HSO4} k_{CO2} k_{HCO3} + k_w k_{SO2} k_{HSO3} k_{HSO4} k_{CO2} \\
& - n_a k_{SO2} k_{HSO3} k_{HSO4} k_{CO2} k_{HCO3} \\
& + k_w k_{SO2} k_{HSO3} k_{CO2} k_{HCO3}) x \\
& + k_w k_{SO2} k_{HSO3} k_{HSO4} k_{CO2} k_{HCO3}
\end{aligned}$$

> **colldenum:=collect(denom(charge),x);** The denominator polynomial

$$\begin{aligned}
colldenum := & x^6 + (k_{SO2} + k_{HSO4} + k_{CO2}) x^5 + (k_{SO2} k_{HSO3} \\
& + k_{SO2} k_{HSO4} + (k_{SO2} + k_{HSO4}) k_{CO2} + k_{CO2} k_{HCO3}) x^4 + (\\
& k_{SO2} k_{HSO3} k_{HSO4} + (k_{SO2} k_{HSO3} + k_{SO2} k_{HSO4}) k_{CO2} \\
& + (k_{SO2} + k_{HSO4}) k_{CO2} k_{HCO3}) x^3 + (\\
& k_{SO2} k_{HSO3} k_{HSO4} k_{CO2} \\
& + (k_{SO2} k_{HSO3} + k_{SO2} k_{HSO4}) k_{CO2} k_{HCO3}) x^2 \\
& + k_{HSO4} x k_{SO2} k_{HSO3} k_{CO2} k_{HCO3}
\end{aligned}$$

Appendix 3.

Henry's law gives

$$H_{\text{SO}_2} = \frac{P_{\text{SO}_2}}{[\text{SO}_2(\text{aq})]}$$

Substituting SO_2 using the dissociation equilibrium relation gives

$$P_{\text{SO}_2} = H_{\text{SO}_2} [\text{SO}_2(\text{aq})] = H_{\text{SO}_2} \left(\frac{[\text{HSO}_3^-][\text{H}^+]}{K_{\text{SO}_2}} \right)$$

In appendix 1 it was found that

$$[\text{HSO}_3^-] = \frac{s_4 \cdot K_{\text{SO}_2}}{\left([\text{H}^+] + K_{\text{SO}_2} + \frac{K_{\text{SO}_2} \cdot K_{\text{HSO}_3}}{[\text{H}^+]} \right)}$$

Inserting this gives

$$P_{\text{SO}_2} = H_{\text{SO}_2} \left(\frac{s_4}{1 + \frac{K_{\text{SO}_2}}{[\text{H}^+]} + \frac{K_{\text{SO}_2} \cdot K_{\text{HSO}_3}}{[\text{H}^+]^2}} \right)$$

Appendix 4.

```

function [y] = ph(x);
%
%       Calculates pH from known concentrations of
%       sulfite, sulfate, sodium and carbonates.
%
%       y=ph(x); where x=[s4,s6,Na,Ctot]
%
%       Describes the charge balance as a rational function and
%       finds the roots of the numerator polynomial, which is a
%       function of the hydrogen ion concentration. Produces a
%       resulting vector of the same size as the input vector.

%Constants:

temp=333;
kw=exp(log(10)*(-(-6.09+4471/temp+0.0171*temp)));
kso2=
khs3=
khs4=
kco2=
khco3=

%Concentrations:

s4=x(1);
s6=x(2);
natot=x(3);
ctot=x(4);

%Coefficients of the numerator polynomial
%(p(1)*[H+]^7+p(2)*[H+]^6....p(7)*[H+]+p(8)):

p(1)=-1;
p(2)=(s6-natot-kco2-khs4-kso2);
p(3)=(kw+s4*kso2-kso2*khs3+s6*kco2-natot*kco2-kso2*khs4+2*khs4*s6+kco2*ctot-
natot*kso2-kso2*kco2-khs4*kco2-kco2*khco3-natot*khs4+s6*kso2);
p(4)=(2*khs4*s6*kso2+s6*kso2*kco2+kw*kso2+kw*kco2-kso2*khs3*kco2-
natot*kso2*khs3+2*s4*kso2*khs3-natot*kco2*khco3-natot*khs4*kco2+s4*kso2*kco2-
kso2*kco2*khco3-kso2*khs4*kco2+2*khs4*s6*kco2-natot*kso2*khs4 +s4*kso2*khs4
+s6*kco2*khco3-khs4*kco2*khco3 +kco2*ctot*kso2+ 2*kco2*ctot*khco3+
kco2*ctot*khs4-natot*kso2*kco2+s6*kso2*khs3+kw*khs4-kso2*khs3*khs4);
p(5)=(kw*kso2*khs3+2*kco2*ctot*khco3*kso2+kw*khs4*kco2+kw*kco2*khco3+
kw*kso2*khs4+2*s4*kso2*khs3*khs4+2*khs4*s6*kso2*khs3+s4*kso2*khs4*kco2-
natot*khs4*kco2*khco3-natot*kso2*kco2*khco3 +2*khs4*s6*kso2*kco2
+2*khs4*s6*kco2*khco3+kco2*ctot*kso2*khs3-natot*kso2*khs3*kco2-
natot*kso2*khs4*kco2-natot*kso2*khs3*khs4+s6*kso2*kco2*khco3

