Modelling and Evaluation of a Waste Incineration Flue Gas Treatment Process

by

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Preface

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Abstract

As environmental awareness is raised, flue gas treatment is gaining more interest and stricter legislation on emissions pushes technological development. Sysav has a waste incineration plant with a flue gas cleaning process which includes removal of acid gases. This is performed by two subsequent scrubbers and following each scrubber a droplet separator is located to prevent transfer of liquid to the next unit. The objective of the report was to study sources to scaling on droplet separators. A literature study reviewed key parameters connected to absorption and scaling, which were compared to Sysav’s operating conditions. It was found that scaling typically consists of calcium sulfite hemihydrate ($CaSO_3$* ½ H_2O) and calcium sulfate dihydrate ($CaSO_4*2H_2O$). Aspen Plus was used to develop a model to represent Sysav’s process and qualitatively assess key parameter influence on absorption of HCl and SO_2, and formation of $CaSO_3$* ½ H_2O and $CaSO_4*2H_2O$. Operational data from the process was implemented from specific time periods. Sensitivity analyses were carried out in which key parameters such as pH, liquid flow, gas flow, temperature and oxygen content were varied. The model successfully modeled absorption of HCl and SO_2 with dependance on key parameters as expected for all key parameters except liquid-to-gas ratio. Calcium sulfite formation was influenced by key parameters according to theory for most parameters but deviating results occurred. Calcium sulfate formation was troubled with unexpected results from the sensitivity analyses. The chemistry for the solid formation in Aspen should be improved in future studies. Actions for scale control in Sysav’s process were proposed such as stabilizing pH, investigating limestone utilization, modifying demister washing procedures and adding particles for seeding.

Sammanfattning

Allteftersom medvetenhet kring miljöfrågor växer får rökgasrening mer uppmärksamhet och striktare lagar på utsläpp gör att teknologin snabbt utvecklas. Sysav har en avfallsförbränning med en rökgasreningsprocess som innefattar avskiljning av sura gaser. Detta sker i två på varandra följande skrubbrar och efter respektive enhet finns en droppavskiljare för att förhindra att vätska överförs till nästkommande enhet. Syftet med denna rapport var att studera källor till uppbyggnaden av beläggningar på droppavskiljarna. En litteraturstudie identifierade nyckelparametrar kopplade till absorption och beläggningar, vilka sedan kunde jämföras med driftsförhållanden i Sysavs anläggning. Det framkom att beläggningar typiskt består mestadels av kalciumsulfithemihydrat ($CaSO_3$*½H_2O) och kalciumsulfatedihydrat ($CaSO_4$*2H_2O). Aspen Plus användes för att utveckla en simuleringsmodell som representerade Sysavs process och kvalitativt kunna utvärdera absorption av sura komponenter samt bildat $CaSO_3$* ½ H_2O och $CaSO_4$*2H_2O. Driftsdata från anläggningen var implementerad från specifika tidsperioder. Känslighetsanalyser genomfördes där nyckelparametrar såsom pH, vätskeflöde, gasflöde, temperatur och syrehalt i rökgasen varierades. Modellen kunde framgångsrikt simulera HCl och SO2 absorption och dess beroende på varierade nyckelparametrar, förutom vätske-gasförhållande. $CaSO_3$* ½ H_2O bildning påverkades av nyckelparametrar på det sätt som beskrevs i teorin för de flesta parametrar, men avvikande resultat förekom. $CaSO_4$*2H_2O bildning hade problem med avvikande beroende på nyckelparametrar. Kemin för kristalliseringen i Aspen Plus borde förbättras i framtiden. Åtgärder för minskning av beläggningar i Sysavs process föreslogs såsom att stabilisera pH, undersöka kalciumkarbonat utnyttjande, modifiera spolningsprocedurer av droppavskiljare och tillsätta fasta partiklar.

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1 Introduction

As incineration is used for handling a variety of society's waste, and environmental awareness is spreading, reduction of air emissions from combined heat and power waste incineration plants has become of growing importance. Stricter legislation has led to rapid development of waste incineration technology over the last 25 years and flue gas cleaning processes have been improved[1]. In Sweden, 4.8 million tons of municipal waste was generated in 2020 of which 47% was incinerated. The category municipal waste includes waste from households as well as similar waste from restaurants, offices and stores[2]. The waste consist of a wide range of compounds and the flue gases will consequently contain emissions which are necessary to remove[1].

Acid compounds, such as sulfur oxides (SO_x/SO_2), are formed during incineration. In *Best Available Techniques (BAT) Reference Document for Large Combustion Plants*[3] it was reported that 66.9% of SO_x/SO_2 emissions originate from thermal power plants and other combustion installations, a category which includes waste incineration plants[3]. As SO_2 is known to have considerable negative effects on both human health and environment, it is enforced by Swedish law to keep emission levels beneath 50 mg/Nm^3 flue gas per 24 hours[4]. Health issues which can arise are breathing difficulties, respiratory diseases, aggravation of cardiovascular disease. Moreover, the acid compounds propagate in the environment by acid rain, resulting in acidification of lakes and streams, as well as damage on trees and agricultural crops[5]. To control emissions, combustion plants implement several post-combustion separation units, often including some type of desulfurization technology[1, 3].

Sysav is one of the 34 existing municipal waste incineration plants in Sweden[1], and is permitted to incinerate 630 000 tons of waste every year[6]. Both municipal and industrial waste is incinerated. The plant has four operating boilers named boiler 1-4. In this report boiler 3 will be studied, which was put into operation in 2003 and produces both electrical power as well as district heating. A scrubber system is used to clean the flue gases. The first scrubber is the "acidic scrubber" in which lime slurry is sprayed through the flue gas with the main purpose to remove HCl, HF, Hg, heavy metals and dust. Similarly, the second scrubber uses lime slurry, however with the aim to separate sulphur dioxide. The pH is higher in this unit giving rise to it being called the "alkaline scrubber". After each scrubber, a demister prevents droplets from being transferred to the next unit.

An identified problem in the scrubber system is the build-up of scaling on the demisters over time. This results in an increased pressure drop and eventually, failure of droplet separation. Thus, regular operational stops for cleaning are necessary. The stops are undesired for both economical as well as work environment reasons.

1.1 Aim

The aim of the project is to conduct a case study of the flue gas cleaning process at Sysav with the objectives to identify key parameters which affect scaling in the demisters and to construct a simulation model in Aspen Plus of the scrubber system. The purpose of the model is to simulate conditions from the facility and analyze absorption and scaling. Finally, it was aspired to propose operational changes in Sysav's facility which could reduce the scaling.

1.1.1 Research questions

The following research questions will be answered in the project.

1. What parameters mainly affect separation efficiency and scaling in a wet flue gas desulphurization (FGD) scrubber system?
2. How can a model be constructed in Aspen Plus which represents Sysav’s scrubber system and can simulate both absorption of acid compounds as well as scaling?
3. What changes can be made in Sysav’s facility which can reduce scaling in the demisters?

1.2 Scope

Only the acidic scrubber (G1), the alkaline scrubber (G2), and liquid droplets separators 1 and 2 (LDS1 and LDS2), were included in the simulation model. The effect on calcium sulfite and calcium sulfate precipitation were studied, excluding other crystal compounds. Furthermore, HCl and SO_2 were only considered as acidic compounds to be absorbed. Numerical verification of the simulation was outside the scope of the project. A qualitative analysis of the results was performed, rather than analyzing numerical results. The simulation model was considered as an early-stage model which can be further developed to improve accuracy.

2 Background

This section aims to provide background on the process and problems related to the case study.

2.1 Process description

An overview of units included in the boiler 3 system at SYSAV is shown in Figure 2.1. The process starts with a bunker in which the waste is dumped as shown by unit number (1) in Figure 2.1. A crane (2) is used to transfer the waste from the bunker to a funnel (3) that leads the waste to the boiler (4) using a pusher. The waste is combusted on a leaning roster which stirs the waste to increase the combustion efficiency. The roster is approximately 100 m^2 and the temperature in the boiler is above 1000 °C. Primary air is injected to the bottom of the boiler, beneath the waste. This is followed by a secondary air injection above the waste to increase the combustion even further by mixing the flue gases. The particles present in the flue gas often adhere to walls in the boiler and are removed by water treatment. The sludge which remains at the bottom, consisting of glass, rock, scrap metal as well as other incombustible material, falls into a water container to cool. Through a sludge discharge (5) the sludge exits the process to become recycled.[6]

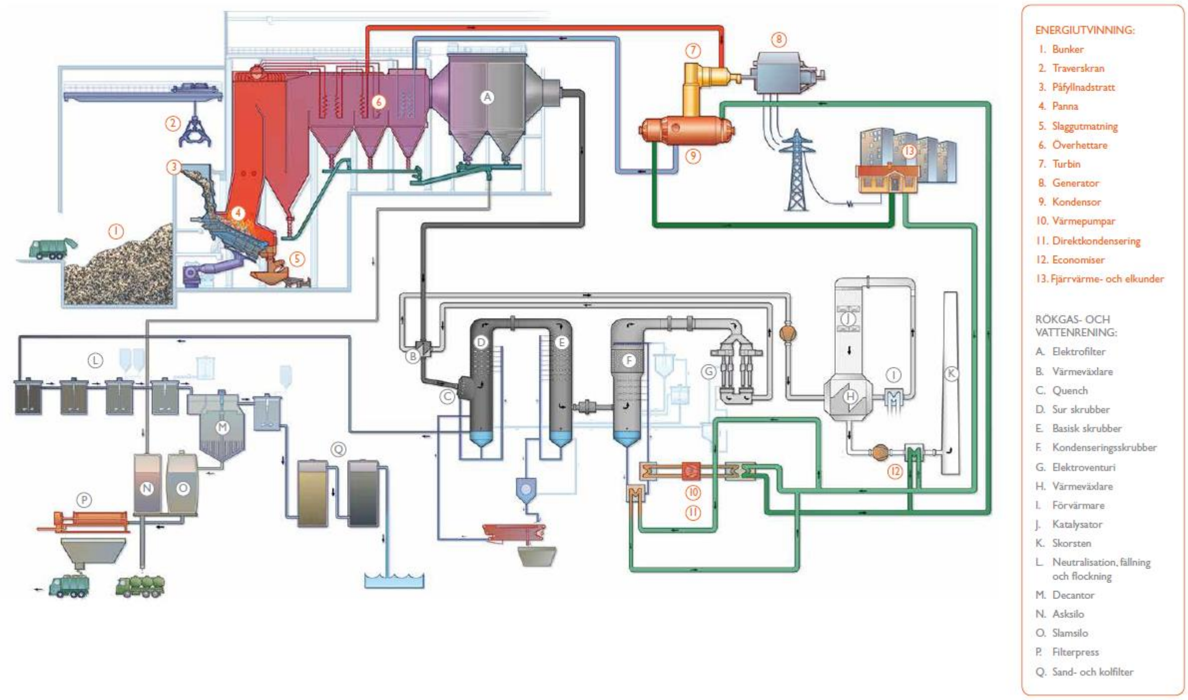


Figure 2.1. An overview of the process for boiler 3 at Sysav. Illustration: Sysav[7].

The waste-to-energy system is initiated with the hot flue gas rising in the boiler and exiting at a temperature of about 850 °C. To accomplish complete combustion of the flue gas, it enters three vertical empty ducts, which consist of boiler tubes with hot walls. Particulates which attach to the walls are removed by a striking apparatus which beats the tubes, causing the particles to fall off. Water flows through the boiler tubes and is heated by the hot flue gas. Thereafter, the flue gas enters a horizontal part of the empty ducts where convection tubes and superheaters (6) make the boiler water reach its highest energy value at 400 °C and 40 bar. The water is now high-pressure steam and is transported to a turbine (7) which produces electrical power using a generator (8). Some of the produced electricity is used for the processes in Sysav's facilities, however, a majority is distributed to the community. The steam is subsequently guided to a condenser (9). Here, district heating water is heated to 80-115 °C, utilizing the energy released from the steam condensing. The heated water is sent to the district heating network (13) and the boiler water is recirculated to the empty ducts. After the district heating water has been used in the municipal network, it is recirculated to the facility. It enters a direct condenser (11), heat pump (10) and a flue gas heat exchanger at a temperature of 40-60 °C. The energy which is recovered in the condenser scrubber (further explained below) is used to increase the temperature of the water 5-10 °C. The last step for the energy recovery system is the economizer (12), which cools the flue gases before being released to the atmosphere, and simultaneously increases the temperature of the water.[6]

The flue gas purification system starts with an electrostatic precipitator (ESP), where ash particles are collected (A). In the filter, the particles are negatively charged by an electrostatic field and can consequently be retained by collection plates, which are positively charged metal sheets. The sheets are shaken periodically, which causes the particles to fall into a dust pocket before being transported to an ash silo. After this unit, the particle content in the flue gas stream is below 20 mg/m^3.[6]

The flue gases are cooled by a heat exchanger (B) before entering the scrubber system. This starts with a quench (C), in which some scrubber water is sprayed into the flue gas to decrease the temperature further and avoid evaporation of the scrubber water in the following step[6]. The temperature is approximately 55 °C, approximately the saturation point of the flue gas[8]. The acidic scrubber (D), referred to as G1, aims to mainly remove acidic gases from the flue gas, such as HCl, HF and SO_3, but also heavy metals such as Hg, as well as remaining particles. Liquid is sprayed at different levels of the scrubber and meets the flue gas in counter-current flow resulting in an absorption of the impurities in the flue gas. The droplets fall to the bottom of the scrubber and a certain level of liquid is maintained in the bottom, which is called the reaction tank or hold tank. Liquid from the reaction tank is recirculated to the spraying nozzles. The pH in this unit is approximately 1.5 as an effect of the dissolution of the acidic compounds in the liquid. To control the pH, alkaline limestone slurry is added to the liquid. A purge stream continuously removes some of the recirculation liquid[6].

After the acidic scrubber follows a liquid droplet separator (LDS1) which has the function to collect droplets and transport them back to the scrubber. This prevents the compounds from disturbing the reactions in the next scrubber. The demister used in Sysav's system is of the vane type which will be further explained later in the report. The captured droplets fall into a pipe, which leads back to the acidic scrubber[6, 9]. The unit is intermittently flushed with process water to decrease coating[10]. Thereafter, an alkaline scrubber, called G2, is used for removal of SO_2 (E). Similarly to the acidic scrubber, it is a spray scrubber, however, co-current flow between sprayed liquid droplets and the flue gas is used. SO_2 dissolves into the droplets which fall into the reaction tank where neutralization with limestone occurs as well as formation of byproducts such as calcium sulfate (gypsum). No air inlet is present, meaning natural oxidation takes place[6, 11]. As in G1, limestone slurry is used for pH control, but a higher pH at approximately 5.8 is desired[12]. The water in the bottom of the scrubber, containing calcium sulfate, unreacted limestone and water, is recirculated to the nozzles for spraying[6]. Calcium sulfite is most likely also present as a byproduct, which will be discussed in the literature review. The purge stream from G2 is led to hydrocyclones which separate gypsum from the liquid. Afterwards, dewatering in a vacuum band filter and eventually, disposal of the gypsum is carried out. A similar demister as LDS1 is placed after the alkaline scrubber for the same purpose, called LDS2[6].

After LDS2, the flue gas enters the third condensation scrubber (F). This aims to condense remaining steam, as well as remove dioxins and any residual SO_2. The scrubber is packed with column packings to increase the contact area. The water condenses on the packing and dioxins follow the water droplets. NaOH is injected to induce final removal of SO_2. [6]

An electroventuri separates the remaining particles from the flue gas (G). The unit consists of 24 pipes which decrease in diameter and in consequence the flow rate increases. The particles are charged negatively by an electrode, in order for them to be collected by a positively charged water mist subsequently.[6]

Prior to the NO_x separation unit, the flue gases are heated in two different heat exchangers, (H and I,) to reach a temperature of 240 °C. NO_x is reduced by a selective catalytic reactor (SCR) unit (J). The unit contains a porous ceramic , which is divided into three levels. NH_3 is injected to the flue gas before it travels through the unit, where NH_3 and NO_x reacts to form N_2 and H_2O. After this final purification step, the flue gases are transported to the stack, where it passes through the economizer before being released to the atmosphere at 70 °C. The system also recirculates 20-30% of the flue gases to decrease NO_x formation in the boiler. The water used in the scrubbers is sent to a separate water purification system.[6]

2.2 Wet scrubbing system

The wet scrubbing system, which will be the focus of this report, consists of the acidic scrubber G1, the first demister LDS1, the alkaline scrubber G2 and the second demister LDS2. Other units in the scrubber system are a quench, prior to G1, and a gypsum separating system of hydrocyclones and tanks after G2. The system is shown in Figure 2.2.

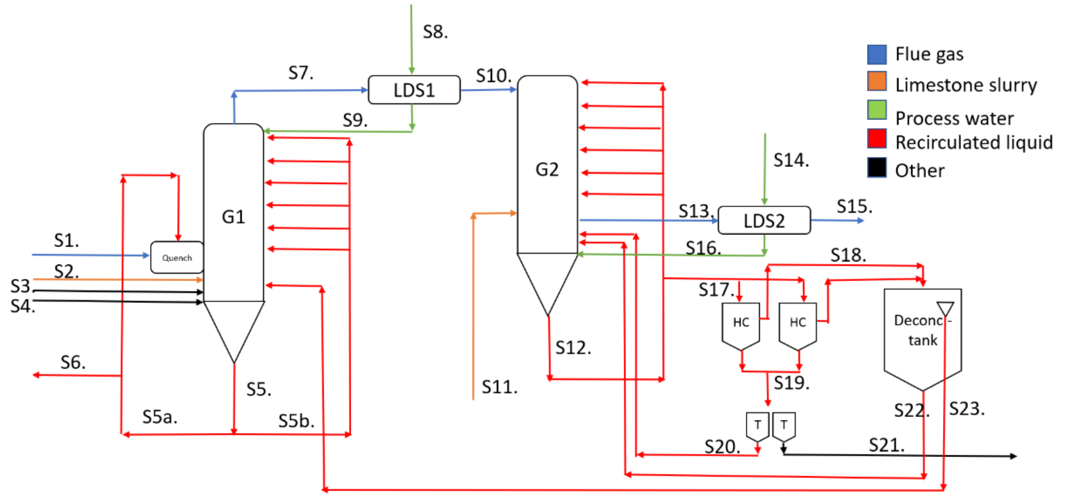


Figure 2.2. The wet scrubbing system. The streams are numbered and further explained in Table 2-1. The illustration was constructed based on flowsheets from the operation unit at Sysav[13].

The streams are summarized in Table 2-1. The inlet streams to G1 are many and include flue gas (S1), limestone slurry (S2), liquid from the gypsum treatment (S3) and liquid from a process water collection tank (S4). Limestone slurry is used to control the pH to 1.5, meaning that injection will only be carried out when the pH is below this value. Another stream enters G1 from LDS1 consisting of entrained liquid droplets which are separated from the flue gas by the unit. In addition, the demister is periodically cleaned using process water (S8) and the outgoing stream enters G1 (S9). Under some conditions, as will be explained later, stream S23 is led to G1 as well.[13]

Liquid from the reaction tank of G1 is recirculated (S5) to the quench to cool the flue gas before entering the scrubber. This ensures that the saturation point is reached to allow for water condensation as well as preventing the spraying liquid from evaporating. It also avoids damage of the scrubber internals. The optimal temperature is 55 °C. However, the actual operating temperature is about 60 °C. A part of S5 however, is used as spraying liquid in the scrubber. The stream is recirculated to spraying nozzles located at different heights in the column to obtain sufficient vapor-liquid contact.[13]

After LDS1 the flue gas will enter G2 at the top of the scrubber. The pH of G2 should be 5.8 and as in G1, limestone slurry injections (S11) are used to counteract pH drops. Liquid from the hold tank of the scrubber is recirculated to spraying nozzles (S12). Like LDS1, LDS2 is cleaned periodically with process water which thereafter enters G2 (S14).[13]

A purge stream (S17) is taken from the recirculation stream and is led to a hydrocyclone. A second hydrocyclone is used as backup in case of malfunction of the first. Gypsum is a byproduct which is formed in G2 and the solid material is separated from the liquid by the hydrocyclone and exits at the bottom of the unit (S19). Depending on the content of gypsum in the stream, which is determined by continuous density measurements, it is either recirculated to G2 (S20) ($\rho < 1025$ kg/m^3) or sent to the gypsum treatment system (S21) ($\rho > 1035$ kg/m^3)[11, 12]. This corresponds to a gypsum concentration of approximately 50 g/L in the recirculation slurry[11]. The liquid which exits the hydrocyclone (S18) enters a deconcentration tank which is necessary to maintain the correct levels of liquid in the bottom of G1 and G2. Primarily, the liquid from the deconcentration tank is sent to G2. However, when a certain level in G2 is reached, no more liquid is allowed to enter this scrubber. Instead, the liquid level in the deconcentration tank will increase until it reaches the inlet tube leading to G1. S23 will in this case lead liquid to the acidic scrubber. The whole process is operated slightly beneath atmospheric pressure.[13]

Table 2-1. Description of the streams in the wet scrubbing system

Stream	Description	Stream	Description
S1.	Flue gas which has passed the ESP and heat exchanger.	**S12.**	Liquid from the hold tank of G2 which is recirculated to the spraying nozzles at different levels of the scrubber.
S2.	Limestone slurry consisting of limestone suspended in water. Same composition as stream 8.	**S13.**	Flue gas exiting G2. It contains droplets and is led to LDS2.

S3.	Water from gypsum treatment.	**S14.**	Process water used for intermediate cleaning of LDS2.
S4.	Liquid from a process water collection (B.M) tank. It is used for collection of process water.	**S15.**	Flue gas exiting LDS2. It is led to scrubber G3.
S5.	Liquid from the hold tank of G1 which is recirculated to spraying nozzles in the quench and at different levels in the scrubber.	**S16.**	Process water exiting LDS2 which is led back to G2.
S5a.	Liquid recirculated to the quench.	**S17.**	Purge stream from the recirculation liquid in G2. It is led to a hydrocyclone for separation of gypsum.
S5b.	Liquid recirculated to the spraying nozzles of the spray column.	**S18.**	Liquid which is separated from the solid gypsum by the hydrocyclone is led to a deconcentration tank.
S6.	Purge stream from the recirculated liquid in G1.	**S19.**	Gypsum which is separated by a hydrocyclone is lead to one of the following tanks. The density of the stream determines which tank.
S7.	Flue gas exiting the scrubber. It contains droplets and is led to LDS1.	**S20.**	If the density of stream S19 is low, the stream is led back to the scrubber.
S8.	Process water used for intermediate cleaning of LDS1.	**S21.**	If the density of stream S19 is high, the stream is led to the gypsum treatment process starting with the vacuum band filter.
S9.	Process water exiting LDS1 which is led back to G1.	**S22.**	From the deconcentration tank the liquid is led back to G2.
S10.	Dry flue gas exiting LDS1 and entering G2.	**S23.**	When the height in the deconcentration tank reaches a certain level, the liquid will be led to G1.

S11.	Limestone slurry consisting of limestone suspended in water. Same composition as stream 2.	

2.3 Scaling problem

As the process is operated, scaling builds up over time on the scrubber internals and the following demisters. The demister scaling is shown in Figure 2.3. If LDS1 has a high amount of scaling, droplet separation efficiency will be reduced, resulting in droplets from G1 transferring to G2. This can lead to reduced pH of G2 and thus, reduced removal efficiency of SO_2. Also, the liquid level in G2 rises. Problems propagate throughout the system, and it is necessary to remove scaling before these effects arise. When cleaning is performed the facility must be stopped, which results in lost income. Moreover, the scaling is hard and difficult to remove, and days of work is required by staff in an inadequate work environment. Both LDS1 and LDS2 are troubled by scaling[14, 15]. Analyses have shown that the main elements present in the scale are calcium and sulfate[16-20].

