

Modeling and validation of the milk of lime production process

Janne Kemppainen

School of Electrical Engineering

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Thesis supervisor:

D.Sc.Habil. Robert Tenno

Thesis advisor:

M.Sc. (Tech.) Timo Fagerström

Author: Janne Kemppainen

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Supervisor: D.Sc.Habil. Robert Tenno

Advisor: M.Sc. (Tech.) Timo Fagerström

Quicklime (CaO) is used in its hydrated form ($\text{Ca}(\text{OH})_2$) to control the pH value in chemical processes. The hydrate, milk of lime, is produced by mixing quicklime and water in an exothermic reaction at a weight ratio of approximately 1:4. The production of milk of lime takes place in a stirred tank reactor that is called a lime slaker. A sufficiently high reaction temperature as well as constant mixing are required to produce a good quality hydrate.

In this thesis a first principles model of a lime slaker was derived to model the slaker temperature based on the lime and water addition rates. Perfect mixing and constant heat capacity, density and volume were assumed. The reaction was assumed to be first order and the possible heat losses were not considered.

The resulting model was able to predict the reactor temperature typically within 1 °C from the measured value. The studied slaker was being operated below the industry recommended temperatures and according to the model a better slaking temperature could be obtained by reducing the water addition rate by 15 %.

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Työn valvoja: D.Sc.Habil. Robert Tenno

Työn ohjaaja: M.Sc. (Tech.) Timo Fagerström

Sammutettua kalkkia ($\text{Ca}(\text{OH})_2$) käytetään teollisissa prosesseissa mm. pH-arvon säätelyyn. Kalkinsammutusprosessissa tuotetaan niin kutsuttua kalkkimaitoa syöttämällä poltettua kalkkia (CaO) ja vettä hyvin sekoitettuun säiliöön noin 1:4 massasuhteessa. Reaktio on vahvasti eksoterminen, joten seoksen lämpötila nousee reaktion edetessä, kunnes nousu tasaantuu reaktion loppumisen merkiksi. Hyvälaatuisen kalkkimaidon tuottaminen vaatii riittävän korkean reaktiolämpötilan sekä kunnollisen sekoittamisen.

Tässä työssä kehitettiin ja identifioitiin kalkinsammutusprosessin fysikaalinen malli, jonka tavoitteena oli estimoida reaktorisäiliön lämpötilaa veden ja kalkin annostelumäärien perusteella. Mallinnuksessa oletettiin täydellinen sekoittuminen, ja että reaktorin lämpökapasiteetti, tiheys sekä tilavuus pysyvät vakioina. Lisäksi oletettiin, että kyseessä on ensimmäisen kertaluvun reaktio. Lämpöhäviöitä ei huomioitu.

Identifioitu malli kykenee ennustamaan reaktorin lämpötilan tyypillisesti noin yhden celsiusasteen tarkkuudella. Tutkittua prosessia ajetaan suosituksia alemmilla lämpötiloilla. Mallin perusteella suositellut lämpötilat voisi saavuttaa vähentämällä vedensyöttöä 15 %.

Avainsanat: kalkki, kalkkimaito, kalkin sammutus, mallintaminen

Preface

I want to thank my supervisor Robert Tenno and my advisor Timo Fagerström for their advice and comments during the writing process. Big thanks to Harri Tikkala for providing the data and process knowledge, and to Osmo Vainio for making all of this possible. Finally, I want to thank my parents for their continuous support throughout my studies.

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Janne Kemppainen

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Symbols and abbreviations

Symbols

A	reactor jacket area (m^3)
c	specific heat capacity ($\text{kJ}/(\text{kg K})$)
C	concentration (mol/l), heat capacity (kJ/K)
ΔH	heat of reaction (kJ/mol)
ΔH_f°	enthalpy change under standard conditions (kJ/mol)
ΔE	activation energy (kJ/mol)
F	flow (m^3/h)
k_0	reaction rate constant ($1/\text{s}$)
m	mass (kg)
M	molar mass (g/mol)
n	amount of substance (mol)
Q	amount of heat (kJ)
r	rate of reaction ($\text{mol}/(\text{l s})$)
r_0	initial sphere radius
R	universal gas constant ($\text{J}/(\text{mol K})$)
R_{DIN}	lime reactivity value ($^\circ\text{C}/\text{min}$)
ρ	density (g/cm^3)
SG	specific gravity (g/cm^3)
t	temperature ($^\circ\text{C}$), time (s)
T	temperature (K)
Δt	temperature change ($^\circ\text{C}$)
ΔT	temperature change (K)
U	overall heat transfer coefficient ($\text{W}/(\text{m}^2 \text{K})$)
V	volume (m^3)

Abbreviations

APC	Advanced Process Control
CCD	Counter Current Decantation
CIL	Cyanide in Leach
CSTR	Continuous Stirred Tank Reactor

1 Introduction

Calcium oxide (CaO) and calcium carbonate (CaCO_3), also known as lime and limestone, are versatile substances that have various uses. They have been known to man for thousands of years as limestone was already used as the main building material for pyramids whereas the Greeks used the highly crystalline form of limestone, marble, for statues and decorations. Lime was also adopted early and it found use for example in construction, bleaching linen or glass manufacture, and it was even used for offensive purposes during war. [1, p. 3-4]

Lime, or quicklime is used in the metal industry to prevent steel from oxidizing, in the construction industry as a building material for restoring old buildings, and in the chemical industry to elevate pH or to bleach paper pulp. Environmental uses include water softening, wastewater treatment and flue gas desulfurization. [2] In the context of this thesis lime is used for controlling the pH value in acid neutralization and cyanide leaching processes at a gold refinery.

Use of quicklime in the pH controlling applications requires the hydrated form of lime that is obtained by mixing water and lime in the slaking process. The strongly exothermic slaking reaction releases heat which warms up the mixture and further accelerates the reaction rate. Maintaining the proper reaction temperature is important to keep the quality of the produced hydrate consistent and to obtain good reactivity as this helps to minimize the environmental impact, and ultimately improve the gold yield.

Despite the wide usage of lime slakers in different industries few mathematical models for determining the temperature of a pure lime slaker can be found from the western scientific literature. There are some applications of advanced process control (APC) systems for the causticizing process in the pulp and paper industry that model the slaker dynamics [3–5], but these include the causticizing reactions and are too complicated for our purposes.

More effort has been put towards modeling lime kilns that are used to produce quicklime from limestone. Models for both traditional shaft kilns as well as rotary kilns have been proposed and model based control schemes have been suggested especially for rotary kilns [6–10].

The aim of this work is to create a computer model of a lime slaker to estimate the reaction temperature based on the system inputs. Then, using the derived model the

effects of alternative control inputs are reviewed to find out what input parameters should be used to achieve a desired reactor temperature.

The studied lime slaker is operated in a batch fashion and the lime and water feeds are set to constant rates and controlled in an on/off manner. Therefore it is not possible to change the rate of either inputs from the control system but only set how long they are kept open. Thus we will not consider active temperature control. The model could still be used in the future as a design aid if it is decided that a control valve should be used at the water inlet feed.

This thesis is divided into five parts. Following this introduction the basic theory behind lime and limestone is covered in the second section. This includes the chemical reactions, equipment, production of quicklime, and most importantly, the theory of lime hydration. This information will serve as the basis of our modeling and set the goals for the slaker operation.

The research material and methods are presented in the third section. First, the studied process equipment are shortly described and the available process data are presented. Next, the modeling equations are derived for the reactor tank assuming perfect mixing and constant density of the reactor contents.

The modeling results are analyzed in the fourth section. The parameter estimations and fit to the process data are assessed and the model is validated against a validation data set. The model is also validated against lime reactivity data and the sensitivity to variations in the initial state estimate is checked. Finally a suggestion to change the slaker operation is given and experiments with alternative input sequences are performed. The findings of the thesis are summarized in the fifth section.

This thesis was conducted at ABB for Agnico Eagle Finland Oy. ABB is a global leader in power and automation technologies [11] and Agnico Eagle is a Canadian mining company that operates the Suurikuusikko gold mine and refinery in Kittilä, Finland [12].

2 Background

This section describes the theoretical background of lime and limestone. The chemical and physical properties are presented and the production of quicklime from limestone is shortly introduced. More emphasis is given to the hydration reaction of quicklime and to the factors that affect the lime reactivity. Finally, different industrial slaking equipment and possible control strategies are discussed.

Figure 2.1 illustrates the cycle of lime that contains the reactions of lime and limestone. Limestone is formed of calcium carbonate (CaCO_3) which in high temperatures releases carbon dioxide and forms quicklime (CaO). When quicklime is mixed with water it hydrates to calcium hydroxide (Ca(OH)_2) simultaneously releasing large amounts of heat. Calcium hydroxide can again react with carbon dioxide contained in the air to form calcium carbonate, finishing the cycle.

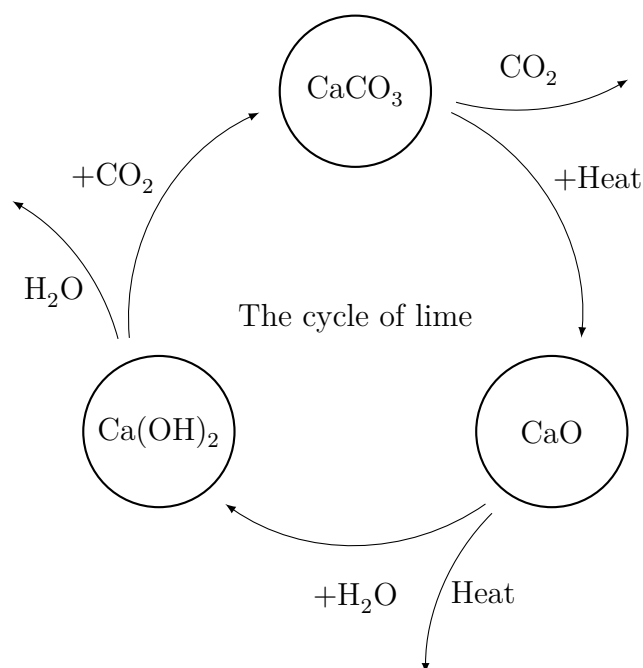


Figure 2.1: Limestone (CaCO_3) releases carbon dioxide (CO_2) at high temperatures and forms quicklime (CaO), which in turn can be hydrated with water to slaked lime (Ca(OH)_2). Slaked lime reacts with CO_2 and forms limestone, finishing the cycle.

2.1 Limestone properties

By definition limestone may be composed of four minerals: [13, p. 7-8]

- Calcite CaCO_3 ,
- Aragonite CaCO_3 ,
- Dolomite $\text{CaMg}(\text{CO}_3)_2$, and
- Magnesite MgCO_3 .

Calcite is the most common of these minerals. The limestones can be classified to two categories, namely high calcium and dolomitic. High calcium contains only calcite or aragonite while pure dolomite is 54.3 % CaCO_3 and 45.7 % MgCO_3 . [13, p. 8-9]

There are many varieties of limestone with different properties and some of those worth mentioning are listed below: [13, p. 9-11]

- *Chalk* is a soft form of calcium carbonate with a small grain size.
- *Dolimitic limestone* in its true form contains 40 to 44 % MgCO_3 and 54 to 58 % CaCO_3 but the name is also used with stones that contain more than 20 % MgCO_3 .
- *High calcium limestone* is mainly composed of calcium carbonate and contains no more than 2-5 % MgCO_3 .
- *Magnesian limestone* contains 5-20 % magnesium carbonate.
- *Marble* is the most beautiful form of limestone. It can be high calcium or dolomitic and due to its structure it is very hard and its surface can be polished smoother than any other stone.

Limestone can contain impurities such as clay, silt and sand. These can be homogeneously mixed within the formation, or be heterogeneously contained in the crevices or between the strata. Silica and alumina are the major impurities and there can also be iron, phosphorus and sulfur contained, but the two latter ones are usually present only in small quantities. Other impurities can be considered as trace elements as their amounts are negligible. [13, p. 18]

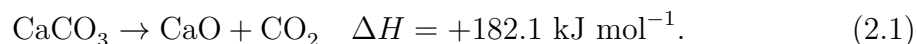
Limestone can contain different amounts of magnesium carbonate. It isn't usually regarded as an impurity unless the application demands a high calcium limestone, and in some cases it can be of equal value with the calcium oxide or it can be

considered as valueless but without adverse effects. The typical requirement of the combined carbonate percentage (calcium and magnesium) is in the range of 95-98 %. [13, p. 19]

The color of pure calcite or magnesite is white but usually even the purest limestones are gray or tan. The gray color is caused by carbonaceous impurities while iron causes the tannish color. All limestones are crystalline but the crystal structures can have large variations resulting in different densities and hardnesses in the stone. Also the porosity of the stone varies greatly as there is typically between 0.3 and 12 % void space in the limestone. [13, p. 20]

2.2 Calcination of limestone

Calcination is the thermal decomposition of limestone into quicklime and carbon dioxide [1, p. 139]. Quicklime is produced with the following endothermic calcination reaction [14]:



Due to the endothermic nature the forward direction of the reaction is favored at high temperatures. The partial pressure of CO_2 in the gas at the limestone surface has to be lower than the temperature dependent decomposition pressure of CaCO_3 for the reaction to proceed. As the reaction releases CO_2 the decomposition of bulky samples can be inhibited due to local high concentrations of CO_2 . [14] The decomposition pressure reaches the atmospheric pressure at approximately 900 °C. [1, p. 140]

The two basic designs for calcination equipment are the shaft kiln and the rotary kiln. In a normal shaft kiln limestone is continuously fed from the top to the kiln and air and fuel are supplied in the middle to the calcining zone. After passing through the cooling zone the end product is collected at the bottom of the kiln. More complicated versions of the shaft kiln can employ inclined walls, multiple chambers or an annular shaft. [6]

The rotary kiln has a long rotating cylinder that is inclined at an angle of 3 to 4°. Limestone is fed from the upper part of the 110 to 140 m long cylinder and fuel and combustion air are supplied from the lower end. Quicklime is gathered at the end and heat from the hot quicklime is used to raise the temperature of the combustion air. [1, p. 176]

The rotary kiln is easier to control and it can produce a wider range of reactivities and lower CaCO_3 concentrations than a shaft kiln. However, shaft kilns can obtain a lower variability of the product reactivity. [1, p. 177]

The final quality of the quicklime depends on the calcination process conditions as well as on the quality of the limestone feed. More porous limestones seem to maintain the structure and produce more porous quicklime. Increasing the process temperature increases the pore radii while the smaller pores are eliminated. Therefore, lower calcination temperatures can yield a more reactive quicklime. [15]

2.3 Properties of quicklime

Quicklime is typically a white-colored micro-crystalline substance that appears to be amorphous under visual inspection. Impurities such as iron and manganese can cause a grey, brown or yellow tint and if solid fuel was used in the production process the surface can have a colored coating. It has an earthy odour. [1, p. 117]

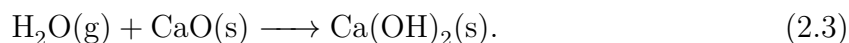
The porosity of the quicklime depends both on the porosity of the limestone as well as on the production process. The volumetrical porosity can reach up to 55 % if porous limestone is burned lightly. In higher temperatures sintering can reduce the porosity to 25 % and in the case of a dead-burned lime it can drop to about 10 %. Different porosities give varying apparent densities for the quicklimes. The mean apparent density of a lime correlates with its reactivity to water. [1, p. 117-118]

Quicklime and calcined dolomite have high melting points so they are refractory substances. They both tend to react with liquid and gaseous water to produce hydroxides. Quicklime is highly reactive with water and it should be properly protected to maintain the chemical properties. [1, p. 119, 221]

Quicklime can react with carbon dioxide, but only at temperatures between 300 and 800 °C. This can happen at the cooling zone at the end of a lime kiln during abnormal operation and it causes the surface of the particles to be carbonated, yielding a less reactive quicklime. [1, p. 122]

In practical situations the reaction with CO_2 can also proceed under ambient conditions if the lime has had contact with atmospheric moisture and it has been partly hydrated. The formation of calcium carbonate from calcium hydroxide releases water that is again available to hydrate the remaining lime particles to keep the reaction going on until the lime has been fully converted. Even relatively low amounts of

reacted quicklime can reduce the overall reactivity significantly. The reactions go as follows: [1, p. 121]



The impurities in quicklime often originate from the limestone it has been produced from. In high-calcium quicklimes the major impurity is calcium carbonate and depending on the application it can be considered as an inert or an active substance. Similarly magnesium oxide is not harmful in steel production but levels above 2 to 5 % can prevent the lime's usage in other applications. [1, p. 122]

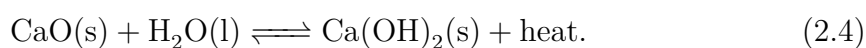
Silicon, aluminium, iron and sulfur can often be found in the limestone but their amounts in the quicklime can be higher if solid fuel is used in the production process. The amounts of trace elements depend on the concentrations in the limestone and high amounts of toxic substances can prevent the lime's usage for example in drinking water treatment. [1, p. 122]

2.4 Lime hydration

Quicklime can be hydrated by mixing it with water which causes an exothermic chemical reaction. This is also called lime slaking. In this section the chemical background as well as the different properties of the lime hydration process are described.

Chemical reaction

High calcium quicklime and water have the following reaction: [13, p. 325]



The enthalpy change ΔH_f° of the reaction under standard conditions can be calculated using the formation temperatures of the reactants and products as follows: [16, p. 115]

$$\Delta H_f^\circ(\text{reaction}) = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \quad (2.5)$$

Table 2.1: Standard enthalpies of the reactants and products. [17, p. 140]

Name	Formula	ΔH° (kJ · mol ⁻¹)
calcium oxide	CaO(s)	-635.5
calcium hydroxide	Ca(OH) ₂ (s)	-986.6
water	H ₂ O(l)	-285.8

Table 2.2: The relative atomic masses of the elements in the reaction. [17, p. 167]

Name	Symbol	Relative atomic mass
Hydrogen	H	1.008
Oxygen	O	16.00
Calcium	Ca	40.08

The standard enthalpies of formation of the compounds in the reaction are listed in Table 2.1. Using these values the enthalpy change in the reaction can be calculated as

$$\Delta H_f^\circ = -986.6 - (-635.5 - 285.8) = -65.3 \text{ kJ} \cdot \text{mol}^{-1}. \quad (2.6)$$

Therefore, when one mole of calcium oxide reacts with water 65.3 kJ of energy is released in the chemical reaction. This causes a temperature rise in the mixture that can be theoretically calculated when it is assumed that there is no heat loss to the environment and the reaction is perfect.

The relative atomic masses of the elements are listed in Table 2.2. With these values calcium oxide (CaO) has a mass of 56.08, water (H₂O) 18.016 and calcium hydroxide (Ca(OH)₂) 74.096. Therefore, theoretically in a perfect reaction 75.7 % of the weight in the calcium hydroxide comes from calcium oxide and the rest 24.3 % comes from the added water. However, practically some amount of excess water is required as part of it evaporates due to the heat of the reaction or becomes adsorbed as free water around the hydrate particles [13, p. 327].