```

```

+s6*kso2*khs03*kco2+2*s4*kso2*khs03*kco2+kco2*ctot*kso2*khs04+kw*kso2*kco2+
2*kco2*ctot*khco3*khs04-kso2*khs04*kco2*khco3-kso2*khs03*kco2*khco3
+s4*kso2*kco2*khco3-kso2*khs03*khs04*kco2);
p(6)=(kw*kso2*khs03*kco2+kw*khs04*kco2*khco3+2*s4*kso2*khs03*kco2*khco3+2*s4*
kso2*khs03*khs04*kco2-natot*kso2*khs03*kco2*khco3 +2*kco2*ctot*khco3*kso2*khs03
+s6*kso2*khs03*kco2*khco3+2*khs04*s6*kso2*khs03*kco2+kco2*ctot*kso2*khs03*khs04
+s4*kso2*khs04*kco2*khco3+kw*kso2*khs04*kco2+kw*kso2*khs03*khs04+kw*kso2*kco
2*khco3-kso2*khs03*khs04*kco2*khco3-natot*kso2*khs04*kco2*khco3+
2*khs04*s6*kso2*kco2*khco3+2*kco2*ctot*khco3*kso2*khs04-
natot*kso2*khs03*khs04*kco2);
p(7)=(2*s4*kso2*khs03*khs04*kco2*khco3+kw*kso2*khs04*kco2*khco3+2*khs04*s6*kso
2*khs03*kco2*khco3+kw*kso2*khs03*kco2*khco3-natot*kso2*khs03*khs04*kco2*khco3+
2*kco2*ctot*khco3*kso2*khs03*khs04+kw*kso2*khs03*khs04*kco2);
p(8)=(kw*kso2*khs03*khs04*kco2*khco3);

```

%Find the roots of the numerator polynomial!

```
r=roots(p);
```

%Choose the correct root! It is positive and real.

```

if (r(1)>0 & imag(r(1))==0)
    h=r(1);
elseif (r(2)>0 & imag(r(2))==0)
    h=r(2);
elseif (r(3)>0 & imag(r(3))==0)
    h=r(3);
elseif (r(4)>0 & imag(r(4))==0)
    h=r(4);
elseif (r(5)>0 & imag(r(5))==0)
    h=r(5);
elseif (r(6)>0 & imag(r(6))==0)
    h=r(6);
elseif (r(7)>0 & imag(r(7))==0)
    h=r(7);
end
end
end
end
end
end

```

%Calculate pH according to the definition!

```

y(1)=-log10(h);
y(2)=0;
y(3)=0;
y(4)=0;

```

Appendix 5.

```

function [y] = scrubber(in);
%
%Calculates the concentrations in the flows out from
%the scrubber as a function of the concentrations in.
%Doesn't consider the absorbtion of CO2 yet!
%
% [y]=[Vut,Lut,so2ut,s4ut,s6ut,natotut,ctotut,pHut]= scrubber(in);
%
%in is a vector with the following content:
%
%in(1)=V, flow of flue gas in to the scrubber, m3/s
%in(2)=L, liquid flow in to the scrubber, litre/s
%in(3)=so2in, concentration of SO2 in the flue gas, ppm
%in(4)=s4in, concentration of sulfites in the liquid, mol/l
%in(5)=s6in, concentration of sulfates in the liquid, mol/l
%in(6)=natotin, concentration of sodium in the liquid, mol/l
%in(7)=ctotin, concentration of carbonatesin the liquid, mol/l
%in(8)=pH in the liquid

%Use variable names for each input
V=in(1);
L=in(2);
so2in=in(3);
s4in=in(4);
s6in=in(5);
natotin=in(6);
ctotin=in(7);
pH=in(8);

%Constants
temp=333;
ox=
R=8.314;
A=          %Cross sectional area of spray tower, m2
z=          %Height of spray tower, m

%Henry's constant with pressures in atm
Hso2=

%Equilibrium constants

kso2=
khsO3=
khsO4=
kco2=
khco3=

```

%Condensing water vapour adds to liquid in

$L_{ut}=L+0.014;$

%Mass transfer coefficient K_{ga}

$K_{ga} =$

$h = \exp(\log(10) \cdot (-pH));$

%Equilibrium partial pressure, ppm

$P_{so2} = H_{so2} \cdot (s4_{in} / (1 + k_{so2} / h + k_{so2} \cdot k_{hso3} / h^2)) \cdot 1e6;$

$expon = K_{ga} \cdot A \cdot z \cdot R \cdot temp / V;$

%Concentrations out from the scrubber

$so2_{ut} = so2_{in} \cdot \exp(-expon) + P_{so2} \cdot (1 - \exp(-expon));$

$s6_{ut} = ox \cdot (V \cdot (so2_{in} - so2_{ut}) \cdot 1e-6 \cdot 101325 / (L_{ut} \cdot 8.314 \cdot temp)) + s6_{in};$

$s4_{ut} = (1 - ox) \cdot (V \cdot (so2_{in} - so2_{ut}) \cdot 1e-6 \cdot 101325 / (L_{ut} \cdot 8.314 \cdot temp)) + s4_{in};$