Some actions have been taken with the purpose of decreasing the scaling. After discussion with the process equipment supplier, gypsum was injected to G1 in boiler 3 at startup summer 2020. The following operational year 2020-2021, cleaning was performed in November and February[15]. The staff claims that 2-3 stops is normal, although lack of documentation on the history of the facility makes it difficult to confirm[14]. Personnel[14] considers the gypsum injections unsuccessful in reducing the amount of scaling. During the spring 2021 a test was carried out in which fresh water was used for flushing LDS1 instead of process water. The result was positive as no more stops were necessary during the spring, however this could also be due to the plant operating at lower load as the weather becomes warmer. Moreover, as mentioned, the gypsum test was carried out during the same operational period and no conclusions can be drawn regarding if any of these actions affected the scaling since no history is available on the number of stops as reference. It should be noted that washing with fresh water is only temporary and cannot be a long-term solution as it requires excessive amounts of fresh water.[14, 15]

During the revision taking place summer 2021, LDS1 was exchanged to a new unit. It was theorized that the surface becomes rougher with time, enhancing particles to stick to it. A more smooth and slippery surface may prevent precipitation from taking place. LDS2 was exchanged in 2015[14]. Pressure drop across LDS1 is measured continuously. LDS2 recently had a pressure measuring device installed[15].

(a) Scaling in droplet separator

(b) Scaling sample

Figure 2.3. Scaling in Sysav's process. Provided by Segerström[21, 22].

3 Technology - Literature Review

The following section contains background of the technologies for acid gas removal, mist eliminators and key parameters which affect the process.

3.1 Alternatives for removal of acid gases

Acid gases, such as HCl, HF and SO_x, are present in the flue gas after combustion. To separate these impurities, absorption or adsorption is often used, and the process can be regenerative or non-regenerative. Non-regenerative technologies can be divided into dry, semi-dry and wet processes[1, 23]. In each category there are further alternatives and the most common are summarized in Figure 3.1. A deeper review will be presented on wet limestone scrubbers, as this technology is employed in Sysav's boiler 3 system. The literature study did not exclusively use information from studies on waste incineration plants, but technologies used in large combustion plants have also been examined as the information is applicable on waste plants as well.

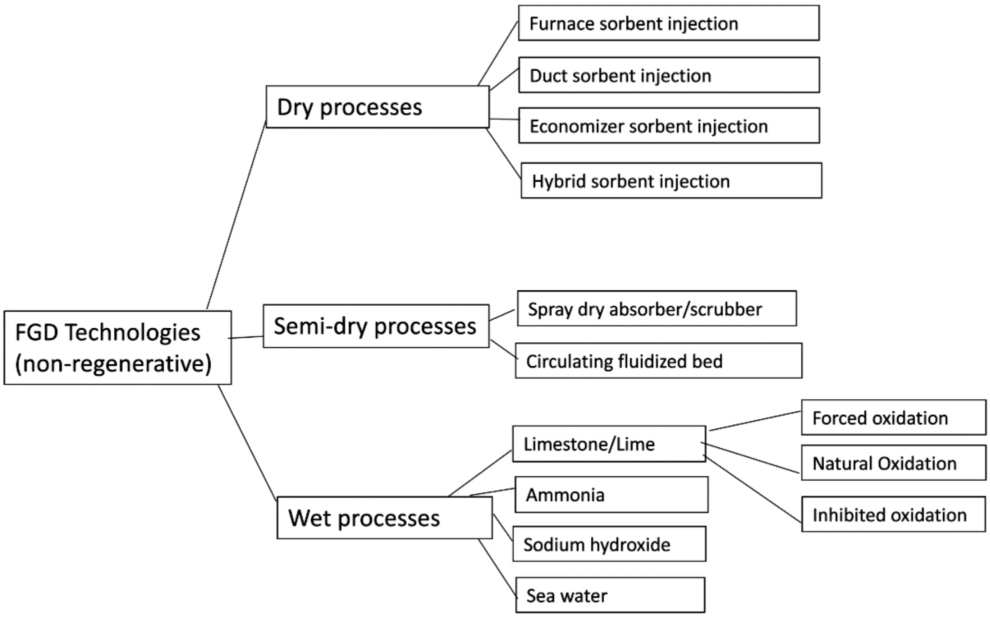


Figure 3.1. Technologies available for flue gas desulphurization. The figure is based on information from literature[3, 5].

3.2 Limestone wet FGD

Limestone wet FGD is the most wide-spread desulphurization system worldwide[24]. Limestone is preferred over lime due to lower cost. Limestone/lime systems use a slurry of the sorption agent and water which comes in to contact with the flue gas and absorbs SO_2. The products will be either a sludge mixture or gypsum depending on the oxidation mode, which will be further explained below. Removal efficiencies up to 99% can be reached[3, 25].

This section provides background on the limestone wet flue gas desulphurization processes specifically. The typical design, chemical reactions taking place, the mass transfer limitations and crystallization mechanisms are reviewed.

3.2.1 Design

Limestone wet FGDs often have at least two steps. The first takes place under acidic conditions and is efficient in removal of HCl, HF and SO_3. However, SO_2 separation is low, due to the presence of HCl disturbing absorption of SO_2, and thus, a second step with higher pH is used for the removal of this. The second stage can also accomplish further removal of the other acidic compounds[1, 23, 26-28]. If bromine or iodine is present in the flue gas the scrubber system tends to remove these impurities as well[1, 23].

Limestone wet FGDs can be divided into the gas-liquid contact zone and the reaction tank. Co-current flow is the most widely spread design and is constructed to have flue gas enter at the bottom of the gas-liquid contact zone and travel upwards due to the low density. Liquid is sprayed through nozzles from the top (and typically at different levels) of the scrubber. The droplets absorb the acidic emissions from the flue gas. The droplets are collected in the reaction tank and limestone slurry is injected as a neutralizing agent due to its alkaline character. Further reactions and formation of byproducts take place in the reaction tank. Some of the liquid is purged to avoid accumulation of the products. To make up for the loss, water and limestone slurry is injected to balance the liquid volume and pH. Liquid is recirculated to the top of the scrubber to be sprayed again.[1, 3] A schematic over a typical scrubber is displayed in Figure 3.2.

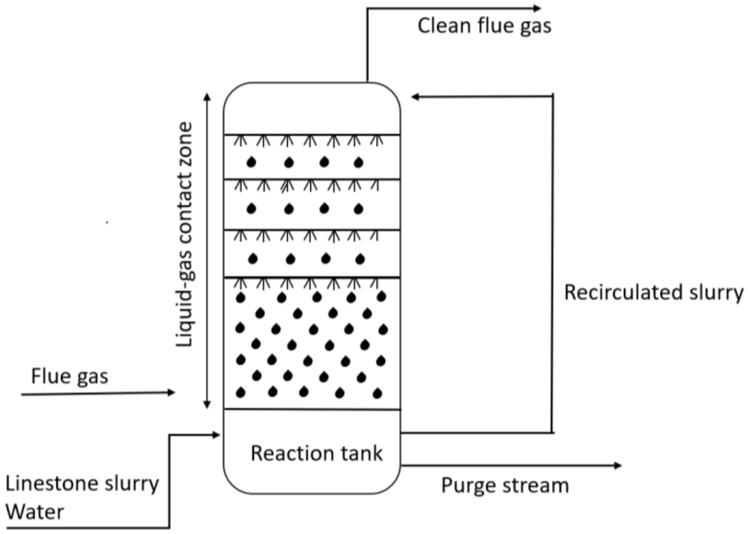


Figure 3.2. A simple drawing of a spray scrubber using limestone as reagent for absorption of SO_2.

3.2.2 Chemistry

The chemistry consists of several equilibrium reactions. The following reactions [1]-[4] take place when the pH is 5-6 in the gas-liquid contact zone and starts with SO_2 dissolution and dissociation[3, 29].

$$SO_{2(g)} \leftrightarrow SO_{2(aq)} \quad [1]$$

$$SO_{2(aq)} + H_2O \leftrightarrow H_2SO_{3(aq)} \quad [2]$$

$$H_2SO_{3(aq)} \leftrightarrow H^+_{(aq)} + HSO^-_{3(aq)} \quad [3]$$

$$HSO^-_{3(aq)} \leftrightarrow H^+_{(aq)} + SO^-_{3(aq)} \quad [4]$$

The reactions involving limestone dissolution and CO_2 phase equilibrium occur simultaneously as shown by reactions [5]-[7].

$$CaCO_{3(s)} + H^+_{(aq)} \leftrightarrow Ca^{2+}_{(aq)} + HCO^-_{3(aq)} \quad [5]$$

$$HCO^-_{3(aq)} + H^+_{(aq)} \leftrightarrow CO_{2(aq)} + H_2O_{(l)} \quad [6]$$

$$CO_{2(aq)} \leftrightarrow CO_{2(g)} \quad [7]$$

The ionic species which are produced from the dissociation reactions together form products and thus, the reactions above can be combined to reaction [8].

$$H_2SO_{3(aq)} + CaCO_{3(s)} \leftrightarrow CaSO_3 + CO_2 + H_2O \quad [8]$$

The calcium sulfite can react further to form gypsum as shown by reaction [9]. The following reactions mainly occur after the liquid-gas contact zone, when the liquid droplets have reached the reaction tank.

$$CaSO_3 + \frac{1}{2}O_2 + 2\,H_2O \leftrightarrow CaSO_4 * 2H_2O_{(s)} \quad [9]$$

The combined reaction of [8] and [9] is reaction [10].

$$SO_2 + CaCO_{3(s)} + \frac{1}{2}O_2 + 2\,H_2O \leftrightarrow CaSO_4 * 2H_2O_{(s)} + CO_{2(g)} \quad [10]$$

The calcium sulfite can also form another byproduct according to reaction [11].[3, 29, 30]

$$CaSO_3 + \frac{1}{2}H_2O \leftrightarrow CaSO_3 * \frac{1}{2}H_2O_{(s)} \quad [11]$$

3.2.3 Mass transfer

In order for the reactions to take place in the liquid, mass transfer from gas to liquid must first occur. SO_2 must diffuse through a gas film and then through a liquid film. $CaCO_3$ must also dissolve. All these processes affect the rate of SO_2 absorption.

SO_2 gas-liquid equilibrium can be described by Henry's law according to equation (1), where $P_{SO2,i}$ is the partial pressure of SO_2 in the gas at the interface, H is Henry's constant and $C_{SO2,i}$ is the concentration of SO_2 in the liquid at the interface.

$$P_{SO2,i} = H * C_{SO2,i} \tag{1}$$

Figure 3.3 illustrates the mass transport of SO_2 through the gas and liquid film according to two-film-theory. The flux of SO_2 through the gas and liquid film must be equal and are described by (2) and (3), assuming steady-state, where k_g and k_l are the mass transfer coefficients, P_{SO2} is the partial pressure of SO_2 in the bulk and C_{SO2} the concentration in the bulk. [31]

Formation of bisulfite as shown in [12] and [13] benefits the driving force for SO_2 to transfer to the liquid and $\Phi$is the enhancement factor which corrects equation (3) to account for the increased mass transfer. The enhancement factor is dependent on SO_2 gas concentration, bulk composition, pH etc. Buffer additives can increase it as more bisulfite is formed which will enhance SO_2 absorption.[31]

$$N = k_g * (P_{SO2} - P_{SO2,i}) \tag{2}$$

$$N = \Phi * k_l * (C_{SO2,i} - C_{SO2}) \tag{3}$$

$$SO_{2(aq)} + H_2O \leftrightarrow H^+_{(aq)} + HSO^-_{3(aq)} \qquad [12]$$

$$SO_{2(aq)} + SO^{2-}_{3(aq)} + H_2O \leftrightarrow 2HSO^-_{3(aq)} \qquad [13]$$

The mass transfer can be summarized as

$$N = K_g * (P_{SO2} - H * C_{SO2}) \tag{4}$$

where K_g is the overall gas-phase coefficient and can be calculated by the following expression.

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{H}{\Phi * k_l} \tag{5}$$

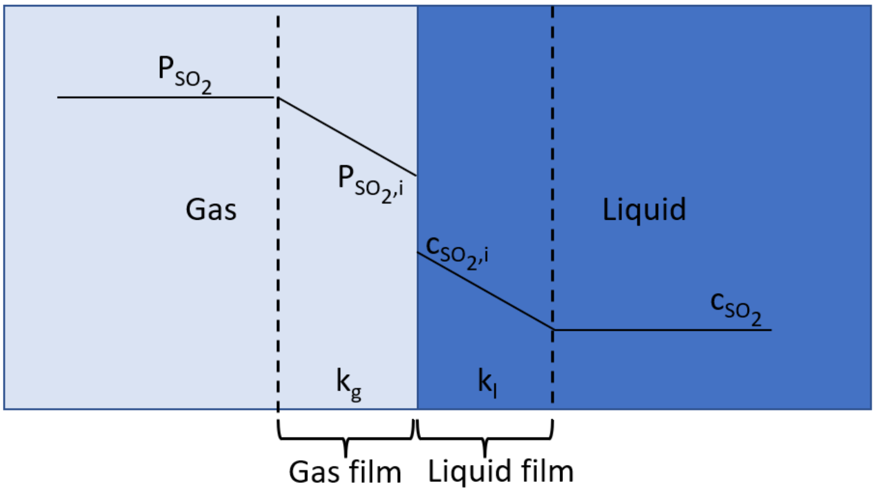


Figure 3.3. Mass transport of SO_2 through the gas and liquid film. The figure is inspired from Nilsson[32].

As seen is in reaction [14] the limestone dissolution reaction can be summarized as

$$CaCO_{3(s)} + 2H^{+}_{(aq)} \leftrightarrow Ca^{2+}_{(aq)} + CO_2 + H_2O \qquad [14]$$

which is a combination of reactions [5] to [7] above. The dissolution of $CaCO_3$ is usually not in equilibrium due to low excess of limestone and short residence time which are parameters inhibiting mass transfer. Many parameters affect the mass transfer, as shown by the equation for dissolution rate (6) in which R_d is the rate of $CaCO_3$ dissolution (mol/s), k_d is the mass transfer coefficient, x_{CaCO_3} is the volume fraction of solids, V is the slurry holdup (m^3), d_{ave} is the mean particle diameter, and pH^* is the equilibrium pH at the surface of the limestone[31]:

$$R_d = k_d * x_{CaCO_3} * V \frac{\pi}{d_{ave}} * (10^{-pH} - 10^{-pH*}) \qquad (6)$$

The presence of sulfite has counteracting effects on limestone dissolution. On one hand, it acts as a buffer, providing H^+ ions and thus enhances dissolution of limestone. On the other hand, at higher concentrations than normal is inhibiting, as $CaSO_3$ precipitates at the surface of the particles and stops dissolution. This is common when large amount of dissolved sulfite is present and little solid $CaSO_3$.[31]

Oxygen is relatively insoluble in water and the mass transfer is the limiting step of oxidation. The mass transfer can be enhanced by the same actions as for SO_2 such as increasing L/G ratio. To limit sulfate oxidation, the scrubber should hence not be overdesigned for SO_2 removal.[31]

3.3 Crystallization

Some background regarding the basics of crystallization is essential for understanding the problems with scaling. For crystallization to take place nucleation must first occur, followed by crystal growth. Simply put, at a certain concentration of solute, crystallization takes place. The solubility is however a function of temperature and for most compounds, solubility increases with temperature. There are three regions of solubility depending on concentration of solute and temperature. The unsaturated region means that the solute is completely dissolved. If the concentration increases or temperature decreases, the solution will eventually reach the equilibrium solubility curve, where the solution is saturated. It might be expected that crystallization starts here, but this is often not the case. Instead, the solution moves into the metastable region where the solution is supersaturated. This is typical if no solid particles are available in the solution, which requires nucleation to occur before crystallization can start. If the concentration continues to rise or the temperature to decline, the solution will reach the supersolubility curve and beyond this, nuclei will start to form spontaneously. This is called the labile region and crystallization will take place as nuclei are formed where crystals can grow.[30]

Nuclei either form through primary or secondary nucleation. The mechanism for homogenous primary nucleation is that solute or molecules come together and start arranging themselves and ultimately come out of solution. As mentioned, this requires that the solution is in the labile region. Heterogenous primary nucleation is when nuclei are formed on solid surfaces e.g. external solid particles. The second mechanism, called secondary nucleation, is when nuclei are formed through attrition of crystals. This means that existing crystals rub against each other or walls and are fractionized, giving rise to nuclei where crystals can grow. Agitation or pumping enables attrition. Addition of solid particles, so called seeding, is another approach to induce secondary nucleation. As a result of these actions, the supersolubility curve moves closer to the equilibrium curve, decreasing the metastable region. [30]

3.4 Crystal compounds

Scaling is the precipitation and buildup of solids on the equipment and generally consists mainly of calcium sulfite hemihydrate and calcium sulfate dihydrate (gypsum). The hemihydrate form of calcium sulfate is sometimes also included [33, 35].

3.4.1 Calcium sulfite

Calcium sulfites usually precipitate as hemihydrate, $CaSO_3$*½ H_2O. Other existing forms are dihydrate, $CaSO_3$*2 H_2O, and tetrahydrate, $CaSO_3$*4 H_2O[34]. The solubility of $CaSO_3$ hydrates is similar and can be approximated to 0.0054 g/100 g water at 25 °C. However, the compound tends to form supersaturated solutions. Increasing temperature or pH reduces solubility of the hemihydrate [34]. The pH dependance can be explained by the dissolution reaction [15].[31]

$$CaSO_3 + H^+ \rightarrow Ca^{2+} + HSO_3^- \qquad [15]$$

The presence of $CaSO_4$ in the solution has a negative impact on the solubility of $CaSO_3$ hemihydrate. A solution saturated with $CaSO_4$ decreases $CaSO_3$ solubility with a mean value of 58%. [34]

In work by Henzel et al.[31] scaling caused by $CaSO_3$ is described based on experience from coal incineration plants. At first, the compound gives rise to scaling which is soft and sticky in texture[31]. However, the soft scale becomes hard if no washing is carried out for a few hours, due to stop in the facility. The calcium sulfite is oxidized to calcium sulfate which is considerably harder[31]. Since calcium sulfite is dissolved at low pH, it has been suggested that when scaling is noticed, the pH of the recycling liquid is lowered temporarly[31].

3.4.2 Calcium sulfate

Three forms of calcium sulfate exist: hemihydrate $CaSO_4$*1/2 H_2O, dihydrate $CaSO_4$*$2H_2O$, and anhydrate $CaSO_4$. The solubility is dependent on temperature for all forms. The hemihydrate and anhydrate solubility declines with temperature. The dihydrate form has a more complex solubility curve as it has increased solubility with temperature up to 40 °C, but at higher temperatures the solubility decreases.[34]

Scaling caused by $CaSO_4$ solids consists of $CaSO_4$*2 H_2O or $CaSO_4$*1/2 H_2O. In order for crystallization to gypsum to take place the solid content or oxidation of sulfite to sulfate must be above 15-20% on a molar basis. This results in a saturation beneath 1 which usually prevents scaling problems. At a relative saturation (further explained in section 3.5.12) above 1.3-1.4 scaling problems typically arise. Calcium sulfate scale is very hard in contrast with calcium sulfite scale. It is controlled by keeping the supersaturation below 1.3 by seeding or by limiting the oxidation. [31]

3.5 Desulphurization efficiency and scaling

Many parameters affect the limestone wet scrubbing process and the main considerations are desulphurization efficiency and scaling[29].

3.5.1 pH

pH is an important factor in the process due to the absorption of SO_2 being strongly influenced by the pH. A low pH will increase limestone dissolution, but at the expense of lower solubility of SO_2 and thus, a reduction of desulphurization efficiency[3, 29, 31, 36]. For a pH of 4.5-5.5 the reactions taking place in the scrubber will mainly form calcium bisulfite $Ca(HSO_3)_2$ instead of calcium sulfite as shown in reactions [16]-[17][3, 29].

$$CaCO_3 + 2\,H_2SO_{3(g)} \rightarrow Ca(HSO_3)_{2(aq)} + H_2O_{(l)} + CO_{2\ (aq)} \tag{16}$$

$$Ca(HSO_3)_{2(aq)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow CaSO_4 * 2H_2O_{(s)} + H_2SO_{4(aq)} \tag{17}$$

Formation of $Ca(HSO_3)_2$ has advantages as it is more soluble than $CaSO_3$ and easier to oxidize to SO_4^{2-} than to SO_3^{2-}, which results in a tendency of less scaling and plugging[29]. Thus, a lower pH decreases $CaSO_3$ scale since it is solubilized as bisulfite instead[35].

A high pH instead has a higher separation efficiency of SO_2, but disadvantages include higher demand of limestone, and higher risk of scaling[29]. Studies have shown that a low pH strongly influences the precipitation of calcium sulfite and maintaining the pH beneath 6 limits scaling considerably[33]. One study recommended a maximum pH of 5.8 for scaling prevention, referring to industrial experience[31].

Moreover, the pH determines the characteristic of the produced crystals. A higher pH will result in smaller and softer crystals, while a more acidic environment will give harder and more rigid crystals.[37] This is explained by higher pH resulting in more calcium sulfite being formed, which becomes a soft scale. At lower pH the rate of calcium sulfate formation will instead increase because more sulfite is solubilized and oxidation to sulfate is favored. [37]

Variations of pH has also been suggested to lead to scaling. If the pH is allowed to drop below 5 and $Ca(HSO_3)_2$ is formed and thereafter the pH increases again, the product could be converted to $CaSO_3$ which is less soluble and could hence cause scaling problems[38]. For these reasons the optimal pH is between 5-6 in wet limestone FGDs and variations should be avoided[29, 31].

3.5.2 Limestone

The reactivity of the limestone affects the separation efficiency of SO_2. The reactivity is determined by the particle size distribution, porosity and purity of the limestone[29]. Moreover, sufficient residence time should be allowed for dissolution of the calcium carbonate and for crystallization to calcium sulfate and sulfite to occur in order to prevent supersaturated liquid entering the scrubber[38].

Recommendations for limestone characteristics were proposed by Henzel et al.[31]. First, it is crucial to choose a limestone with a high purity. More than 90% $CaCO_3$ and less than 5% MgCO3 is recommended[31]. If the gypsum bi-product is to be used for commercial purposes, the purity of the $CaCO_3$ should be at least 95%[29]. Secondly, small particle size is desirable as this will increase limestone utilization and as a result, SO_2 absorption. The size found to be effective in the report[31] was that in which 90% of the weight fit through a 325 mesh screen. This corresponds to a particle size of 149 µm. However, other studies found that 100 mesh was enough (= 44 µm)[38]. An article from 2015[29] states that conventional limestone wet systems use a particle size of 5-20 µm. Although different sizes are proposed by different sources it can be concluded that particle size has a great impact on the dissolution of limestone and hence the SO_2 absorption[29]. High utilization is usually accomplished at lower pH. Except for high SO_2 absorption, a good utilization will also result in less solids in the recirculation liquid, which, according to Henzel et al., is a method for scale control [31].

Another factor which influences the limestone dissolution is the presence of other compounds. Earlier studies have found that without any sulfite present, the dissolution of limestone is controlled by mass transfer. However, when sulfite is present both mass transfer and surface kinetics will play a role and sulfite will inhibit the limestone dissolution rate. [39] Other known inhibitors are zink, magnesium, copper, manganese, scandium, phosphate, iron, Al^{3+} and F^- [39]. Heavy metals can inhibit limestone utilization by forming insoluble carbonates on the limestone particle surface[31].

The stochiometric ratio (SR), i.e., the ratio between the actual amount of $CaCO_3$ and the theoretical amount needed for neutralization should be kept below 1.2 to avoid scaling. This is because a too high stochiometric ratio can lead to $CaCO_3$ and $CaSO_3$* 1/2 H_2O forming scale. The excess reagent can also be carried to the demister where it will react with SO_2 and form scale. Testing at a facility has shown that demister scaling was controlled when SR was below 1.18 [31]. Another example is the Duck Creek FGD system where it was concluded that improving the limestone utilization was important to solve demister scaling problems[40].