Due to the loss of water the theoretical amount of water would lead to an incomplete hydration and unstability of the hydrate as there would still be oxides left within the hydroxides. For a complete hydration reaction of an average quicklime the amount of added water should be at least 52 % of the solid weight of the lime. The exact minimum amount depends on the quality and purity of the quicklime. [13, p. 327]

Hydrated forms of lime

The hydrated forms of lime can be grouped depending on the amount of excess water they contain: [13, p. 327-329]

- *Dry hydrate* contains the least excess water as it is produced by adding only the amount of water that is needed for the hydration reaction and the loss of water through evaporation. Typically in the making of dry hydrate one part of weight of quicklime is mixed with 0.5-0.75 parts of water.
- *Putty* is a wet plastic form that can be molded. It contains 30-45 % of free water and can be produced by adding 1-1.4 parts water by weight to 1 part of quicklime, or by adding water to dry hydrate. Thorough mixing is important to obtain a homogenous putty.
- *Slurry* can be described as having the consistency of a thick cream. Compared to putty it will flow and it is pumpable. Slurry contains approximately 60-73 % free water and is usually produced by adding one part of quicklime to two parts of water or adding water to a putty.
- *Milk of lime* is thinner than slurry and its consistency can be compared to whole milk. The concentration can vary greatly, the typical amount of lime solids is between one and twenty percent. It can be prepared by mixing quicklime and water in ratios from 1:3 to 1:4.5 at temperatures of approximately 65 °C to 80 °C. Often it is prepared by diluting a slurry, putty or dry hydrate.
- *Lime water* is a saturated or unsaturated solution of calcium in water. The solubility of calcium decreases with increased temperature.
- *Air-slaked* lime is produced when moisture in the air comes into contact with the quicklime and a slow hydration reaction starts. Simultaneously CO_2 from the atmosphere is absorbed which results the air-slaked lime to be a mixture of hydroxides, oxides and carbonates.

Hydration rate

The rate of the hydration reaction depends on various properties and conditions of the process. Much of the variation rates of hydration and the final physical properties of hydrates depend on the used quicklime, whose quality in turn is dependent on the limestone it has been produced from. The optimal hydration conditions must be

tested empirically for each quicklime source and the instructions from the manufacturer should be followed to achieve a good quality. It may be needed to accelerate or slow down the reaction to have certain properties required by the customer. [13, p. 329]

Highly reactive high calcium slakes fast and produces a lot of heat and turbulence in the water. On the other hand hard-burned high calcium or dolomitic limes have slower hydration reactions. Depending on the lime quality the reaction can occur in seconds or it can take hours or even months. Especially overburned, recarbonated, impure or hydraulic lime can require a long time to hydrate. [13, p.332] The soft-burned porous limes react more rapidly as the water molecules are able to penetrate the particles more easily and the steam produced by the reaction heat breaks the structures to even smaller particles [18].

In addition, the following factors influence the rate of reaction: [13, p. 332-334]

- *Purity.* High lime purity increases the reaction speed. Impurities in the lime clog the pores or they can partially coat the particles and therefore block the water contact.
- *MgO content.* Higher contents of magnesium oxide cause slower reaction rates.
- *Size.* A fine particle size results in a faster slaking process compared to a more coarse lime feed.
- *Temperature.* The reaction rate is increased in higher temperatures and for some limes it is doubled when the water temperature is increased by 10 °C. For many limes the peak of the reaction rate is obtained with steam.
- *Amount of water.* Adding more water reduces the rate of hydration and the produced heat.
- *Agitation.* Mixing of the lime and water mixture helps to break the particles and increases the reaction rate significantly.
- *Air-slaked.* Partial air-slaking or recarbonation of the quicklime makes the reaction sluggish.

The reaction starts fast when the lime and water make contact and the temperature jumps instantaneously. After the initial jump the temperature rises until it plateaus indicating that the reaction is complete. [13, p. 334]

Fast addition of a large amount of excess water to lump or pebble quicklime can cause so called drowning where the lime becomes hydrated on the surface but the

water does not penetrate to the inside of the particle. With too much water the initial temperature rise is not enough to break the particles to smaller pieces which can cause delayed or incomplete hydration. [13, p. 334]

With too little added water the temperature can rise too high and cause so called burning of the hydrate. This means that some of the hydrated lime can become unhydrated again. The crystal structure of the particles may stay intact and the hydrated surface can prevent the interior from hydrating and as a result the structure is coarser than in a normal dry hydrate. [13, p. 334]

Particle size and specific surface

The surface area as well as the particle size and gradation of the calcium hydroxide particles depend on the process conditions during slaking and the qualities of the quicklime. In most cases fine particle size with a restricted size distribution is preferred. [13, p. 338] Higher surface area is desirable as it correlates with better efficiency and lower lime consumption requirements. [19]

Lime hydroxides are only slightly soluble in water, but still a hundred times more soluble than limestone. The solubility decreases in higher temperatures and it follows a straight line ranging from 1.4 g CaO/l at 0 °C to 0.5 g at 100 °C. In acid neutralization the lime ionizes into Ca^{2+} and OH^- ions that form calcium salts with the acid ions that have a negative charge. As salt is being formed the excess lime dissolves until all of it has been consumed or the acid has been neutralized. [20]

The surface area of the solid lime particles is the most important factor affecting the utilization of the lime slurry and it depends on the porosity and the shape of the solid particles. The importance of high surface area is due to the fact that ionization only happens on the solution interface of the particle. [20] This means that the slaking conditions should be designed such that a large surface area is obtained.

Generally, the knowledge and experience of the slaker equipment manufacturers should be utilized to produce good quality lime. Typically quicklime and water are added at controlled rates to achieve a high slaking temperature and a desired slurry density. [20] It has been suggested that dispersion of the hydrate particles is improved when a large amount of excess water is used which leads to smaller particle size and slower settling qualities. If too little water is used the fine hydrate particles will agglomerate into coarse particles that have a lower chemical reactivity. [13, p. 340]

Despite the larger amount of water the reaction temperature should be maintained at a reasonably high level and the mixture should be thoroughly agitated to achieve fine particle sizes. There is some disagreement on the optimal temperature but for wet slaking the typical recommendation is about 71-93 °C. [13, p. 340] The requirements for excess water and reaction temperature are somewhat conflicting as adding more cold water will inexorably cool down the reaction.

In his paper from 1926 Whitman studied hydrates that were produced under different conditions. His first observation was that the use of excess water resulted in much finer particle sizes than with the theoretical water amount or vapor. Further increasing the excess water amount decreased the particle size a little. He also observed that boiling increased fineness notably, and that agitation is needed to produce a fine final product as it prevents the crystals from clustering. [21]

Whitman concludes that rapid hydration results in fine particles as the chances for agglomeration or crystal growth are reduced. He also suggests that the addition of excess water has three effects: [21]

1. individual crystals are separated which reduces agglomeration and prevents the crystals from growing,
2. local overheating is prevented and
3. the rate of hydration is increased at the presence of excess water at all temperatures.

Increasing the reaction temperature accelerates lime hydration without increasing crystal growth correspondingly which leads to smaller individual crystals. High temperature also prevents the crystals from agglomerating into larger particles. [21]

Higher temperatures can have an opposite effect when only little excess water is used as the reaction heat is transferred to a mass of a low heat capacity, causing a rapid rise in temperature and eventually overheating the particle. At temperatures above 547 °C the hydration reaction does not happen at atmospheric pressure anymore and the hydrated lime will start to lose water and dehydrate. As the temperature approaches the dehydration temperature the hydration reaction becomes slower and the rate depends largely on the heat loss which can be quite slow in larger lumps of quicklime. This results in larger particles and eventually worse product quality. [21]

Another significant factor is the purity of the process water. Recycled or polluted water may contain accelerators or retarders that affect the hydration reaction. Accelerators

are ions that form soluble salts with calcium whereas retarders form insoluble compounds. For example sulfite or sulfate ions may react on the surface of the lime particles and block water from penetrating thus leading to an incomplete hydration reaction. However, when slurry is diluted after slaking the presence of retarders in the dilution water has a very minimal effect. This is why the effect of retarders doesn't need to be considered when preparing slurry from dry hydrated lime. [20]

Slaking temperature

As already mentioned, higher temperatures tend to make the reaction occur faster and yield smaller particle sizes. In laboratory tests it has been shown that using hot water in the slaking process increases the temperature rise and reduces the size of the hydrated lime particles [22].

In practice there is no need to use heated water as this can actually decrease the quality of the slurry. In laboratory tests the dry lime is added directly to the hot water thus increasing the reactivity. In practical applications the water feed is mixed with the hot slurry so the added lime doesn't come to direct contact with the raw water feed, effectively giving the same result. However, if heated water is used the slurry may start boiling which can cause operational and safety problems. Therefore more water is needed and the resulting slurry will be thinner which may be unwanted. Heating of the water feed may be necessary when the slaker is run significantly below its full rated capacity. [22]

In 1960 Miller [23] studied the reaction between calcium oxide and water. He calculated the theoretical temperature rise with different water-to-lime ratios followed by experimental results. The theoretical temperatures with different water-to-lime ratios can be calculated by using the specific heat capacities of calcium hydroxide and water and by distributing the heat of the reaction between the produced calcium hydroxide and the excess water. The practical temperatures were naturally systematically lower than the theoretical temperatures as Miller didn't account for the radiation losses in the theoretical results.

Miller compared the settling time, specific surface and viscosity of samples of slaked lime that were produced with different starting temperatures and water-to-lime ratios. He concluded that generally high temperatures and low ratios of water produced higher specific surfaces. This is true especially with lower initial water temperatures as a smaller amount of water will result in a higher final temperature. With higher

initial temperatures the variation of specific surfaces was small with all ratios. [23]

2.5 Slaking equipment

Different types of slaking equipment are available to produce various qualities of slaked lime. The main differences of the slaker types are the designed water-to-lime ratio and the choice between continuous or batch production. Common to all slaking equipment there is some sort of an agitated vessel with controlled water and lime feeds and temperature monitoring.

A slaker has three basic requirements for its operation, namely (1) the ability to mix a correct amount of water and quicklime, (2) hydrate the quicklime, (3) and separate any impurities or grit from the final product, the calcium hydroxide slurry. [18] The addition of water and lime should be uniform and continuous with enough time for the particles to come into contact and hydrate completely. The ability to remove grit from the suspension improves the product quality but also protects the pumps and tanks against abrasion. [13, p. 363]

A short overview of available slaking equipment is given below.

Slurry slaker

A slurry slaker, also called detention type slaker, operates with a lime-to-water ratio of 1:3.3 to 1:5 and it typically comprises of two chambers where the slurry is transferred by gravity from one chamber to the other. The water and quicklime are mixed in the first chamber where the slaking reaction occurs. The second chamber is used to remove the grit by adding cold water which decreases the slurry viscosity and lets the grit settle at the bottom to be collected away. [18]

At full rated capacity the retention time of such slakers is usually ten minutes. This means that a particle entering the slaker spends ten minutes on average in the first chamber before exiting to the grit removing chamber. It is the most common type used in Europe and the USA. [18]

Paste slaker

Paste slakers operate with a lower lime-to-water ratio of 1 to 2.5 which results in a paste form of the slaked lime. Horizontal rotating paddles need to be used to push the paste towards the discharge point because it is too thick to flow gravitationally. After exiting the slaker the paste is diluted for grit separation. [18]

Paste slakers use less water which means that heat is generated more rapidly and the slaking is accelerated. Faster slaking allows for a more compact design for the same full rated capacity when compared to slurry slakers. [13, p. 363] Paste slakers are mainly used in the USA. [18]

Ball mill slaker

Ball mill slakers are derived from ball mills that were designed for wet and dry grinding. They are used when the required capacity is large, no grit discharge is allowed or the amount of sulfites or sulfates is too high in the slaking water for regular slakers. They are more expensive than the other types of slakers. [18]

Batch slaker

Batch slakers are similar to slurry slakers but they are operated in batches. First the required water and lime amounts are calculated. At the start of the batch the calculated amount of cold water is added to the reactor tank. Then the quicklime is added and the mixture is agitated until it reaches a preset temperature. The slurry is moved to a second tank to be used or for grit removal. [18]

After emptying the tank water is added and the slaker is put to standby mode waiting for the next batch cycle. The batch slaker is used when a continuous slaker can't be used and lime slurry is needed periodically in small batches. [18]

2.6 Control of the slaking process

The available literature on controlling and optimizing the slaking process is rather scarce. Hassibi [18] emphasized that the reaction temperature has the largest impact on the specific surface of the hydrate. He proposed that the optimal way to operate a slaker would be to use the lime-to-water ratio to control the reaction temperature.

Attempting to maintain a constant lime-to-water ratio or slurry consistency would result in larger quality variations due to the variability of the lime reactivity and the incoming water and lime temperatures. [18]

According to Boynton, the process temperature should generally be maintained below the boiling point but above 82 °C. The most precise control of the slaking temperature can be obtained with a thick slurry suspension or a thin putty which would correspond to a water-to-lime ratio of 3:1 \pm 25 %. In a continuous slaker a thermostatically controlled water valve that responds to a 2.5 °C temperature change can be used to maintain the proper temperature. The concentration of the suspension can be verified with a hydrometer. [13, p. 360-361]

Attard [24] described the operation of a batch slaker. In the described batch slaker warm or hot water is first added to the reactor tank and its temperature is measured. Depending on the water temperature a lime-to-water ratio is selected using predetermined rules and the necessary amount of water is added. Then the lime feed screw is operated until the desired combined weight is reached. The slaking timer is started and after it has expired the final slaking temperature is measured. An alarm is displayed if the temperature is below a threshold value. Finally the product is diluted to the final dilution weight and discharged.

The batch slaker described by Attard is based purely on pre-calculating the required amounts and mixing the contents for a predetermined time, and there is no on-line temperature control. Still, the batch slaking system was a vast improvement over the previous equipment. Some initial problems were experienced when the high water starting temperature resulted in boiling during the first thirty seconds of the batch. Also, the lack of grit removal caused some problems but this was solved by using finer lime. [24]

3 Research material and methods

3.1 Kittilä gold mine

Located in Lapland, Northern Finland the Kittilä gold mine site is one of the largest gold deposits and the largest gold mine in Europe. It is operated by the Canadian mining company Agnico Eagle Mines Limited that acquired it in 2005. Annually about 6,000 kg of gold is extracted from 1.4 million tonnes of ore. Currently the ore reserves are estimated to last until 2036 but this can be extended if new deposits are found by exploration. The mine has 400 employees and over 100 contractor personnel. [12]

The Suurikuusikko gold deposit was discovered already in 1986, yet mining began with two open pits "Suuri" and "Roura" in 2008. After 2012 mining has only taken place underground. [12]

The mineral is processed on-site at the local mineral processing plant. Because the ore is refractory, i.e., the gold is locked inside sulphide mineral grains it is challenging to process. Cyanidation is the only economically viable option to process such ore. [12]

Mineral processing plant overview

Figure 3.1 describes the overall process of the Kittilä gold mine. The refining process starts with crushing of the large ore particles to a smaller size in the jaw crusher. The feed is forwarded to the semi-autogenous grinding (SAG) mill where the wetted ore is grinded with the help of metal balls inside the mill. The particles that are small enough are captured by the cyclones and the ones that are too heavy are returned to the SAG mill. The goal of the grinding is to have 75 % of the particles to be smaller than $75\mu m$.

Next, there are two phases of flotation. In a flotation cell air is blown into a mixer which generates small bubbles. Hydrophobic particles attach to these bubbles and they can be collected from the overflowing foam. The other particles sink to the bottom of the cell and are collected from there. The properties of the foam and the selectivity of the flotation can be adjusted with special additives as well as air flow and agitation speed.

In carbon flotation organic carbon is separated from the ore as it has a negative

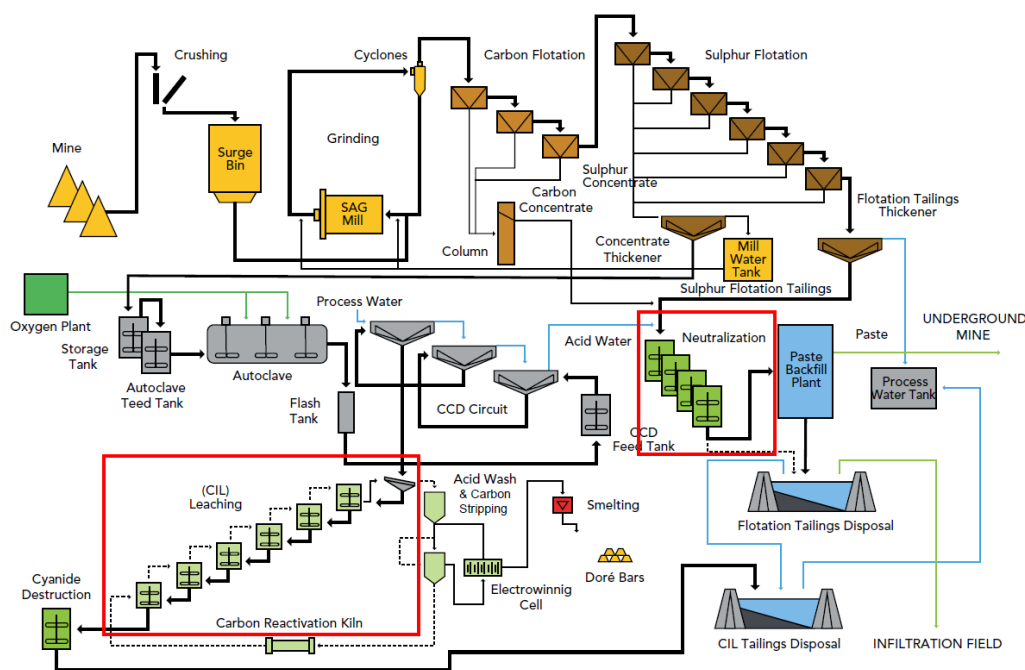


Figure 3.1: Process flow of the Kittilä gold mine. The produced milk of lime is used in the cyanide leaching and acid neutralization processes (highlighted red). [12]

effect in later processes. The overflow of the flotation is forwarded to the sulphur flotation cells.

The gold is encapsulated within the sulphide mineral phase so in sulphur flotation the sulphur concentrate is taken for further processing. The overflowed flotation tailings are neutralized with quicklime and treated in the paste backfill plant to produce paste that is used to fill the empty stopes in the mine. [12]

The concentrate is thickened and washed from chloride before it is fed to the autoclave where the sulphur structures are oxidized in high pressure and in a temperature of 200 °C. Because of the added oxygen the sulphide minerals burn and disintegrate and the gold inside them is freed. [12]

In the counter current decantation (CCD) process the percent solids in the slurry is increased and the concentrate is washed with a stream of water in the opposing direction.

In the carbon in leach (CIL) circuit gold is leached from a solid matrix with cyanide to form a gold cyanide complex. At the same time activated carbon is used for adsorption of the gold cyanide complex from the slurry. The simultaneous leach and adsorption minimises the so-called preg robbing where the gold attaches to natural

absorptive carbon instead of the active carbon. [25] The granules of activated carbon where the gold has been attached are collected by sieving from the slurry. [12]

The gold is gathered in the electrowinning cell and then smelted to doré bars that contain 92-95 % gold. The remaining slurry that is rich in cyanide is oxidated to a non-harmful form before being disposed of to the CIL tailings pond. [12]

Lime usage in the plant

The mineral processing plant has its own lime slaking equipment to produce milk of lime that is used in two locations, namely in the cyanide leaching and neutralization processes to control the pH value. As the price of lime is relatively low, the possible decrease in lime consumption is not the driving factor to optimize the production process but the indirect benefits are gained from increased safety, more consistent operation, larger throughput and reduced environmental stress in the leaching and neutralization processes.

Especially the cyanide leaching plant requires good quality milk of lime as the process pH control is critical for safety. During normal operation the pH value is kept between 9 and 9.5. The flows in the process are large, so the pH value can change fast if the lime of milk is not working properly. If the pH value of the NaCN solution drops to 7 extremely toxic hydrogen cyanide gas (HCN) starts to form. On the other hand, if the pH is too high the chemical SMBS that is used to destroy the cyanide ceases to work properly and the dosage has to be increased which is expensive.

Neutralization is the last phase of the process. Anything that leaves the neutralization plant is directed to flotation tailings disposal and from there to the infiltration field and eventually to the surrounding environment. Therefore a malfunctioning neutralization process can cause acidification of nature.

3.2 Process and equipment description

A simplified schematic of the slaking process is shown in Figure 3.2. The main components of the system are the CaO storage silo and two reactor tanks. Lime is added with a screw conveyor and fresh water is supplied with appropriate piping and valves.