$ctot_{ut} =$ %Later $ctot_{ut} = ctot_{in};$

$natot_{ut} = L \cdot natot_{in} / L_{ut};$

$V_{ut} = V;$

$x = [s4_{ut}, s6_{ut}, natot_{ut}, ctot_{ut}];$

$pH_{ut} = phvpoly(x);$

$y(1) = V_{ut};$

$y(2) = L_{ut};$

$y(3) = so2_{ut};$

$y(4) = s4_{ut};$

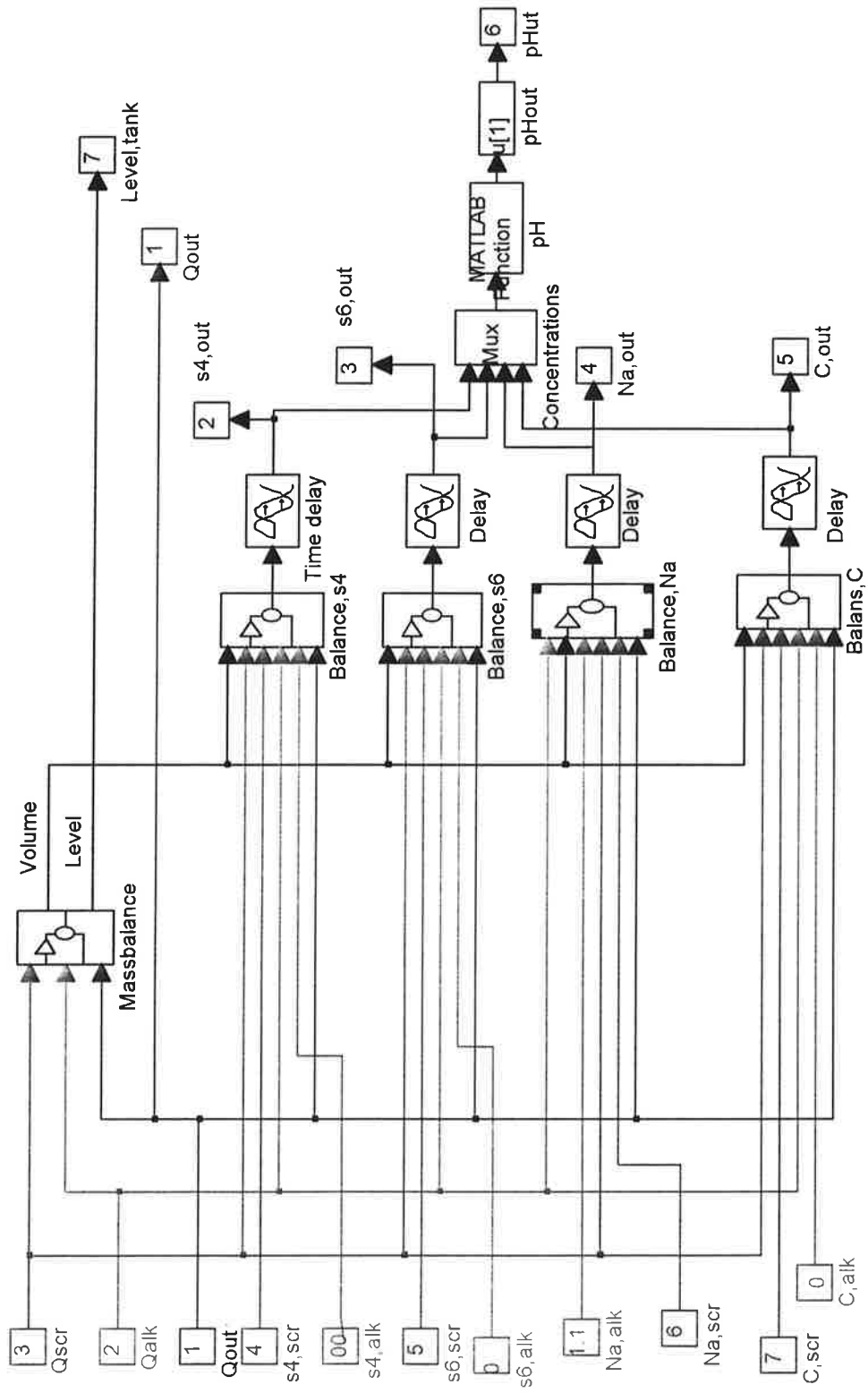
$y(5) = s6_{ut};$

$y(6) = natot_{ut};$

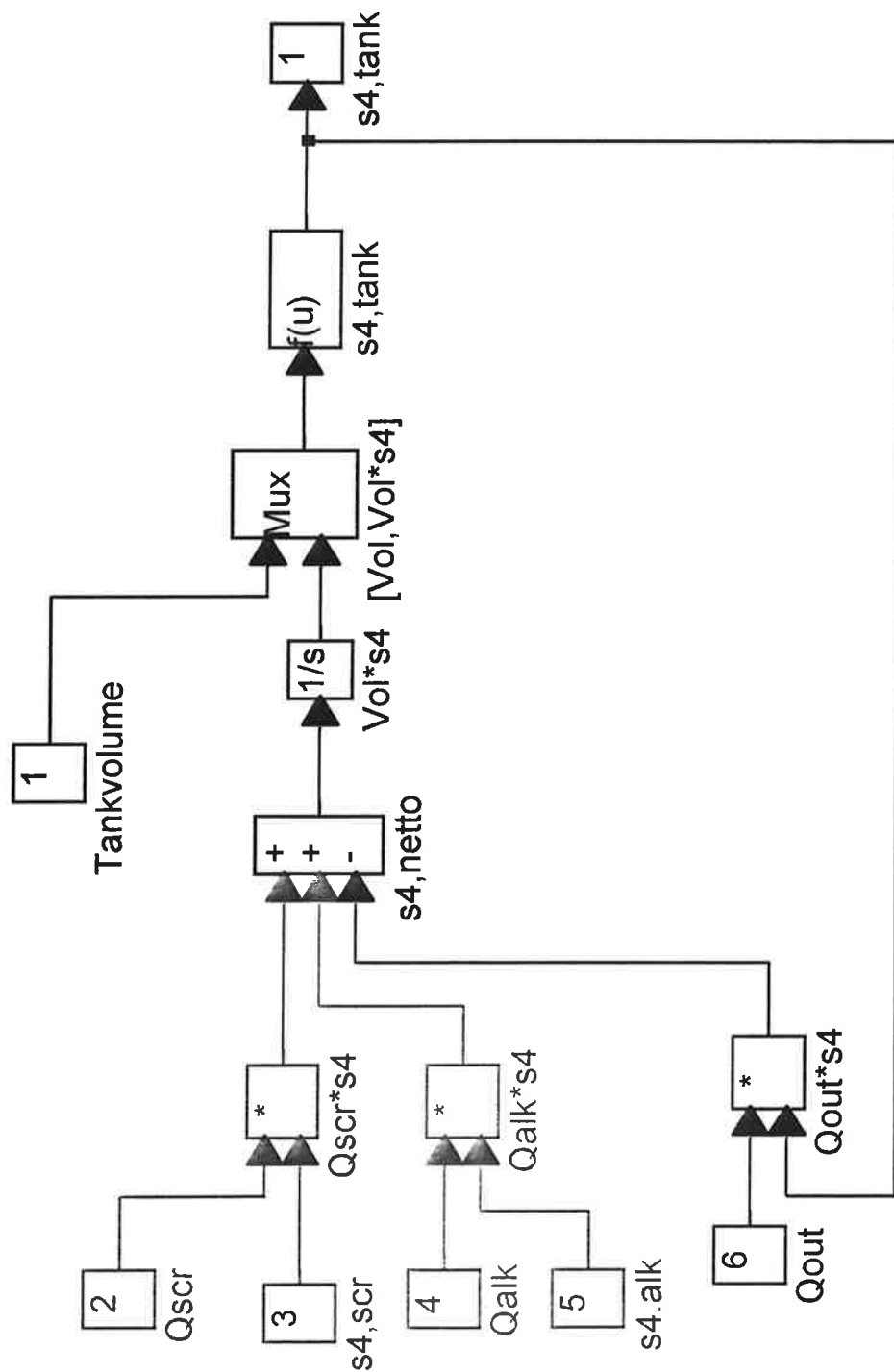