Utilization of limestone is proportional to the added amount. Some excess is necessary for SO_2 absorption and 100% utilization is not possible. The utilization can be improved by a large effluent hold tank and finer particles. The scrubber can be designed to enhance limestone utilization. In countercurrent flow, the pH is lowest at the inlet of the gas flow, which is located at the bottom of the scrubber. The limestone is usually injected here as a low pH will favor dissolution and utilization. Utilization can also be improved by separating and recycling unreacted limestone or by addition of buffers. [31]

3.5.3 Temperature

In a wet scrubber it is necessary to cool the flue gases to the saturation temperature, i.e. the temperature at which water condenses. This is to prevent sprayed water from evaporating, which would result in a temperature decrease[36]. Moreover, the temperature in the scrubber affects the reaction kinetics, meaning the rate of the reactions will increase with temperature. Diffusion also occurs more quickly at higher temperature which affects H^+ ions that travel towards the limestone particles. The temperature also affects the solubility of the gases. A high temperature results in a decrease of SO_2 solubility and hence, reduced separation efficiency of the compound. Likewise, CO_2 , which is formed in the reaction between limestone and acidic compounds, becomes less soluble at higher temperatures[29].

The temperature has also been shown to affect scaling. Experiments carried out comparing the scaling rate at 38 °C and 52 °C concluded that the rate was three times higher at the higher temperature. To limit the scaling as well as achieving higher desulphurization efficiency, it is recommended to operate at a low temperature[33, 35]. A report by Henzel et al. reviewed several FGD facilities and found 54 °C to be the conventional value for limestone spray scrubbers. It should be noted that the review focused on high-sulfur coal processes[31].

3.5.4 Liquid-to-gas ratio

The molar liquid-to-gas ratio (L/G) describes the relationship between amount of liquid slurry and flue gas entering the scrubber. The separation efficiency of SO_2 increases with higher L/G, but so do the operational costs. Hence, a low value is strived for, which may be accomplished by making up for the loss of efficiency by increasing the pH.[5, 29, 37] Some ambiguity exists regarding typical L/G values for limestone processes. One report [41] stated that 8-13 dm^3/m^3 is conventional, and in other works[31] the operational L/G was found to be in the range 2.5-9.1 dm^3/m^3 for nine investigated FGDs. In both studies the investigated plants were coal combustion plants.

L/G ratio can be increased to control scaling. A higher ratio leads to more mechanical washing of the column which limits the scaling by partially reversing the precipitation of calcium sulfite[33, 35]. Except for mechanical cleaning, it also contributes to less calcium sulfite per pass, which inhibits supersaturation[35].

3.5.5 HCl and HF

When HCl or HF dissolves in the liquid it decreases pH which has a negative effect on the desulphurization efficiency. Therefore, it is advantageous to use a pre-scrubber for removal of HCl and HF to prevent disturbances from the compounds in the desulphurization scrubber[29]. If water is used as injection in the pre-scrubber, typically the pH is 0-1[1]. In a limestone process HF could also form byproducts such as CaF_2, $CaAlF_3(OH)_2–CaF_2$ and $NaMgAlF_6·H_2O$ which could coat the limestone particles and cause reduced separation efficiency[29].

3.5.6 Additives

It has been shown that the addition of organic acids as buffers can improve the process. The compounds will counteract the drop in pH which occurs as SO_2 dissolves and thus maintain a higher pH. In result, a higher desulphurization efficiency can be achieved. This enables the use of a lower stochiometric ratio of limestone which can lead to reduced scaling[29, 36]. Examples of such additives are: adipic, glycolic, maleic, acrylic, and formic acids and dibasic acid. However, disadvantages include higher operational costs[36].

Magnesium oxide is a common additive which has a different mechanism to improve SO_2 absorption. It forms salts with the acidic compounds in the slurry which are more soluble than the calcium-based salts. This leads to more alkalinity being available in the slurry, enhancing the SO_2 removal.[41]

Another study investigated potential scale-preventing compounds and concluded that Calnox 214 DN, made from sodium polyacrylate and lignosulfonates, and Calgon CL-14, consisting of amino methylene phosphorate, were especially effective for limestone wet scrubbing systems[33]. Polyphosphates and polyacrylates were discussed as promising alternatives in another study[35].

3.5.7 Residence time

A long residence time in the liquid-gas-contact zone of the scrubber leads to a higher separation efficiency as the acid compounds have more time to be absorbed. This can be performed by increasing the liquid flowrate and decreasing the gas flow rate[5, 29]. The size of the scrubber also influences the capture of SO_2 since a larger size consequently gives longer residence time and thus, a higher SO_2 separation[31].

The residence time in the reaction tank affects scaling. A longer residence time enhances the limestone dissolution and calcium sulfite and calcium sulfate precipitation in the tank. This in turn prevents supersaturated liquid from being recirculated in the scrubber, which can lead to scaling[31, 35] . To increase the residence time it is important to have an adequate liquid level in the reaction tank[31]. One article proposes a minimum residence time of 8 minutes for single loop systems (with fly ash removal in the scrubber) and 5-7 minutes in a double loop system (without fly ash removal in the scrubber)[31].

3.5.8 Solid content

It has been shown that circulating some solid particles reduces scaling. This action, called seeding, prevents supersaturation by promoting the precipitation to take place on the solid particles which act as sites for nucleation and crystallization, instead of precipitating on surfaces in the scrubber. It is desired to use a solid of the same polymorph as the precipitating compounds and hence, gypsum is often used in FGDs for this purpose. In one study it was concluded that 1% gypsum content reduces scaling with 40% and a higher content will not decrease the scaling any further[33, 35]. Studies are contradicting however, and another source claims that a minimum of 8% solids should be maintained in the solution to prevent scaling[31].

3.5.9 Oxidation

The oxidation determines the byproducts from the limestone FGD process. Oxidation will lead to formation of $CaSO_4*2H_2O$ (gypsum), while a limited oxidation will cause the majority of the product to be constituted of $CaSO_3*½\ H_2O$. In general, the oxidation level depends on the ratio of O_2 to SO_2 in the flue gas. It will also increase in the presence of certain trace metals[31]. A low pH also typically favors oxidation since more HSO_3^- is available which, as explained earlier, is easier to oxidize[5, 36, 38]. However, the extent to which this parameter affects the oxidation is contradicting by different studies[33].

In theory, oxidation can have two effects on scaling in the scrubber. Limited oxidation leads to less calcium sulfate and more calcium sulfite scaling. This is advantageous since sulfate scale is more difficult to remove than sulfite. However, if on the other hand, higher degree of oxidation occurs, more gypsum is present which acts as seeding which may reduce scaling. In one incineration plant study[35], a quick buildup of scaling was observed when 4% oxygen was present in comparison to no oxygen. It has been proposed that to prevent scaling of calcium sulfite and sulfate it is often best to either limit oxidation of sulfite to sulfate to not exceed 15-20% or to have complete oxidation (= forced oxidation)[31].

The oxidation of SO_3^{2-} or HSO_3^- to SO_4^{2-} has a high reaction rate and is enhanced by presence of Mn and Fe, which is commonly found in FGD processes. Instead of being kinetically controlled, the oxidation is mass transfer controlled since the solubility of O_2 in water is low. Therefore, the oxidation mainly depends on parameters which affect the mass transfer rather than the reaction kinetics, such as oxygen content in the flue gas, gas/liquid contact, and amount of SO_2 removed [31].

Today mainly two types of oxidation modes are used in limestone FGD technologies: natural and forced oxidation. In natural oxidation, no air inlet to the scrubber is present, and only the excess oxygen in the flue gas after incineration will be available for oxidation. As a result, the product will contain 50–60% $CaSO_3*½\ H_2O$ and $CaSO_4*2H_2O$ in a sludge form. The crystals are in the size of 1–5 μm, which are difficult to dewater[29]. The degree of oxidation depends on the amount of oxygen available in the flue gas meaning it is relatively uncontrolled.[31]

In forced oxidation, air is injected to the reaction tank of the scrubber or a separate hold tank[5, 29]. The product will consist of 90% $CaSO_4*2H_2O$ (gypsum) with crystal size 1–100 μm. As the crystals are larger the product will be easier to dewater. Lately many processes have converted from natural to forced oxidation due to the enhanced gypsum quality which can be commercialized. However, factors such as upstream particulate control, content of F^- and Cl^- ions, purity of limestone, conversion efficiency etc. affects the final quality of the gypsum[29]. Furthermore, in forced oxidation there is less risk of scaling due to the controlled oxidation taking place in the reaction tank, preventing supersaturation. An example found in literature[31] reported that during testing, gypsum scaling was minimized when air was injected to a separate hold tank.

Another alternative is inhibited oxidation in which emulsified sodium thiosulfate ($Na_2S_2O_3$) is injected to the reactor to prevent gypsum formation in the absorber[5]. It acts as an oxidation inhibitor[31].

3.5.10 Entrainment

The number of droplets which follow the gas as entrainment is primarily determined by the gas velocity. When droplets are sprayed, they first accelerate due to gravitation, but eventually they reach a point where drag forces balances gravitational forces. If the gas velocity is higher than this final velocity, called terminal settling velocity, entrainment will be high. The terminal settling velocity is influenced by droplet diameter, and smaller droplets will have a lower value and thus, higher risk for entrainment[31]. However, small droplets have the advantage of providing larger area for mass transfer to occur and the size is therefore a trade-off between the effects[31]. A high entrainment leads to more liquid coming in contact with the droplet separator surfaces and thus, could potentially give more scaling.

3.5.11 Scrubber design

It is important to design the scrubber system to prevent solid deposits. If a high concentration of solid occurs somewhere, there is a risk that deposits will form, which grow. Stagnant liquid should be avoided. Typical risk areas are rough areas, at bends of pipes, behind packing etc.[35] Intermediately wet and dry areas can also lead to scaling. The areas which are in contact with liquid should be well irrigated. Demisters are therefore a risk zone, and effective washing is very important, but difficult to accomplish. Thus, periodical mechanical removal might be unavoidable.[35]

3.5.12 Relative saturation

The rate of crystallization is a function of the relative saturation ratio (RS). The relative saturation ratio of calcium sulfate and calcium sulfite is thus important for scale control. The RS is the product of calcium and sulfate ion activities (concentration) divided by the solubility constant according to equation (7)[31]. Ratios above 1 means supersaturation. In order to obtain scale-free operation this value should be below 1.4 for calcium sulfate and 6 for calcium sulfite. This is controlled through L/G ratio and pH.[31]

$$RS_{CaSO4*2H2O} = \frac{a_{Ca^{2+}} * a_{SO_4^{2-}}}{K_{SP_{CaSO4*2H2O}}} \tag{7}$$

The rate of crystallization can be described by equation (8). R_c is the rate of crystallization (mol/s), k_c is the crystallization rate constant, β the specific surface area of solids (m^2/g), V_R is the volume of slurry, W_s is the slurry solid content (g/m^3). [31]

$$R_C = k_c \beta V_R W_S (RS - 1) \tag{8}$$

3.6 Demisters

There are a variety of demisters used in industry, the most frequently utilized being of the impingement type. Common for this group is that they enhance the gravitational force by increasing the droplet size. Included in this category are mist eliminators using baffles, wire mesh and microfibres[42]. Sysav has mist eliminators of the baffle type[43].

Baffle demisters consist of multiple baffles, vanes or plates which form channels through which the flue gas must travel. Directional changes of the channels cause the droplets to hit the walls and are separated based on the mass moment of inertia[42]. The technology is widely used due to the construction taking up little space, having high separation efficiency, even for smaller droplets, and a low pressure drop[44]. In addition, high flue gas velocity is possible if the vanes are directed horizontally towards the gas flow, instead of vertically. Another positive feature is that it can handle solids in the liquid, as well as high liquid loads. However, compared to wire mesh and microfiber mist eliminators, the removal of very small droplets is less efficient [42].

3.6.1 Demister scaling

The problem with scaling in limestone FGDs has been recognized for a long time and particularly on demisters. Karlsson et al.[45] wrote already in 1980 that it is common that scaling and plugging first becomes a problem in the mist eliminators. The problems can be prevented by having higher amounts of liquid withdrawn from the scrubber, which allows for more washing of the mist eliminator with fresh water. This in turn, can limit the buildup rate of deposits. The amount of solids, which can be increased by the presence of fly ash, can lead to more rapid scaling of demisters. At last, the material of the demister has an impact on the rate of scale formation[45]. Demisters made from fiberglass seemed to reduce scaling in one study [35]. However, washing and removal of scaling was still necessary.

Washing procedures of demisters are important for scale control. Wash water type, direction, duration, flow rate and water pressure should be considered. The type of water should ideally be fresh water, but in a closed process it is impossible to only use this. However, it is possible to limit the usage of contaminated water by injecting all makeup water for the process to the demister washing system. The rest of the water necessary, should be obtained from the solids dewatering system and mixing with fresh makeup water. Demisters can be either horizontal or vertical and depending on the configuration, spraying is possible from different angles. If washing takes place counter currently to the gas flow, large amounts of mist might be generated and a second stage mist eliminator is recommended. Washing of demisters can be continuous or intermediate. Intermediate washing typically removes hard scale, while continuous prevents scale buildup. It is possible to have a separate loop for washing of demisters if they are horizontal. Then the amount of washing water can be increased and if necessary continuous washing can be implemented without disturbing other parts of the process. The wash water pressure have been reported to vary greatly and values differ between 20-100 psig.[31]

A study at the Shawnee test facility[31], a coal incineration plant, investigated demister scaling problems. The demister setup was different from Sysav as the flue gas entered vertically into a three-stage horizontal demister. The study concluded that improving alkali utilization to be above 85% had a reducing effect on the buildup of scaling. It was recognized that the issue was that unreacted neutralizing agent follows the droplets to the demisters and formed deposits which further reacted with SO_2, causing scaling. If utilization cannot be improved, which is typical for limestone processes which commonly have lower utilization than 85%, another approach for scale inhibition was found to be lower pH (however at the cost of reduced SO_2

absorption). Washing was also adapted to reduce scaling of the mist eliminators. Depending on the utilization level of the alkali, washing was either performed intermediately or continuously. The flow, area, number of nozzles and specific wash rate on the bottom and top-side were varied.[31]

The successful wash protocols from the study, were to have the top side of the demister washed separately with a washing time of 3 minutes followed by 7-minute paus. The bottom side had a continuous wash flow. The specific rate was 0.09085 m^3/h per square feet on the bottom side (0.98 $m^3/h*m^2$) and 0.120376 m^3/h per square feet (1.3 m^3/m^2*h) on the top side wash. The total value is 2.28 m^3/m^2*h. Each nozzle sprayed with 1.82 m^3/h[31]. Although a different mist eliminator design was used, the findings can still be relevant as reference in absence of data from more resembling facilities.

3.7 Summary of key parameters

The literature review of the technology and key parameters effect on SO_2 absorption and scaling can be summarized according to Table 3-1. Nonetheless, the reader should be aware that the table is a generalization and to understand the complete effect of a varying parameter a full explanation is available in sections 3.4, 3.5 and 3.6.

Table 3-1. Key parameters in limestone wet FGD processes. The table is bases on findings from the literature review in sections 3.4, 3.5 and 3.6. The effect of an increase of a parameter on absorption and scaling is generalized as + (= increase), - (= decrease) or 0 (= no effect).

Increased parameter	**SO_2 absorption**	**Scaling**
pH	+	+
Limestone utilization	0	-
Temperature	-	+
L/G	+	-
Residence time in reaction tank	0	-
Solid content	0	-
Relative saturation	0	+
Demister washing frequency	0	-
Oxidation	0	+ (if natural oxidation) - (if forced oxidation)
Additives	+	-
Entrainment	0	+

4 Modelling – Literature Review

To aid in the development of an Aspen Plus simulation model of Sysav's scrubber system, literature sources were studied. The review aimed to answer which physical property method is suitable for the system and which unit operation(s) should be selected to simulate absorption scrubbers.

4.1 Aspen Plus

Aspen Plus is a simulation software which is a tool to model chemical processes. A flowsheet is defined by the user and can for example include a reactor as well as pre- and post-treatment steps. This enables a simulation of a process plant from raw material to product. Examples of unit operations available in Aspen Plus is distillation, absorption, extraction, heating/cooling and various reactors. [46]

4.2 Physical property model

In Aspen Plus all kinetic, physical, thermodynamical and transport properties are based on a chosen physical property method. As the case process involves ions and salts, the model must be applicable for electrolytes. An electrolyte system includes compounds which can dissociate in a polar medium and therefore, demands calculations to consider the equilibrium between ionic and condensed form of each compound [46-48]. ELECNRTL, ENRTL-RK and ENRTL-SK are all physical property methods appropriate for electrolyte systems that can handle the non-ideal mixing properties which is caused by the ionic species. They are all effective for mixed solvents at varying concentrations. Yet, ELECNRTL is the most versatile[48]. In addition, Aspen guide documents recommend using ELECNRTL not only for general electrolyte systems [46-48], but also for acid gas absorption using water and lime specifically[47]. Studies of similar simulated scrubbing systems have selected the method as well[49-52].

When the ELECNRTL method is used, Aspen generates possible electrolyte reactions with the Electrolyte wizard tool for the selected compounds and the formed ionic species and salts from these reactions are added to the list of compounds. The chemistry of the system is thus implemented meaning all compounds will be present in equilibrium with their ionic form throughout the model.

When using the Electrolyte wizard for generating electrolyte reactions and components, the user can choose to have either symmetric or unsymmetric reference state for ionic components. The unsymmetric option means that equilibrium constants are calculated from the reference state Gibbs free energies of the components. Moreover, infinite dilution in water is assumed when calculating the activity coefficients[48]. This is typically used for solutes with low concentrations[53]. If the symmetric option is selected, the equilibrium constants must be entered manually[48]. This option is appropriate to describe the activity coefficient of the solvent e.g. water[53]. Besides this, the choice between true or apparent components must be made. This refers to if the results of components should be reported as ionic species or as base components[48].

4.3 Absorption modelling

There are different approaches to simulating an absorption scrubber. The simplest model is to use a FLASH2 unit, in which two streams are mixed and then separated, allowing for the selected electrolyte reactions to take place. Calculations on thermal and phase conditions are performed and it models a single stage separator[47]. This means that a FLASH2 describes the vapor-liquid equilibrium, including the absorption of the acid compounds to the water[54]. The unit has been used previously to simulate SO_2 absorption in work by Galbe[55].

A different method is to use the column model RADFRAC for the simulation. Previous studies[49] on absorption have been carried out utilizing a RADFRAC. RADFRAC is a rigorous model which can effectively model any liquid-vapor process and is recommended by Aspen guides for simulating absorption[47]. In the unit, vapor and liquid streams meet, and the selected electrolyte reactions occur as the compounds transfer between the phases and are thus absorbed. The main difference from the FLASH2 is that the number of theoretical stages must be specified, meaning that several equilibrium stages exist between gas and liquid. In addition, more details for the column can be provided if desired[47, 56]. A drawback is that it is more difficult for the system to converge.

A RATEFRAC has also been reported to be used to model absorption[50]. It is similar to the RADFRAC, however is rate-based instead of assuming equilibrium for the separation process. This means that separation efficiency depends on the rate of mass and heat transfer as well as rate of reaction[47].

Other studies have used a combination of reactor units to simulate absorption with limestone. An RSTOIC reactor to model dissolution of limestone in water, followed by two RCSTR blocks was used in studies by Lim and co-workers[51, 52]. The first unit modelled the vapor-liquid contact zone and the second modelled the reaction tank, in which gypsum was formed[51, 52]. In all reactor blocks it is necessary to specify the reaction(s), although, it should be noted that the electrolyte chemistry, which is implemented by selecting the ELECNRTL method, will also be present. In RSTOIC, the kinetics are not accounted for. The stoichiometry and conversion are instead specified and will determine the composition of the outlet stream. RCSTR stands for rigorously continually stirred tank reactor. The selected reactions can be either kinetic or equilibrium, but if kinetic is chosen, the user must provide kinetic parameters. In addition, either reactor volume or residence time is specified. More features are possible to add to the block[47]. The disadvantage with using reactor blocks is that converging errors often arise.

4.4 Evaluation of equilibrium constants

The equilibrium constant has a temperature dependence according to (9).

$$\ln(Keq) = A + \frac{B}{T} + C * \ln(T) + E * (\frac{P - Pref}{Pref}) \tag{9}$$

Aspen Plus generates equilibrium constants for the electrolyte equilibrium reactions. Equilibrium constants for a limestone-acid gas system can be obtained from literature sources as well. Neveux and Le Moullec[57] used equilibrium constants when modelling limestone FGD which differed somewhat from Aspen generated constants. The equilibrium constants from Aspen Plus and Neveux and Le Moullec[57] can be viewed in Appendix A: Equilibrium Constants.

4.5 Kinetic data for oxidation

The oxidation reaction used in the model is described in reaction [19]. Two sources[58, 59] report kinetic data. Karatza et al. claimed that $k_0 = 1.19*10^{-4}$ $m^{3/2}/mol^{½}$ s at T = 45 ˚C[58]. However, Pisu et al.[59] used $k_0 = 19.5*10^9$ $m^{3/2}*mol^{½}$ s for the relevant temperature range and E = 86 000

J/mol. Both sources report zero order of reaction with regard to oxygen, and 3/2 order of reaction for the bisulfite ion. The influence of the kinetic constant (k_0), activation energy (E) and temperature on rate of reaction (r) is according to (10) and (11).

$$HSO_3^- \ + \ 0.5\, O_2 \ + \ H_2O \rightarrow \ SO_4^{2-} \ + \ H_3O^+ \qquad [19]$$

$$r \ = \ k * (HSO_3^-)^{3/2} \qquad (10)$$

$$k \ = k_0 * e^{E/RT} \qquad (11)$$

4.6 Stream Class

The conventional stream class in Aspen is CONVEN. This is recommended when no solids are present or if the solids are electrolyte salts. MIXCISLD is another option which is applicable when conventional inert solids are present, but the particle size distribution is not implemented. Conventional solids, on the contrary to non-conventional, are solids with known and homogenous composition. Both calcium sulfite and calcium sulfate are conventional solids. An example of non-conventional solids are biomass and ash. [46]

5 Methodology

The methodology contains an investigation in which the process conditions at Sysav are compared to literature recommendations. Next follows a description of the model development phase and at last, the implementation of the case process conditions to the model and sensitivity analyses which were carried out.

5.1 Evaluation of process

From the literature study in section 3.4 key parameters were described which affected the absorption of acid gases as well as the scaling of calcium sulfite and calcium sulfate. Many of these were reviewed from Sysav's process. Some were however difficult to evaluate due to lack of information.

5.1.1 pH

The pH of the scrubbers was evaluated by analyzing measurement data[60] from November 2020 to January 2021.

5.1.2 Temperature

The temperature was examined during the time period from November 2020 to January 2021[60]. Data could be retrieved from temperature measurements in the quench. It is assumed that this temperature is relatively constant over the scrubber system.

5.1.3 Residence time

The residence time of the liquid in the reaction tank in the scrubbers was evaluated. The residence time was calculated by estimating the volume of the bottom liquid in each scrubber and then calculating using the formula:

$$Residence\ time\ = V/F \tag{12}$$

where V is the volume of the liquid in the bottom of the scrubber and F is the volumetric flowrate. This is applicable assuming the bottom tank is an ideal tank reactor, in which all parts of the liquid have the same residence time i.e., perfect mixing.[61] The calculations are presented in Appendix B: Calculation of Reaction Tank and Residence Time.

The height of the scrubbers was 6.7 m in G1 and 7.5 m in G2, according to the operators[12] and it is assumed that the measurement is from the bottom of the scrubber to the surface of the liquid. Dimensions of the scrubbers were gathered from drawings for line 4 in Sysav's process[62, 63]. However, the scrubbers for line 3 and 4 were assumed to be alike.

5.1.4 Demister washing frequency

The time during which the demisters are washed was measured manually on site. Also, the time between washes was documented. It was assumed that all demisters are washed in a sequence and have the same on/off times. The dimensions of the demisters were given from layout documents of the demisters[43]. Since the facility was built, the two demisters have been exchanged, but the new units should have similar dimensions. The number of tubes were found in scrubber documentation[62, 63]. The number of spraying nozzles is uncertain, but personnel claims it to be 6 spraying nozzles per tube[64]. From this, the specific rate could be calculated by dividing the total flow with the area of the demisters to give a flow per square meter. The flow per nozzle was also calculated. The calculations are displayed in Appendix C: Demister

Washing Calculations. The results were compared to findings by Henzel et al. [31] who in their work described tests done at Shawnee test facility from which successful washing protocols of demisters were determined.