The process is operated in a batch fashion. At the beginning of the sequence the

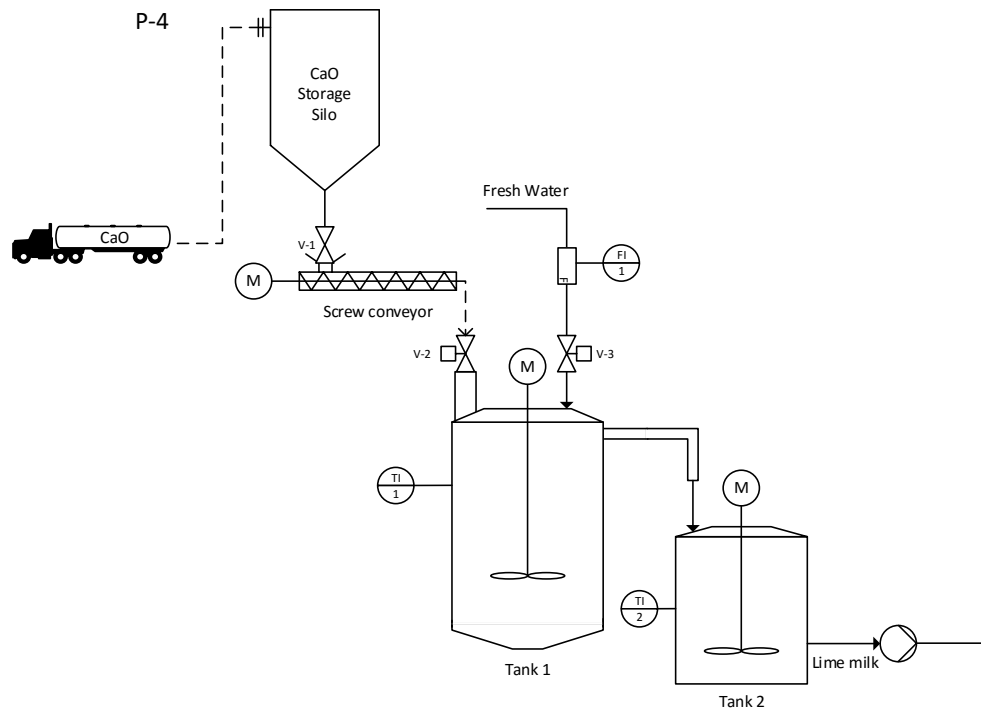


Figure 3.2: Simplified schematic of the milk of lime production process.

binary water inlet valve opens, the screw conveyor starts adding lime and the agitator starts mixing. The amount of water is measured with a flow meter and the screw conveyor is operated for a preconfigured time. The CaO storage silo has weighing equipment so the amount of added lime can be verified. After the reactants have been added a washing sequence starts where the lime feed shut-off valve is rinsed to prevent blockage. After every fifth batch cycle a valve at the bottom of the tank is momentarily opened to dispose of the solids that have not been dissolved such as sand. A new batch sequence starts when the washing sequence is finished and the level of the second tank is low enough.

The transport of the mixture from the reactor tank to the dilution tank happens on an overflow basis. The first tank has internal piping that prevents the raw water and lime feeds from directly overflowing as the outflow needs to reach the bottom of the tank before exiting.

The volume of the mixing tank is 21 m^3 and in one batch approximately one tonne of lime and four tonnes of water are added. Therefore each batch replaces approximately 20 – 25 % of the reactor contents.

3.3 Lime reactivity testing

Different limes can have various reactivities depending on their origin and the production process. Reactivity testing is needed to verify that the lime sample has the needed properties for its application. A standard reactivity testing procedure and apparatus has been described in the European standard EN 459-2:2010 [26] and the determination of the chemical properties, constituents and trace elements has been described in the standard EN 12485:2010 [27].

Proper handling of the lime sample is essential to obtain correct results as the reactivity of the sample can be changed in the presence of moisture and carbon dioxide from the atmosphere. [1, p. 199]

The reactivity test describes how fast the lime reacts with water. A reactivity value R_{DIN} ($^{\circ}\text{C}/\text{min}$) classifies the lime's reactivity as: [28]

- $R_{\text{DIN}} > 30$: highly reactive lime,
- $10 < R_{\text{DIN}} < 30$: reactive lime,
- $R_{\text{DIN}} < 10$: unreactive lime.

The standard testing apparatus consists of a heat insulated Dewar vessel, stirrer motor, stand and support, blade stirrer, lid and a calibrated thermometer. In the test procedure the Dewar vessel is filled with 600 ± 1 g of distilled water at 20°C . A sample of 150 ± 0.5 g of lime is weighed and added all at once while the stirrer is running. The temperature is measured periodically and the wet slaking curve can be drawn. The result is the time that is required for the mixture to reach a temperature of 60°C . [26]

The R_{DIN} value can be calculated by dividing the temperature rise of 40°C by the time in minutes that was required for the temperature rise to occur. [28] The R_{DIN} value therefore describes the rate of the temperature rise as degrees per minute during the initial reaction.

Samples of lime taken on different days were analyzed by measuring the time it takes for the temperature to rise by forty degrees. Also the final temperatures were recorded. The raw data is included in Appendix A.

The R_{DIN} values were calculated for each sample and they are plotted in Figure 3.3. The measurements indicate that the used lime is in the lower end of the reactivity scale. The values are typically in the range of 10 to $17^{\circ}\text{C}/\text{min}$ but the last four

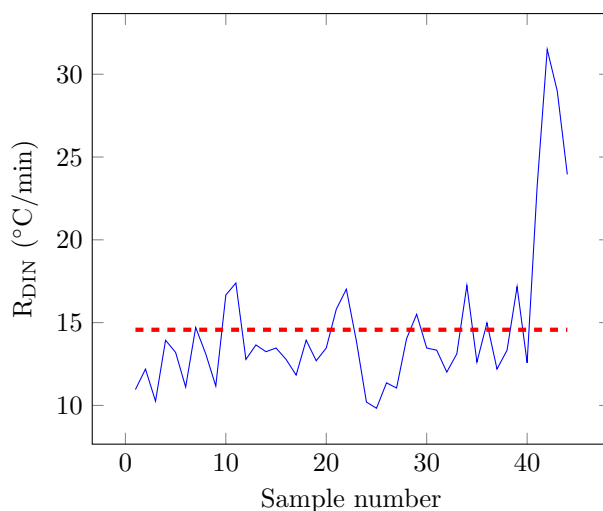


Figure 3.3: Lime reactivity rates of 44 samples taken during September and October 2015 (blue) and their mean (red).

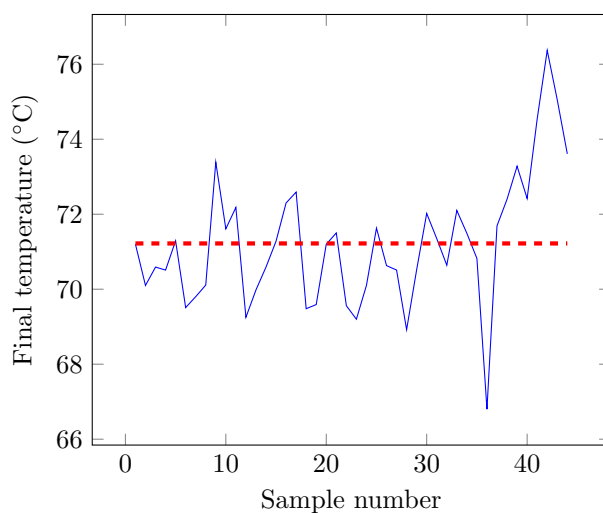


Figure 3.4: Final slaking temperatures of 44 samples taken during September and October 2015 (blue) and their mean (red).

samples show noticeably greater reactivity. The mean reactivity value of this data set is 14.6 °C/min.

The final slaking temperatures of the samples are shown in Figure 3.4. The mean final temperature is 71.2 °C and the measured values stay mostly within two degrees from this value.

3.4 Process data

91 hours of production data was available starting from April 29th, 2016 14:06:26. Three measurement values were gathered: the water infeed flow, reactor temperature and lime silo weight. The temperature of the incoming water is not measured.

The measurement data didn't have constant sampling intervals. Due to the way the automation system stores the time series data the time differences between samples were varying. Therefore the data needed to be resampled to obtain a constant time difference between samples and to synchronize the sample times between measurements. The Matlab function *synchronize* [29] was used for this purpose by doing pair-wise synchronizations between each of the timeseries objects.

Silo weight

The weight measurement data in Figure 3.5a shows the weight of the silo in tonnes. The whole data can't be directly used for modeling purposes as the silo can be simultaneously filled while lime is fed to the slaker. However, the lime feed screw is always operated at the same constant speed so the lime addition rate can be calibrated from the weighing data.

The data is somewhat noisy. During lime addition the weight should be monotonously decreasing as lime cannot be taken back to the silo, and when the screw is not operated the value should stay constant. The measured value shows rapid local changes which means that simply differentiating the data to obtain the lime addition rate would not work and some pretreatment is required.

As a first pass the data was denoised using the *wden* [30] wavelet denoising function from the Matlab Wavelet Toolbox. As seen in Figure 3.5c this resulted in much smoother data for further processing and during lime addition the values were monotonously decreasing as desired.

Next, the times where the values stayed relatively constant were found using a sliding window during which all the values had to be within a threshold value from each other. For each identified set of subsequent near constant values the mean of the set was used as a replacement.

Linear regression was performed separately on all areas that were not identified to be constant. The first and last ten samples of each region were excluded from

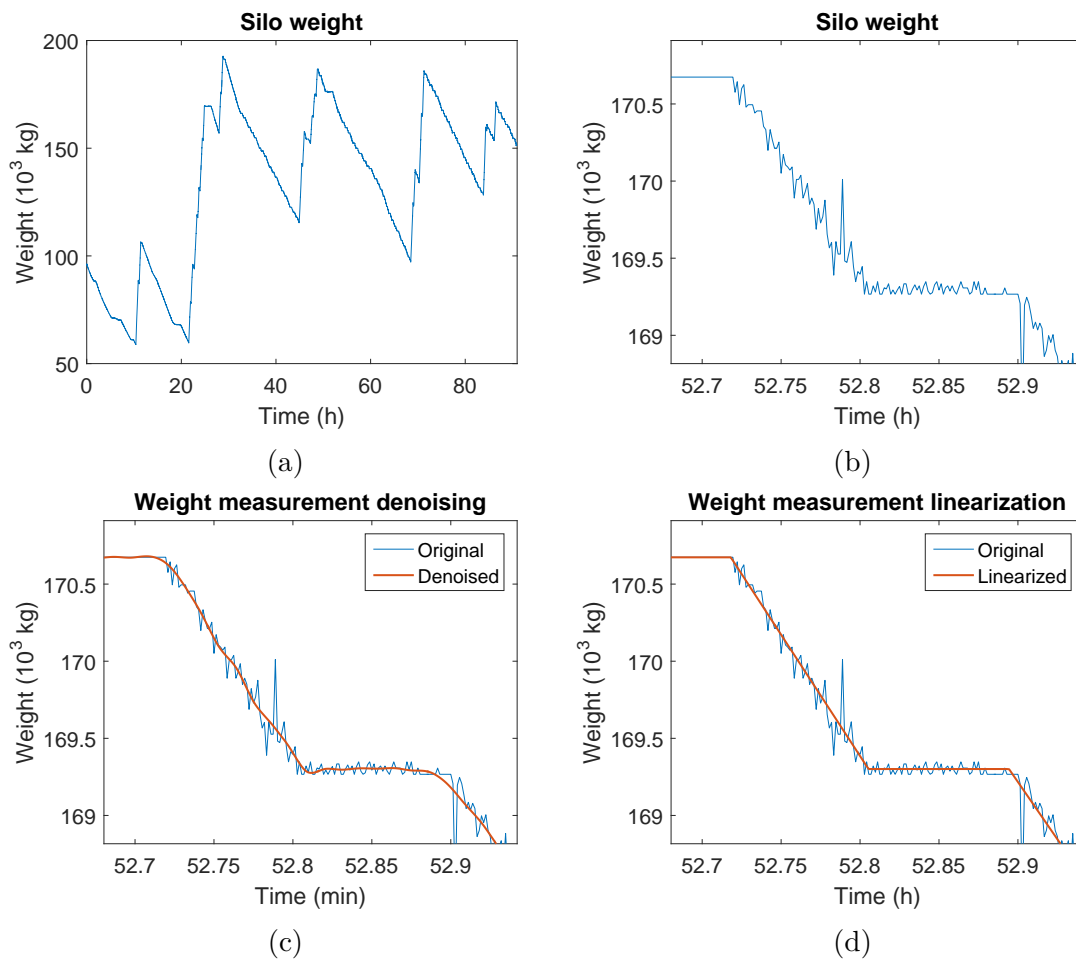


Figure 3.5: Modified weight data: (a) whole data, (b) zoomed in data, (c) wavelet denoising, (d) linearization.

the calculation of the regression coefficients to obtain a better fit to the data. The calculated values of the neighboring constant areas were used as minimum and maximum values in the regression to obtain a good transition between the stages. Due to the window thresholding the constant areas were usually a little shorter than they should be giving enough room for the linear regression to collide to the minimum and maximum values. The transition points can be interpreted as the start and stop times of the lime feed screw as the motor running data was not available. The result is illustrated in Figure 3.5d.

Water feed

The water feed data is shown in Figure 3.6. The water feed is controlled with a binary valve which doesn't allow fine control of the flow rate. At the open position

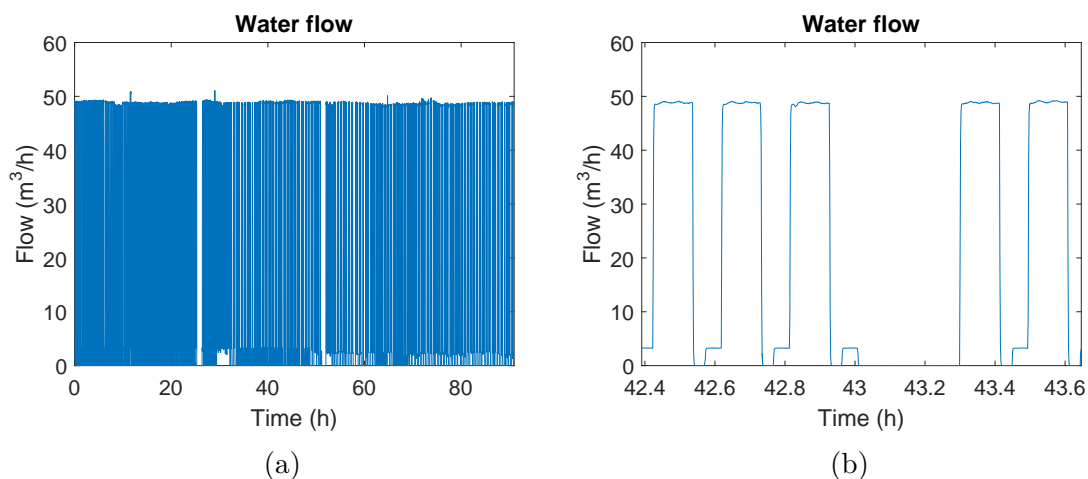


Figure 3.6: Water flow data: (a) whole data, (b) zoomed in data.

the flow rate is restricted to approximately $50 \text{ m}^3/\text{h}$. During each batch the valve is kept open until the desired amount of water has been added to the reactor tank. There is also a flushing sequence where a smaller water flow is used to rinse the equipment to prevent blockage.

Temperature

The temperature measurement data is shown in Figure 3.7. There are relatively large global variations in the process temperature. Locally the batches are quite similar but depending on the frequency of the batch runs the temperature may or may not have enough time to settle.

At the beginning of each batch the reactor temperature starts to drop rapidly as cold water enters the reactor. During the water feed phase the temperature measurement is quite noisy. This is probably caused by imperfect initial mixing of the incoming water at the temperature sensor location.

The addition of lime is not enough to keep the temperature from dropping so the temperature keeps decreasing until the water feed is turned off. There are some variations between batches but typically the lime feed screw is still operated for approximately one to one and a half minutes after the water feed has been shut down. A rapid rise in temperature follows, followed by a period where the temperature settles to the final value. In some cases the next batch starts before the reaction has finished.

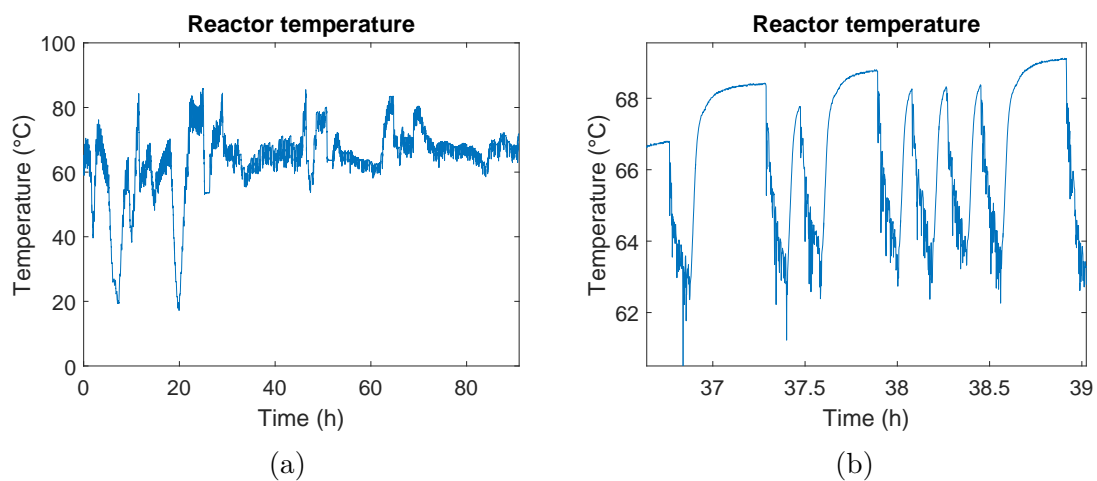


Figure 3.7: Temperature data: (a) whole data, (b) zoomed in data.

3.5 Reaction temperature

The enthalpies of formation are given in the standard temperature of 25 °C (298 K) and standard pressure 100 kPa. [16, p. 114] The initial mixture composition differs from the final state as CaO and H₂O react to Ca(OH)₂. Therefore one has to be careful when calculating the final temperature of the system if the initial temperatures are not the same.

In this section we calculate the theoretical final temperature of the system with different starting temperatures and water to CaO ratios assuming no heat loss to the environment and a perfect reaction. We also determine the impact of the varying heat capacity of the mixture.

Theoretical temperature rise

If we assume that the initial temperatures of CaO and H₂O differ from the standard temperature we can calculate the amount of energy that needs to be added to/removed from the system to bring the reactants to the standard temperature. This amount is then subtracted from the heat generated by the reaction and finally the temperature rise from 25 °C can be calculated by distributing the heat between the water and the calcium hydroxide.

The amount of heat Q (J) required to change the temperature of a substance is [17]

$$Q = cm\Delta t, \quad (3.1)$$

where m is the mass of the substance (kg), c is the specific heat capacity (kJ/(kg K)), and Δt is the temperature change (K).

Therefore, the initial heat requirement Q_{init} to bring the reactants to 25 °C can be calculated from

$$Q_{\text{init}} = c_{\text{H}_2\text{O}}m_{\text{H}_2\text{O}}(t^\circ - t_{\text{H}_2\text{O}}) + c_{\text{CaO}}m_{\text{CaO}}(t^\circ - t_{\text{CaO}}), \quad (3.2)$$

where $c_{\text{H}_2\text{O}}$ is the specific heat capacity of water, $m_{\text{H}_2\text{O}}$ is the initial amount of water, $t_{\text{H}_2\text{O}}$ is the initial temperature of water, c_{CaO} is the specific heat capacity of calcium oxide, m_{CaO} is the mass of the calcium oxide, t_{CaO} is the initial temperature of calcium oxide, and t° is the standard temperature 25 °C. If Q_{init} is negative heat would need to be removed to bring the reactants to the standard temperature.