$y(7) = ctot_{ut};$

$y(8) = pH_{ut}(1);$

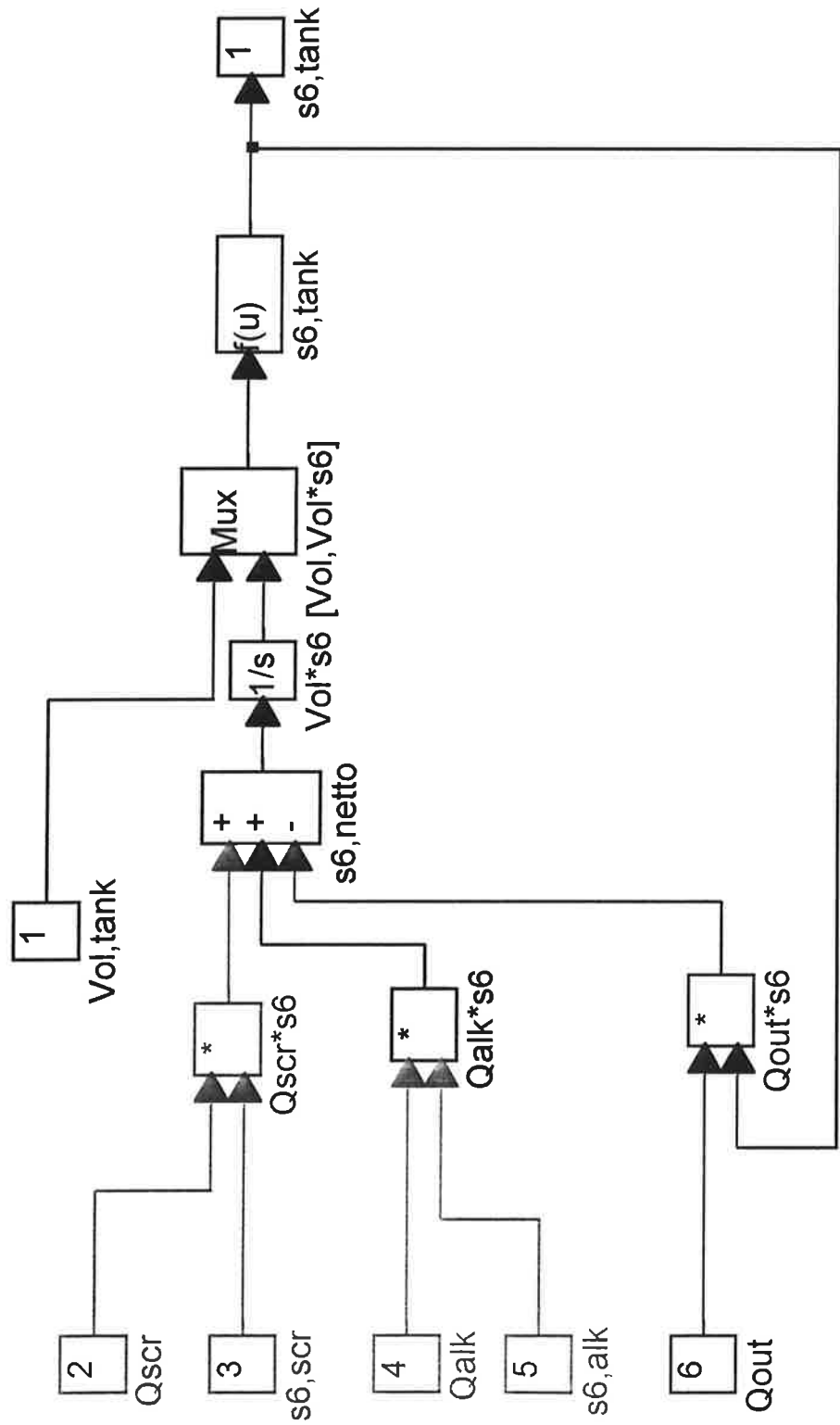
Appendix 6. The tank



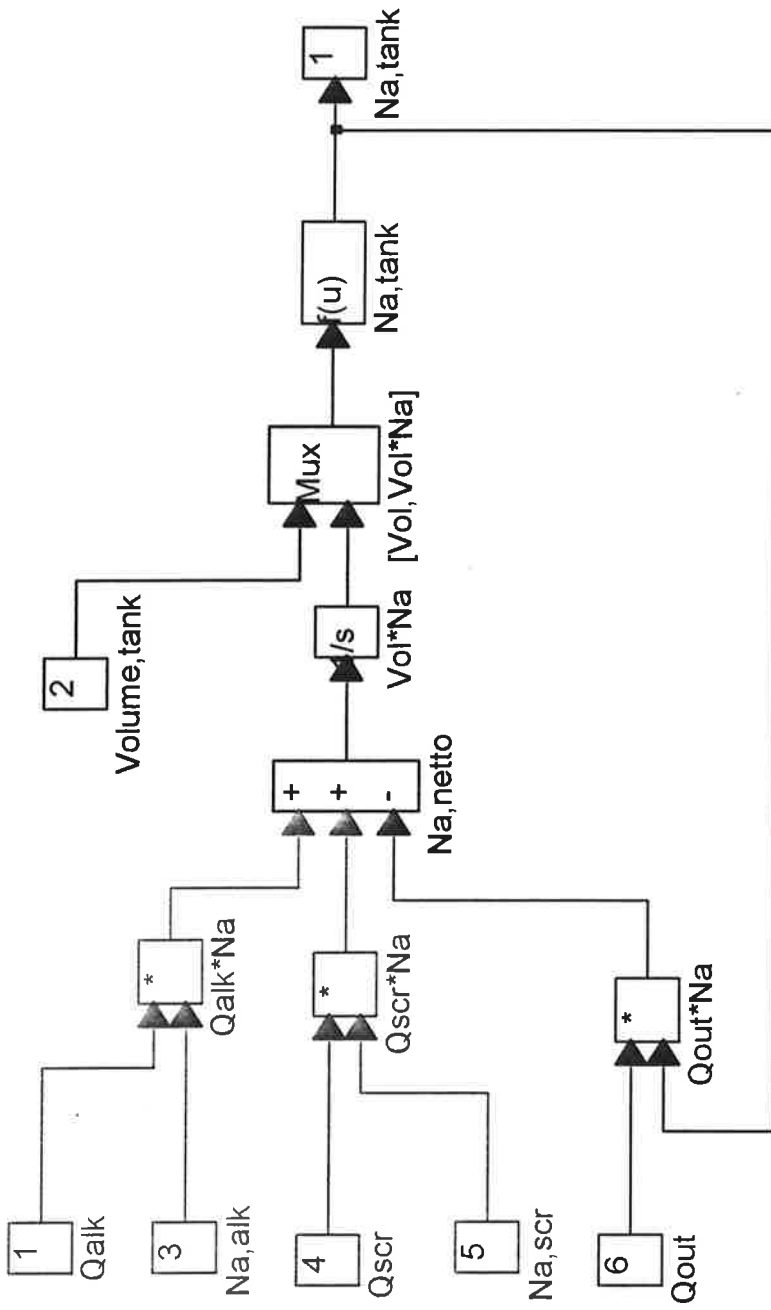
Balance on sulfite