5.1.5 Gypsum content

The gypsum content in the recirculated liquid is controlled by density measurements[12]. The density of the liquid corresponds to a gypsum content (g/L)[11] which can be compared to literature sources.

5.1.6 Limestone specifications

The limestone purity and particle size distribution were obtained from a supplier specification sheet[65]. The characteristics were compared to reference values found in the literature study.

From the literature study it was revealed that the stochiometric ratio has great impact on scaling and that excess limestone should be avoided. The added amount is however unknown and thus it is impossible to evaluate.

5.1.7 L/G ratio

The liquid-to-gas ratio was evaluated based on flue gas flow and recirculated liquid in the scrubbers. The flue gas flow was estimated with the assumption of constant waste composition, referred to as “nominal waste” which was determined based on operation year 2020-2021[66]. See section 5.3.1 for more information regarding the nominal waste. The recirculated liquid in each scrubber was found in pump specifications[67-69].

The flue gas flow at nominal waste was determined to be 180 460 Nm^3/h upstream from G1[66]. At 60 ° C and 1 atm, this corresponds to 220122 m^3/h. Details on calculations can be read in Appendix D: Calculations of Flue Gas Flow at Nominal Load. It was assumed that the flue gas flow is unchanged when entering G2, as the temperature and pressure does not change significantly and the compounds absorbed in G1 constitute only a small portion of the total flue gas flow. In G1, 1020 m^3/h liquid is sprayed[68] and to the quench two pumps are operated, each pumping 85 m^3/h of liquid[67]. The total amount of liquid that comes in contact with the gas is thus 1190 m^3/h. The recirculation liquid flow in G2 is 220 m^3/h[69]. The L/G ratio was determined by dividing the recirculation flow with the flue gas flow. The computed ratios were based on the flue gas flow at nominal load, and as the facility occasionally is run at lower load, while the liquid flow is constant, the L/G will increase. The calculated values are thus minimum values. However, during the winter season full load is standard procedure, making this ratio relevant to evaluate.

5.1.8 Oxygen content

The oxygen content is a key parameter which affects the formation of calcium sulfate, as described in the literature study. Thus, it was of importance to evaluate the oxygen content available in the flue gas. However, lack of measurements prohibited the evaluation and only the calculated value from the nominal waste could be used as basis for discussion.

5.2 Model development

The aim of the model development phase was to find unit operation blocks in Aspen Plus which could model the absorption taking place in the scrubber and the precipitation of calcium sulfite and calcium sulfate proceeding in the demister. The objective was to get results on HCl and SO_2 removal as well as formation of the solid compounds. It was reviewed if the results had the correct dependance on parameters as found in the literature study. This was considered enough for verification in this early development stage of the model. The target was to obtain a model which functioned and gave results on the mentioned parameters. This can in the future be verified and modified using experimental data.

5.2.1 Selection of physical property method

As was described in section 4.1.1 the system contains ions and salts, which are electrolytes. Hence, the appropriate physical property method to describe the system is ELCNRTL.

5.2.2 Chemistry

As ELECNRTL is chosen as the physical property method, the choice of equilibrium reactions is of importance. The electrolyte wizard tool in Aspen was used to generate the relevant equilibrium reactions. The unsymmetric and true components options were selected. The reactions which were generated and used in the model were:

$$H_2O + HSO_3^- \leftrightarrow H_3O^+ + SO_3^{2-} \quad [20]$$

$$2\,H_2O + SO_2 \leftrightarrow H_3O^+ + HSO_3^- \quad [21]$$

$$CaOH^+ \leftrightarrow Ca^{2+} + OH^- \quad [22]$$

$$HCl + H_2O \leftrightarrow Cl^- + H_3O^+ \quad [23]$$

$$H_2O + HSO_4^- \leftrightarrow H_3O^+ + SO_4^{2-} \quad [24]$$

$$H_2SO_4 + H_2O \leftrightarrow H_3O^+ + H\,SO_4^- \quad [25]$$

$$H_2O + HCO_3^- \leftrightarrow CO_3^{2-} + H_3O^+ \quad [26]$$

$$2\,H_2O + CO_2 \leftrightarrow HCO_3^- + H_3O^+ \quad [27]$$

$$2\,H_2O \leftrightarrow OH^- + H_3O^+ \quad [28]$$

The following salt reactions were also included in the model:

$$CaSO_4 * 2\,H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2\,H_2O \quad [29]$$

$$CaSO_4 * 0.5\,H_2O \leftrightarrow 0.5\,H_2O + Ca^{2+} + SO_4^{2-} \quad [30]$$

$$CaSO_3 * 0.5\,H_2O \leftrightarrow 0.5\,H_2O + Ca^{2+} + SO_3^{2-} \quad [31]$$

$$CaSO_4 \leftrightarrow Ca^{2+} + SO_4^{2-} \quad [32]$$

$$CaSO_3 \leftrightarrow Ca^{2+} + SO_3^{2-} \quad [33]$$

$$CaCl_2 * 2\,H_2O \leftrightarrow Ca^{2+} + 2\,H_2O + \; 2\,Cl^-$$ [34]

$$CaCl_2 * 4\,H_2O \leftrightarrow Ca^{2+} + 4\,H_2O + \; 2\,Cl^-$$ [35]

$$CaCl_2 * 6\,H_2O \leftrightarrow Ca^{2+} + 4\,H_2O + \; 2\,Cl^-$$ [36]

$$CaCl_2 * \; H_2O \leftrightarrow Ca^{2+} + \; H_2O + \; 2\,Cl^-$$ [37]

$$CaCl_2 \leftrightarrow Ca^{2+} + \; 2\,Cl^-$$ [38]

$$Ca(OH)_2 \; \leftrightarrow \; CaOH^+ + \; OH^-$$ [39]

$$CaCO_3 \leftrightarrow \; CO_3^{2-} \; + Ca^{2+}$$ [40]

Dissociation reactions included were:

$$CaCO_3 \rightarrow \; CO_3^{2-} \; + Ca^{2+}$$ [41]

$$CaSO_4 * 2\,H_2O \; \rightarrow \; Ca^{2+} + \; SO_4^{2-} \; + \; 2\,H_2O$$ [42]

$$CaSO_3 * 0.5\,H_2O \; \rightarrow \; 0.5\,H2O \; + \; Ca^{2+} + \; SO_3^{2-}$$ [43]

The components used in the model were all included in the above reactions. The equilibrium constants which were generated by Aspen was compared to the values presented by Neveux et al.[57] An attempt to modify the equilibrium constants to the proposed values was carried out since Aspen occasionally generates false values. However, due to convergence errors, the Aspen-generated constants were used nevertheless, as it was necessary to move on with the model development. It was not prioritized to put more effort into the chemistry constants in the early-stage model. It is possible that after verification, these values should be modified to adapt the model to reality.

As will be explained in the following section, the chemistry was adapted to different parts of the flowsheet. The final absorption model did not include the salt reactions, while the precipitation model included all above reactions, as well as additional reactions for calcium sulfite and calcium sulfate formation and oxidation. The Henry components were CO_2, SO_2, HCl, O_2, N_2.

5.2.3 Selection of absorption model

For the absorption, RCSTR, FLASH and RADFRAC units were tested in Aspen. Due to convergence problems at higher temperatures, the RCSTR unit could not find any solutions at 60 °C (corresponding to the process temperature) and this unit was thus rejected as an alternative for the simulation. It should be noted that this was at an early stage in the project and later other methods for helping Aspen with solving problems which at first attempt, did not converge, were discovered. It is possible that the block could have been used with modification of convergence method and chemistry. This was however not tested, due to time limit of the project and as other units were found to be successful for the scope of this project.

The FLASH could converge and successfully model absorption. However, the absorption of SO_2 was approximately 100% which was unreasonable under the tested conditions. Moreover, the recommendation from the literature study and professors[70] was to use RADFRAC for the absorption and thus more effort was not laid on the FLASH. Nevertheless, it should be emphasized that the block showed potential as the SO_2 absorption was limited by the presence of HCl. It is possible that the unit could be of useful if further developed.

The RADFRAC could model absorption of acid gases, however the unit only converged if the salt reactions were excluded from the electrolyte chemistry. Based on problems with the two earlier tested operational units and the fact that RADFRAC is the recommended choice for modelling an absorption scrubber, this was selected for the final model. The number of stages was varied, but as this had no effect on the result, 10 stages were used.

5.2.4 Selection of precipitation model

To resemble the process at Sysav, a part of the recirculation liquid in the scrubber should enter the demister. The flue gas exiting the scrubber should also be led to the demister block, allowing for components of the liquid and gas stream to transfer between the phases and possibly form calcium sulfite and calcium sulfate. Moreover, an oxidation reaction was to be implemented. Three blocks were tested for the purpose: a FLASH, a CRYSTALLIZER and an RCSTR. The reaction set which was implemented besides the reactions in the chemistry section, were calcium sulfite/sulfate formation and oxidation of HSO_3^-. The oxidation reaction was [19]. The salt reactions were entered according to reactions [44] - [47] and equilibrium was assumed. MIXED means that it is a conventional compound, while CISOLID is a conventional inert solid compound, meaning that it is present in the CISOLID substream.

$$Ca^{2+} + SO_3^{2-} + 0.5\,H_2\,O \leftrightarrow CaSO_3 * 0.5\,H_2\,O(MIXED) \tag{44}$$

$$Ca^{2+} + SO_4^{2-} + 0.5\,H_2\,O \leftrightarrow CaSO_4 * 2\,H_2\,O(MIXED) \tag{45}$$

$$CaSO_3 * 0.5\,H_2\,O(MIXED) \leftrightarrow CaSO_3 * 0.5\,H_2\,O(CISOLID) \tag{46}$$

$$CaSO_4 * 2\,H_2\,O(MIXED) \leftrightarrow CaSO_4 * 2\,H_2\,O(CISOLID) \tag{47}$$

Tests with the CRYSTALLIZER block did not form any calcium sulfite or calcium sulfate. The block was tested with and without the oxidation reaction implemented as well as the reactions being specified through chemistry or based on solubility data. This option was thus neglected. Similar problems emerged when using the FLASH block. No salts were formed. The FLASH block was consequently also considered unfit for the model. The RCSTR block was tested and could successfully form both calcium sulfite and calcium sulfate. At first the oxidation reaction was implemented as an equilibrium reaction, but this was changed to kinetic to improve the reaction dependence on oxygen content, as is expected from literature. Kinetic data was implemented on the oxidation reaction from Pisu et al.[59]. Moreover, the residence time was specified to be 0.25 h, equal to the time between washings in Sysav's process.

5.2.5 Solids in Aspen

Solids in Aspen is complex to simulate. Since the solids in the model are electrolyte salts it should be sufficient to use the stream class CONVEN. However, it was decided to use MIXCISLD instead. This is recommended when simulating solids with known composition in combination with liquids. The selection was motivated by the fact that when the salts are formed, they act as inert components, which is simulated by MIXCISLD. Therefore, this was considered a better estimation of the precipitation behavior. Verification is necessary to further determine if this was a good guess or if the other stream class is closer to reality.

5.2.6 Convergence

Due to the complexity of the model, convergence errors were a persistent problem. To get the calculations to converge the RADFRAC was specified to be calculated with the standard convergence method and changed to an Absorber in the advanced settings. Moreover, it was common to change the general convergence method between Wegstein, Direct, Broyden and Newton. By re-running the script several times and changing the convergence method, the model usually could converge eventually.

5.2.7 Assumptions

Calculations by Aspen plus are made with some assumptions.

- The process is assumed to be at steady state. As follows, all stream flows and compositions are constant. The system is in reality a dynamic process and large variations in waste composition results in the flows of the flue gas cleaning to vary consequently. However, to rectify the assumptions, different operational conditions were simulated.
- Phase equilibrium is assumed. The gaseous compounds are considered to follow a solubility of Henry’s law as the concentrations are low.
- Equilibrium reactions (except for oxidation) is assumed. The assumption was made to simplify the simulation. However, to accurately simulate the crystallization, kinetics should be implemented as well as the mass transfer limitations.
- A limited number of reactions are included in the simulation model. The literature study concluded the main reactions of importance in limestone scrubbing and they were all included in the simulation model. Besides these, other reactions were generated by Aspen Plus Elecwizard tool as well and it was assumed that all possible reactions for the system were found and thus, these were all used in the final model.
- The droplets in the demisters are assumed to behave as a continuously stirred tank reactor. This is a large assumption as a concentration gradient is likely to be present. However, for the purpose of this project it is a good approximation.
- Pressure drop and heat losses are neglected. In Sysav’s process the temperature and pressure is relatively constant.
- Mass transfer kinetics are not considered. The solubility of the gases is assumed to follow Henry’s law and reach equilibrium.
- Co-current or counter-current flow is not considered.
- No solids are present in the recirculation liquid.
- Instantaneous dissolution of $CaCO_3$ is assumed and thus, the reactivity is not considered.
- Washing of the demisters is neglected in the model. The purpose is to get an indication of precipitation during varying operational conditions and although washing can inhibit the buildup of scaling, it is impossible to estimate to what extent. Thus, this was neglected as an operational parameter in the model and it is instead discussed in the evaluation of the process with the literature study as reference.
- The water entering the scrubbers is assumed to be clean. In reality, the process water contains impurities since the process water comes from the condensation scrubber.

However, in the already complex model, it was necessary to simplify this flow. Also, the exact concentration of impurities in the water varies and to accurately model this, varying compositions should have been implemented, which was considered overly time consuming and was not prioritized in the project.

- Notable is that supersaturation is not modelled. The crystallization occurs only based on the equilibrium reactions and constants. The results of crystal formation should be regarded as a maximum value on the contrary to the process in reality, in which all of this might not precipitate and instead a supersaturated solution will form. The supersaturated liquid comes with the risk of precipitating on surfaces such as demisters and therefore it was considered as accurate to model that equilibrium occurs and that precipitation is not limited.

5.3 Process inputs

The objective was to implement values from Sysav's process into the Aspen plus model. It is however complex to determine flows and compositions because of the large variations in incinerated waste. A "base case" was developed with estimated streams, and the composition was later varied from the base case according to measurement data to have a sufficient representation of the actual process.

5.3.1 Base case model

Although deviation in the flue gas flow and composition occur, an estimation of a representative flow was necessary to determine. For this aim, two sources were reviewed. Original documentation of the facility contains the expected flue gas flow and composition, which the process was dimensioned for[71]. However, since the facility was started, the maximum load has been increased with approximately 10%[14]. Moreover, the waste is likely to have changed over the past 20 years in composition. This means that the actual flue gas flow at full load has increased since startup, and the composition presumably differs from what was estimated by the supplier. Thus, the original documentation was deemed as non-representative of current conditions.

Another source for determining the flue gas flow and composition is using nominal waste incinerated during the year 2020[66]. The estimated nominal composition of the waste is shown in Table 5-1. The main flows of the process and a lower and higher heating value had been calculated for nominal waste. This was regarded as a better estimation of the current operating conditions than those obtained by the original documentation. Therefore, these values were used in the simulation as a "base case". Naturally, this is a rough estimation as the waste varies in composition and heating value. Using this data, means assuming that the flue gas constantly has the composition from incineration of nominal waste and that the heating values do not change.

Table 5-1. Nominal waste at Sysav 2020. [66]

Component	Weight fraction
Ash	22.66%
Moisture	25.85%
C	27.71%
H	3.87%
O	18.70%
N	0.55%
S	0.14%
Cl	0.52%

Nominal waste 2020 conditions were used to calculate a flue gas composition which was provided by Sysav[66] . The composition was adapted to the simulation model and the conversion is shown in in Appendix E: Stream Data at nominal Load. The modified flue gas composition is presented in Table 5-2. Modifications included using the nominal waste load of 32.3 kg/h and neglecting HF, CO and NH_3 in the flue gas, as the amounts were low. Cl in the waste is assumed to form only HCl. After passing the quench, the entering flue gas to G1 is saturated and at 60 °C. To adjust the composition to meet the criteria, the water content was increased to 15% of the flue gas flow. N_2 was used to balance the flue gas to the correct total flow since it constitutes the majority of the flue gas and is an inert component.

Table 5-2. Flue gas composition used in the simulation model.

Component	Mass fraction
H_2O	0.15
CO_2	0.1437
O_2	0.07827
NO_x (as NO_2)	0.0002665
HCl	0.0006781
SO_2	0.0001903
N_2	0.6269

The liquid flows to G1 and G2 had been calculated in previous work[66] from an assumed stoichiometry between limestone and acid compound and assumption of SO_2 and HCl, HF content in the flue gas. The entering water and bleed of G1 had been calculated based on the maximum allowed chloride concentration in the stream. Specified in the Aspen model was the amount of ingoing water to G1, 10 433 kg/h[66]. The $CaCO_3$ was assumed to have ideal reactivity and thus, in the model was only used to obtain the correct pH. The calculated stream data entering and exiting G1 can be viewed in Appendix E: Stream Data at Nominal Load. As described in section 2.2 many flows are present in reality, however the flows vary considerably and thus, the estimation was considered adequate. It should be noted that the original documentation of the process states that the purge stream from G1 (S6) should be 4.2 m^3/h[8]. However, according to staff it is operated at higher values today[14]. The ingoing and outgoing flows are thus uncertain.

The recirculation liquid was determined based on original documentation[67-69] of the pumps in the system. It was found that in G1 the sprayed liquid is 1020 m^3/h and to the quench 85 m^3/h per pump is transferred. This means that the total amount of recirculated liquid of G1 is 1190 m^3/h. The arguments for using the quench liquid as well as the sprayed liquid in the model were that 1) it is important that the total amount of liquid in which the dissolved ions can be dissolved is correct and 2) some absorption might take place in the quench simultaneously as the flue gas is cooled and saturated. In G2, the recirculation flow was 220 m^3/h.

The streams which were implemented in the model are summarized in Figure 5.1. The system was divided into two separate files: one with G1 and LDS1, and the other containing G2 and LDS2. The system was combined by manually modifying the entering flue gas stream to G2 to have the composition and size of the outgoing flue gas stream from G1. The complete input data to Aspen Plus is shown in Appendix F: Input to Aspen Plus – Base Case. The stream inputs and operational conditions were used according to Table 5-3.

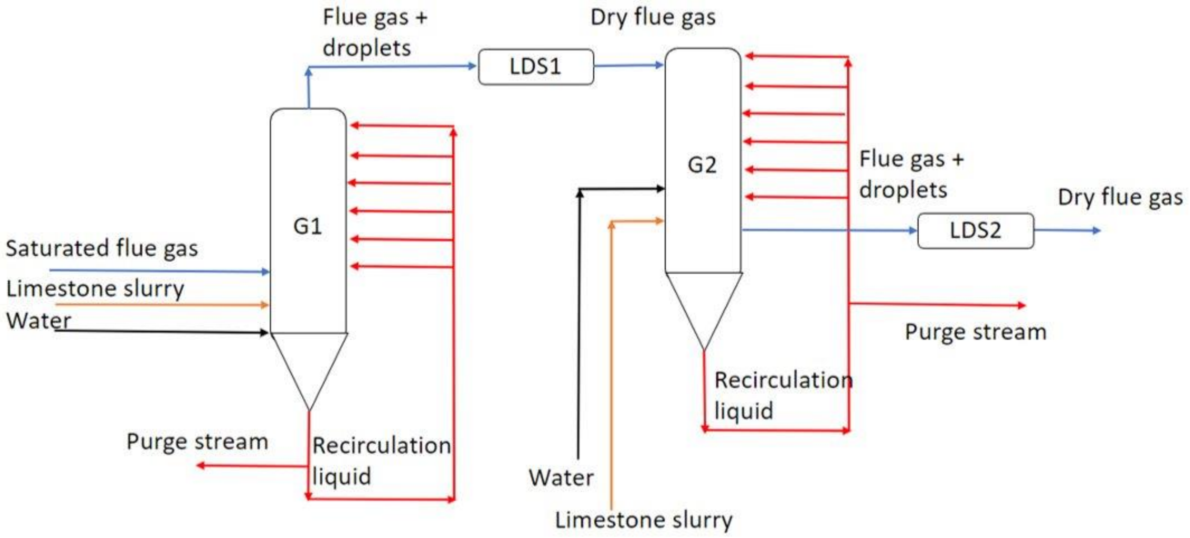


Figure 5.1. The units and streams included in the Aspen Plus model.

Table 5-3. Process conditions which were used in the simulation model.

Parameter	**Input value**
Temperature	60 °C
Pressure	1 atm
Flue gas flow	229 104 kg/h
Recirculation liquid G1	1190 m^3/h
Recirculation liquid G2	220 m^3/h
Liquid into G1	10 433 kg/h
Liquid into G2	3120 kg/h

5.3.2 Cases

Except for the base case composition of the flue gas, signal data was reviewed to collect operational conditions during specific time periods from 2020-2021[60]. Studying the pressure drop over heat exchanger 1, corresponding to the pressure drop over the scrubber system, gives an indication of when scaling starts to occur in the demisters. During November 2020 to January an increase in pressure drop could be observed which is illustrated in Figure 5.2. Short periods when peaks in HCl content, SO_2 content and pH occurred were selected during this time period and used as cases to be studied using the simulation model in Aspen Plus. The peaks which were chosen for the case studies are shown in Figure 5.3 and are illustrated by the red markings. The objective was to find times when key parameters differed from nominal values. Ideally, the model can be used to evaluate operational conditions which should be avoided. The straight line in the graphs for HCl and SO_2 content is due to defective measurements.