The effective amount of heat that is used to change the temperature of the products can be calculated as

$$Q_{\text{eff}} = -Q_{\text{reaction}} - Q_{\text{init}}, \quad (3.3)$$

where Q_{reaction} is the heat of the reaction. The amount of released heat can be calculated as

$$Q_{\text{reaction}} = n_{\text{CaO}} \cdot \Delta H_f^\circ, \quad (3.4)$$

where n_{CaO} is the amount of substance of CaO (mol) and ΔH_f° is the heat of reaction (kJ/mol). The sign of Q_{reaction} in Equation 3.3 is negative as ΔH_f° is negative for exothermic processes.

In wet slaking the reaction happens with excess water and lime is the limiting factor in the reaction. Let us assume that the lime reacts perfectly. We already calculated the relative atomic masses for calcium oxide and water that numerically coincide with the molar masses. The amount of substance n (mol) can be calculated from [17, p. 131]

$$n = \frac{m}{M}, \quad (3.5)$$

where m is the mass (g), and M is the molar mass (g/mol) of the substance. According to the reaction in Equation 2.4 the reactants have the same coefficients so the following holds:

$$n_{\text{CaO}} = \frac{m_{\text{CaO}}}{M_{\text{CaO}}} = \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} = n_{\text{H}_2\text{O}}, \quad (3.6)$$

where n_{CaO} is the amount of substance, m_{CaO} is the mass, M_{CaO} is the molar mass of CaO, and $m_{\text{H}_2\text{O}}$ is the mass, $M_{\text{H}_2\text{O}}$ is the molar mass, and $n_{\text{H}_2\text{O}}$ is the amount of substance of the reacted water. The mass of the reacted water can therefore be calculated from

$$m_{\text{H}_2\text{O}} = \frac{M_{\text{H}_2\text{O}}}{M_{\text{CaO}}} m_{\text{CaO}}. \quad (3.7)$$

Let us denote the initial mass of water as m_1 , the initial mass of CaO as m_2 , the final mass of water as m'_1 , and the mass of produced $\text{Ca}(\text{OH})_2$ as m_3 . Due to the preservation of matter the sum of the masses has to remain the same before and after the reaction:

$$m_1 + m_2 = m'_1 + m_3. \quad (3.8)$$

It can be thought that the the water attaches to the calcium oxide in the reaction increasing its mass. Using Equation 3.7 the final masses can be calculated satisfying

the preservation of matter as

$$m'_1 = m_1 - \frac{M_{\text{H}_2\text{O}}}{M_{\text{CaO}}}m_2 \quad \text{and} \quad m_3 = m_2 + \frac{M_{\text{H}_2\text{O}}}{M_{\text{CaO}}}m_2. \quad (3.9)$$

Assuming no heat loss to the surroundings the temperature change caused by the reaction can be calculated from the relation

$$Q_{\text{eff}} = c_1 m'_1 \Delta t + c_3 m_3 \Delta t, \quad (3.10)$$

where c_1 is the specific heat capacity of water, c_3 is the specific heat capacity of calcium hydroxide, and Δt is the change in temperature. Solving for the temperature change we obtain

$$\Delta t = \frac{Q_{\text{eff}}}{c_1 m'_1 + c_3 m_3}. \quad (3.11)$$

Using Equations 3.3 and 3.9 this becomes

$$\Delta t = \frac{-Q_{\text{reaction}} - Q_{\text{init}}}{c_1 \left(m_1 - \frac{M_{\text{H}_2\text{O}}}{M_{\text{CaO}}}m_2\right) + c_3 \left(1 + \frac{M_{\text{H}_2\text{O}}}{M_{\text{CaO}}}\right)m_2}, \quad (3.12)$$

and by reordering we obtain

$$\Delta t = -\frac{Q_{\text{reaction}} + Q_{\text{init}}}{c_1 m_1 + \left(c_3 + \frac{M_{\text{H}_2\text{O}}}{M_{\text{CaO}}}(c_3 - c_1)\right)m_2}. \quad (3.13)$$

By adding the equations for Q_{reaction} and Q_{init} , and substituting c_{CaO} with c_2 we get the following equation:

$$\Delta t = -\frac{\frac{m_2}{M_{\text{CaO}}}\Delta H_f^\circ + (c_1 m_1 (t^\circ - t_1) + c_2 m_2 (t^\circ - t_2))}{c_1 m_1 + \left(c_3 + \frac{M_{\text{H}_2\text{O}}}{M_{\text{CaO}}}(c_3 - c_1)\right)m_2}. \quad (3.14)$$

As the temperature change is calculated from the standard temperature the final temperature can be obtained by summation with the standard temperature t° 25 °C as

$$t_{\text{final}} = t^\circ + \Delta t. \quad (3.15)$$

For simplicity let us assume that 1 kg of CaO is slaked. The selection of the exact

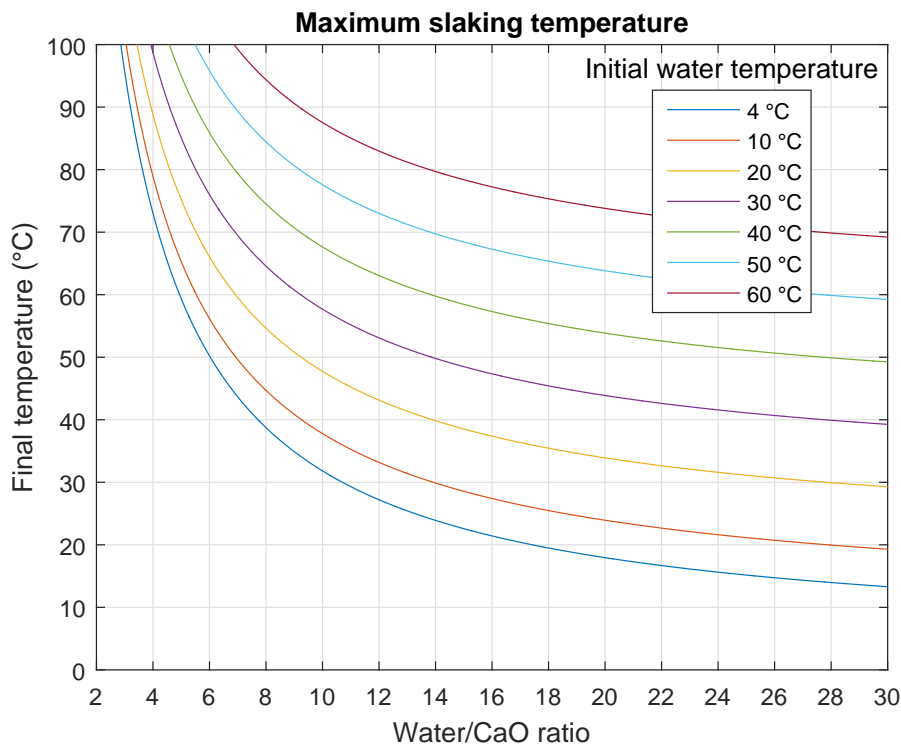


Figure 3.8: Theoretical final slaking temperatures with different water starting temperatures and CaO initial temperature at 25 °C.

amount is arbitrary as the temperature depends only on the ratio of water and lime.

$$n_{\text{CaO}} = \frac{1000 \text{ g}}{56.08 \text{ g/mol}} \approx 17.8 \text{ mol.} \quad (3.16)$$

The enthalpy change in the hydration reaction was calculated in Equation 2.6 to be $\Delta H_f^\circ = -65.3 \text{ kJ} \cdot \text{mol}^{-1}$. Using this information we can calculate the amount of heat Q_{reaction} released when 1 kg of CaO reacts with a sufficient amount of H₂O:

$$Q_{\text{reaction}} = n_{\text{CaO}} \cdot \Delta H_f^\circ = 1164 \text{ kJ.} \quad (3.17)$$

Figure 3.8 shows how the initial water temperature affects the theoretical final slaking temperature. The final temperatures were calculated with different mass ratios of water and calcium oxide. The initial temperature of CaO was kept at a constant 25 °C value. It is clear that the initial water temperature has a great effect on the final temperature.

At a 4:1 water ratio a 10 °C difference in the initial water temperature shows as a 9.87 °C difference in the final temperature which means that 98.7 % of the initial

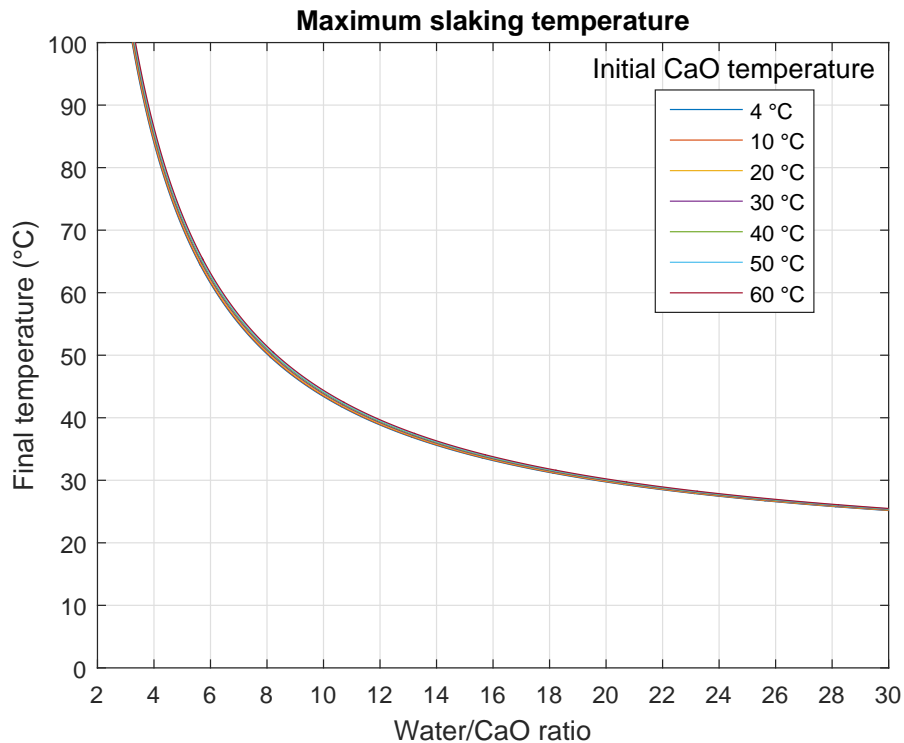


Figure 3.9: Theoretical final slaking temperatures with different CaO starting temperatures and initial water temperature at 16 °C.

water temperature goes towards the final temperature. Decreasing the water ratio to 1:1 yields 95.05 % and increasing the ratio naturally moves the percentage closer to 100 %.

Figure 3.9 shows the effect of the initial temperature of the quicklime. It can be seen that the temperature variations are considerably smaller. At a 4:1 ratio the temperature difference between the smallest and largest value is only 2.5 °C.

Conclusion: The initial temperature of CaO has only a small effect and it can be safely left out from the model.

Heat capacity variation

As the reaction advances the composition of the mixture changes inexorably which causes the heat capacity of the system to change also. Therefore the temperature change incurred by the same amount of reaction heat varies depending on the reaction state.

Table 3.1 lists the specific heat capacities of the reactants and products. Let us

Table 3.1: Specific heat capacities of reactants and products at standard pressure and 298.15 K. [31]

Name	Formula	c_p (J mol ⁻¹ K ⁻¹)	c_p (J g ⁻¹ K ⁻¹)
calcium oxide	CaO(s)	42.0	0.749
calcium hydroxide	Ca(OH) ₂ (s)	87.5	1.18
water	H ₂ O(l)	75.3	4.18

assume that we are mixing 4 kg of water to 1 kg of quicklime. Using Equation 3.7 we can calculate the mass of reacted water:

$$m_{\text{H}_2\text{O}} = \frac{M_{\text{H}_2\text{O}}}{M_{\text{CaO}}} m_{\text{CaO}} = \frac{18.016 \text{ g/mol}}{56.08 \text{ g/mol}} \cdot 1 \text{ kg} = 0.321 \text{ kg}. \quad (3.18)$$

The heat capacity C (J/K) of a mass m of a substance depends on the specific heat capacity c as [17, p. 120]

$$C = cm. \quad (3.19)$$

The total heat capacity of the system is a sum of the heat capacities of the reactor contents and can be calculated as

$$C = c_{\text{H}_2\text{O}} m_{\text{H}_2\text{O}} + c_{\text{CaO}} m_{\text{CaO}} + c_{\text{Ca(OH)}_2} m_{\text{Ca(OH)}_2}. \quad (3.20)$$

At the beginning of the reaction there is only water and CaO present so the initial heat capacity is

$$C_{\text{init}} = c_{\text{H}_2\text{O}} m_{\text{H}_2\text{O}} + c_{\text{CaO}} m_{\text{CaO}} \quad (3.21)$$

$$= 4.18 \frac{\text{J}}{\text{g} \cdot \text{K}} \cdot 4,000 \text{ g} + 0.749 \frac{\text{J}}{\text{g} \cdot \text{K}} \cdot 1,000 \text{ g} \quad (3.22)$$

$$= 17,469 \frac{\text{J}}{\text{K}}. \quad (3.23)$$

At the end of the reaction all of the CaO has reacted and transformed to Ca(OH)₂ while the amount of water has been reduced by 0.321 kg. Because mass is conserved the weight of calcium hydroxide is 0.321 kg larger than the CaO weight, correspondingly.

Therefore the final heat capacity is

$$C_{\text{final}} = c_{\text{H}_2\text{O}}m_{\text{H}_2\text{O}} + c_{\text{Ca(OH)}_2}m_{\text{Ca(OH)}_2} \quad (3.24)$$

$$= 4.18 \frac{\text{J}}{\text{g} \cdot \text{K}} \cdot 3679 \text{ g} + 1.18 \frac{\text{J}}{\text{g} \cdot \text{K}} \cdot 1321 \text{ g} \quad (3.25)$$

$$= 16,937 \frac{\text{J}}{\text{K}}. \quad (3.26)$$

The heat capacity of the system reduces by 532 J/K which is 3 % of the initial heat capacity of the system. The values can be transformed to the specific heat capacity of the mixture by dividing by the total mass 5 kg. This yields the initial specific heat capacity of 3.49 kJ/(kg K) and the final specific heat capacity of 3.39 kJ/(kg K).

The true heat capacity of the system is a combination of all three heat capacities and changes constantly as the reaction advances and the reactants are fed to the tank. As the water is fed slightly faster than the quicklime the specific heat capacity of the system will shift towards that of water and start to decrease once the water feed is stopped and only lime is added.

The mixing tank in our system is rather large compared to the amount of added reactants within a single batch sequence. Therefore the true specific heat capacity should stay closer to that of the final products.

Conclusion: If we assume that the lime-to-water ratio remains approximately constant between batches then the specific heat capacity of the reactor contents can also be considered as constant. This will help to keep the model simpler.

3.6 Reaction model

A reaction model is required to describe how fast the reaction occurs at each time instant. In this section we will examine the reaction kinetics and select a reaction model that is suitable for modeling purposes.

Shrinking sphere model

Ritchie and Xu (1990) made experiments with rotating quicklime disks to study the reaction mechanism between quicklime and water with different amounts of sodium hydroxide. In the experiment the rotation speed of the disks was varied to determine if the reaction rate is under chemical or diffusion control. [32]

They found out that the reaction rate seemed to be approximately constant for each given disk rotation speed which suggests that the reaction is inherently zero order, i.e. the reaction advances at a constant rate if the reacting area stays the same. The reaction rate was strongly dependent on the rotation speed which could be caused by diffusion of reactants to the oxide surface or diffusion of products away from the surface. They noted that the reaction can be broken down into three distinct steps: [32]

1. conversion of calcium oxide to calcium hydroxide,
2. dissolution of calcium hydroxide to calcium and hydroxide ions in the solution,
3. diffusion of the ions in the solution.

Ritchie and Xu deduced that the reaction has to be diffusion controlled at step 3 because the reaction is strongly dependent on the disc rotation speed and it has a low activation energy. Also, the rate constants are too small for the first step with a high bulk concentration to be the rate limiting one. [32]

Ritchie and Xu continued with lime powder studies to model the reaction kinetics. They assumed that the oxide particles were initially spheres with a radius r_0 and that the reaction is zero order as they found out in the rotating disc experiments. They defined the extent of reaction as [32]

$$x = \frac{\Delta T}{\Delta T_\delta}, \quad (3.27)$$

where ΔT is the temperature change after time t , and ΔT_δ is the temperature change at the end of the reaction. Next, they fit the data to the shrinking sphere equation [32]

$$1 - (1 - x)^{1/3} = k_0 t / r_0, \quad (3.28)$$

where x is the extent of reaction, k_0 is the reaction rate constant, t is the elapsed time and r_0 is the initial radius of the spheres.

To test whether the shrinking sphere model would work with the available production data temperature measurements from seven different time periods were selected. Each selected period contains 140 sample values starting from the point when the reactor temperature started to rise, i.e. the water feed was cut off. Only periods where the next batch didn't start within the sample time were included. The data is plotted in Figure 3.10.

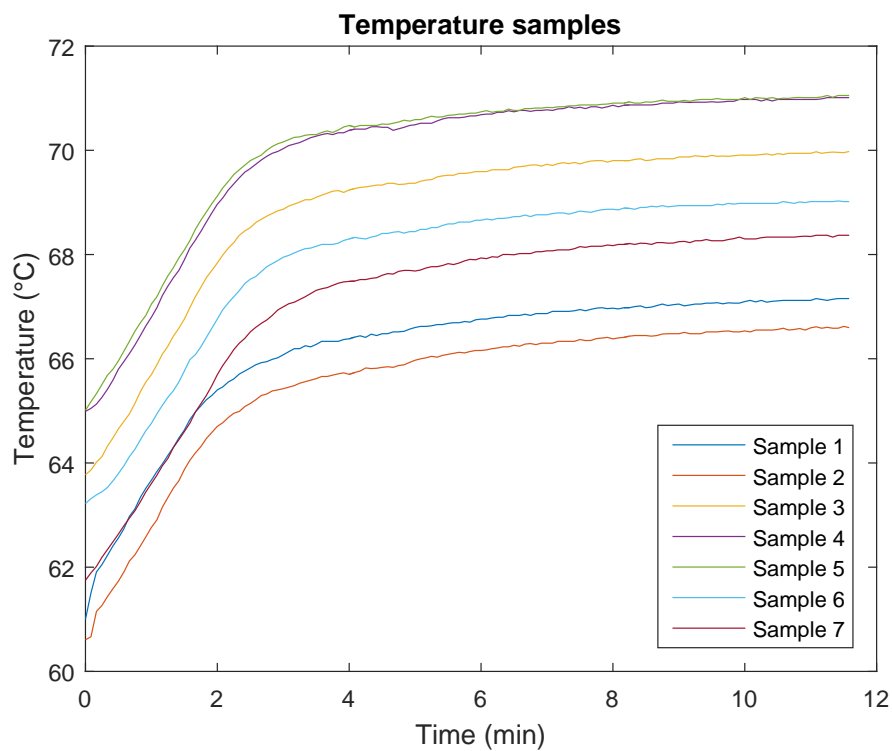


Figure 3.10: Temperature samples for the shrinking sphere model.