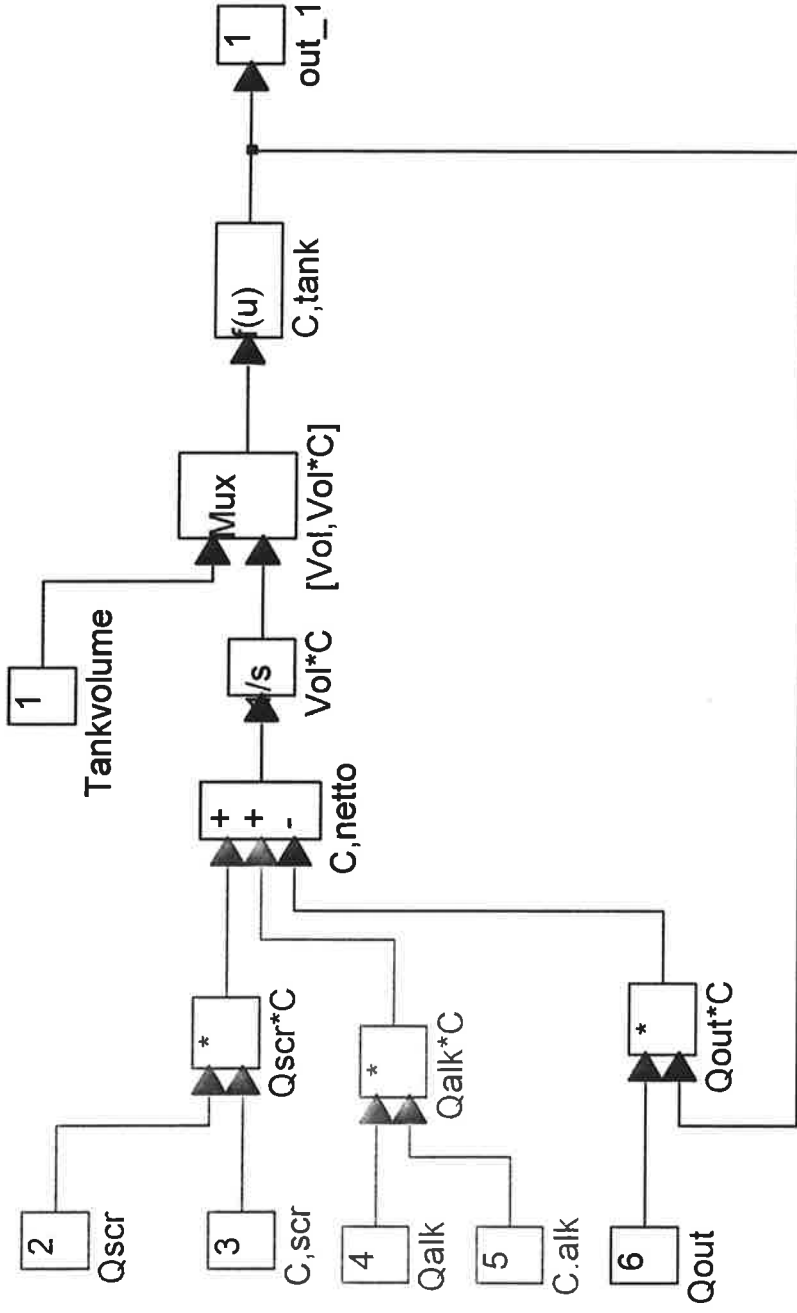
Balance on sulfate



Balance on sodium

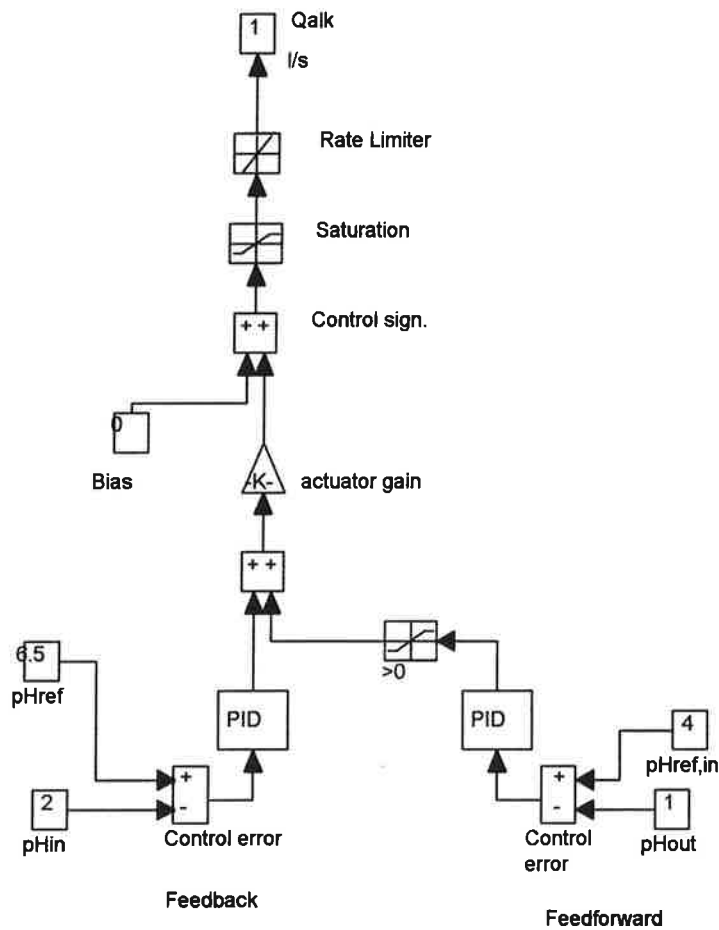


Balance on carbonates

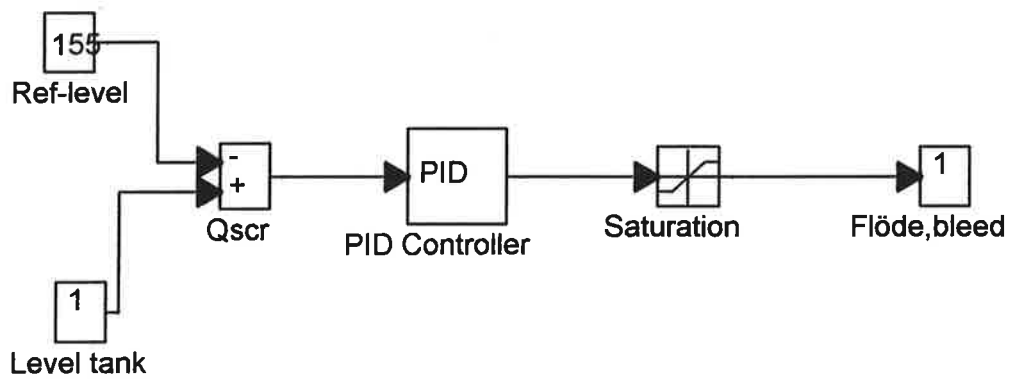


Appendix 7.