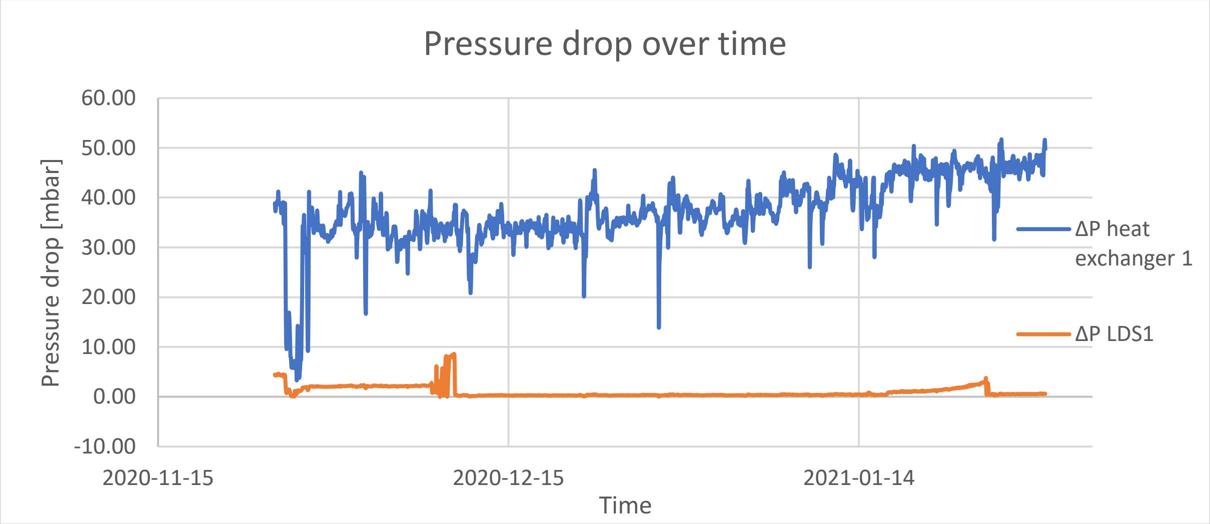
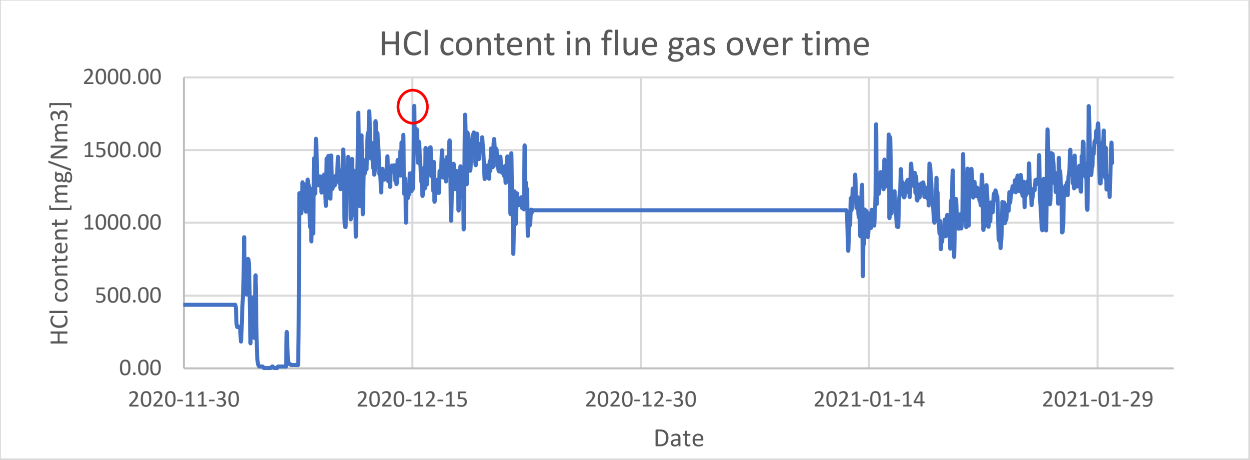
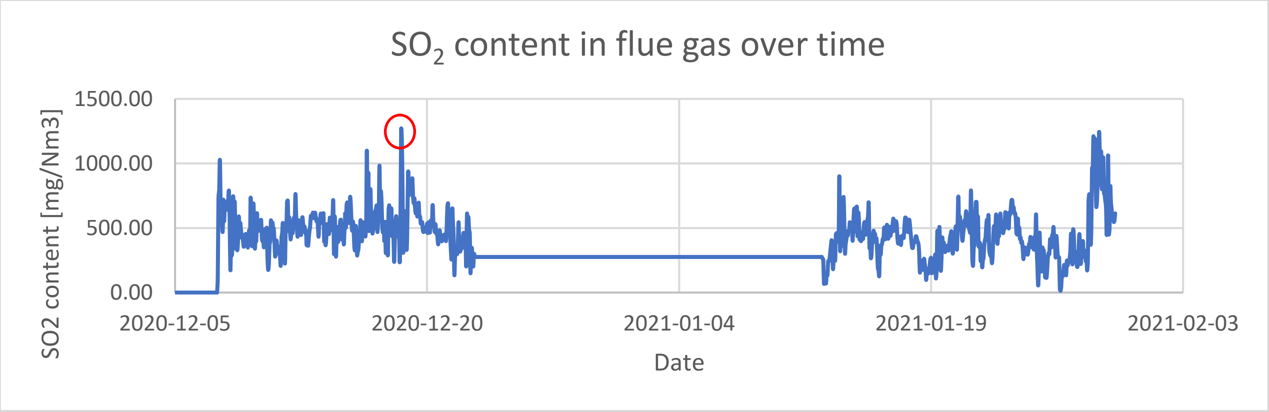


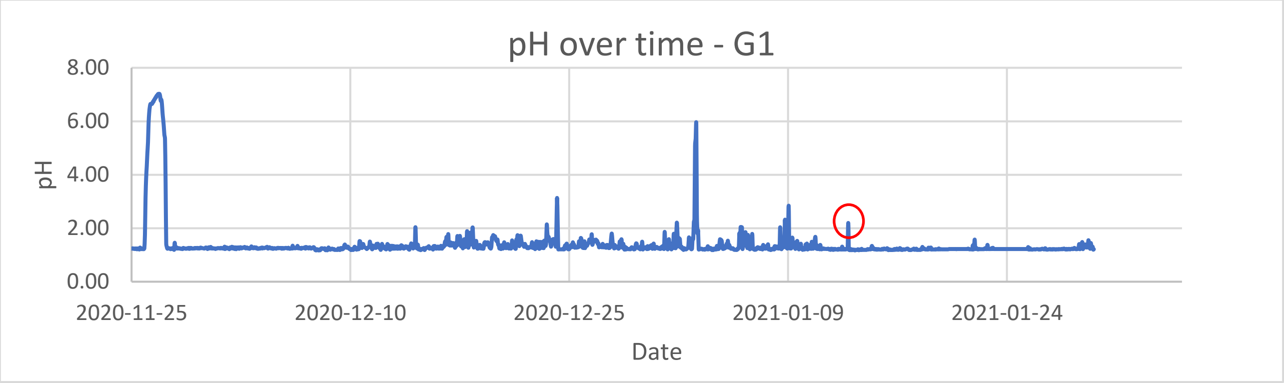
Figure 5.2. Pressure drop over heat exchanger 1 (blue) and over LDS2 (orange).



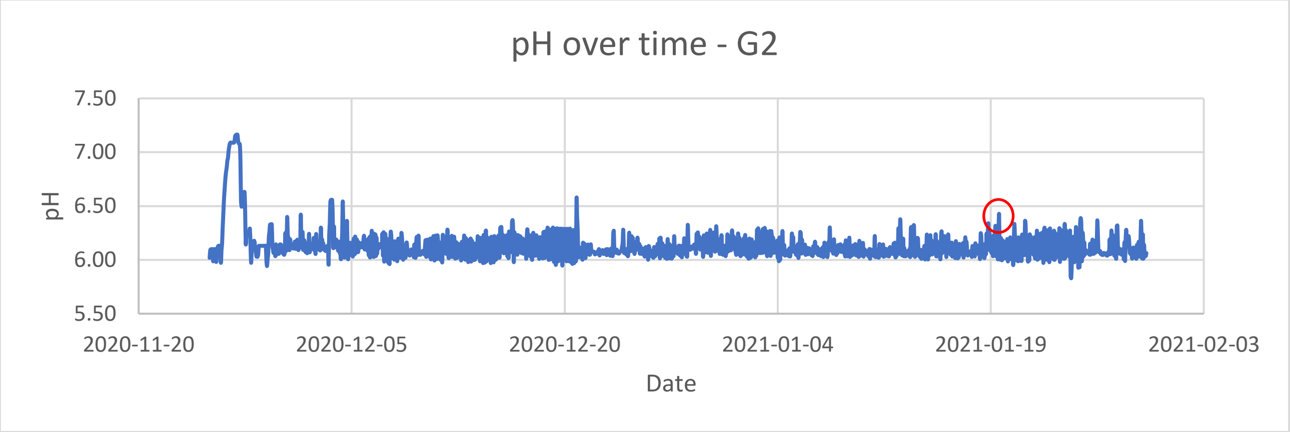
(a) HCl content.



(b) SO_2 content.



(c) pH in G1.



(d) pH in G2.

Figure 5.3. Measurement data from Sysav's process. The red circles marks the selected time periods which were used in the simulation model.

The pH and content of SO_2 and HCl were specified in the flue gas in the model according to measured values during the examined time period. The total flue gas flow was assumed to be constant, based on examination of the steam production which can be used to determine which load the process is operated at. It was concluded that the mean steam production was 110 ton steam/h with a standard deviation of 17 ton/h, indicating that the process was run at maximum load during the majority of the examined timeline. It was ensured that steam production specifically during the case periods did not deviate considerably from this value. The model was modified with the parameters in Table 5-4. The correct pH for the cases was implemented by manually varying the $CaCO_3$ content in the inlet stream until the correct pH was obtained.

Table 5-4. The cases tested in the simulation model. They are based on operational data from Sysav's process.

Case	**Description**	**Steam production [ton/h]**	**HCl content [mg/Nm^3]**	**SO_2 content [mg/Nm^3]**	**pH in G1**	**pH in G2**
Base Case	Estimation of composition with incineration of nominal waste	110	815	229	1.5	5.8
Case 1	HCl peak	114.37	1804.83	612.67	1.22	6.00
Case 2	SO_2 peak	112.90	1731.15	1260.43	1.28	6.02
Case 3	Peak in pH in G1	112.85	1213.34	282.90	2.20	6.05
Case 4	Peak in pH in G2	113.77	765.40	167.75	1.21	6.43

5.4 Sensitivity analyzes

A number of sensitivity analyzes were carried out. The pH, flue gas flow, recirculation liquid flow, temperature and oxygen content in the flue gas were varied. The aim of this was to study the trends of the results and compare to findings from the literature study. The results of HCl and SO_2 removal as well as salt formation were documented for all sensitivity analyses. Once the trends are verified, results from the case study can be interpreted as indications for undesirable operation parameters.

5.4.1 pH

By varying the $CaCO_3$ content entering the scrubbers, the pH was varied for the base case as well as cases 1-4 in both G1 and G2. At most it was adjusted 1.2 up and 0.7 down (absolute value) from the case pH. The flue gas composition for each case was maintained.

5.4.2 Temperature

The temperature was varied in the base case model. 50, 60 and 70 °C were tested by modifying the temperatures of all flows and units as well as the water content in the flue gas to reach saturation.

5.4.3 Load

As the incinerated load varies in the facility, the size of the generated flue gas flow differs consequently. A sensitivity analysis in which the flue gas flow was varied was thus carried out to investigate how the HCl removal efficiency, SO_2 removal efficiency and scaling is affected. The flue gas flow was varied between 70-110% of the flue gas at nominal load with respect to the mass flow. Only the base case was tested with varying flue gas flow. The composition remained unchanged. As the flue gas flow changes, the L/G ratio is consequently affected. Therefore, it is expected that the absorption will increase and scaling decrease when the flue gas flow is reduced.

5.4.4 Recirculated liquid flow

The liquid flow which is recirculated to the scrubber was run at two different modes. For G1, the recirculated liquid was either 145 m^3/h or 1190 m^3/h. In G2, the corresponding flow was 58 m^3/h or 220 m^3/h. The higher recirculation flow is the flow used in Sysav’s process, while the exact numerical values of the lower liquid flows were not important, only that they were lower than 1190 m^3/h and 220 m^3/h respectively so that the effect of a change in L/G could be studied. The flows were varied by changing the split fraction to the purge stream. This means that the incoming liquid and purge stream remained similar in all runs. The base case and cases 1-4, as described in Table 5-4, were run at these two operating modes to evaluate the model sensitivity to the parameter. As the recirculation liquid flow is increased, so is the L/G and thus, according to literature as described in section 3.5.4, the expected effects are increased absorption at higher liquid flow and decreased scaling. The pH was maintained at the case pH by modifying the amount of entering $CaCO_3$.

5.4.5 Oxygen

The oxygen content was varied into the RCSTR to investigate the precipitation dependance on oxygen. According to theory[31], more gypsum should be formed when more oxygen is available for oxidation. Separator and mixer blocks were used to vary the oxygen content up and down. To maintain the same total flue gas flow, the inert component N_2 was added or removed from the stream, correcting for the changed O_2 mass. Only the effect on formation of $CaSO_3 * \frac{1}{2} H_2O$ and $CaSO_4 * 2H_2O$ was studied.

The runs were made with a recirculated liquid of 145 m^3/h to G1 and 58 m^3/h to G2, which differs from the values in the final model. However, since the aim of the sensitivity analysis was simply to investigate the oxygen dependance on the precipitating salts, the numerical values on recirculation flow is unimportant. The volume percent of oxygen was varied between 5-7% for G1 and 7-8% in G2.

6 Results and Discussion

6.1 Evaluation of process

In this section results regarding the evaluation of Sysav's process compared to recommendation from literature sources are presented.

6.1.1 pH

The pH is set to 1.5 in G1 and 5.8 in G2. The actual pH varies over time however due to varying acid gas content in the flue gas. The pH from November 2020 to January 2021 in the two units was displayed in section 5.3.2 in Figure 5.3 (a) and (b). The maximum, minimum, mean, median, and standard deviation of the pH is shown in Table 6-1.

Table 6-1. Summary of pH variations in scrubbers G1 and G2.

	pH G1	**pH G2**
Target	1.5	5.8
Maximum	7.02	7.16
Minimum	1.17	5.83
Mean	1.41	6.14
Median	1.25	6.10
Standard deviation	0.76	0.15

The target pH value for G2, the unit which removes SO_2, is in line with literature source values claiming that a maximum pH of 5.8 should be used to avoid scaling[31]. For G1, which is called a pre-scrubber in the literature, typical values were pH 0-1 if water was injected only[1]. It is unclear how a higher value affects the unit. The results of mean pH over time was 1.41 in G1 and 6.14 for G2 implying that the pH control is insufficient, the target pH is not maintained. The mean is obviously affected by deviating operation periods such as stops in the facility which occurs in the beginning of the studied time period, but also the median differs, further confirming that deviation from the target value is common. The standard deviation is 0.76 in G1 and 0.15 in G2, a variation which can affect absorption and scaling considerably. Lower pH increases calcium sulfite solubility. When the pH is increased periodically the solubilized calcium sufite precipitates and there is a risk for scaling on the demisters. A higher pH overall enhances calcium sulfite precipitation and if the target pH would be increased in G2, there would be a great risk of increased scaling on demisters. Moreover, the calcium sulfite which is formed might further oxidize by the oxygen available in the flue gas passing, resulting in undesired hard scale.

6.1.2 Temperature

The temperature in the quench is continuously measured in the process at Sysav[60]. The measurement from November 2020 to January 2021 is shown in Figure 6.1. The low temperature in the beginning is due to a stop in the facility.

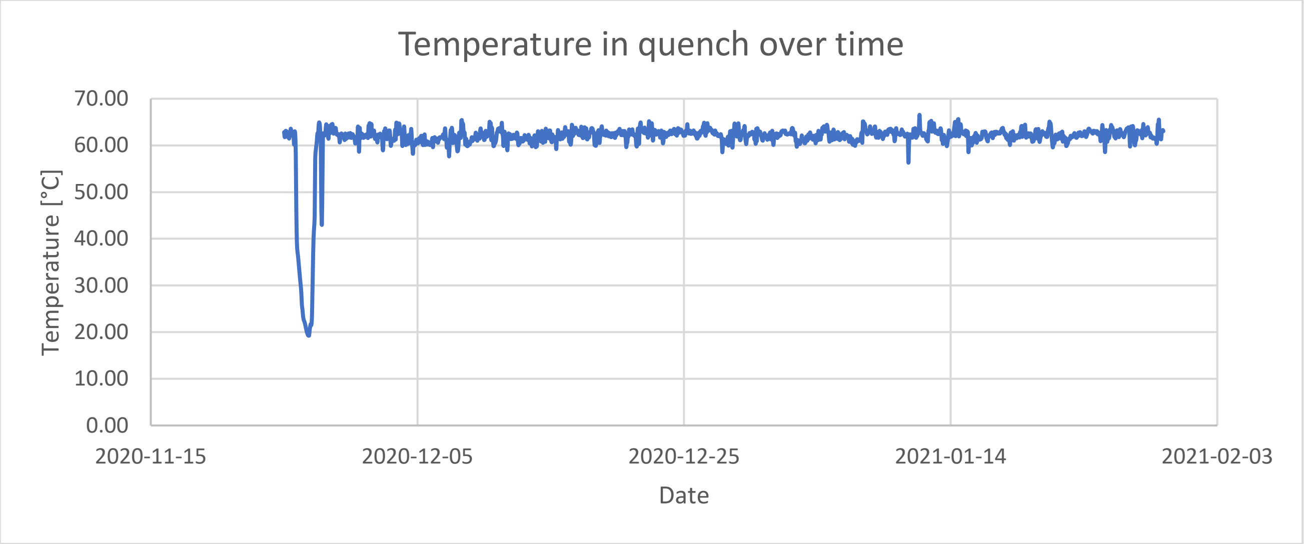


Figure 6.1. Temperature of the flue gas measured in the quench in Sysav's process.

During the studied time period, the mean temperature is slightly above 60 °C with a standard deviation of 5.27 as shown in Table 6-2. In the literature[31], 54 °C was reported as the conventional temperature for facilities similar to Sysav's. As previously mentioned, scaling can be reduced and absorption increased by lowering the temperature which should be considered for solving the issue at Sysav. Nevertheless, this requires modifications of the system. Either the upstream heat exchanger must be modified, or the quench must be more effective in lowering the temperature, increasing both investment and operational costs.

Table 6-2. Flue gas temperature in the quench in Sysav's process.

	Flue gas temperature in quench [°C]
Mean	61.43
Median	62.24
Standard deviation	5.27

6.1.3 Residence time

The dimensions of the scrubbers are illustrated in Figure 6.2. The calculated volumes of G1 and G2 reaction tanks were 88.3 m^3 and 127.60 m^3 respectively. The corresponding residence times were calculated to 4.45 and 34.8 minutes. According to literature[31], the residence time should be above 5-7 minutes for scrubbers without simultaneous fly ash removal and if not, 8 minutes, to prevent supersaturated liquid to be recirculated. Ideally, no fly ash should enter the scrubber system at Sysav as it is removed in the upstream electrostatic filter. However, problems have occurred in the past when fly ash has been present the scrubbers. Regardless of if fly ash is present or not, the residence time in G1 is lower than the recommended values. The comparison is presented in Table 6-3. However, since SO_2 is not absorbed here, the risk of supersaturation is low, and precipitation will most likely not occur in the tank despite the low residence time. In G2, the residence time is longer than 8 minutes. The risk of supersaturation is higher in G2 as a substantial amount of SO_2 is absorbed here. It is important to enable a sufficient residence time in this unit, which seems to be fulfilled.

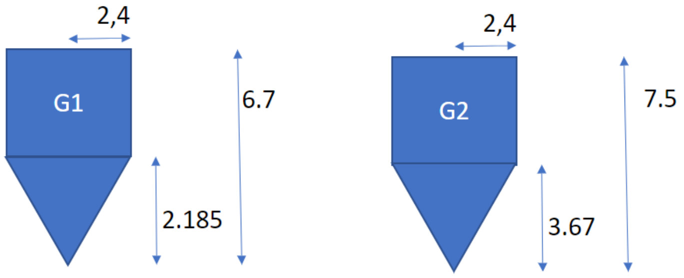


Figure 6.2. Dimensions of scrubbers G1 and G2.

Only one source of recommended residence time was found in the literature study, and it should be noted that more reports should be reviewed to get a broader range of values for comparison, as the successful time might vary in different plants.

Table 6-3. Residence time of scrubbers G1 and G2 compared to a literature value.

Unit	**Residence time [min]**
G1	4.45
G2	34.8
Literature[31]	< 8

6.1.4 Demister washing frequency

A summary of the washing parameters at Sysav, compared to findings in literature from tests at Shawnee facility[31] is presented in Table 6-4. The measurements at Sysav revealed a 3-minute washing time, followed by 15-minute paus. It was assumed that LDS1 and LDS2 are washed in the same intervals. The flowrate varied. For G1 it was usually approximately 7.5 m^3/h, but during a few seconds it increased to 16 m^3/h. G2 varied between 8-10 m^3/h but mostly it remained at 8 m^3/h. G1 has 6 tubes with 6 nozzles per tube which sprays the liquid. The washing liquid stream passes through one tube at a time in a sequence. Thus, each tube sprays liquid for 0.5 minutes. LDS2 consists of two demisters which are sprayed from 12 tubes. The actual time which each tube sprays liquid is hence 0.25 minutes. The 6 nozzles on each tube sprays simultaneously[64]. Thea area of the demisters at Sysav are 3.55 m^2/demister[43].

Table 6-4. The results from the demister washing frequency test.

**The calculated value is based on the demister area 3.55 m^2. It is unclear if the calculations should be done with the double area since LDS2 consists of two demisters.*

***Calculated from the top and bottom flow rates: 0.98 m^3/m^2*h + 1.3 m^3/m^2*h.*

	Sysav	**Literature**[31]
Washing time	3 minutes (30 seconds per tube and 6 nozzles in G1) (15 seconds per tube and 6 nozzles in G2)	3 minutes (top side) and Continuous (bottom side)
Paus time	15 minutes	7 minutes (top side) and Continuous (bottom side)
Flowrate G1	7.5 m^3/h (periodically 16 m^3/h)	-
Flowrate G2	8-10 m^3/h (mostly 8 m^3/h)	-
Washing time per nozzle G1	30 seconds	
Washing time per nozzle G2	15 seconds	
Area demister	3.55 m^2	
Specific rate G1	2.11 m^3/m^2*h	
Flowrate per nozzle G1	1.25 $m^3/h*nozzle$	
Specific rate G2*	2.25 m^3/m^2*h	2.28 m^3/m^2*h **
Flowrate per nozzle G2	1.3 m^3/h	1.82 m^3/h

The values at Sysav are somewhat lower than at the Shawnee test facility for specific flow rate, and it is possible that a higher flow could reduce the scaling, although only one source has been used as reference and more examples should be examined to draw certain conclusions. Moreover, it is possible that 3.55 m^2 *2 should have been used as the total area as 2 demisters are present in LDS2. If so, the specific area is considerably lower than literature values. The stops are longer at Sysav also and only intermediate washing is performed. During long pauses it is possible that calcium sulfite is formed and further oxidized to calcium sulfate. It is possible that a higher frequency of washing would decrease the scaling. The tubes being washed in a sequence consequently gives low washing times per tube and nozzle. If the uncertain calculations are correct, the washing time is only 30 seconds in G1 and 15 seconds in G2, which is low compared to 3 minutes, the washing time reported in literature, and may not be long enough to remove scaling.

It should be noted that there is an ambiguity regarding the procedure of the calculations done at the Shawnee facility. It is unclear if all nozzles sprayed at the same time or if they were used in a sequence. In Sysav's process each tube is operated in a sequence and the total flow is divided with 6 nozzles, which is the number of nozzles in operation simultaneously. At the Shawnee test facility, the calculations are done by dividing the total flow with the total number of nozzles. The Shawnee test facility seems to have a different system for washing of the demisters, as they separate the washing of the top side and the bottom side. This means that the results should be regarded as uncertain and only interpreted as a suggestion that the washing procedures influences the buildup of scaling and that modifications can be done to achieve improved scale control.

6.1.5 Gypsum content

The density of the recirculated slurry in G2 is controlled by continuous density measurements to approximately 1030 kg/m[3,12]. This corresponds to a gypsum content of 50 g/L[11]. The gypsum content in the solution is hence 4.9%. Different sources have found different values to be effective, but some have reported that at least 8% solids is necessary for preventing scaling[31]. The results are summarized in Table 6-5. Other sources[33] found 1% to be effective, and that a higher value did not reduce the scaling any further. This indicates that different results can be obtained, and it is unclear what value should be used at Sysav. However, it is possible that modifying the target density to a higher value could reduce scaling.

Table 6-5. Density control determines the solid content in the liquid. The solid content in Sysav's process can be compared to literature values.

	Sysav	**Literature sources**
Density	1030 kg/m^3	-
Concentration	50 g/L	-
Solid content	4.9%	8%[31].
		1%[33]

6.1.6 Limestone specifications

The specification for the limestone used in Sysav's process is summarized in Table 6-6, together with recommended values from different sources.

Table 6-6. Summary of limestone characteristics of limestone used at Sysav and recommendations from literature.

	Sysav	Literature sources
Carbonate ($CaCO_3$ + $MgCO_3$)	98.8%	> 90% $CaCO_3$[31] < 5% $MgCO_3$ [31]
Particle diameter	d98% = 20 µm part < 2 µm = 30-45%	44 µm[31] 149 µm[38] 5-20 µm[29]
Stochiometric ratio	Unknown	< 1.2 [31]

No conclusions can be drawn regarding the purity since the exact $CaCO_3$ content is unidentified. The size is in the same range as the literature values, however since porosity, purity and size altogether affect the reactivity, more information or testing is necessary to determine the utilization.

The amount of excess $CaCO_3$ is not known and could be a factor that contributes to the scaling according to the literature study. The stochiometric ratio should be determined to evaluate if the reactivity is sufficient of the limestone and if not, explore the possibility of improving the parameter to reduce scaling.

6.1.7 L/G ratio

The calculated L/G ratios for the units at Sysav are presented in Table 6-7. It is debatable if the liquid to the quench in G1 should be included in the calculations, and the result can be either 5.4 dm^3/m^3 if the liquid to the quench is included or 4.6 dm^3/m^3 if not. Literature reference values[41] of the parameter is also included in Table 6-7 for comparison.

Table 6-7. Liquid-to-gas ratio in scrubbers G1 and G2. Conventional values according to literature are included as reference.