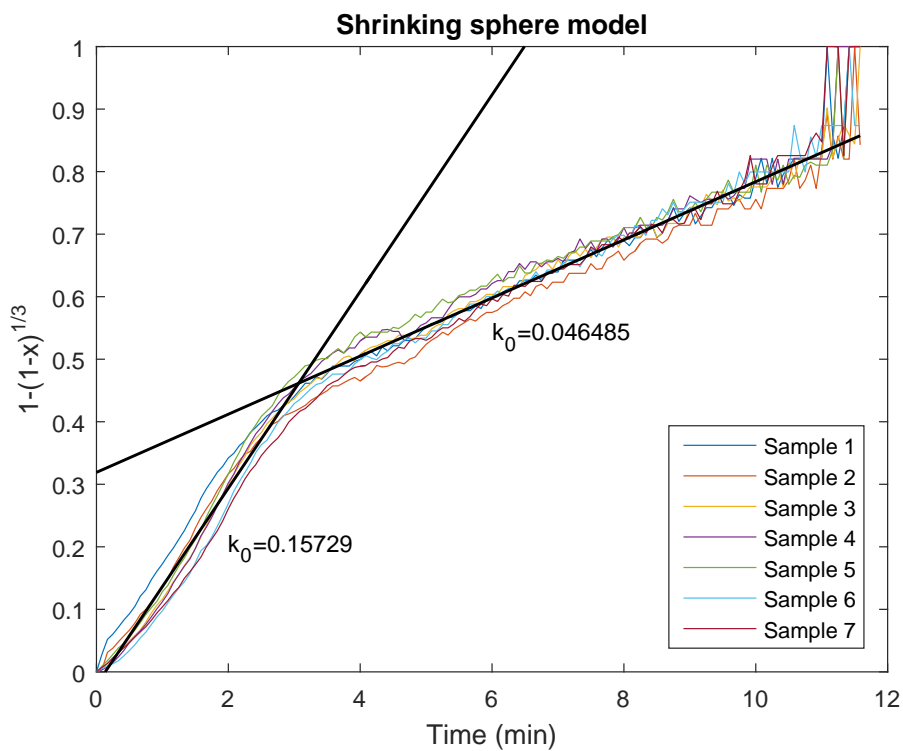


Figure 3.11: Temperature data fit to the shrinking sphere model.

In the selected samples the lime feed screw was still operating for approximately one and a half minutes after the water feed had been shut off. At two minutes the lime feed was off for all samples. This causes the quite linear looking behavior in the beginning as new lime particles are being fed to the reactor at a constant rate.

The same data is plotted in Figure 3.11 according to the shrinking sphere equation (Equation 3.28). Ideally, the data should fit a straight line through the origin in order to follow the model. After four minutes the data seems to follow a straight line quite well. However, between two and four minutes there is a clear curvature in the plot which means the shrinking sphere model fails to explain what is happening.

If we set the initial radius of the particles to one we can calculate the rate constant by performing linear regression on the data between four and ten minutes. Similarly a straight line can be fitted to the first two minutes of the data to compare the change of the reaction rate. The numerical values for the initial and final rate constants are $k_0 = 0.157$ and $k_0 = 0.0465$, respectively. The reaction seems to occur over three times faster at the beginning.

The shrinking sphere model assumes that the particles start at some homogeneous initial radius. However, in practice the feed is quite heterogenous with various initial particle sizes. Also, the larger particles consist of many smaller particles and are therefore very porous and react more quickly than the model predicts. [32]

The shrinking sphere model seems to describe the end of the reaction rather well but fails to describe the transient behavior. In the lime powder experiments Ritchie and Xu mixed only 0.2 g of quicklime to 200 ml of water [32] which is a significantly smaller ratio than in our data.

Another problem with the shrinking sphere model is the applicability to a continuous process model. It assumes some initial radius for the particles but with a continuous feed of lime there will be particles of various radii in the reactor. Therefore a distinct starting point for the reaction would be difficult to determine.

As the shrinking sphere model is defined based on the extent of the reaction as realized temperature change over total temperature change, the final temperature estimate should be continuously updated. To make matters even more complicated, the addition of water and its effect in the initial temperature as well as the lime concentration should also be included in the model.

Conclusion: The shrinking sphere model is not suitable for our purposes.

First order reaction

In the previous section we came to the conclusion that the shrinking core model is not feasible for our purposes. It was also mentioned that the reaction seems to be inherently zero-order if the reacting area is kept constant. This would work for modeling if the calcium oxide was a catalyst to some other reaction and the area would always remain the same.

We are going to assume that the reaction is first order in relation to the concentration of CaO. Because we have excess water we are going to further simplify the reaction by assuming that the water is an inert and use the notation



where A is CaO, B is Ca(OH)₂ and k_A is the reaction rate constant .

3.7 Reactor model

A chemical reactor is the most important unit of operation in the chemical industry which makes them generally interesting subjects to study in chemical engineering. One typical type of a chemical reactor is the continuously stirred tank reactor (CSTR) which has continuous input and output streams of fluids. In the case of a CSTR it is usually assumed that the reactor is perfectly mixed which means that the concentrations and temperatures are uniform throughout the reactor and that these properties also apply directly to the exit stream. [33, p. 560]

Bequette shows the derivation of a CSTR model with a cooling jacket [33, p. 560]. We will partially follow this procedure in this thesis while making some adjustments to fit our problem case. As a difference to the example in Bequette's book our reactor has no active cooling. There is probably some heat loss to the environment but we are going to assume that the effects of these losses are negligible. Another key difference is that we have two input streams, one of which is a feed of solids.

In this section we will develop the required equations for the reactor model. We will determine the material balances, especially the volumetric flows of substances in and out of the constant volume reactor. The reaction rate depends on the concentration of CaO so we will also form an equation to describe the chemical reaction. Lastly, the energy balance equation describes the reactor temperature over time.

Material balance

The rate of accumulation of material in a well stirred reactor depends on the difference of the inflows and outflows according to [33, p. 562]

$$\frac{dV\rho}{dt} = F_{in}\rho_{in} - F_{out}\rho, \quad (3.30)$$

where V is the volume of the material, ρ is the material density in the reactor (mass/volume), ρ_{in} is the incoming material density, F_{in} the volumetric flow rate of material (volume/time), and F_{out} the flow rate out of the system respectively.

To simplify the equation we assume that the density ρ stays constant, i.e. $\rho_{in} = \rho$, and we obtain

$$\frac{dV}{dt} = F_{in} - F_{out}. \quad (3.31)$$

Due to the overflow discharge the volume of our system is constant so the derivative is zero. Therefore we have

$$F_{in} = F_{out} = F. \quad (3.32)$$

We don't have a measurement of the outflow or the tank level available so without the constant density assumption there would be two unknowns in the equation. This way we obtain an estimate of the outflow that doesn't violate the constant volume restriction.

The volumetric inflow is a combination of the lime and water feeds. The water feed is already in the correct units but for the lime feed we only have the mass transfer rate. We approximate the volumetric feed rate by dividing the mass rate \dot{m}_{CaO} (tonnes/h) with the density of CaO as

$$F_{CaO} = \frac{\dot{m}_{CaO}}{\rho_{CaO}}. \quad (3.33)$$

Therefore the total volumetric inflow can be expressed as

$$F = F_{H_2O} + \frac{\dot{m}_{CaO}}{\rho_{CaO}}. \quad (3.34)$$

The true specific gravity of calcium oxide is between 3.25 and 3.38 g/cm³. Due to porosity the apparent density is smaller and some porous limes can have a value as low as 1.4 g/cm³. [1, p. 117-118] Boynton gives values between 2.0 and 2.20 for typical commercial oxides. [13, p. 195]

The third density measurement would be the bulk density that is again lower than the apparent density as it describes the whole bulk of the lime. Pebble or lump size limes have lower values than pulverized limes because of the added space between particles [13, p. 196]. This value is not useful for us as the lime is dispersed in the water and the space between particles is filled with water molecules.

The specific gravity of calcium hydroxide is 2.24 g/cm³ which is smaller than for calcium oxide. If we only consider the true specific gravities then the volume of one mole of calcium hydroxide is

$$V_{\text{Ca(OH)}_2} = \frac{nM_{\text{Ca(OH)}_2}}{SG_{\text{Ca(OH)}_2}} = \frac{1 \text{ mol} \cdot 74.096 \text{ g/mol}}{2.24 \text{ g/cm}^3} = 33.08 \text{ cm}^3. \quad (3.35)$$

Similarly, the absolute volume of one mole of calcium oxide would be

$$V_{\text{CaO}} = \frac{nM_{\text{CaO}}}{SG_{\text{CaO}}} = \frac{1 \text{ mol} \cdot 56.08 \text{ g/mol}}{3.34 \text{ g/cm}^3} = 16.79 \text{ cm}^3. \quad (3.36)$$

when the specific gravity value given by Boynton [13, p. 195] is used. Also one mole of water is used in the reaction. The specific gravity of water is one so the volume has the same numerical value as the molar mass, 18.016 cm³. The ideal change in volume would therefore be

$$\Delta V = V_{\text{Ca(OH)}_2} - V_{\text{CaO}} - V_{\text{H}_2\text{O}} \quad (3.37)$$

$$= 33.08 \text{ cm}^3 - 16.79 \text{ cm}^3 - 18.016 \text{ cm}^3 \quad (3.38)$$

$$= -1.726 \text{ cm}^3, \quad (3.39)$$

If we want to add water in a mass ratio of 4:1 compared to the quicklime, then the required total amount of water for one mole of lime is

$$V_{\text{H}_2\text{O,tot}} = 4 \cdot \frac{n_{\text{CaO}}M_{\text{CaO}}}{SG_{\text{H}_2\text{O}}} = 4 \cdot \frac{1 \text{ mol} \cdot 56.08 \text{ g/mol}}{1 \text{ g/cm}^3} = 224.32 \text{ cm}^3. \quad (3.40)$$

This means that 8 % of the water reacts with the quicklime. The total initial volume given the calculated values would be 241.11 cm³, and the volume change -1.726 cm^3 would therefore correspond to -0.7% of the total initial volume.

This calculation did not take the possible effects of porosity into account. It is likely that the CaO powder has initially more pore space than what is left in the calcium hydroxide particles after reaction. To keep the model as simple as possible we are

going to neglect any possible changes in the volume. If the true volume after reaction is smaller than at the beginning the amount of substance in the reactor will still stay the same. On the other hand, if the required volume is larger the ratios of quicklime, hydrated lime and water will still stay the same because we assume perfect mixing.

Balance on CaO

In Section 3.6 we made the assumption that the reaction is first order to the concentration of calcium oxide and adapted the notation to use A for the calcium oxide and B for calcium hydroxide. Assuming a constant volume reactor the material balance of component A can be expressed as [33, p. 562]

$$V \frac{dC_A}{dt} = FC_{Af} - FC_A - rV, \quad (3.41)$$

where C_{Af} is the concentration of CaO in the feed stream (mol/l), C_A concentration of CaO in the reactor and r the rate of reaction per unit volume.

The rate of reaction per unit volume is temperature dependent and described by the Arrhenius equation [33, p. 563]

$$r = k_0 \exp\left(\frac{-\Delta E}{RT}\right) C_A, \quad (3.42)$$

where k_0 is the rate constant of the reaction, ΔE is the activation energy, R is the universal gas constant and T the absolute temperature in kelvins. This equation describes how the reaction rate changes with respect to temperature. The values for the rate constant and activation energy need to be determined to fit the model.

The total feed stream flow is a combination of the water and lime feeds. Let us use the notation

$$F = F_w + F_A, \quad (3.43)$$

where F_w and F_A are the volumetric flow rates (m³/h) of water and lime, respectively.

For the concentration we consider the water and lime feeds separately. In the water feed stream the molar concentration of CaO is naturally zero. The lime stream is considered to be pure calcium oxide so its concentration can be directly calculated based on the specific gravity SG_A and the molar mass M_A of CaO. The molar

concentration C_{Al} of CaO in the pure lime feed is then

$$C_{Al} = \frac{SG_A}{M_A}. \quad (3.44)$$

The concentration of CaO in the whole inlet stream is

$$C_{Af} = \frac{F_A C_{Al}}{F_w + F_A} = \frac{F_A C_{Al}}{F}. \quad (3.45)$$

The volumetric flow can be calculated from the mass flow by dividing with the specific gravity:

$$F_A = \frac{\dot{m}_A}{SG_A}. \quad (3.46)$$

Therefore the inflow part of Equation 3.41 can be written as

$$FC_{Af} = F_A C_{Al} = \frac{\dot{m}_A}{M_A}. \quad (3.47)$$

The whole balance equation then becomes

$$\frac{dC_A}{dt} = \frac{\dot{m}_A}{VM_A} - \frac{F_w + F_A}{V} C_A - r. \quad (3.48)$$

We see that the inlet feed value is not dependent on the specific gravity but SG_A affects how much of the reactor contents are displaced by the added lime through the F_A term.

Energy balance

When constant volume, specific heat capacity and density are assumed the energy balance of a system can be calculated with [33, p. 562]

$$V \rho c_p \frac{dT}{dt} = F \rho c_p (T_f - T) + (-\Delta H) V r - UA(T - T_j), \quad (3.49)$$

where T is the system temperature (K), ρ is the density (kg/m^3), c_p is the specific heat capacity ($\text{kJ}/(\text{kg K})$), T_f is the feed temperature (K), ΔH is the heat of reaction (kJ/mol) and r is the rate of reaction per unit volume ($1/\text{m}^3$). The $(-\Delta H) V r$ term is the rate of energy from the exothermic reaction. As the temperature of the

surrounding environment is not known we will ignore any possible heat losses and assume that the heat exchange term through the reactor jacket $-UA(T - T_j)$ is zero.

The energy balance can then be written in the following form:

$$\frac{dT}{dt} = \frac{F}{V}(T_f - T) + \frac{-\Delta H}{\rho c_p}r. \quad (3.50)$$

The total flow is a combination of the water and lime flows. We will assume that the addition of lime does not affect the temperature and that only the water feed has a significant effect. The final form of the energy balance equation is then

$$\frac{dT}{dt} = \frac{F_w}{V}(T_w - T) + \frac{-\Delta H}{\rho c_p}r, \quad (3.51)$$

where T_w is the incoming water temperature.

3.8 Data selection

Two sets of data, each spanning a little over twelve hours, were selected for building and validation of the process model. The linearized weight measurement data was differentiated and converted to tonnes per hour to obtain the lime addition rate. The inlet water flow measurement and the reactor temperature measurement were left unmodified.

Figures 3.12 and 3.13 show the input and output data of the model building dataset, respectively. The batches are operated at varying frequencies. At the beginning the slaker is operated as fast as possible as the next batch is started right after the flushing sequence has ended. Later on the batches are run more infrequently.

The temperature measurement contains rapid local variations as well as long term changes. During the water addition period the temperature data is especially noisy but after the water inlet valve has been shut the it becomes smooth. The temperatures are plotted in degrees Celsius to make them easier to comprehend but kelvins were used for modeling.

The validation data is presented in Figures 3.14 and 3.15. Generally, the behavior is similar to the estimation dataset but there are larger changes in the average temperature. There also seem to be some differences in the lime feed rate.

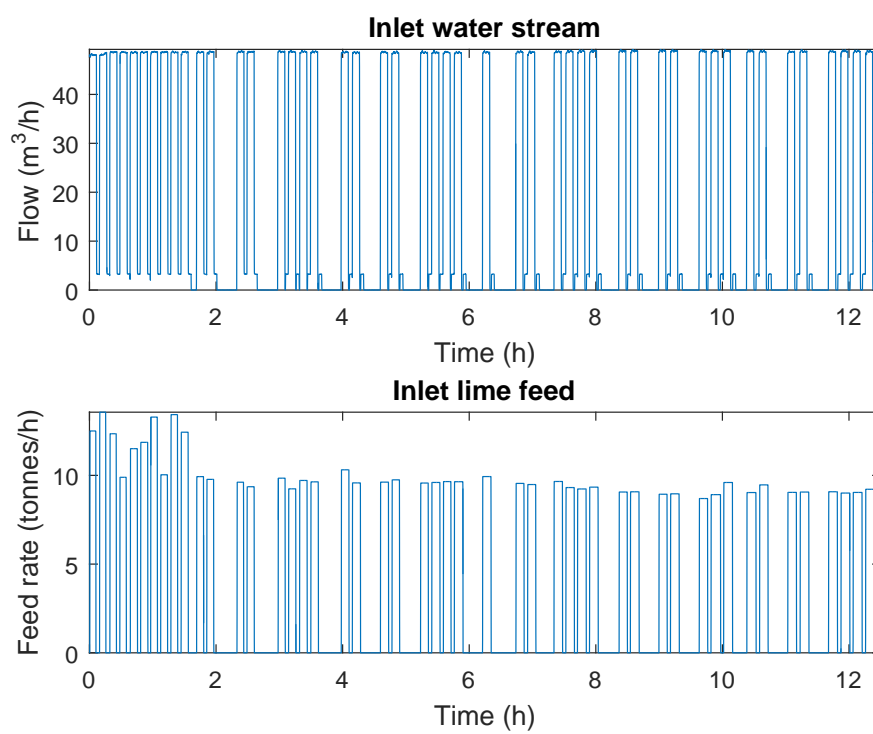


Figure 3.12: Water feed and lime addition rate data for model building.

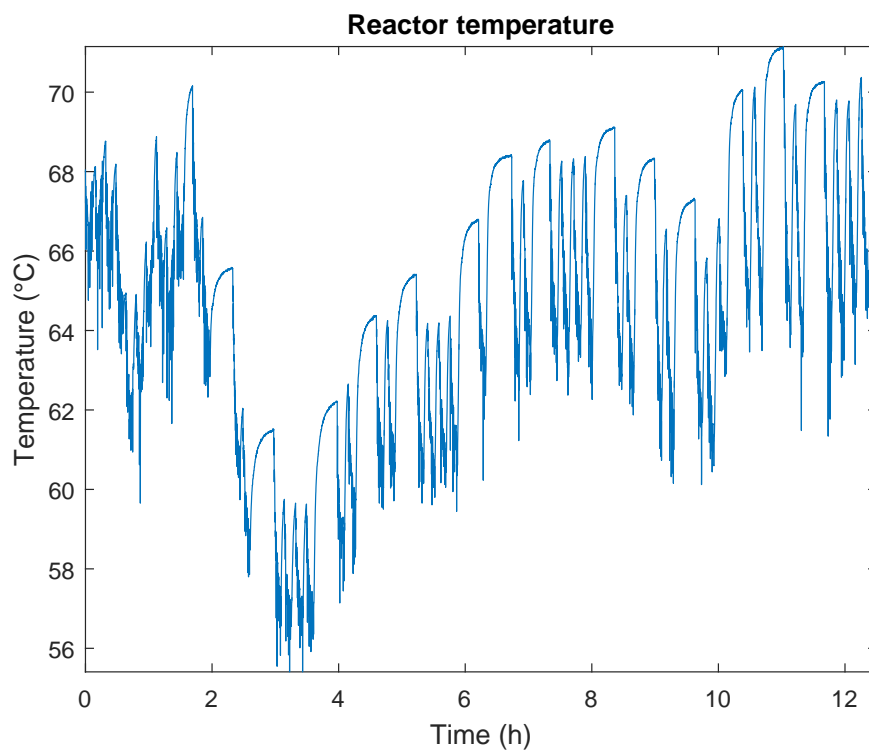


Figure 3.13: Temperature measurement data for model building.

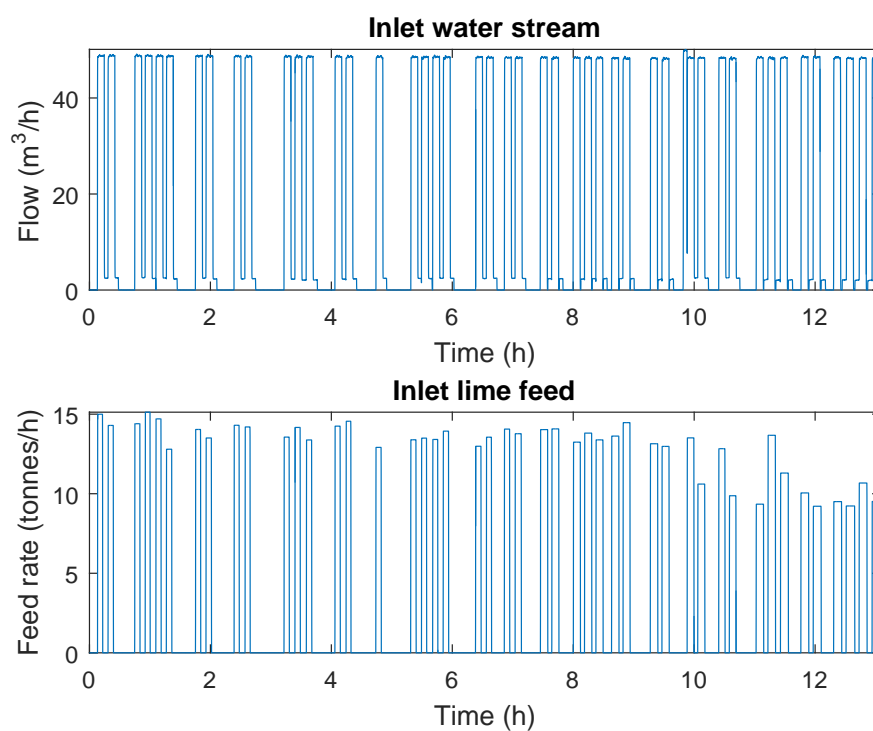


Figure 3.14: Water feed and lime addition rate data for model validation.