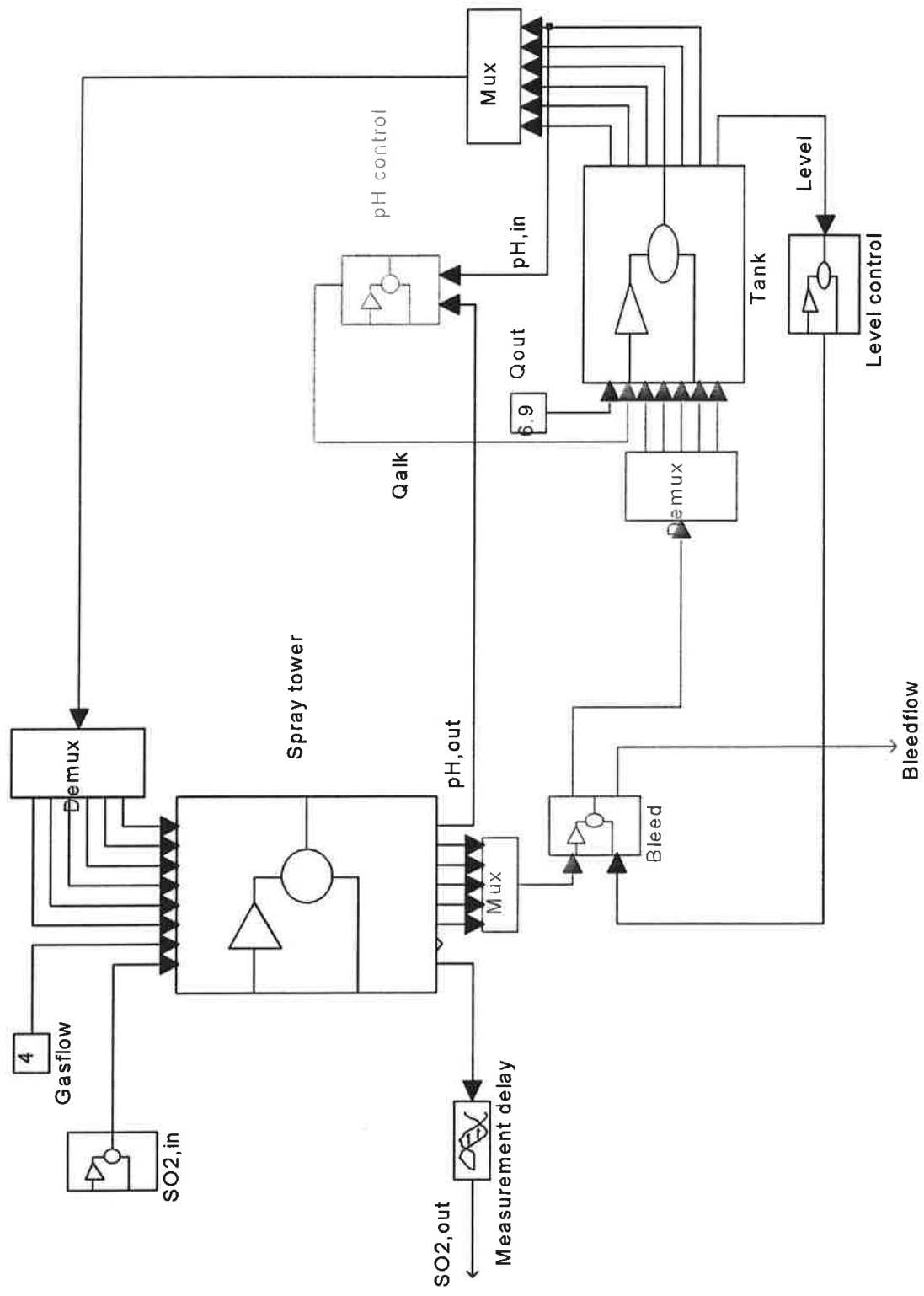
pH control



Level control



Appendix 8.



Appendix 9.

This appendix refers to information that can be found in a technical report at ABB Fläkt Industri AB. The report has number TR V-95.012E.

Appendix 10.

This appendix refers to information that can be found in a technical report at ABB Fläkt Industri AB. The report has number TR V-95.012E.

Appendix 11.

This appendix refers to information that can be found in a technical report at ABB Fläkt Industri AB. The report has number TR V-95.012E.

Appendix 12.

The dynamics of the model is described by equation 28

$$\frac{d}{dt}(V \cdot \bar{c}) = Q_{scr} \cdot \bar{c}_{scr} + Q_{alk} \cdot \bar{c}_{alk} - Q_{out} \cdot \bar{c}$$

Assuming that the level control is good the volume is constant, i.e

$$\frac{d(\bar{c})}{dt} = \frac{Q_{scr}}{V} \cdot \bar{c}_{scr} + \frac{Q_{alk}}{V} \cdot \bar{c}_{alk} - \frac{Q_{out}}{V} \cdot \bar{c}$$