	Sysav	Literature
L/G G1	> 5.4 or 4.6 dm^3/m^3	-
L/G G2	> 1.0 dm^3/m^3	8-13 dm^3/m^3 [41]

No data can be found in the literature regarding L/G ratio for the pre-scrubber, corresponding to G1. One can assume however, that similar values should be applicable on this unit since sufficient absorption of the acidic compounds must take place. The L/G ratios at nominal load for both scrubbers are lower than conventional values found in literature. It is possible that the low L/G ratio limits the absorption efficiency of the absorbate species as well as enhances scaling.

6.1.8 Oxygen content

The oxygen content in the flue gas when calculating from nominal waste was 8 mass% or 7 vol%, although it varies in the real process. The oxygen content is not measured and can thus not be compared to recommended values. In the literature study it was described that to minimize calcium sulfate scaling, the oxidation should be controlled to either a minimum value (natural oxidation), or a maximum value (forced oxidation). One study[35] reported rapid formation of calcium sulfate scaling already at an oxygen content of 4%, implying that the estimated O_2 content in the flue gas is high and enables scaling. As mentioned, this estimation is uncertain and the parameter should be measured and controlled in Sysav's process, particularly since the observed scale has been very hard periodically, indicating that oxidation to calcium sulfate occurs.

6.2 Simulation results

The results obtained from the Aspen Plus simulation are presented in the following section. The final model which was obtained from the model development phase is shown in Figure 6.3. The figure shows the general model consisting of a scrubber, recirculation, and demister. G1 + LDS1 and G2 + LDS2 were computed in separate files, both using the general model setup according to the figure, however with individual process conditions as described in the model development section. "Scrubber" in the figure is a RADFRAC modelling absorption, "dropsep" is an RCSTR unit modelling crystallization and oxidation in LDS1, the "mix" and "split" units are used to mix incoming liquid streams to the scrubber and the latter for splitting the recirculation flow to either be sent for recirculation, sent to the droplet separator or purged.

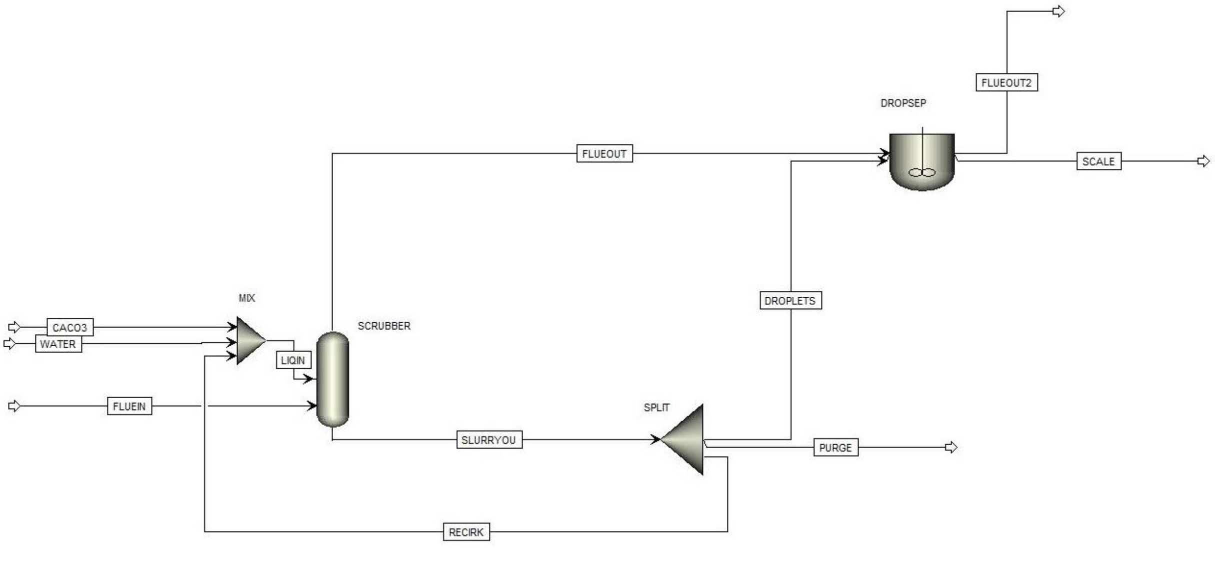


Figure 6.3. Aspen Plus simulation model. G1 and LDS1 are displayed. G2 and LDS2 has the same setup.

6.2.1 Case study

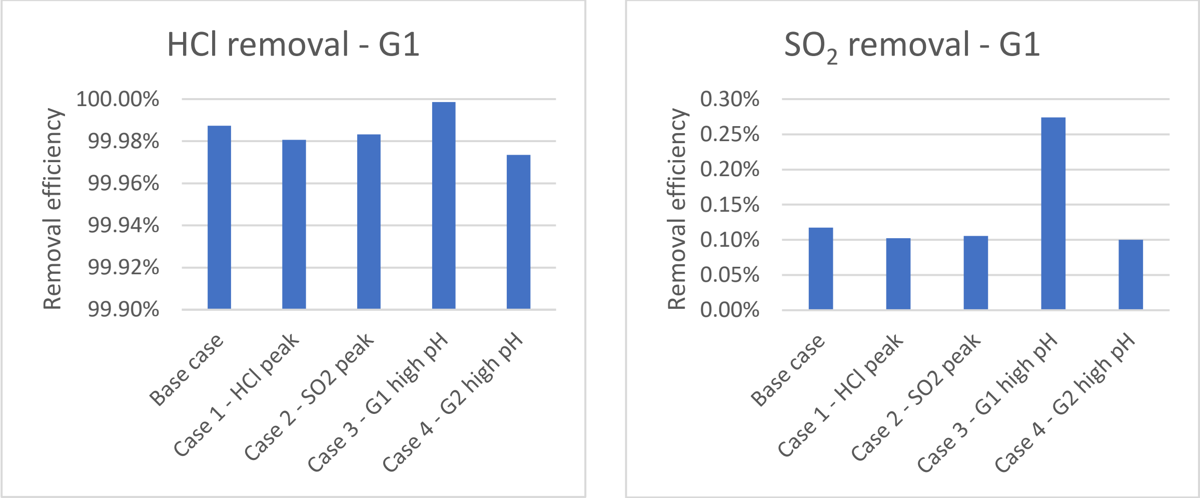
Input to the five cases was implemented according to Table 5-4 and the results of SO_2 and HCl removal efficiency as well as $CaSO_3$*½ H_2O and $CaSO_4$*2H_2O formation were recovered. The

Aspen Plus results report for the base case includes results for all streams and operational units and is displayed in Appendix G: Results report from Aspen Plus – Base Case. Numerical results for all cases from G1 and G2 models can be read in Appendix H: Case Study Raw Data.

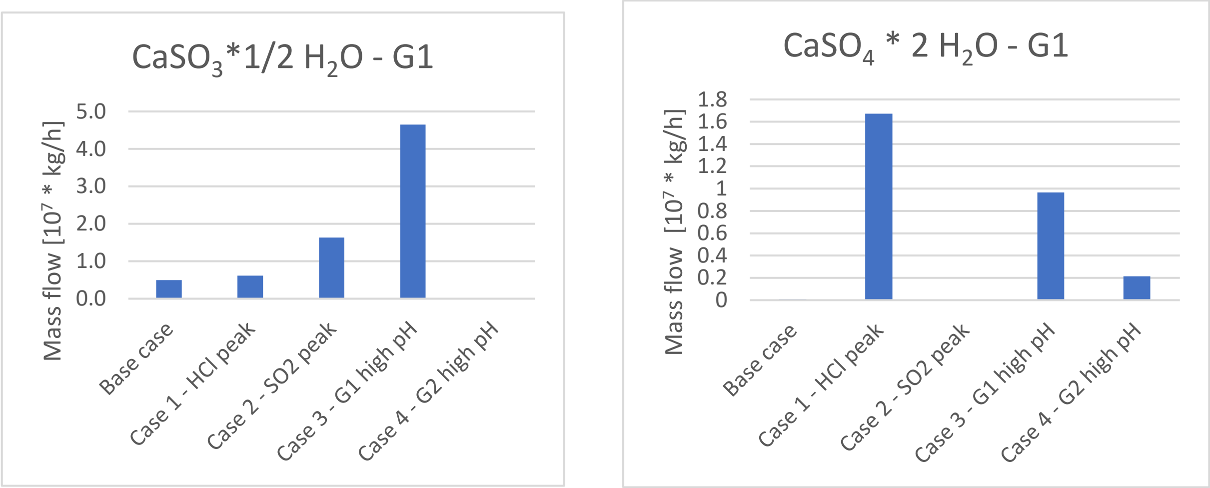
Results from G1 are presented in Figure 6.4 and shows high HCl removal efficiency for all cases, while the SO_2 removal is low. This is expected as a higher pH is necessary for SO_2 absorption to be efficient. In case 3, the pH was higher and consequently a somewhat higher SO_2 removal takes place.

The calcium sulfite and sulfate formations are low in the LDS1 model for all cases, contradicting what has been observed in the facility. Very low amounts of SO_2 are absorbed in this scrubber, caused by the low pH, leading to low crystal formation due to the limitation of available reactant. This is supported by the fact that in case 3, a higher amount of $CaSO_3*½ H_2O$ is formed, which corresponds to the case when a higher SO_2 removal is observed.

The results of low crystal formation in the model, on the contrary to the high buildup on the demisters in reality, indicate that something excluded from the model affects the crystal buildup. Not accounted for in the model is the excess $CaCO_3$ in the recirculated slurry. The excess $CaCO_3$ has been reported in literature to enhance scaling as it reaches the demister where it can further react with SO_2. If excess $CaCO_3$ is collected in the droplets in the demister, the pH in the droplets will be higher which will further enhance SO_2 dissolution and consequently more SO_2 and $CaCO_3$ will form salts. In this model perfect utilization of $CaCO_3$ is assumed and it possibly that this is a key parameter for scaling in demisters. The model fails in simulating unreacted $CaCO_3$ and further dissolution of SO_2 leading to scale formation in the demister.



(a) HCl removal efficiency. (b) SO_2 *removal efficiency*

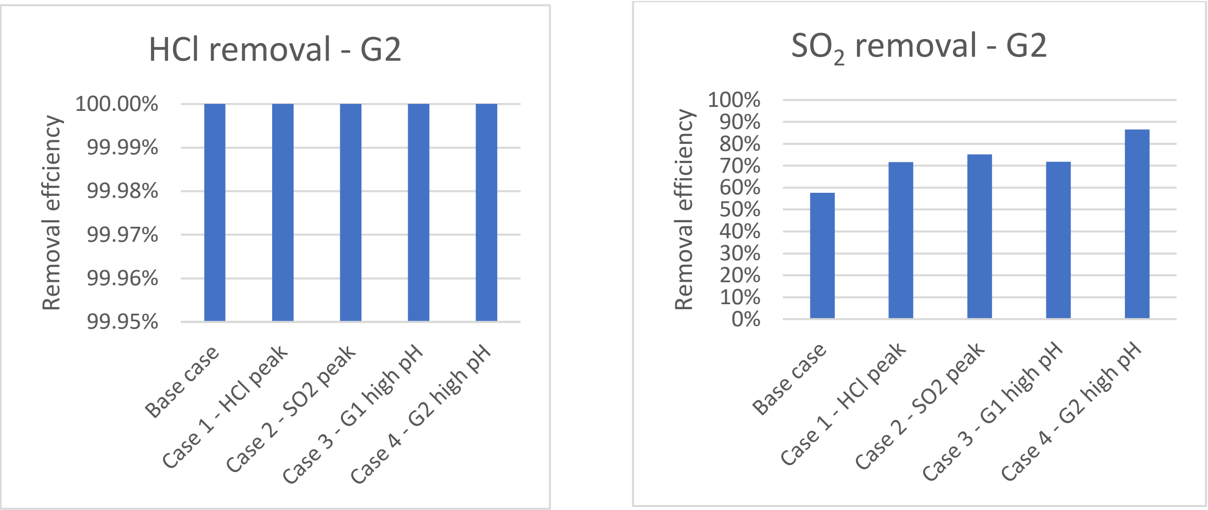


(c) Calcium sulfite hemihydrate. *(d) Calcium sulfate dihydrate*

Figure 6.4. Results from the G1/LDS1 model for all cases on HCl removal, SO_2 *removal,* $CaSO_3*1/2H_2O$ *and* $CaSO_4*2H_2O$ *formation.*

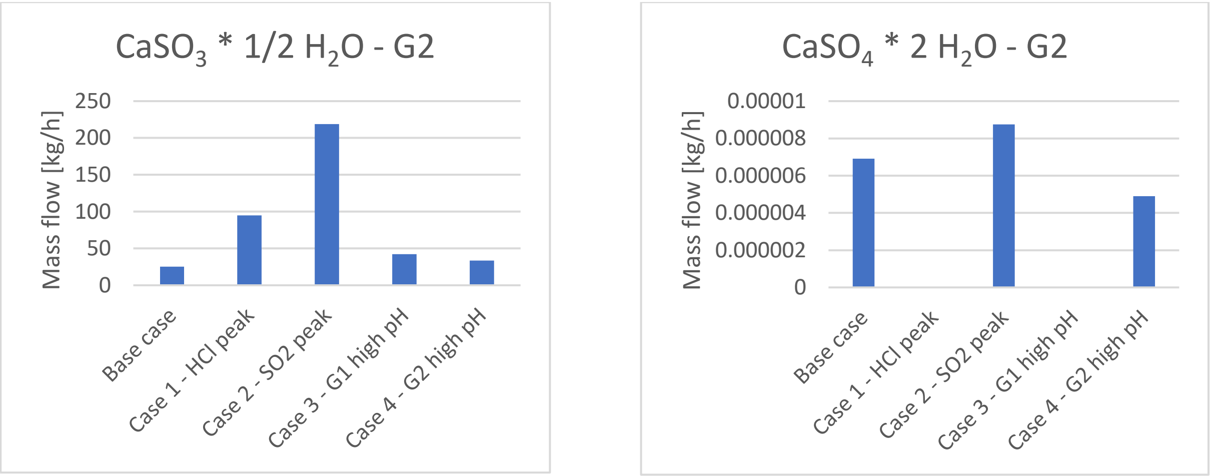
The same parameters were studied from G2 according to Figure 6.5. Also in G2 a high HCl removal is obtained. The ingoing amount is however rather low as most of the compound is removed in G1. The SO_2 removal varies between 57-87%. The results indicate that pH is the most influencing factor as the SO_2 absorption is considerably higher for case 4, which was run at higher pH.

The $CaSO_3$*½ H_2O formation is higher in G2 compared to G1, which likely is caused by the high pH enhancing the SO_2 removal. Higher concentration of SO_2 is absorbed to the liquid and more salt product is obtained. It seems that, as was indicated by the results from G1, SO_2 is the limiting factor for formation of $CaSO_3$*½ H_2O. Furthermore, the highest amount is observed for case 2, corresponding to the SO_2 peak in the flue gas. Although somewhat higher than in G1, low amounts of $CaSO_4*2H_2O$ are also formed in G2. The highest amounts are formed for the base case and cases 2 and 4. It should be remembered that the numerical values have not been confirmed, and the sensitivity analyzes results must be used to assess the model reliability before any conclusions regarding operation can be made from the case results.



(a) HCl removal efficiency.

(b) SO_2 *removal efficiency.*



(c) Calcium sulfite hemihydrate.

(d) Calcium sulfate dihydrate.

Figure 6.5. The results of HCl and SO_2 *removal efficiency in G2 and the crystal compound formation in LDS2 derived for input from 5 different operational conditions.*

6.2.2 pH dependance

The HCl and SO_2 removal efficiencies as a function of pH were summarized in two graphs according to Figure 6.6 and Figure 6.7. Numerical data is provided in Appendix I: pH Sensitivity Analyze Raw Data. The removal of SO_2 increases with pH as expected and follows a clear trend except for some outliers. The SO_2 absorption is in the same range as was presented by Henzel et al.[31] and thus legitimate. The results of HCl removal shows that the absorption of this compound is also increased with pH. This is logical as a higher pH means that more alkalinity is available which enhances the driving force of absorption.

The deviating results are likely caused by Aspen calculations finding false solutions. This is a dilemma for complex problems as the solutions may be more than one and sometimes unreliable results are generated. Furthermore, convergence problems were common, and the model was “forced” to converge by re-running the simulation with varied convergence methods which eventually led to a solution being generated. It is however a risk that a false solution is found using this approach.

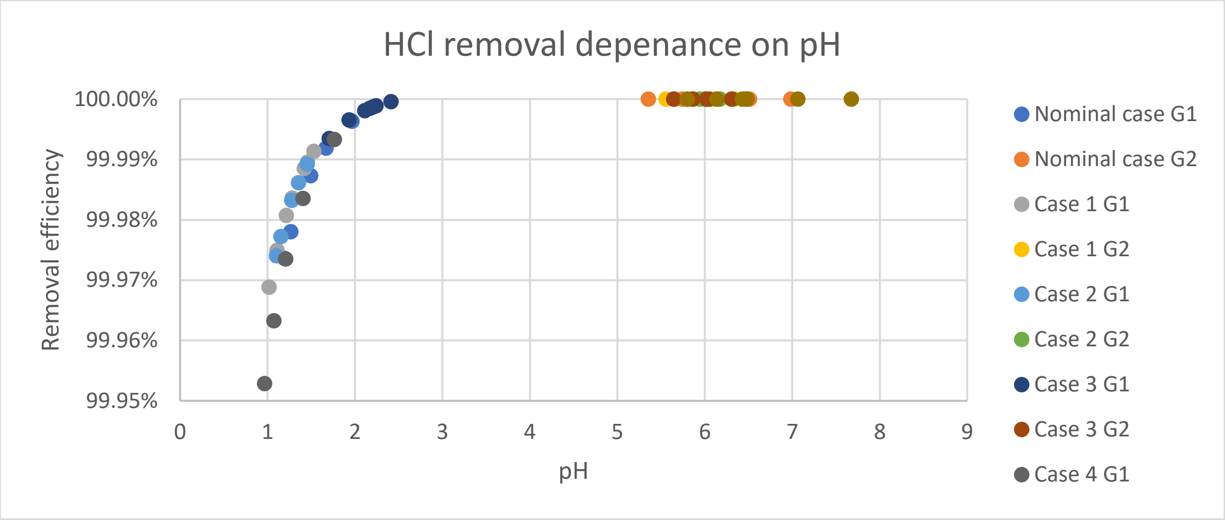


Figure 6.6. HCl removal efficiency as function of pH.

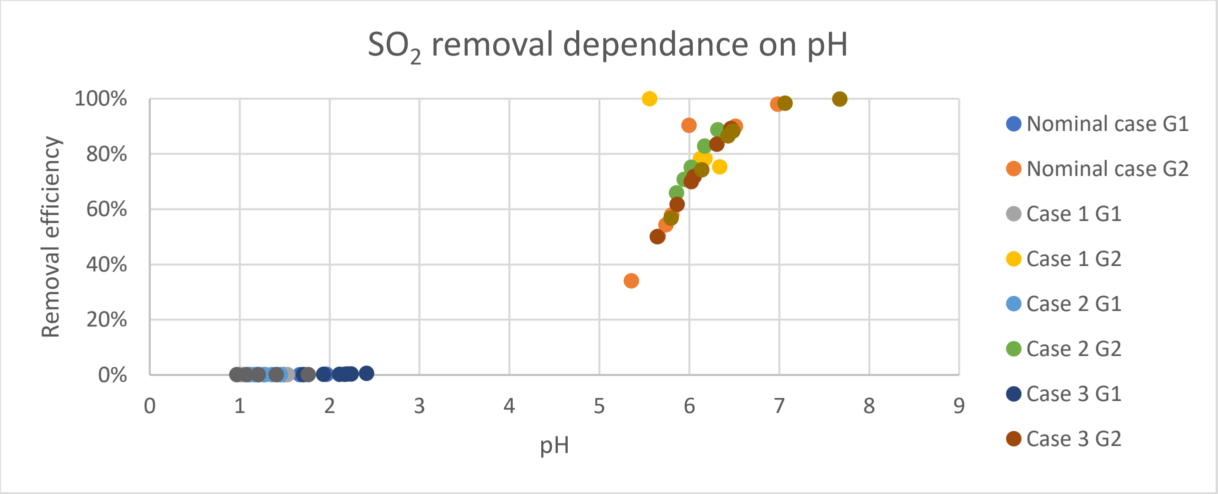


Figure 6.7. SO_2 removal efficiency as function of pH.

Likewise, the formation of $CaSO_3*½ H_2O$ and $CaSO_4*2H_2O$ as a function of pH is illustrated in graphs as presented in Figure 6.8 and Figure 6.9. The sulfite production increases with pH as anticipated. The gypsum ($CaSO_4*2H_2O$) results are more widespread and, as was seen in the case study, the numerical values are close to zero. The values are higher in the G2 model (at pH around 6), but still a scattering occurs in the result. Either the results are too low and consequently very sensitive to changes, causing the deviation, and/or the reaction is not simulated correctly. The second option means that chemistry constants obtained from Aspen Plus databanks should be reviewed and altered manually.

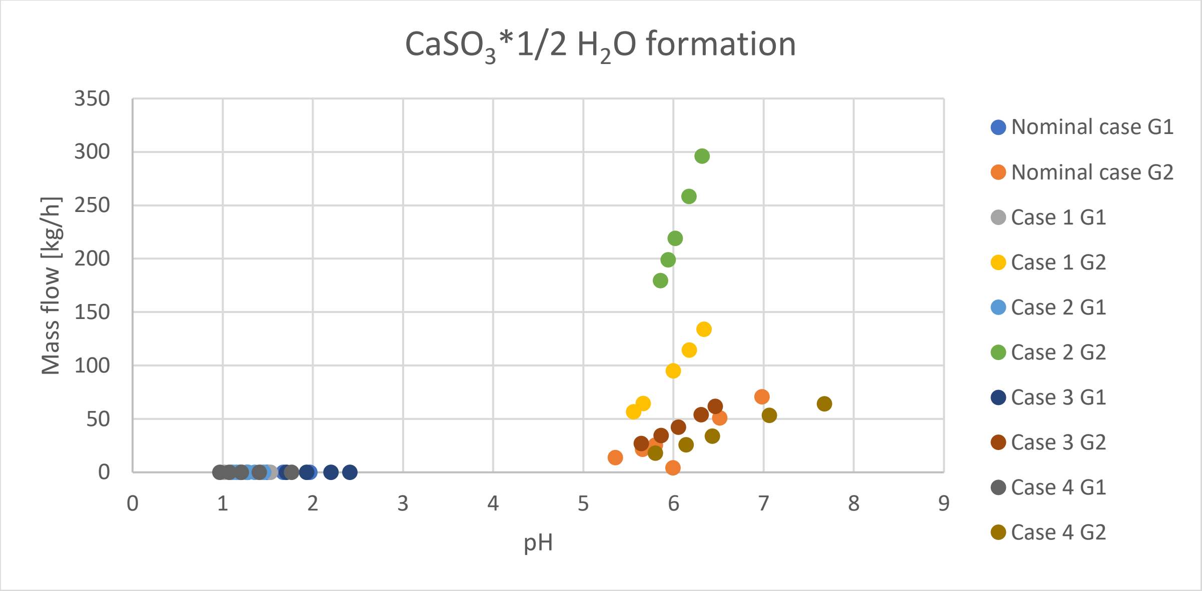


Figure 6.8. Calcium sulfite hemihydrate formation as a function of pH.