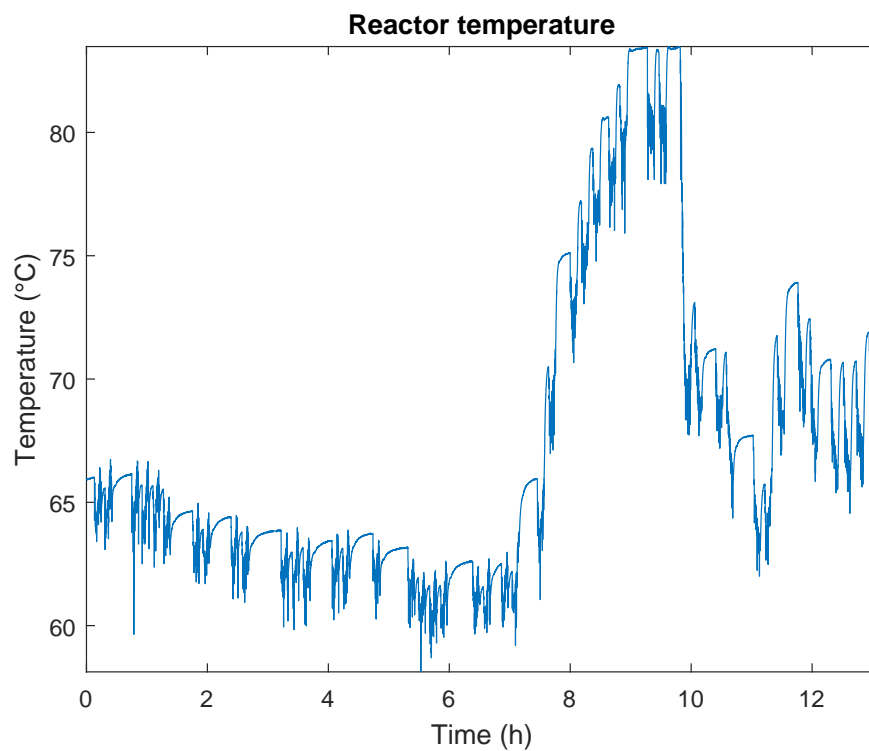


Figure 3.15: Temperature measurement data for model validation.

4 Estimation results

In this section we observe the results of the model estimation and validate the model against the validation data set. We also experiment with different input sequences to find out how the model behaves; especially how the reactor temperature depends on the amount of water.

The three balance equations 3.42, 3.48 and 3.51 were implemented in Matlab and the model parameters were estimated using grey-box estimation methods. The practical part of the modeling is described in more detail in Appendix B.

4.1 System parameters

There were eight different modeling parameters, four of which were fixed to known values based on process knowledge or information obtained from the literature. The values for the remaining four parameters needed to be estimated. The obtained final model values are shown in Table 4.1.

The fixed parameters were the reactor volume, heat of reaction, activation energy and the universal gas constant. The reactor volume was known to be 21 m³ and the heat of reaction was calculated in Section 2.4 as -65.3 kJ/mol. The activation energy of the reaction was set to 16 kJ/mol based on the theoretical estimate by Ritchie and Xu [32] and the gas constant has a value of 8.3145 J/(mol K) [17, p. 71].

The four free parameters were the water temperature, specific gravity of quicklime, heat capacity times density and the pre-exponential nonthermal factor. They were first initialized with values that were likely to be in the neighborhood of the true values before running the estimation procedure.

Table 4.1: Model parameters.

Symbol	Description	Value
T_w	Water feed temperature	277.281 K
V	Reactor volume	21 m ³
SG_A	Specific gravity of quicklime	3.995 g/cm ³
ρc_p	Heat capacity times density	3993.52 kJ/(m ³ K)
k_0	Pre-exponential nonthermal factor	11617.3 1/h
ΔE	Activation energy	16000 J/mol
R	Gas constant	8.3145 J/(mol K)
ΔH	Heat of reaction	-65.3 kJ/mol

The water is being taken from a small pond outside so the initial guess for the incoming water temperature was set to 4 °C. The specific gravity of quicklime was given an initial value of 2.5 g/cm³ based on the discussion in Section 3.7. The heat capacity times density was initialized using the corresponding values for pure water and the k_0 factor was arbitrarily selected based on initial experiments with the modeling.

The water feed temperature was restricted between zero and twenty degrees Celsius and the specific gravity of quicklime between two and four grams per cubic centimeter. Other parameters were constrained to positive values with the exception of the heat of reaction that is a negative constant.

The estimated water feed temperature stayed close to the initial 4 °C guess. Setting the initial guess to 8 °C before parameter estimation didn't change the situation significantly.

The original estimate of the heat capacity times density parameter was based on the values for water at 4174.37 kJ/(m³ K) but after fitting to the process data the value was decreased to 3993.52 kJ/(m³ K). Using the heat capacity of calcium hydroxide 1.18 J/(g K) from Table 3.1 and the specific gravity 2.24 g/cm³ the heat capacity times density parameter would be 2643.2 kJ/(m³ K) for pure calcium hydroxide. Therefore it is logical that the estimated value is smaller than the initial guess.

The lime specific gravity parameter was bounded between 2 and 4 g/cm³. The optimizer hit the upper limit and the standard deviation of the estimate was rather large. After setting the upper limit to infinity the optimizer ended up with a value of 650 g/cm³ which is unrealistic. The specific gravity parameter affects only how much of the reactor contents are displaced by the added lime and larger values mean denser material and smaller displacement. It seems that only the water volume is relevant for the model.

The pre-exponential term k_0 in the Arrhenius equation was estimated at 11617.3 h⁻¹. In the initial optimization attempts the activation energy was not fixed and the estimated value was approximately 35 kJ/mol. This caused a strong temperature dependency for the reactivity and the k_0 parameter was accordingly larger. The initial estimate of k_0 with the smaller activation energy of 16 kJ/mol was then calculated directly from the Arrhenius equation to give the same reaction rate at a selected temperature within the normal reactor operating range.

4.2 Model equations

By using the estimated parameter values from Table 4.1 the reactor model can be realized. The balance of CaO (Equation 3.48) becomes

$$\frac{dC_A}{dt} = \frac{\dot{m}_A}{0.0012 \text{ (m}^3 \text{ tn)/mol}} - \frac{F_w + \frac{\dot{m}}{3.995 \text{ tn/m}^3}}{21 \text{ m}^3} C_A - r, \quad (4.1)$$

where C_A is the concentration of CaO (mol/m³), \dot{m} is the mass rate of the CaO feed (tonnes/h), and F_w is the water inlet flow (m³/h). Note that tonnes per cubic meter were used as units for the lime specific gravity.

The Arrhenius equation (Equation 3.42) is

$$r = 11617.3 \frac{1}{\text{h}} \cdot \exp\left(\frac{-1.9243 \text{ K}}{T}\right) C_A, \quad (4.2)$$

where T is the system temperature (K).

Finally, the energy balance (Equation 3.51) can be written as

$$\frac{dT}{dt} = \frac{F_w}{21 \text{ m}^3} (277.281 \text{ K} - T) + 0.0164 \frac{\text{m}^3\text{K}}{\text{mol}} \cdot r \quad (4.3)$$

Discrete forms of these equations with a sampling time of five seconds were used in the practical modeling.

4.3 Fit to process data

The results of the model estimation are displayed in Figure 4.1. The model seems to capture the process characteristics relatively well. Especially when there are only short delays between the batch runs the model follows the data closely.

To describe how well the model fits the data the Matlab function *compare* calculates the normalized root mean square error (NRMSE) fit using [34]

$$\text{fit} = 100 \left(1 - \frac{\|y - \hat{y}\|}{\|y - \text{mean}(y)\|} \right), \quad (4.4)$$

where y is the validation data, \hat{y} is the model output and $\|$ marks the 2-norm of the vector.

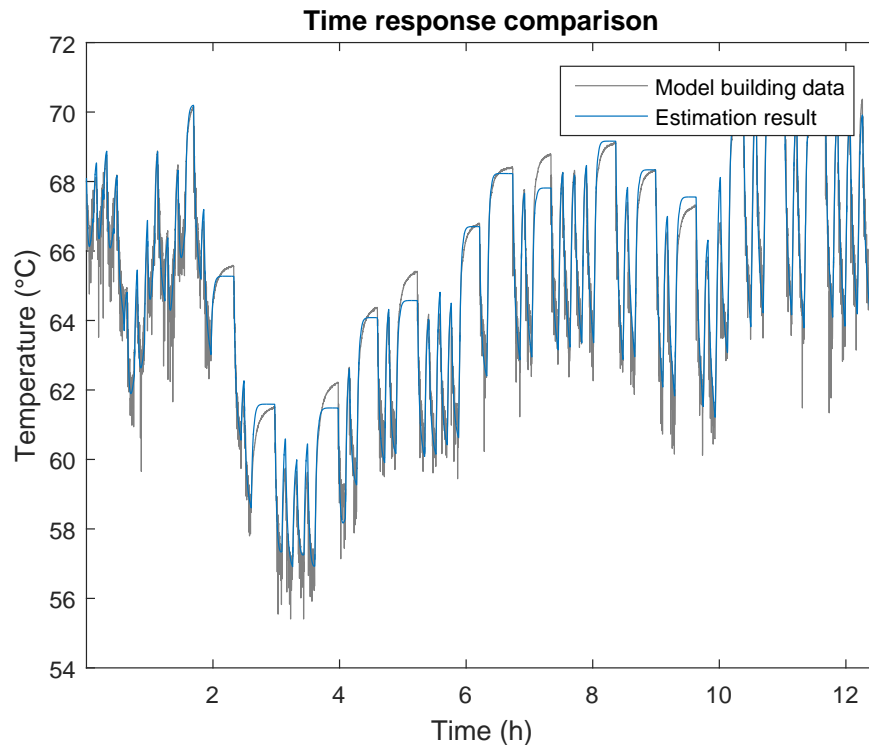


Figure 4.1: Model building data: model output (blue) and process temperature measurement (gray).

In the model building data set the model achieves a 84.6 % fit. In comparison, when the temperature measurement data is run through the wavelet denoising function and compared to the original temperature data the corresponding fitness value is 90.4 %.

With longer delays between batches the model seems to reach its final temperature faster than the actual process. As we found out in Section 3.6 the end behavior of the batch follows the shrinking sphere model which is generally slower than our exponential assumption.

Most of the temperature peaks in the model follow closely the real values but for some batches there is an unexplained one degree difference between the real and the estimated value. Even if the estimate for one peak is wrong the following peaks will still give correct results.

The validation results are presented in Figure 4.2. For the validation data set the model obtains a fitness value of 86.02 %. This is better than what was achieved for the estimation data but the inter-batch differences of the estimated and true final temperatures are more frequent than during the estimation phase. Between two and

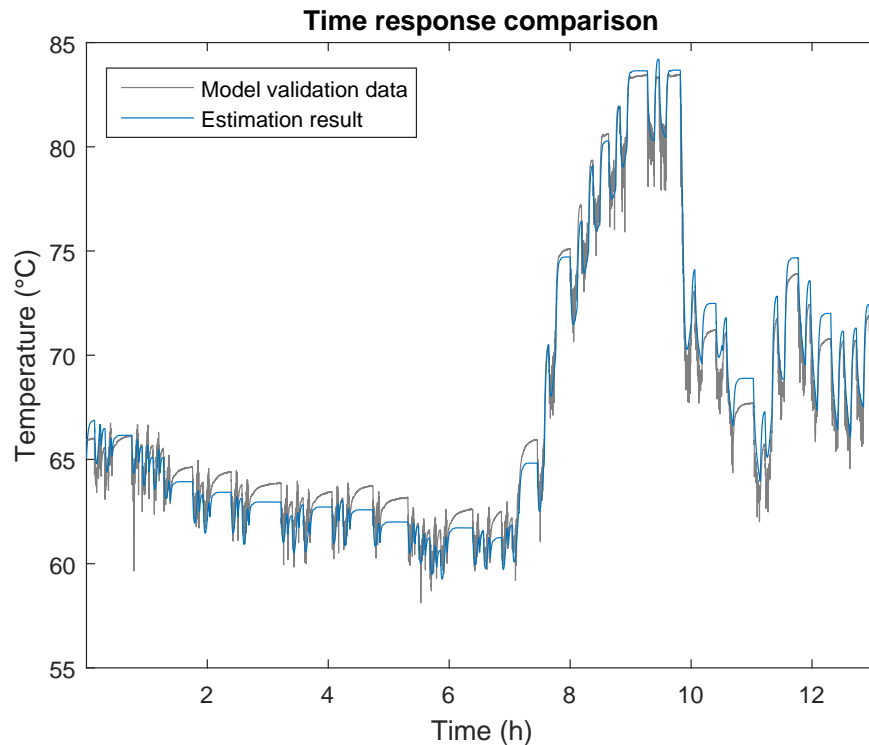


Figure 4.2: Model validation data: model output (blue) and process temperature measurement (gray).

eight hours the model gives consistently lower final temperatures compared to the real process. The long term average is still well described.

The NRMSE fit value normalizes the fitness based on the norm of the deviations from the mean value. The standard deviation of the estimation data set is 3.30 while the validation data set has a higher value of 6.19. Therefore the better fit according to the NRMSE value is partly due to the higher variance and the resulting effect of normalization. Still, the model seems to work satisfactorily also with this wider temperature range.

4.4 Model reactivity test

For further verification of the results the model was subjected to an artificial reactivity test where the initial temperature was set to 20 °C and the lime concentration to 200 g/l (3.56 mol/l). It was assumed that this value would approximately correspond to a 4:1 water to lime ratio. The model was then simulated for a ten minute period.

As defined for reactivity testing in Section 3.3 the time that it takes for the process

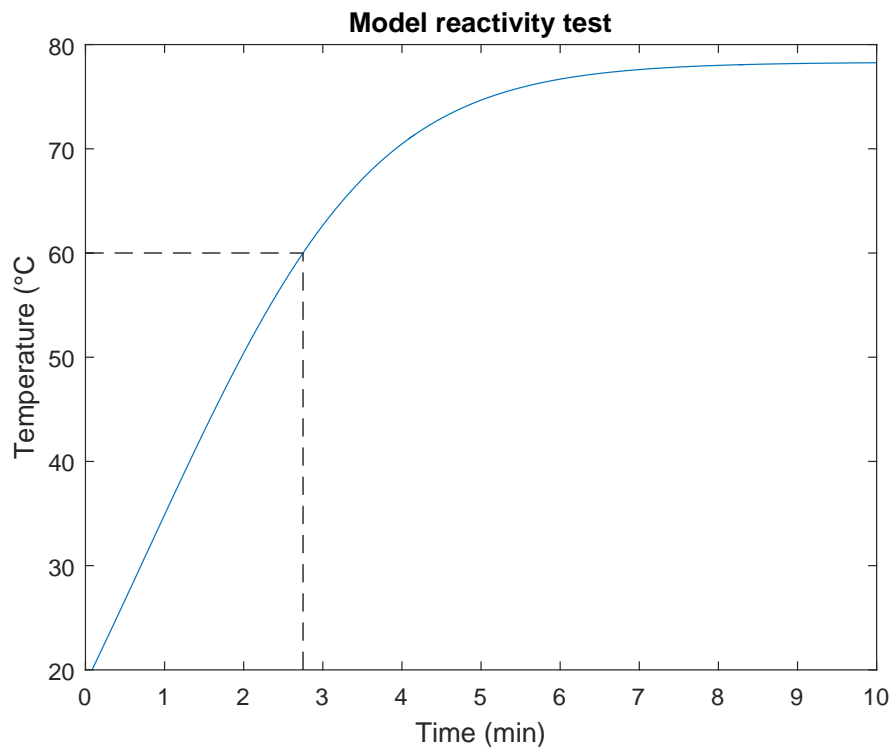


Figure 4.3: Model response to an artificial reactivity test.

to reach 60 °C and the final temperature were measured. The simulated process took 2 minutes 45 seconds to reach the 60 °C mark and reached a final temperature of 78.2 °C. The resulting reactivity value is 14.5 °C/min which is practically identical with the mean reactivity of the tested lime samples where we had the value 14.6 °C/min. The mean final temperature of the tested samples was 71.2 °C which is 7 °C lower than the model estimate. One sample did reach 76.37 °C in the reactivity test data but the majority of the samples stayed within 69 – 73 °C. The model seems to overestimate the final temperature while the initial reactivity is spot on.

The results are somewhat sensitive to the initial concentration estimate as dropping the concentration to 180 g/l drops the final temperature to 72.4 °C and the slaking time to reach 60 °C is increased to 3 minutes 20 seconds. Conversely, starting with 220 g/l gives a final temperature of 84.1 °C and 60 °C is reached in 2 minutes 20 seconds. The results with the starting concentration of 180 g/l actually correspond quite closely with the sample from 17.9.2015 in Appendix A.

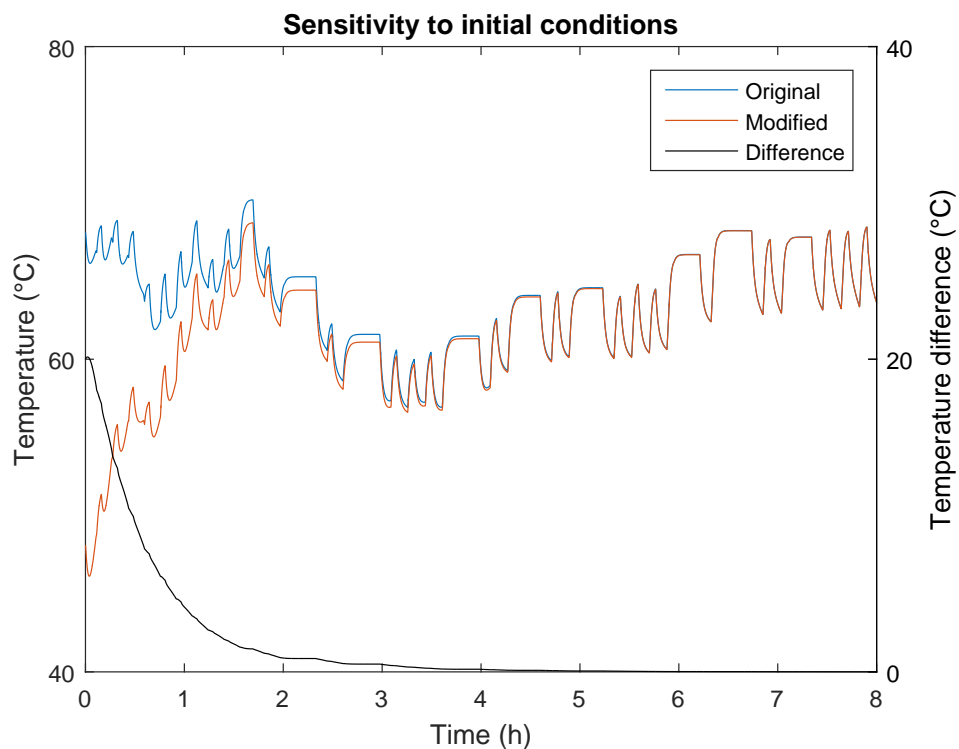


Figure 4.4: Model sensitivity to initial conditions; original estimated initial state (blue) and initial temperature shifted by 20 °C (orange).