\bar{c}_{scr} is depending on \bar{c} according to the nonlinear function

$$\bar{c}_{scr} = f_{scr}(\bar{c}, G_c)$$

where G_c is the flue gas concentration of SO_2 . Using a Taylor series expansion and truncating after first order terms gives

$$c_{scr} \approx f_{scr}(\bar{c}, G_c) + \left(\frac{\partial f_{scr}}{\partial x} \right) dx + \left(\frac{\partial f_{scr}}{\partial G_c} \right) dG_c \approx x_{scr}^o + B_3 \Delta x + B_4 \Delta G$$

$$B_3 = \begin{bmatrix} \frac{\Delta s4_{scr}}{\Delta x_1} & \frac{\Delta s4_{scr}}{\Delta x_2} & \frac{\Delta s4_{scr}}{\Delta x_3} & \frac{\Delta s4_{scr}}{\Delta x_4} \\ \frac{\Delta s6_{scr}}{\Delta x_1} & \frac{\Delta s6_{scr}}{\Delta x_2} & \frac{\Delta s6_{scr}}{\Delta x_3} & \frac{\Delta s6_{scr}}{\Delta x_4} \\ \frac{\Delta Na_{scr}}{\Delta x_1} & \frac{\Delta Na_{scr}}{\Delta x_2} & \frac{\Delta Na_{scr}}{\Delta x_3} & \frac{\Delta Na_{scr}}{\Delta x_4} \\ \frac{\Delta C_{scr}}{\Delta x_1} & \frac{\Delta C_{scr}}{\Delta x_2} & \frac{\Delta C_{scr}}{\Delta x_3} & \frac{\Delta C_{scr}}{\Delta x_4} \end{bmatrix} \quad B_4 = \begin{bmatrix} \frac{\Delta s4_{scr}}{\Delta G_c} \\ \frac{\Delta s6_{scr}}{\Delta G_c} \\ \frac{\Delta Na_{scr}}{\Delta G_c} \\ \frac{\Delta C_{scr}}{\Delta G_c} \end{bmatrix}$$

x_{scr}^o is the stationary concentrations out from the spray tower and

$\Delta x = [s4 - s4^o, s6 - s6^o, Na - Na^o, C - C^o]^T$ where $s4^o$, $s6^o$, Na^o and C^o are the stationary concentrations. The numerical derivatives in matrices B_3 and B_4 can be evaluated using the MATLAB scrubber function. The pH function can also be evaluated using Taylor series expansion.

$$pH = f(x) \approx f(x^o) + C \cdot \Delta x, \quad C = \begin{bmatrix} \frac{\Delta pH}{\Delta x_1} & \frac{\Delta pH}{\Delta x_2} & \frac{\Delta pH}{\Delta x_3} & \frac{\Delta pH}{\Delta x_4} \end{bmatrix}$$

Changing variables according to

$$y = pH - pH^\circ, u = Q_{\text{alk}} - Q_{\text{alk}}^\circ \text{ and } Z = G_c - G_c^\circ$$

the model can now be written

$$\dot{x} = A_1 \cdot x + B_1 \cdot u + B_2 \cdot (B_3 \cdot x + B_4 \cdot Z) = (A_1 + B_2 \cdot B_3) \cdot x + B_1 \cdot u + B_2 \cdot B_4 \cdot Z$$

$$y = C \cdot x$$

where

$$A_1 = -\frac{Q_{\text{out}}}{V} I$$

$$B_1 = \frac{1}{V} \bar{c}_{\text{alk}}$$

$$B_2 = \frac{Q_{\text{scr}}}{V}$$

Ignoring changes in the flue gas concentration the state space model is obtained

$$\frac{dx}{dt} = Ax + Bu$$

$$y = Cx$$

where

$$A = A_1 + B_2 \cdot B_3$$

$$B = B_1$$

Appendix 13.

```

%      An m-file that calculates the real part and the complex part of
%       $G=G_p*G_c$  and plots the Bode diagram for the open loop system.
%      Uses the state space matrices A,B,C and D and the controller
%      parameters K, Ti and Td. All must be global variables.
%      Uses the function g2 to get the transfer function.

w=logspace(-6,0,1000);
s=w*i;
%Calculate the transfer function for the open loop system

[Gnum,Gden]=g2(A,B,C,D,K,Ti,Td);

%Calculate amplitude and phase for 1000 different points along the imaginary axis.

for m=1:1000
    yAmp(m)=(abs(polyval(Gnum,s(m))/polyval(Gden,s(m)))));
    yfas(m)=angle(polyval(Gnum,s(m))/polyval(Gden,s(m)))*180/pi;
end

%Plot a Bode diagram

subplot(211)
loglog(w,yAmp,'w-');
grid
subplot(212)
semilogx(w,yfas,'w-');
grid

```

```

function [Gnum,Gden] = g2(A,B,C,D,K,Ti,Td)

```

```

%      This function creates the transfer function
%       $G=G_p*G_c$  from the state space description
%       $dx/dt=Ax+Bu$ ,  $y=Cx+Du$  for the process
%      and the controller parameters K,Ti and Td
%      in a PID controller. The result is numerator
%      and denominator polynomials for the transfer function
%      of the open loop system.

```

```

%Transfer function for the process
[num,den]=ss2tf(A,B,C,D);

```

```

%Transfer function for the controller
N=40;

```

```
b1=(Ti*Td+K*Ti*Td/N);  
b2=(Td/N+K*Ti);  
b3=1;  
a1=Td*Ti/N;  
a2=Ti;  
a3=0;  
PIDnum=[b1,b2,b3]*0.083;  
PIDden=[a1,a2,a3];
```

```
%Transfer function for the open loop system.
```

```
n=conv(num,PIDnum);  
d=conv(den,PIDden);  
Gnum=n;  
Gden=d;
```