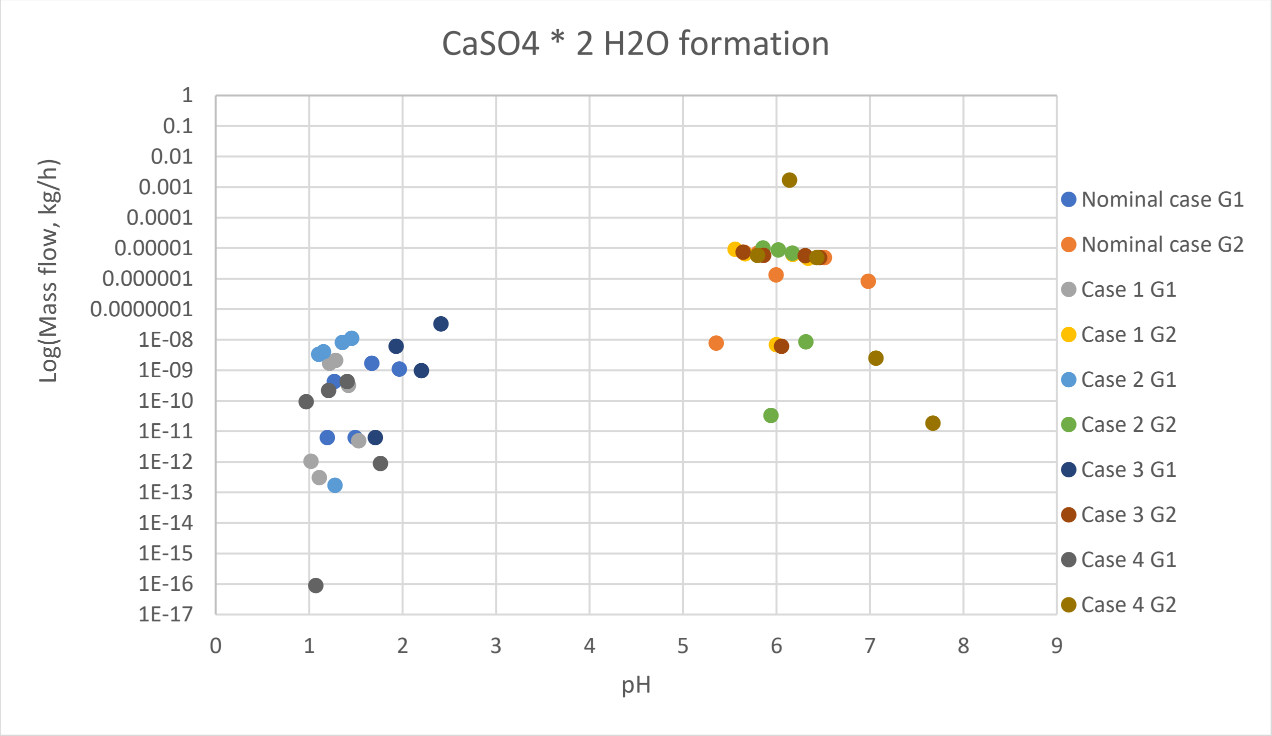
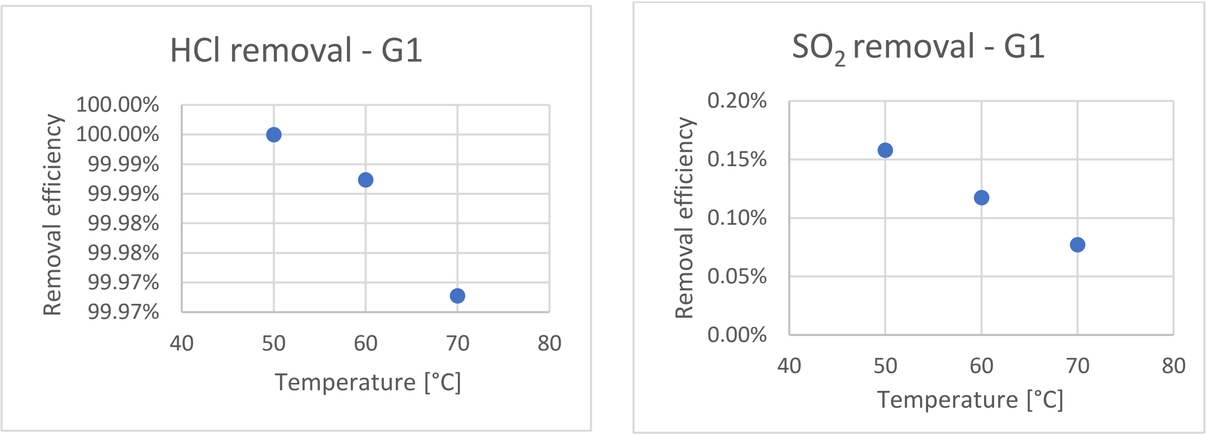


Figure 6.9. Calcium sulfate dihydrate formation as a function of pH. The y-axis is logarithmic.

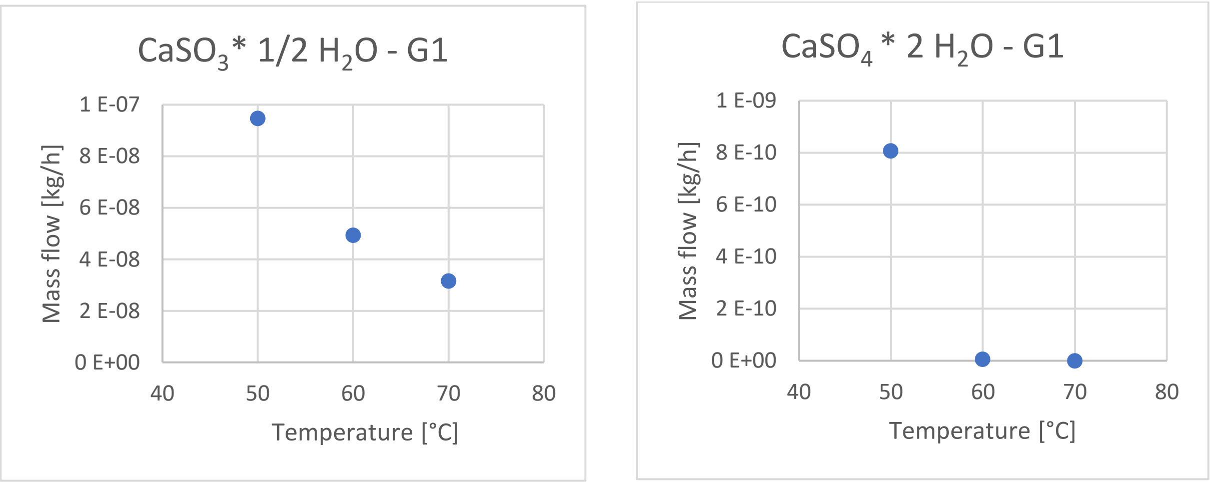
6.2.3 Temperature

The HCl and SO_2 removal efficiencies decreased with temperature, which was predicted from the literature study, as shown in Figure 6.10 for G1 and Figure 6.11 for G2. On the contrary, the $CaSO_3$*½ H_2O formation decreased with temperature in both G1 and G2, conflicting with literature sources. This indicates that the dependence on available SO_2 in the liquid dominates over the temperature dependance in the model. As previously observed, the $CaSO_4$*$2H_2O$ formation is numerically small and the results are random in G1. The values are higher in G2 and a maximum occurs at 60 °C which cannot be explained. This further supports that the $CaSO_4$*$2H_2O$ results are unreliable. Raw data is displayed in Appendix J: Temperature Sensitivity Analyze Raw Data.

Although only 3 data points were reviewed it could be confirmed that the model has the correct temperature dependance for the absorption for the temperature range tested. More studies regarding the temperature influence on crystal formation should be conducted.

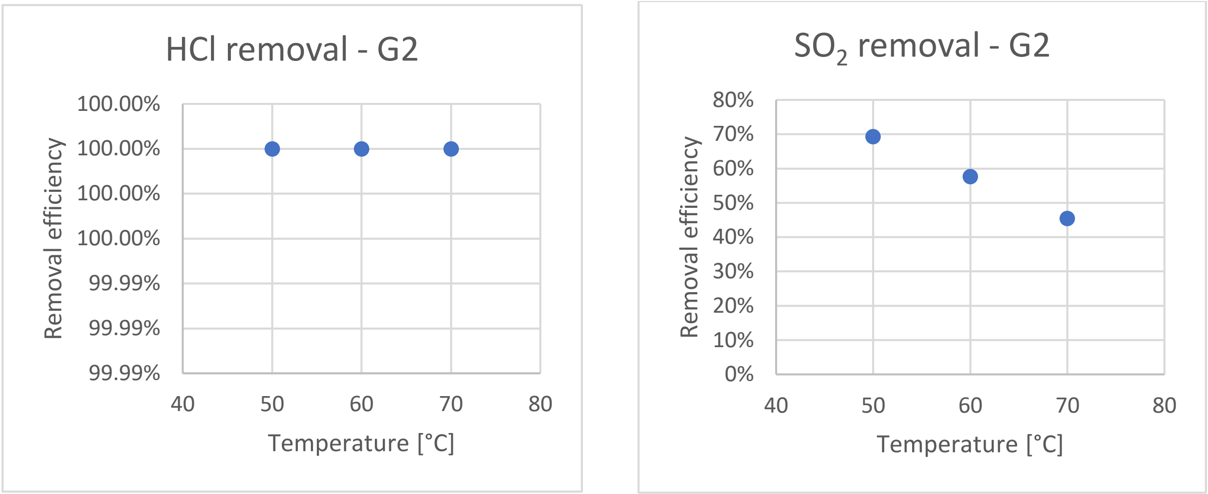


(a) HCl removal efficiency. *(b) SO_2 removal efficiency.*



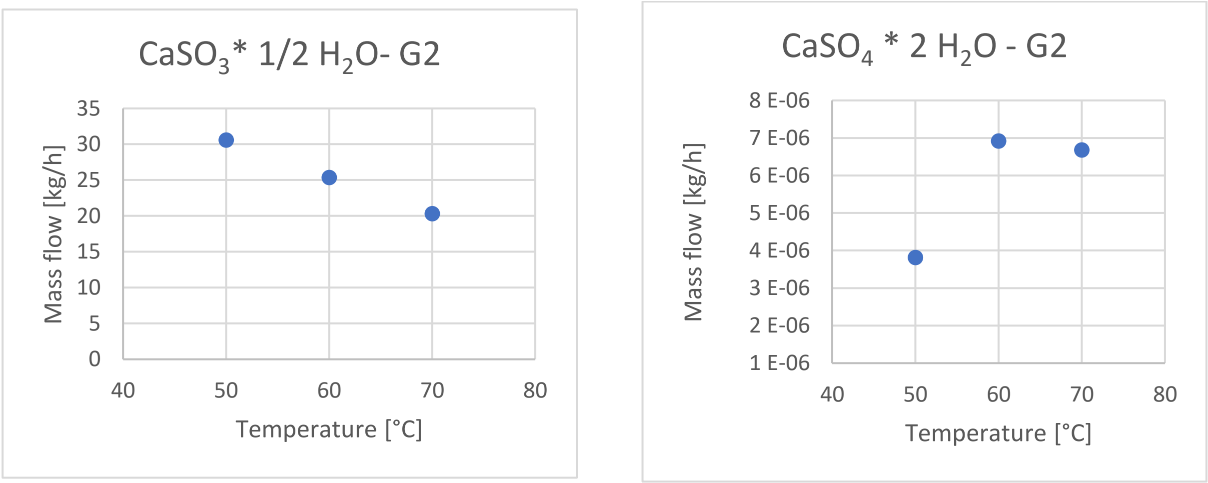
(c) Calcium sulfite hemihydrate. *(d) Calcium sulfate dihydrate.*

Figure 6.10. Absorption and solid formation as a function of temperature for the simulation model containing G1 and LDS1.



(a) HCl removal efficiency.

(b) SO_2 *removal efficiency.*



(c) Calcium sulfite hemihydrate.

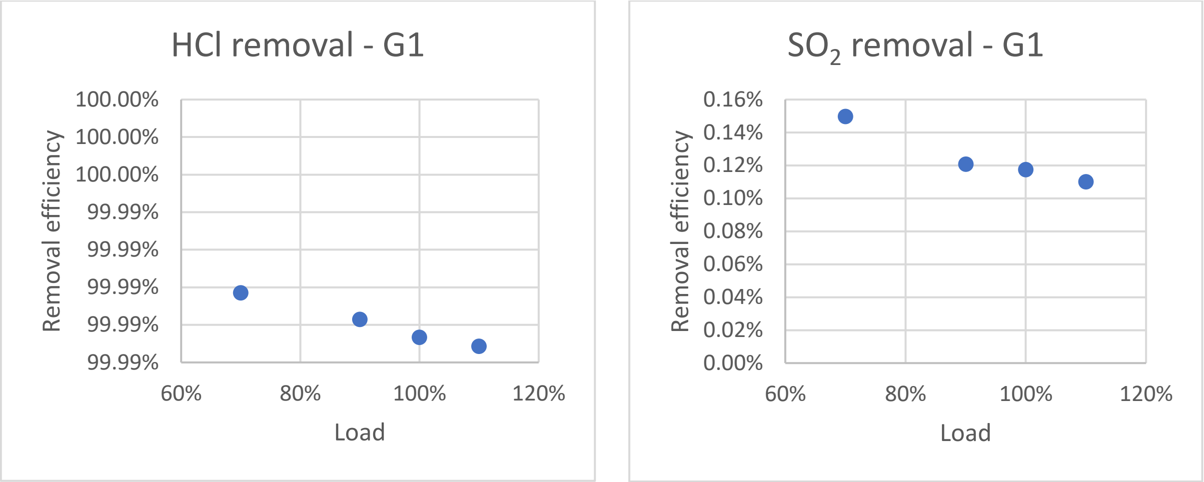
(d) Calcium sulfite dihydrate.

Figure 6.11. The absorption and solid formation as function of temperature for the simulation model containing G2 and LDS2.

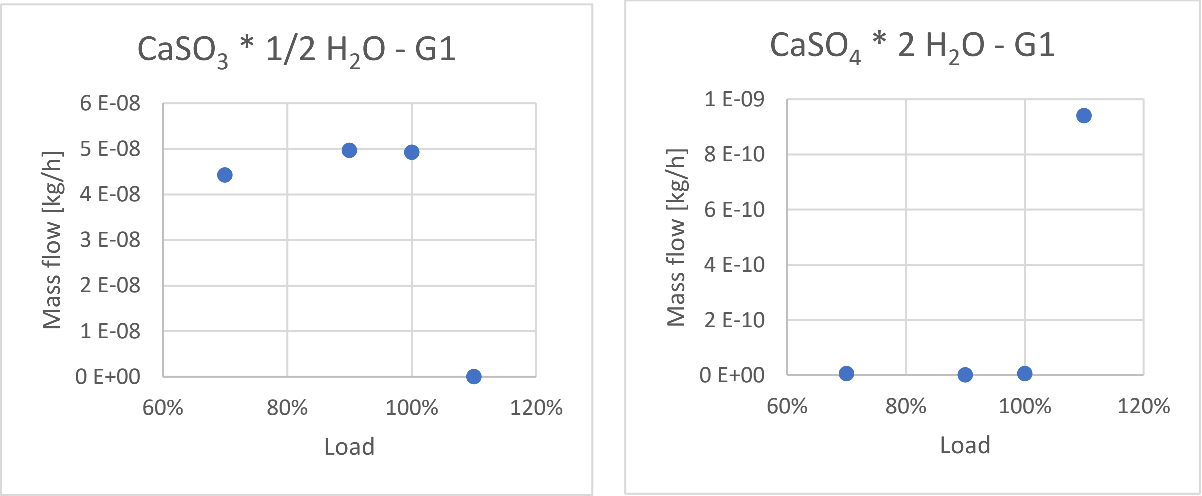
6.2.4 Load

As the flue gas flow is varied, the L/G ratio changes as well. Thus, it is expected that the absorption should decrease with increased load if the recirculated liquid remains unchanged. Moreover, the salt formation was proposed in the literature to decrease with higher L/G by two main mechanisms: more mechanical washing and less calcium sulfite per pass. It was expected that the model would respond accordingly, but only because of less calcium per pass as the mechanical washing is not included in the model.

The results for G1 are shown in Figure 6.12 and for G2 in Figure 6.13. HCl and SO_2 absorption showed a decrease in removal efficiency with higher flue gas flow. This trend was observed both in G1 and G2, although more clearly in G2 for SO_2. The results could nevertheless be due to the amount of available HCl and SO_2 to start with varying as the flue gas follow varies. The result of both $CaSO_3$*½ H_2O and $CaSO_4$*$2H_2O$ at 110% load varied from the other results in G1. It is perhaps due to Aspen finding another available solution, and although it is not reasonable, the solution is generated by the program without errors. Except for this deviating result, the tendency of $CaSO_3$*½ H_2O is to increase at higher load, as was theorized. The $CaSO_4$*$2H_2O$ results are, as in previous tests, small and the variations even smaller consequently supporting that the model fails in simulating this compound correctly. The graphs are plotted from numerical data, which can be found in Appendix K: Load Sensitivity Analysis Raw Data.



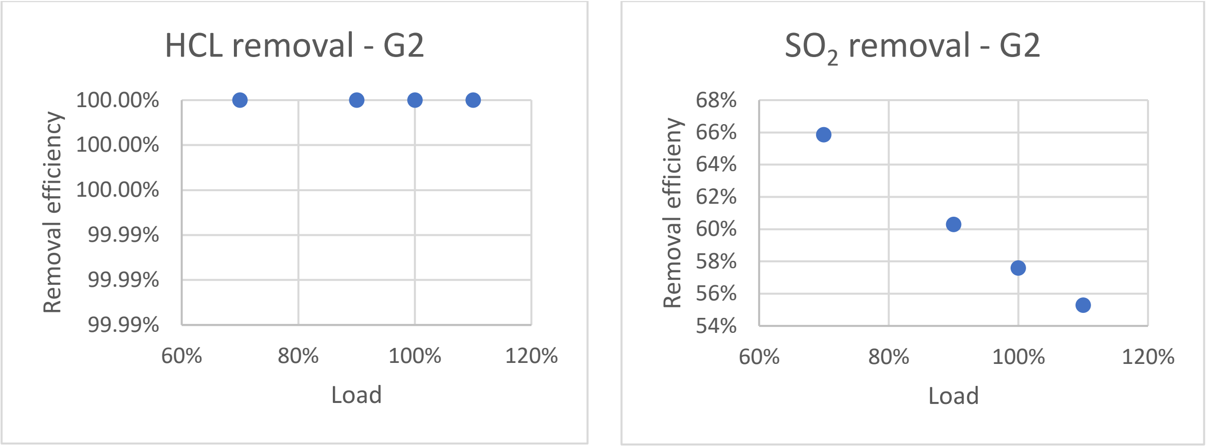
(a) HCl removal efficiency. *(b)* SO_2 *removal efficiency.*



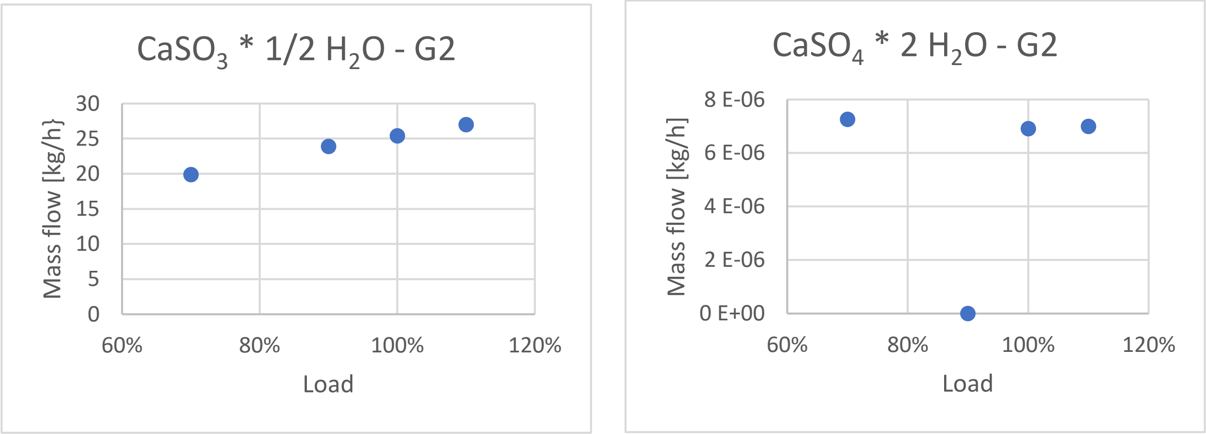
(c) Calcium sulfite hemihydrate. *(b) Calcium sulfate dihydrate.*

Figure 6.12. Absorption and solid formation as function of load. Results from the model containing G1 and LDS1.

In G2, an increased flue gas flow, likewise enhanced $CaSO_3$*½ H_2O formation which was desired. Results of the $CaSO_4$*$2H_2O$ formation obtained one outlying point for the run at 90% load. The other values have a small decrease with load on the contrary to the literature review findings, however, as mentioned earlier, the behavior of the $CaSO_4$*$2H_2O$ in the model is likely incorrect.



(a) HCl removal efficiency. *(b)* SO_2 *removal efficiency.*



(c) Calcium sulfite hemihydrate. *(d) Calcium sulfate dihydrate.*

Figure 6.13. Absorption and solid formation as a function of load. The results are from the model with G2 and LDS2.

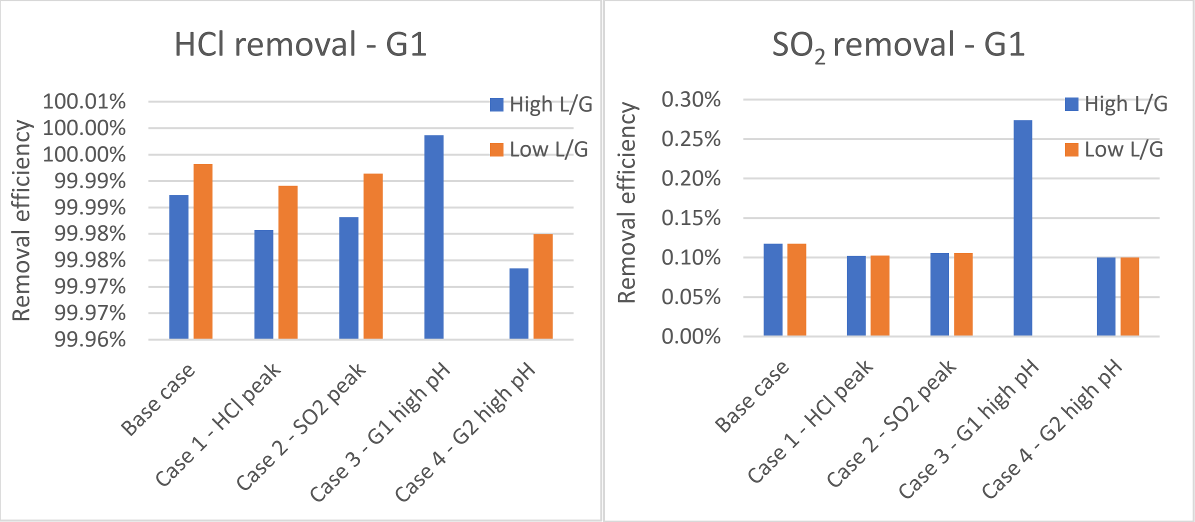
6.2.5 Recirculated liquid flow

Removal efficiencies and solid formation for all cases for high and low liquid flow recirculated is shown in Figure 6.14 and Figure 6.15. Raw data can be found in Appendix L: Recirculation Liquid Flow Sensitivity Analysis Raw Data. Case 3 was not run at the lower liquid flow. In this analysis the L/G ratio was varied by changing the liquid flow, on the contrary to the results above in section 6.2.4 in which the flue gas flow was varied and the recirculation flow was constant. The results from varying the recirculation liquid are more reliable to test the model dependance on L/G ratio than by varying the flue gas flow as done in section 6.2.4. This is because varying the flue gas flow also consequently varies the amount of HCl and SO_2, giving uncertain results of the absorption efficiency.

The removal efficiency obtained limited effect in G1 when varying the recirculated liquid, while the flue gas flow was constant. The effect that could be seen, although small, was that the absorption decreased at the higher L/G mode. The effect was clearer for the results from G2. This is contradicting literature which clearly states that the efficiency is increased by increasing the sprayed liquid. Thus, the results indicate that the absorption dependency on the amount of liquid and gas is not correct. This effect was not seen in the results in section 6.2.4 when the flue gas flow was varied, which supports the theory that variations of SO_2 and HCl amounts affects the results on absorption efficiency.