4.5 Model sensitivity to initial conditions

The model is able to follow the process relatively well even if it occasionally deviates from the true data as was seen in Figure 4.2. Therefore it is of interest to verify how sensitive the model is to differences in the initial state estimate.

Figure 4.4 shows the modeling result with the input data from the estimation data set with different initial process states. The blue line shows the original state estimate given by the optimizer and the orange line was calculated by decreasing the initial temperature by 20 °C and setting the concentration to zero before running the simulation. The black line shows the difference between these two state estimates at any given time.

The temperature difference between the estimates seems to decrease exponentially and after five hours the lines are identical for all modeling purposes. Therefore the model is able to forget its history and deviations from the true value do not accumulate over time. This is important if the model were to be used on-line.

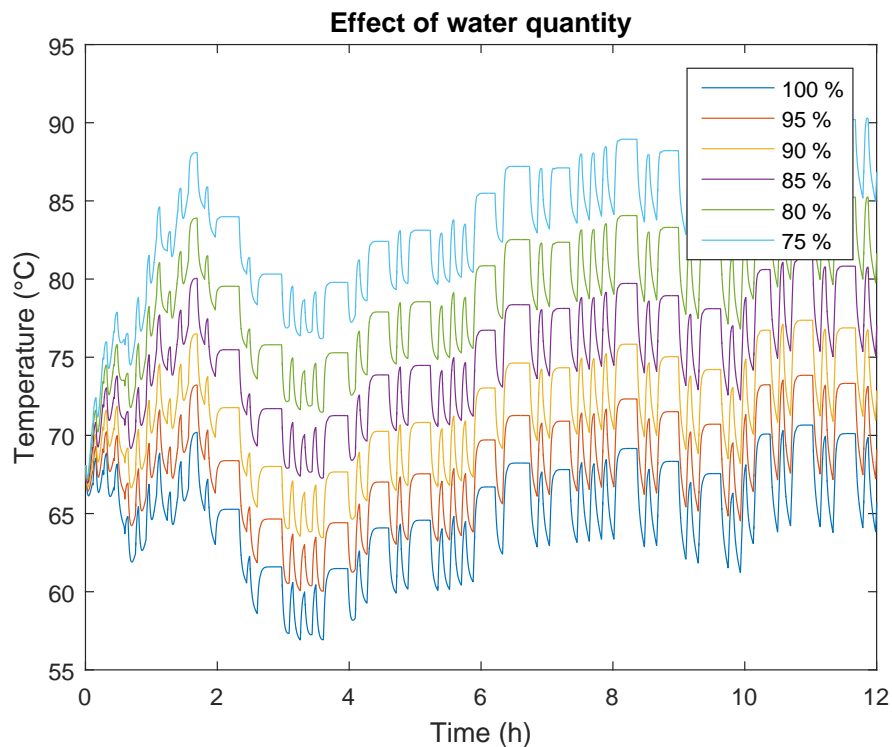


Figure 4.5: The effect of different water amounts to the slaking temperature.

4.6 Selecting the lime-to-water ratio

The recommended temperature for wet slaking is 71-93 °C [13, p. 340]. In our data set the slaker temperature is approximately 65 °C on average so the process is being operated below the recommended range. The control strategy should be modified so that the slaker will operate at slightly higher temperatures to potentially increase the hydrate quality. Using the model we are able to test different operating scenarios without having to do experiments with the true process. As there is no control valve available for the water feed such tests would require other means to limit the water addition rate.

A natural way to increase the reaction temperature is to reduce the incoming water amount so that the cold inlet water will absorb less heat from the process. To maintain the water-to-lime ratio of the final product the reduced initial water amount can be compensated by adding water straight to the dilution tank after the slaker. This will also help cool down the dilution tank contents to prevent agglomeration of the hydrate crystals [19].

The water amount reduction was simulated by adjusting the peak values of the water

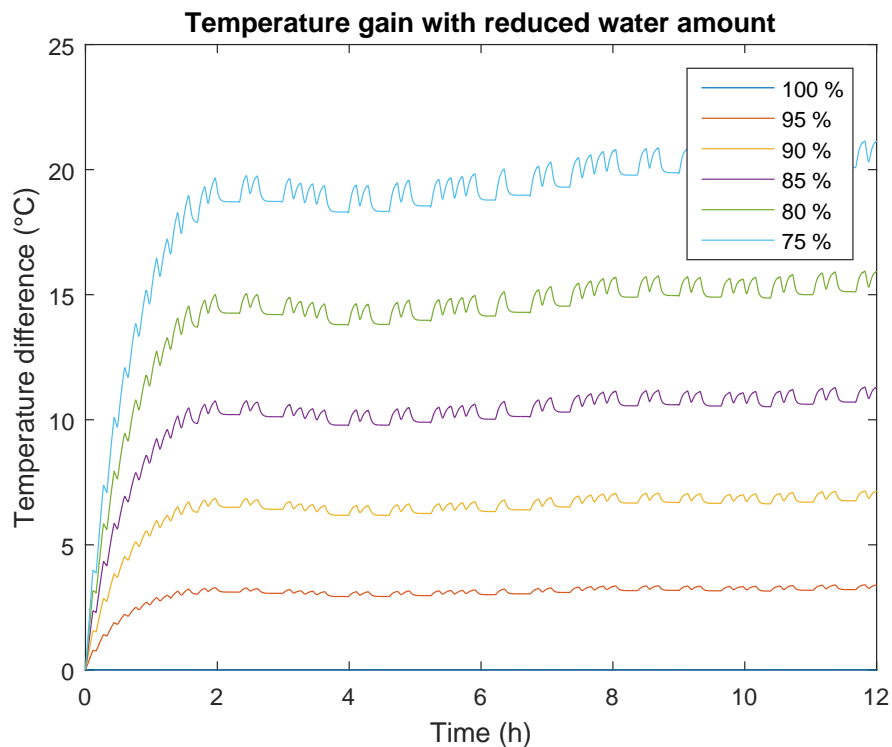


Figure 4.6: Temperature gain with reduced water amount.

addition rates by a reduction factor. The lime addition rates were maintained at the current levels. The same initial state was used for all simulations and as we found out in Section 4.5 after five hours the estimates will have reached their own true trajectories. These results are shown in Figure 4.5.

Figure 4.6 shows the differences between the original model and the results with the reduced water amount. It can be seen that decreasing the water amount by 15 % from the current setting would increase the slaking temperature by 11 °C, bringing it to 76 °C on average. A 20 % decrease in the water amount would increase the average temperature by 15.5 °C. Trying to increase the temperature further could lead to boiling in some circumstances.

By numerically integrating the water and lime addition rates the cumulative amounts were obtained. There are 46 complete batch runs within the estimation data set where in total 266.9 m³ of water and 57 tonnes of lime were mixed. On average 5.82 m³ of water and 1.24 tonnes of lime were used in one batch which corresponds to a lime-to-water ratio of 1:4.68.

Reducing the water amount by 15 % would decrease the lime-to-water ratio to 1:3.98 which should still give a well flowing milk of lime. A twenty-percent reduction in the

water amount would yield a ratio of 1:3.74. For preparation of milk of lime directly from quicklime it has been recommended that a ratio from 1:3 to 1:4.5 should be used at a temperature between 65.5 and 82 °C [13, p. 328].

As a conclusion it is suggested that the water addition amount should be reduced by 15-20 % to obtain a 11-15 °C increase in the slaking temperature. This would give process values that follow more closely the industry recommendations and have the potential to increase the overall milk of lime quality.

4.7 Alternative control inputs

More experiments were performed with the model by testing the steady state operation and the effect of delaying either of the system inputs. The results are discussed in the subsections below.

Steady state operation

The steady state behavior of the model was tested by calculating the mean values of the input sequences in the model building data and using these as constant inputs for the model. The input values were alternately scaled up or down every six hours, and each time the scaling amount was increased by 10 percentage points. Additionally, four different simulations were performed with different lime-to-water ratios. In the first simulation the average ratio of the model building data set was used and in the subsequent simulations the water amount was reduced to 95 %, 90 % and 85 %. All of the simulations were initialized at the steady state of the original reactant ratio where the lime concentration was 98.47 mol/m³ and the temperature was 64.78 °C.

The test input is shown in Figure 4.7 and the corresponding system states in Figure 4.8. This test reveals two properties of the system. Firstly, in continuous operation the steady state temperature stays close to the mean temperature from batch operation (65.02 °C) if the mean lime-to-water ratio from the batch operation is used. Secondly, higher flows result in slightly lower temperatures but the ratio of the reactants is the most deciding factor of the system temperature.

The temperature differences between the different total flow rates are due to the corresponding lime concentrations. At higher flows the reactants exit the slaker faster and there is less time for the lime to react.

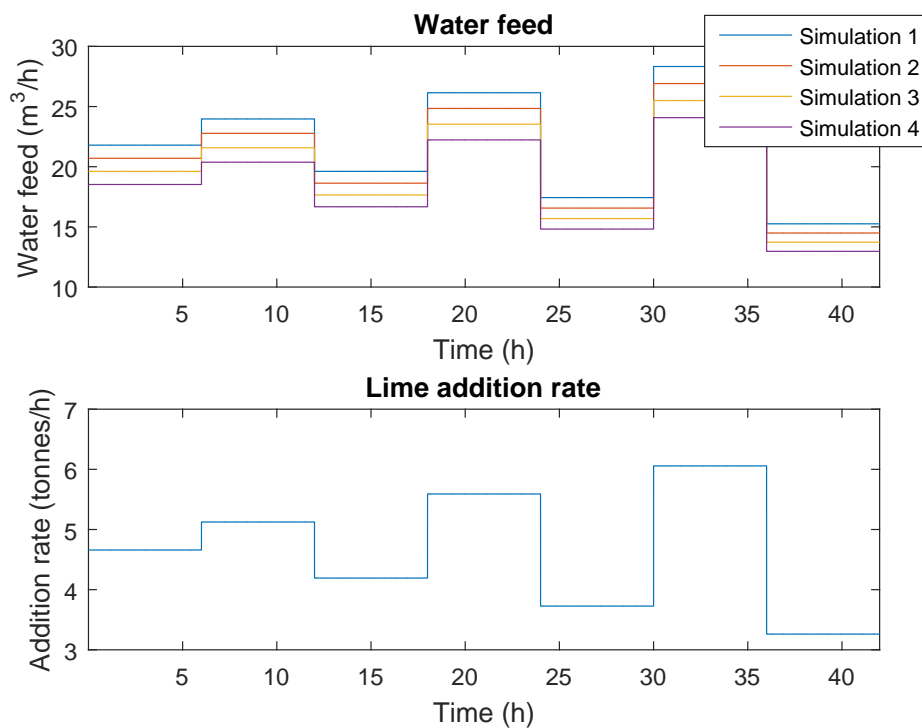


Figure 4.7: Continuous operation test input.

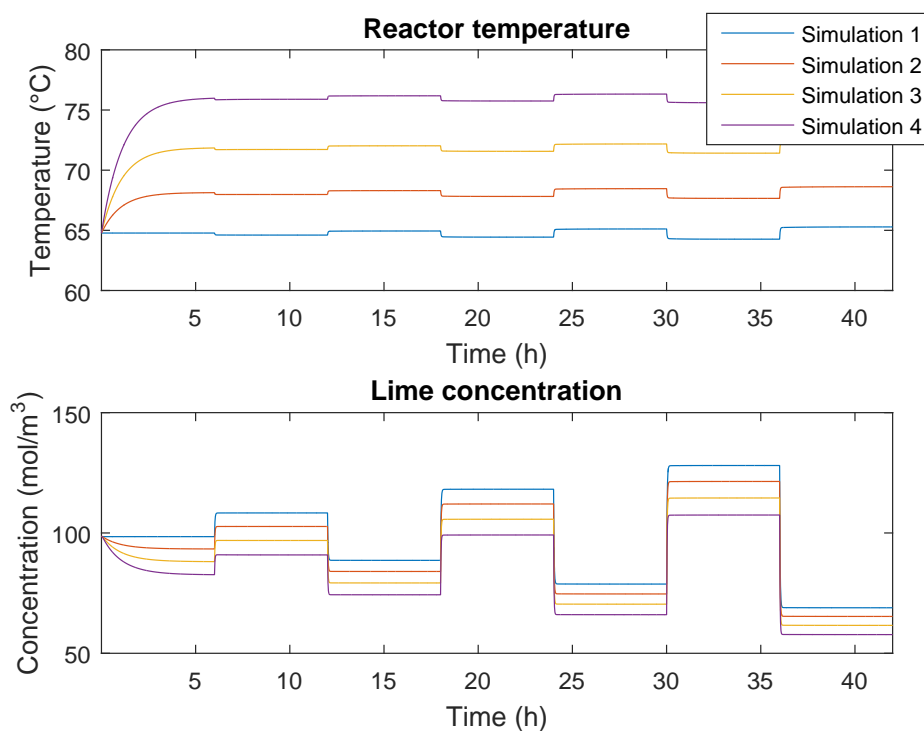


Figure 4.8: System states with the continuous operation test input.

Delayed inputs

One way to alter the process without changing the reactant rates or ratios is to modify the feed timings. Figures 4.9 and 4.10 show the effects of delaying the water or lime addition by one minute. The original model output is also shown as a reference.

It seems that delaying the water feed reduces the final slaking temperature by approximately two degrees Celsius and the lowest temperature of a batch seems to be only minimally higher. On the other hand delaying the lime feed by one minute results in a two degree increase in the final temperature and the temperature at the end of the water addition is only slightly lower than the reference.

According to these experiments the final slaking temperature could be increased by delaying the lime addition but this also increases the temperature variations. Delaying the water feed gives a lower final temperature but reduces the temperature variability which could also mean lower quality variations in the final product. The model suggests that by combining a delayed water feed with a reduced water amount higher temperatures with lower variability could be obtained.

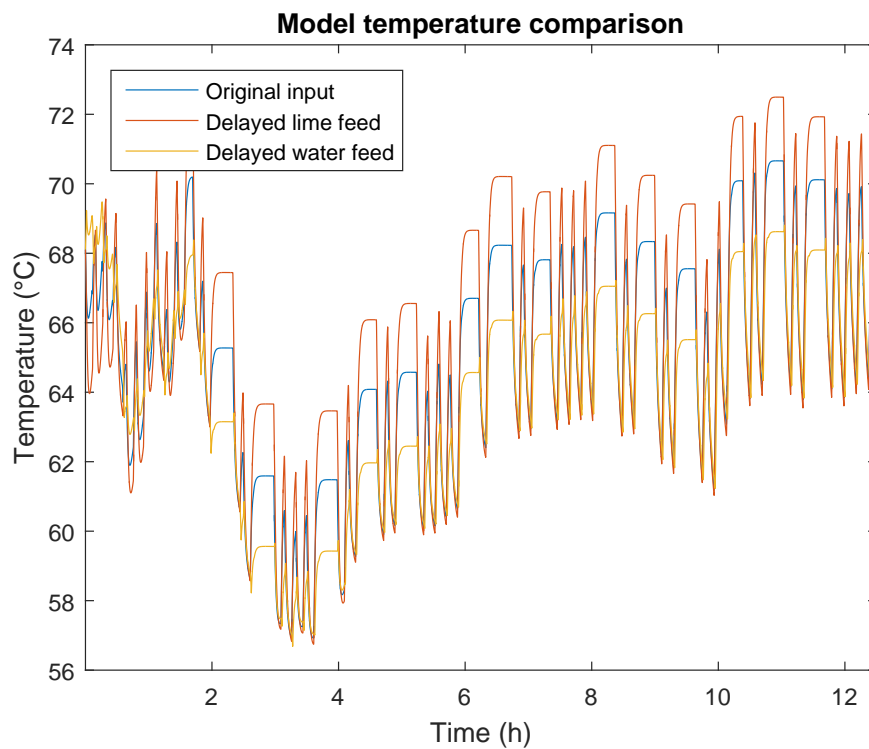


Figure 4.9: Model output with the model building data (blue), delayed lime feed (orange) and delayed water feed (yellow).

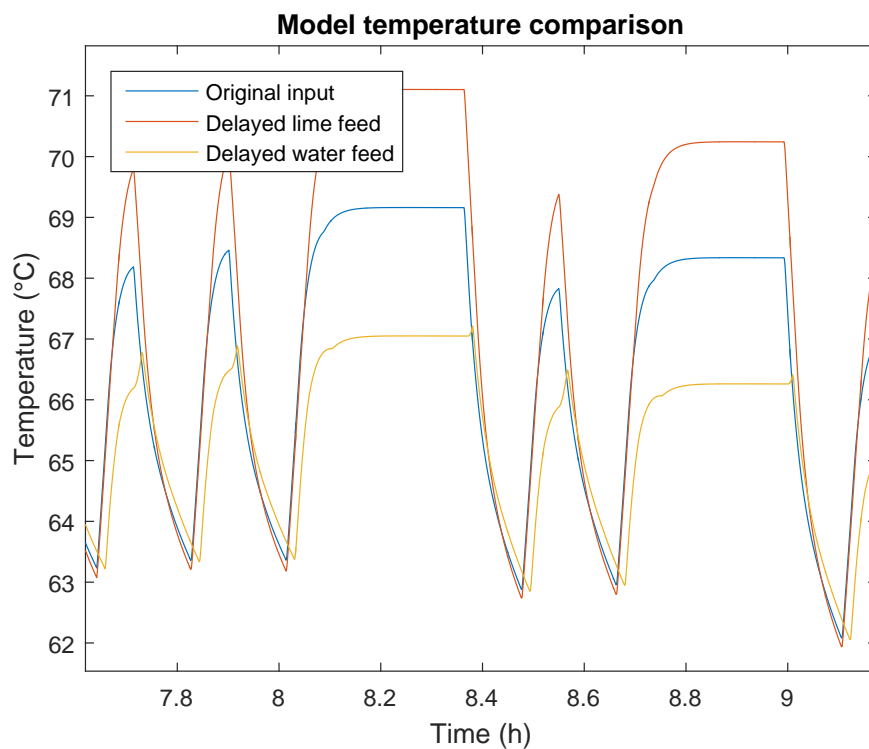


Figure 4.10: Closer view on the delay comparison.

5 Summary

The purpose of this thesis was to create a computer model of a quicklime slaker to potentially improve its performance. In the modeling it was assumed that the volume, density and heat capacity remain constant and perfect mixing keeps the temperature and lime concentration identical everywhere in the reactor. It was also assumed that the reaction between quicklime and water is first order, the temperature of the added lime doesn't have an impact and that there are no heat losses to the environment. All these assumptions were found to be feasible.

The modeling equations were derived for a continuous stirred tank reactor. The concentration of quicklime in the reactor depends on the amount of lime from the inlet feed, flow of unreacted lime through the reactor outlet and the reaction rate. Due to overflow discharge in the slaker the volume of the reactor contents stays constant and the volumetrical flows to and from the reactor are always identical. The rate of reaction depends on the concentration of lime and temperature in the reactor tank as per the Arrhenius equation.

The energy balance of the reactor is based on two effects: the difference between the water feed and reactor temperatures, and the amount of heat generated by the exothermic reaction. The reaction rate from the concentration calculation was also used to calculate the corresponding amount of released heat. The effect of the heat losses through the reactor jacket was considered negligible and this didn't cause any problems in practice.

The available data for modeling were the water feed rate, lime storage silo weight and reactor temperature. The lime weight measurement needed to be transformed to a lime addition rate. Measurements of the reactor outflow, water feed temperature or the concentration of lime in the reactor were not available.

Separate sets of data were selected for model building and validation. The system parameters were estimated with the Matlab grey-box estimation tools. Predetermined fixed values were used for the reactor volume, reaction activation energy, ideal gas constant and the heat of reaction. The remaining four parameters that were left to be identified were the water feed temperature, specific gravity of lime, heat capacity times density, and the pre-exponential nonthermal factor of the Arrhenius equation.

The identified model was able to describe the model building dataset well. Some temperature peaks in the measurement data couldn't be described by the model but

the difference between the estimate and the measurement remained mostly within one degree Celsius. These momentary deviations didn't seem to affect the temperature estimation of the following batches.

The validation dataset contained larger temperature variations but the model was still able to predict the reactor temperature satisfactorily. Deviations from the measured value were more frequent but the temperature difference between the model output and the measurement stayed typically below one degree Celsius.

The slaker was found to be operating around 65 °C according to the temperature measurement data. This was below the recommended temperature range as higher temperatures generally yield a more reactive hydrate. The model was used to estimate how much the water feed rate should be decreased in order to reach the desired temperatures. In the model building dataset the slaker was operated with an average lime-to-water ratio of 1:4.68. It was found out that by reducing the ratio by 15 % to approximately 1:4 the average temperature could be raised by 11 °C while still maintaining the consistency of the milk of lime.

Due to the lack of a control valve making adjustments to the water feed rate is not possible while the plant is in operation. The proposed water amounts can be tested by reducing the time that the water inlet valve is kept open, and the process modifications could be performed during the next maintenance break. While the average temperature could be raised without changing the feed rate, distributing the water addition over a longer period decreases the rapid temperature impact.

All the used data was from late spring so it would have been interesting to see how much the process behavior changes during the extremely cold winter periods. It is possible that with outside temperatures below -35 °C the heat losses to the environment might become more significant. The available data from the historical database did not have enough resolution to allow proper performance comparisons.

Overall, the goals of the thesis were fulfilled. The derived model was able to describe the process dynamics with a reasonable accuracy. Then, using the model a new recommendation for the water amount was quantified.

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A Lime reactivity tests

Lime reactivity test data was available from lime samples taken in September and October 2015 and the results are shown in Table [A1](#).

In the reactivity test quicklime and water were mixed with a 1:4 ratio and the time that it took for the temperature to rise from 20 °C to 60 °C was measured. The results are shown on the slaking time column as minutes.

The final slaking temperatures are shown on the Temperature T_{\max} column.

Table A1: Lime reactivity test data

Date	Slaking time 60 °C (min)	Temperature T_{\max} (°C)
1.9.2015	3.65	71.2
2.9.2015	3.28	70.1
3.9.2015	3.9	70.59
4.9.2015	2.87	70.51
5.9.2015	3.03	71.29
7.9.2015	3.6	69.51
8.9.2015	2.72	69.8
9.9.2015	3.05	70.11
10.9.2015	3.58	73.39
11.9.2015	2.4	71.61
11.9.2015	2.3	72.18
12.9.2015	3.13	69.25
13.9.2015	2.93	69.98
14.9.2015	3.02	70.59
15.9.2015	2.97	71.28
16.9.2015	3.13	72.3
17.9.2015	3.38	72.59
18.9.2015	2.87	69.48
19.9.2015	3.15	69.59
21.9.2015	2.97	71.2
22.9.2015	2.53	71.5
22.9.2015	2.35	69.56
22.9.2015	2.88	69.2
22.9.2015	3.92	70.1
23.9.2015	4.07	71.63
24.9.2015	3.52	70.63
25.9.2015	3.62	70.51
26.9.2015	2.85	68.92
27.9.2015	2.58	70.52
28.9.2015	2.97	72.02
29.9.2015	3	71.35
30.9.2015	3.33	70.64
1.10.2015	3.05	72.1
2.10.2015	2.32	71.49
3.10.2015	3.17	70.82
4.10.2015	2.67	66.8
5.10.2015	3.28	71.69
6.10.2015	3	72.4
8.10.2015	2.33	73.28
9.10.2015	3.18	72.42
16.10.2015	1.72	74.54
17.10.2015	1.27	76.37
18.10.2015	1.38	75.05
19.10.2015	1.67	73.61

B Matlab model

Here the Matlab model of the reactor is described. Also the essential .m scripts that were used for modeling are included.

B.1 Model construction

The practical model fitting of the reactor data was implemented in the Matlab [35] numerical computing environment from Mathworks. The model fitting was performed using the System Identification Toolbox [36] that enables modeling of dynamic systems from input-output data. In particular, the grey-box modeling functionality was utilized to find the proper parameter values for the derived equations.

The concentration and energy balance equations from Section 3.7 were implemented as the function *cstr_m.m* which calculates the time derivative of the system given the current system state, control values and a set of parameters. The function definition is as follows:

```
function [ dx, y ] = cstr_m( t, x, u, T_w, V, SG, HD, k_0
    , E, R, H, varargin )
```

The function returns two values. The first return value *dx* is a vector that contains the concentration of CaO in moles per cubic meter and the reactor temperature in kelvins. The temperature measurement is stored in the variable *y* and is equal to *x*(2). This redundancy is required for the Matlab System Identification Toolbox function *idnlgrey* that was used to build the nonlinear grey box model and estimate its parameters.

Table B1: Model parameters for the *cstr_m* function.

Parameter	Symbol	Description	Units
<i>T_w</i>	T_w	Water feed temperature	K
<i>V</i>	V	Reactor volume	m ³
<i>SG</i>	SG	Specific gravity of quicklime	g/cm ³
<i>HD</i>	ρc_p	Heat capacity times density	kJ/(m ³ K)
<i>k_0</i>	k_0	Pre-exponential nonthermal factor	1/h
<i>E</i>	ΔE	Activation energy	J/mol
<i>R</i>	R	Gas constant	J/(mol K)
<i>H</i>	ΔH	Heat of reaction	kJ/mol
<i>varargin</i>	-	Not used	-

Also the function parameters have to follow the toolbox requirements which means that the current time \mathbf{t} , current state \mathbf{x} and control value \mathbf{u} have to be defined before the modeling parameters. These parameters and their respective units are listed in Table B1.

The model parameter initialization, selection of estimation and validation data and fitting the model to the data was performed in a script called *modeling.m*.

The scripts follow the example case given in the Matlab online documentation for performing grey-box estimation of a continuously stirred tank reactor [37]. The problem that is considered in the documentation is the same one that was presented by Bequette [33].

In the example case the inlet feed stream remains constant but the inlet feed stream temperature and the concentration of the reactant in the inlet feed stream are controlled. The reactor jacket is simultaneously cooled and the coolant temperature is controlled. [37] In comparison, we have only two input values, namely the flow rate of water and mass rate of quicklime.

The system states are identical in both cases. The first state is the concentration of the reactant while the second one is the reactor temperature. In the example case the concentration is also measured and modeled to fit the input-output data. [37] Only the temperature measurement was available to us so the concentration remained as an internal state.

The workflow for the modeling can be broken down into the following steps:

1. Load data and calculate mass flow from lime weight data.
2. Select data for estimation and validation.
3. Set initial guesses for the system states and parameters.
4. Create the model object.
5. Set parameter and state constraints.
6. Estimate model.
7. Display results.

The model had eight different parameters in total, four of which were given fixed values based on knowledge of the process and the reaction. The values for the four remaining parameters were then found by running the model estimation procedure.

The parameters, constraints and the model function were used to construct the *idnlgrey* object. Also the names and units of the input and output variables were defined. [38] The additional parameters can be used to select the ordinary differential equation (ODE) solver and the related properties [39] but the selection was left at the automatic setting and the Runge-Kutta(4,5) solver *ode45* was used as a result.

The model parameters were estimated with the *nlgreyest* routine from the Matlab System Identification Toolbox. The function takes the estimation data set and the model object as parameters and tries to find the parameter values that best match the data [40]. The maximum number of optimization iterations was set to 25.

B.2 Estimated parameters

Four of the eight system parameters were fixed to known values and the remaining four parameters were left to be estimated. The optimizer required nine iterations before the change in the cost function was smaller than the threshold. The optimization yielded the following model:

```
nlgr =
Continuous-time nonlinear grey-box model defined by 'cstr_m' (MATLAB file):

    dx/dt = F(t, u(t), x(t), p1, ..., p8)
    y(t) = H(t, u(t), x(t), p1, ..., p8) + e(t)

with 2 inputs, 2 states, 1 output, and 4 free parameters (out of 8).

Inputs:
  u(1) Inlet water stream(t) [m^3/h]
  u(2) Inlet lime feed(t) [tonnes/h]
States:
  x(1) Concentration of A in reactor tank(t) [mol/m^3]
  x(2) Reactor temperature(t) [K]
Output:
  y(1) Reactor temp.(t)
Parameters:
  value      standard dev
  p1 Water feed temperature [K]      277.281  0.227719 (est) in [273.15, 293.15]
  p2 Reactor volume [m^3]            21       0 (fix) in [0, Inf]
  p3 Specific gravity [g/cm^3]       3.99544  4.85138 (est) in [2, 4]
  p4 Heat capacity times density [kJ/(m^3*K)] 3993.52  15.6486 (est) in [0, Inf]
  p5 Pre-exponential nonthermal factor [1/h] 11617.3  117.614 (est) in [0, Inf]
  p6 Activation energy [J/mol]       16000    0 (fix) in [0, Inf]
  p7 Ideal gas constant [J/(mol K)]   8.3145   0 (fix) in [0, Inf]
  p8 Heat of reaction [kJ/mol]       -65.3    0 (fix) in [-Inf, 0]

Name: Stirred tank reactor

Status:
Termination condition: Change in cost was less than the specified tolerance.
Number of iterations: 9, Number of function evaluations: 10

Estimated using Solver: ode45; Search: lsqnonlin on time domain data "Estimation data".
Fit to estimation data: 84.6%
FPE: 0.2583, MSE: 0.258
More information in model's "Report" property.
```

B.3 Model scripts

The main part of the modeling was performed with the *cstr_m.m* function and the *modeling.m* script. They are included in the subsections below. The different test case scripts that were used are not included here.

B.3.1 cstr_m.m

```
function [ dx, y ] = cstr_m( t, x, u, T_w, V, SG, HD, k_0
    , E, R, H, varargin )
%CSTR_M Continuous Stirred Tank Reactor
%
% Input variables:
% x: current state
%     x(1) C_A: concentration of CaO [mol/m^3]
%     x(2) T: reactor temperature [K]
% u: input signals
%     u(1) F_w: water flow [m^3/h]
%     u(2) F_l: lime feed [tonnes/h]
% y: output signal
%     y(1) T: reactor temperature [K]
% T_w: water temperature [K] (fixed)
% V: volume [m^3] (fixed)
% SG: specific gravity of the lime [g/cm^3]
% HD: heat capacity times density [kJ/(m^3*K)]
% k_0: pre-exponential nonthermal factor [1/h]
% E: Activation energy [J/mol]
% R: Gas constant [J/(mol*K)]
% H: heat of reaction [kJ/mol]
%
%
% Output variables:
% dx: state derivative
% y: measurements
%
% Equations:
```

```

% CaO balance:
%
% 
$$\frac{dC_A}{dt} = \frac{F_l}{V} C_{Af} - \frac{F_w + F_l}{V} C_A - r$$

%
% Energy balance:
%
% 
$$\frac{dT}{dt} = \frac{F_w}{V} (T_w - T) + \frac{-\Delta H}{\rho c_p} r$$

%
% Rate of reaction:
%
% 
$$r = k_0 \exp(-\Delta E / (R T)) C_A$$

%
% Initialize variables
M = 56.08e-6;           % Molar mass of CaO [tonnes/
    mol]
% Note: use tonnes/mol to be compatible with the
% units of the mass flow
% of CaO

C_A = x(1);           % Concentration of CaO [mol/m^3]
T = x(2);             % Tank temperature [K]
F_w = u(1);           % Water flow [m^3/h]
F_lm = u(2);          % Lime mass flow [tonnes/h]
F_l = F_lm/SG;        % Volumetric lime flow [m^3/h]

% Output equations
y = T;               % reactor temperature

% Arrhenius equation
r = k_0*exp(-E/(R*T))*C_A;

% State equations

```

```

dC = F_lm / (V*M) - (F_w + F_l)/V * C_A -r;
dT = F_w / V * (T_w - T) - H / (HD) * r;
dx = [dC; dT];

```

```
end
```

B.3.2 modeling.m

```

%% Modeling script
% This script is used for modeling of the reactor.

%% Load data
addpath('utils');
load('modelingDatasets');
T = c2k(T); % transform temperature from
             Celsius to Kelvin

%% Modify weight data to be suitable for modeling
% differentiate, use negative sign to give positive flow
  rates
% use the gradient function to maintain the vector length
W_d = -gradient(W); % tonnes/5s (sampling time 5s)
% transform to tonnes/h
samplingTime = 5; % sampling time in seconds
sInHour = 60*60; % seconds in an hour
samplesPerHour = sInHour / samplingTime;
W_d = W_d*samplesPerHour; % tonnes/h

%% Create estimation and validation data
range_estimation = 22000:31000;
range_validation = 39530:48950;

F_e = F(range_estimation); % estimation water flow
T_e = T(range_estimation); % estimation temperature
W_e = W_d(range_estimation); % estimation lime feed rate

F_v = F(range_validation); % validation water flow
T_v = T(range_validation); % validation temperature

```

```

W_v = W_d(range_validation);% validation lime feed rate

%% Initial states and parameters
C_init = 0;           % Initially no CaO in reactor [mol/l]
T_init = T_e(1);     % Starting temperature [K]
T_w = c2k(4);        % Incoming water temperature assumed
    4 C [K]
V = 21;              % Reactor volume [m^3]
SG = 2.5;            % Specific gravity of lime [g/cm^3]
    or [tonnes/m^3]
H = -65.3;           % Heat of reaction [kJ/mol]
k_0 = 1.32e4;        % Pre-exponential factor [1/h]

R = 8.3145;          % Gas constant [J/(mol K)]
E = 16e3;            % Activation energy [J/mol]

% Initial heat capacity times density
C_w = 4.1819;        % water heat capacity [kJ/(kg K)]
rho = 998.2;         % water density [kg/m^3]
HD = C_w*rho;        % heat capacity times density
    estimate [kJ/(m^3 K)]

%% Create model
FileName = 'cstr_m';% File describing the model structure
.
Order = [1 2 2];     % Model orders [ny nu nx].
Parameters = [T_w; V; SG; HD; ... % Initial parameters.
    k_0; E; R; H];
InitialStates = [C_init; T_init]; % Initial states.
Ts            = 0;           % Time-continuous
    system.
nlgr = idnlgrey(FileName, Order, Parameters,
    InitialStates, Ts, 'Name', ...
        'Stirred tank reactor', ...
        'TimeUnit', 'hours');

```

```

nlgr.InputName = {'Inlet water stream' ... % u(1)
                 'Inlet lime feed'};      % u(2)
nlgr.InputUnit = {'m^3/h' 'tonnes/h'};
nlgr = setinit(nlgr, 'Name', ...
               {'Concentration of A in reactor tank' ... % x(1)
                'Reactor temperature'});    ... % x(2)
nlgr = setinit(nlgr, 'Unit', {'mol/m^3' 'K'});
nlgr = setinit(nlgr, 'Fixed', {false false});
nlgr.OutputName = {'Reactor temp.'};      % y(1)
nlgr.OutputUnit = {'K'};

nlgr = setpar(nlgr, 'Name', ...
              {'Water feed temperature' ... % T_w
               'Reactor volume' ... % V
               'Specific gravity' ... % SG
               'Heat capacity times density' ... % HD
               'Pre-exponential nonthermal factor' ... % k_0
               'Activation energy' ... % E
               'Ideal gas constant' ... % R
               'Heat of reaction' ... % H
              });
nlgr = setpar(nlgr, 'Unit', {'K' 'm^3' 'g/cm^3' ...
                             'kJ/(m^3*K)' '1/h' 'J/mol' 'J/(mol K)' 'kJ/mol'});

%% Set parameter constraints

nlgr.Parameters(2).Fixed = true; % Fix V.
nlgr.Parameters(6).Fixed = true; % Fix E
nlgr.Parameters(7).Fixed = true; % Fix R.
nlgr.Parameters(8).Fixed = true; % Fix H.

nlgr.Parameters(1).Minimum = c2k(0); % T_w.
nlgr.Parameters(1).Maximum = c2k(20);
nlgr.Parameters(2).Minimum = 0; % V
nlgr.Parameters(3).Minimum = 0; % SG.
nlgr.Parameters(3).Maximum = 4; % SG.

```



```

nlgr.Parameters(4).Minimum = 0;    % HD
nlgr.Parameters(5).Minimum = 0;    % k_0
nlgr.Parameters(6).Minimum = 0;    % E
nlgr.Parameters(7).Minimum = 0;    % R.
nlgr.Parameters(8).Maximum = 0;    % H.

% Concentration must not be negative
nlgr.InitialStates(1).Minimum = 0;
present(nlgr);

%% Create iddata objects
Ts = 1 / samplesPerHour;          % sampling time in hours

% Estimation data
ze = iddata(T_e, [F_e W_e], Ts, 'Name', 'Estimation data'
);
ze.InputName = nlgr.InputName;
ze.InputUnit = nlgr.InputUnit;
ze.OutputName = nlgr.OutputName;
ze.OutputUnit = nlgr.OutputUnit;
ze.Tstart = 0;
ze.TimeUnit = 'hours';
ze.ExperimentName = 'Estimation';

% Validation data
zv = iddata(T_v, [F_v W_v], Ts, 'Name', 'Validation data'
);
zv.InputName = nlgr.InputName;
zv.InputUnit = nlgr.InputUnit;
zv.OutputName = nlgr.OutputName;
zv.OutputUnit = nlgr.OutputUnit;
zv.Tstart = 0;
zv.TimeUnit = 'hours';
zv.ExperimentName = 'Validation';

%% Plot estimation data

```

```

plotiddata(ze)

%% Plot validation data
plotiddata(zv)

%% Estimate model
opt = nlgreyestOptions('Display','on');
opt.SearchOption.MaxIter = 25;
nlgr = nlgreyest(ze, nlgr,opt);

%% Present model results
present(nlgr)

%% Display model with estimation data
figure
compare(ze,nlgr);

%% Display model with validation data
figure
compare(zv,nlgr);

```

B.4 Utility functions

The small helper functions that were used to streamline the modeling script are shown in this section. The function that was used to fit the process data to the shrinking sphere model is also included here.

B.4.1 k2c.m

```

function [ t ] = k2c( T )
%K2C Kelvin to Celcius
% Transform from K to C
t = T - 273.15;
end

```

B.4.2 c2k.m

```
function [ T ] = c2k( t )
%C2K Celsius to Kelvin
% Transform from C to K
T = t + 273.15;
end
```

B.4.3 plotiddata.m

```
function plotiddata( z )
%PLOTIDDATA
%Plot the input and output data of an iddata object
figure('Name', [z.Name ': input data']);
subplot(2,1,1)
plot(z.SamplingInstants, z.InputData(:,1));
title('Inlet water stream');
xlabel('Time (h)')
ylabel('Flow (m3/h)')
axis tight

subplot(2,1,2)
plot(z.SamplingInstants, z.InputData(:,2));
title('Inlet lime feed');
xlabel('Time (h)')
ylabel('Feed rate (tonnes/h)')
axis tight

figure('Name', [z.Name ': output data']);
plot(z.SamplingInstants, k2c(z.OutputData(:,1)));
title('Reactor temperature')
xlabel('Time (h)')
ylabel(['Temperature (' char(176) 'C)'])
axis tight

end
```

B.4.4 shrinking_sphere.m

```
function [ y_out ] = shrinking_sphere( Tm )
%SHRINKING_SPHERE
% Fit data to shrinking sphere model
if (isvector(Tm))
    y_out = calc_T(Tm);
else
    y_out = zeros(size(Tm));
    for i = 1:size(Tm,2)
        y_out(:,i) = calc_T(Tm(:,i));
    end
end
end

function y = calc_T(T)
    T0 = min(T);
    Tend = max(T);

    dT = Tend - T0;
    T = T - T0;

    x = T / dT;

    y = 1 - (1-x).^(1/3);
end
```