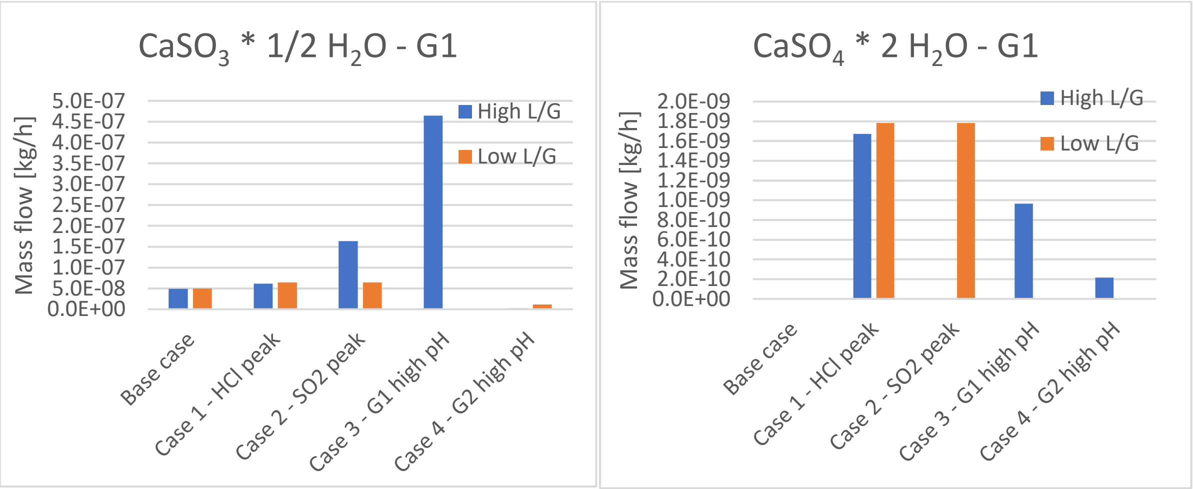
This could be due to the mass transfer kinetics not being accounted for (equation (4)). The liquid-gas ratio affects the contact area which would increase mass transfer and consequently enhance absorption. In the model, equilibrium is assumed and SO_2 dissolution in the liquid will follow Henry's law. What was observed initially when altering the liquid flow upwards was that the pH increased, due to the concentration of SO_2 decreasing in the higher solute volume. To investigate only the L/G ratio effect on the process, the pH was modified to be the same as at the low L/G test by decreasing the amount of $CaCO_3$ entering the process. This in turn means that the stochiometric ratio is lower which decreases the driving force of SO_2 absorption. It seems that the effect of lower stochiometric ratio is observed rather than the effect of higher liquid flow. Perhaps if the $CaCO_3$ dissolution and mass transfer kinetics were accounted for in the model, the increased L/G would affect the absorption in the way that was expected.

The $CaSO_3$*½ H_2O precipitation was higher at lower L/G for the nominal case and cases 1, 2 and 4 in G2. This is supported by theory. In G1 the results are more ambiguous, however, this can be explained by the low amount which are formed are sensitive to changes and therefore not reliable. Similarly, the $CaSO_4$*$2H_2O$ formation is random, half of the results are higher at lower L/G and half lower. In general, only the $CaSO_3$*½ H_2O in G2 seems to have the expected dependance on L/G ratio.



(a) HCl removal efficiency.

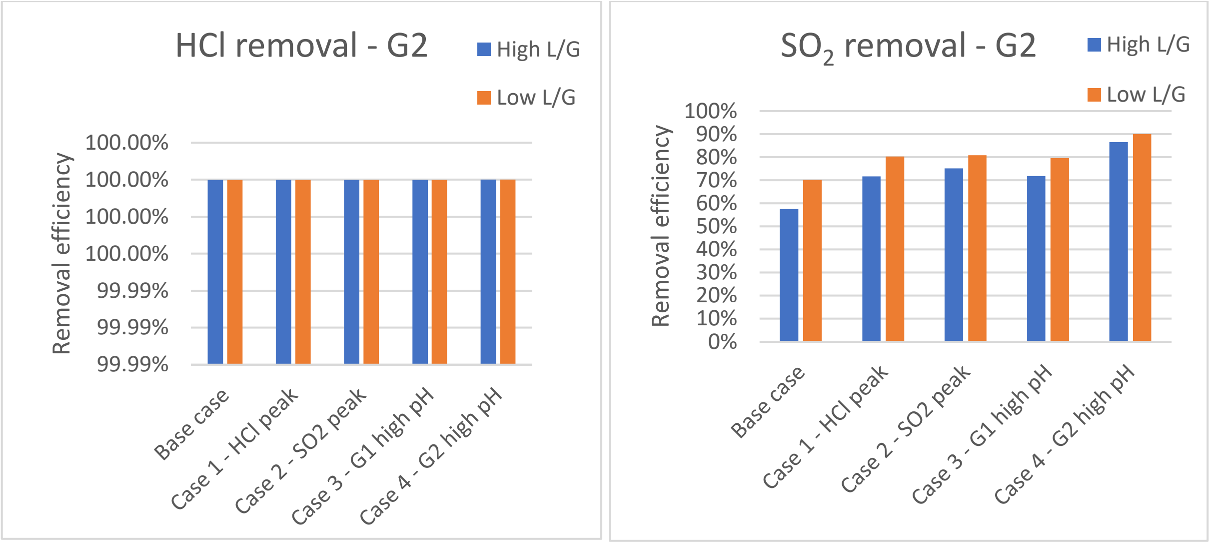
(b) SO_2 *removal efficiency.*



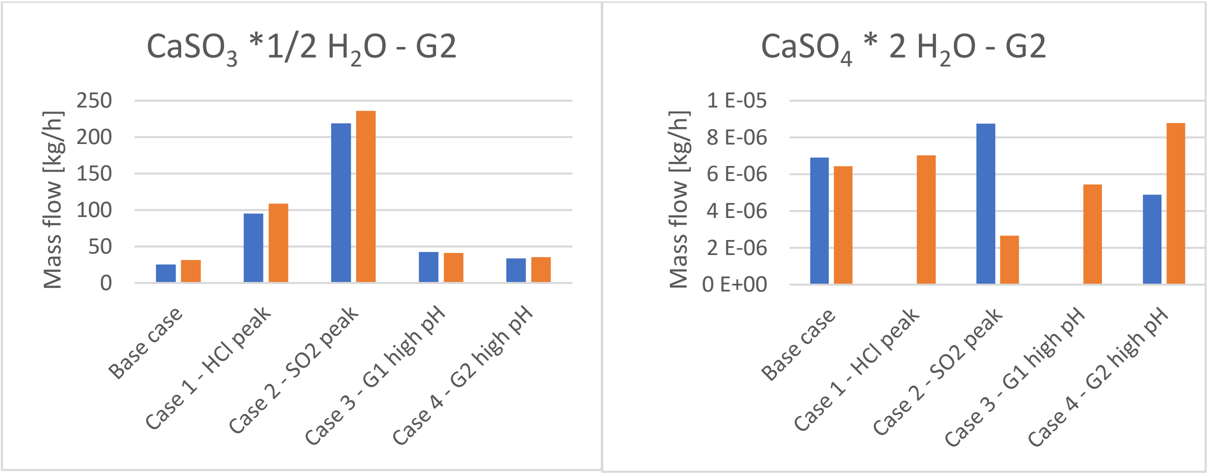
(c) Calcium sulfite hemihydrate.

(d) Calcium sulfate dihydrate.

Figure 6.14.Results from G1 simulation runs with 5 cases of operating conditions with high or low flow of recirculation liquid.



(a) HCl removal efficiency. *(b)* SO_2 *removal efficiency.*

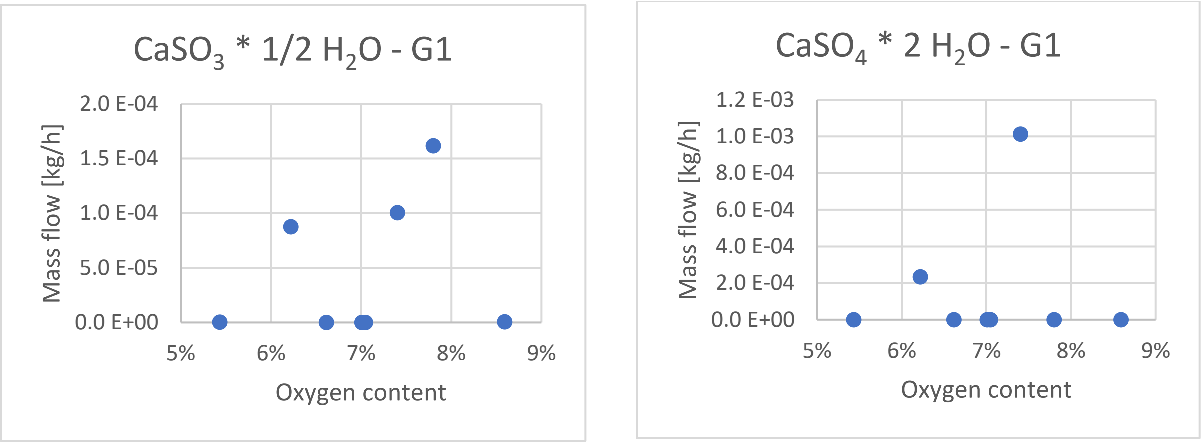


(c) Calcium sulfite hemihydrate. *(d) Calcium sulfate dihydrate.*

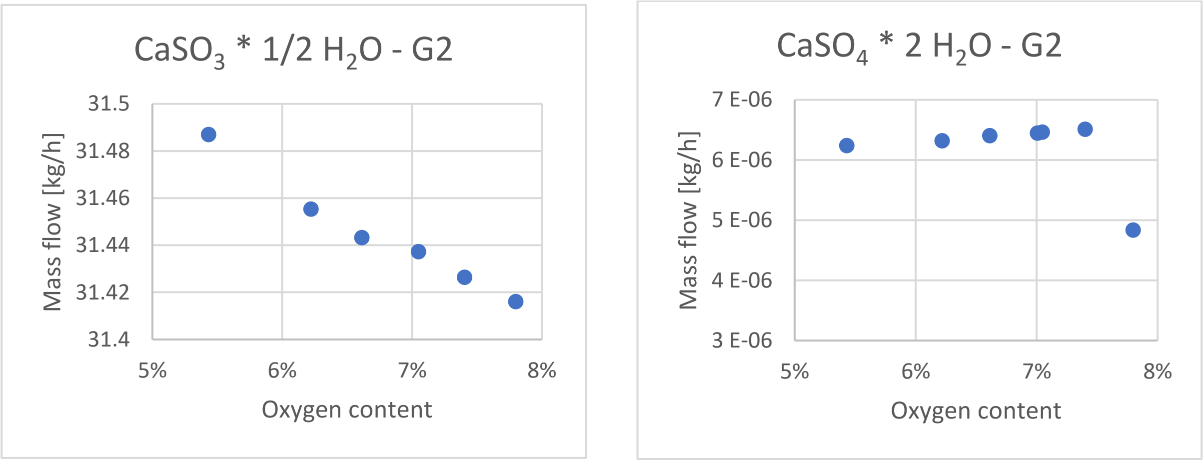
Figure 6.15. Results from G2 simulation runs with 5 cases of operating conditions with low and high recirculation liquid flow.

6.2.6 Oxygen

Results from varying oxygen content in the flue gas is exhibited in Figure 6.16. The formation of calcium sulfite and sulfate does not have a clear oxygen dependance when observing the results from G1. This is probably due to the overall low amounts formed, making the results sensitive to the effect of the numerical methods used. However, in G2, less $CaSO_3$*½ H_2O is produced at higher oxygen content and the $CaSO_4$*$2H_2O$ production is instead increased which is accurate. However, to evaluate the numerical values, experimental data is necessary. It can be suspected that although the trend is correct, the values are wrong, especially for $CaSO_4$*$2H_2O$ which is considerably smaller than $CaSO_3$*½ H_2O. At the highest oxygen content, the $CaSO_4$*$2H_2O$ result deviated, possibly because of the extensive convergence problems that occurred. The model was run several times with changed convergence method to overcome the problems before a result was generated.



(a) Calcium sulfite hemihydrate after G1. *(b) Calcium sulfate dihydrate after G1.*



(a) (c) Calcium sulfite hemihydrate after G2. *(d) Calcium sulfate dihydrate after G2.*

Figure 6.16. Solid formation as a function of oxygen content in the flue gas. G1 and G2 models were both tested.

6.2.7 Strengths and weaknesses

$CaSO_3$*½ H_2O mostly follows the trends that are expected from literature. $CaSO_4$*$2H_2O$ have more doubtful results as the expected trends are not retrieved by the simulation. Moreover, small amounts are formed, which is not what occurs in reality. Both compounds are suspected to form the wrong numerical values, but as no experimental data is available for validation it is impossible to evaluate this.

The crystallization is simplified in the model and to increase the accuracy, more data such as solubility constants should be implemented in the model. This might improve the amount of formed $CaSO_4$*$2H_2O$ and its dependance on the key parameters.

Neither of the results of HCl or SO_2 absorption efficiencies have been numerically verified and thus, the values should not be relied on. However, it seems that the simulation is successful in qualitatively modelling the removal dependance on the tested parameters as the trends of the results followed expectations based on the literature study. The exception is the L/G ratio influence, which probably demands mass transfer kinetics to be implemented to get the correct correlation.

More uncertainties regarding the model are the ingoing and outgoing liquid flows. These flows have not been measured in the real process but were only calculated based on assumptions of waste composition and maximum ion concentrations in the liquid.

7 Conclusion

In the literature study it was concluded that the following parameters influence the absorption performance: pH, L/G ratio, temperature and limestone utilization. Buildup of scaling was found to be connected to these, but also to residence time in the reaction tank, oxidation, solid content, relative saturation, washing procedures and scrubber design.

These key parameters in Sysav's process were compared to literature recommendations. The target pH agrees with other facility examples, although great variations occur over time and better control is necessary. If possible, a temperature decrease could potentially increase absorption and decrease scaling. Other conclusions were that the residence time is sufficient. The found parameters that were unsatisfactory compared to suggested values were the gypsum content, the L/G ratio and demister washing frequency. Limestone characteristics and oxygen content were not possible to evaluate due to lack of information.

In the Aspen simulation, sensitivity analyses were performed on some of the key parameters - pH, temperature, L/G ratio and oxygen. The flue gas flow was also varied, as an attempt to test operational conditions at Sysav when the process is run beneath full load. The absorption of the acidic compounds followed expected trends for all parameters except L/G ratio where it increased with L/G, instead of decreasing which was expected from the literature review. This is probably an effect of the exclusion of mass transfer kinetics in the model. The formation of $CaSO_3*½ H_2O$ seemed to be strongly influenced by the amount of SO_2 dissolved. Increased absorption of SO_2 to the liquid gave higher amounts of $CaSO_3*½ H_2O$. In consequence, low amounts were recovered in G1 and higher in G2. $CaSO_3*½ H_2O$ formation had the correct relationship to varied parameters except for temperature, oxygen and L/G ratio in the LDS1 model. It can be partly explained by the formed low amounts being sensitive, but also to convergence problems which might gave generated unreliable results. In the G2/LDS2 model the correlation between the varying parameter and formed $CaSO_3*½ H_2O$, was according to theory except for temperature. The $CaSO_4*2H_2O$ formation was in general low for both units. The results were inconclusive regarding its dependance on all parameters except for oxygen content in the G2/LDS2 model, where the expected trend was obtained: increased formation at higher oxygen content. The chemistry constants and crystal formation should be reviewed to improve the model.

Operational cases from Sysav's process were implemented in the simulation model and the results revealed that the SO_2 content in the flue gas is a risk factor as it enables enhanced scaling. Moreover, it showed that higher pH greatly influences the absorption of acid compounds and that pH variations should be avoided.

7.1 Recommendations

Recommendations to Sysav to control scaling are the following:

- Investigate the limestone utilization and ensure that the stochiometric ratio does not exceed critical values.
- Improve pH control and run the process at the target value.
- Wash the demisters more frequently.
- Measure oxygen content and limit oxidation.
- Increase the solid content in the recirculation liquid.

- Minimize operational stops since sulfite deposits might harden and oxidize during these times.
- Decrease the pH during short times when scaling builds up to reverse the calcium sulfite precipitation.
- Use additives such as magnesium.

It is emphasized that operational changes in the process should be systematically tested. It is necessary to quantify the scaling for example by measuring the thickness of the depositions after a certain time period. If the operational changes do not reduce the scaling sufficiently, modifications in the facility could be made:

- Increase L/G ratio by enhancing the liquid flow to the scrubbers.
- Modify the process to forced oxidation mode.
- Implement higher wash flow to the demisters and perhaps continuous washing.

7.2 Future work

Future studies should focus on numerically verifying the model by collecting experimental data. Ideally the flue gas flow and composition must be known before G1, between the units and after G2. Moreover, the liquid flows in and out from the scrubbers should be determined at site, instead of by calculations which are uncertain as was done in this project.

After this, it is possible to evaluate what additional information should be implemented in the model. It is suspected that the reaction and mass transfer kinetics must be added for accuracy. Moreover, the crystallization chemistry should be reviewed as it was shown to be flawed already in this early-stage model.

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Appendix A: Equilibrium Constants

The equilibrium constants for the electrolyte reactions generated from Aspen Plus are shown in Table A-1. In the limestone FGD model by Neveux and Le Moullec[57] the equilibrium constants for the reactions used are presented in Table A-2.

Table A-1. The equilibrium constants for the reactions in a model generated from Aspen Plus databanks.

	Reaction	**A**	**B**	**C**	**D**
Equilibrium	$2H_2O = HO^- + H_3O^+$	132.90	-13446	-22.477	
	$2H_2O + SO_2(aq) = HSO_3^- + H_3O^+$	-5.9787	637.40	0	-0.015134
	$H_2O + HSO_3^- = SO_3^{2-} + H_3O^+$	-25.291	1333.4		
	$2H_2O + SO_3(aq) = HSO_4^- + H_3O^+$	Not included			
	$H_2O + HSO_4^- = SO_4^{2-} + H_3O^+$	0	0	0	0
	$2H_2O + CO_2(aq) = HCO_3^- + H_3O^+$	231.47	-12092	-36.782	
	$H_2O + HCO_3^- = CO_3^{2-} + H_3O^+$	216.05	-12432	-35.482	
	$H_2O + HCl(aq) = Cl^- + H_3O^+$	0	0	0	0
	$H_2O + NH_3(aq) = NH_4^+ + HO^-$	Not included			
	H2SO4 + H2O <--> H3O+ + HSO4-	0	0	0	0
	CAOH+ <--> CA++ + OH-	0	0	0	0
Salts	$CaSO_4$*2H_2O	354.91	-14056.4	-59.450	0.042882
	CASO4*1:2W:A	0	0	0	0
	$CaSO_3$*½H2O	0	0	0	0
	CASO4	0	0	0	0
	$CaSO_3$	0	0	0	0
	CaCl2*2H2O	-1504.3	44596	257.01	-0.376
	CaCl2*4H2O	42.359	0	-10.992	0.049194

	CaCl2*6H2O	1397.4	-31788	-255.46	0.52674
	CaCl2*H2O	5.9522			-0.01806
	CaCl2	0	0	0	0
	Ca(OH)2	0	0	0	0
	$CaCO_3$	0	0	0	0

Table A-2. Equilibrium constants used by in a limestone FGD model by Neveux and Le Moullec[57]*.*

	A	**B**	**C**	**D**
$2H_2O = HO^- + H_3O^+$	140.93	-13446	–22.477	
$2H_2O + SO_2(aq) = HSO_3^- + H_3O^+$	-1.932	-3 768.0	-20.0	
$H_2O + HSO_3^- = SO_3^{2-} + H_3O^+$	-21.274	1 333.4		
$2H_2O + SO_3(aq) = HSO_4^- + H_3O^+$	6.908			
$H_2O + HSO_4^- = SO_4^{2-} + H_3O^+$	-4.490			
$2H_2O + CO_2(aq) = HCO_3^- + H_3O^+$	235.48	-12 092	-36.782	
$H_2O + HCO_3^- = CO_3^{2-} + H_3O^+$	12.450	-6 286.9		-0.050628
$H_2O + HCl(aq) = Cl^- + H_3O^+$	18.421			
$H_2O + NH_3(aq) = NH_4^+ + HO^-$	2.760	-3 335.7	1.4971	-0.037057

Appendix B: Calculation of Reaction Tank and Residence Time

The volume of the reaction tank (i.e. bottom part of the scrubber containing liquid) was calculated using the dimensions of the scrubber and the flow of the recirculation liquid. The cylindrical and cone shaped parts of the bottom were calculated respectively. See Figure 6.2 for explanation of the design and dimensions of the scrubbers.

The measurements and calculations on G1 reaction tank are summarized here.

Height of cone = H_{co} = 2.185 m

Height of cylinder = H_{cy} = 6.7-2.185 = 4.515 m

Diameter = 2*r = 2.4 m

$$Volume\ of\ cylinder\ =\ A*h_{cy}\ =\ pi*r^2*h_{cy}\ =\ 75.1m^3 \tag{B.1}$$

$$Volume\ of\ cone\ =\ A*h_{co}/3\ =\ 13.2\ m^3 \tag{B.2}$$

$$Total\ volume\ =\ 75.1\ +\ 13.2\ =\ 88.3\ m3 \tag{B.3}$$

$$Residence\ time\ = \frac{V}{F} = \frac{88.3}{1190} =\ 0.0742\ h\ =\ 4.45\ min \tag{B.4}$$

Similarly, the volume and residence time was calculated for G2 reaction tank.

Hcy = 7.5 – 3.67 = 5.83 m

H_{co} = 3.67 m

$$Volume\ of\ cylinder\ =\ pi*r^2*h_{cy}\ =\ 105.5\ m^3 \tag{B.5}$$

$$Volume\ of\ cone\ =\ A*h_{co}/3\ =\ 22.14\ m^3 \tag{B.6}$$

$$Total\ volume\ =\ 105.5\ +\ 22.1\ =\ 127.60\ m^3 \tag{B.7}$$

$$Residence\ time\ =\ 127.6/220\ =\ 0.58\ h\ =\ 34.8\ min \tag{B.8}$$

Appendix C: Demister Washing Calculations

The specific rate, meaning the flow per area unit, was calculated for each demister. The area was determined to 3.55 m2 and the flow to LDS1 was approximately 7.5 m^3/h and to LDS2 8 m^3/h. G1 has 6 tubes and G2 12 tubes with 6 nozzles per tube. The tubes are operated in a sequence and it is assumed that the total flow goes to one tube at a time. The flow per nozzle was also calculated.

Specific rate LDS1 = 7.5/3.55 = 2.11 m^3/m2*h

Per nozzle LDS1 = 7.5/6 =1.25 m^3/nozzle

Specific rate LDS2 = 8/3.55 = 2.25 m^3/m2*h

Per nozzle LDS2 = 8/6 = 1.3

(However it is not clear if the flow to LDS2 is divided on the two demister surfaces on LDS2 and if so, the specific rate and flow per nozzle should be divided by 2.)

Appendix D: Calculations of Flue Gas Flow at Nominal Load

To calculate the L/G ratio presented in section 6.1.7 the normalized flue gas flow at nominal load was converted to a volumetric flow at 60 °C and 1 atm. It had been determined by Sysav[66] that the flue gas flow after the electrostatic filter is 180 460 Nm^3/h when operating with nominal waste.

Ideal gas law is assumed to apply.

$$pV = nRT \tag{D.1}$$

Normalized flow means that the pressure is 101325 Pa and the temperature 273 K. The volumetric flow at the process conditions is calculated as follows.

$$P_1V_1/RT_1 = P_2V_2/RT_2 \tag{D.2}$$

The pressure and R is unchanged, the simplification can be made.

$$V_1/T_1 = V_2/T_2 \tag{D.3}$$

The original volume and temperature is V_1 = 180460 m^3/h and T_1 = 273 K. The new temperature is T_2 = 273 + 60 = 333 K.

$$V_2 = 333 * 180460/273 = 220122\, m^3/h \tag{D.4}$$

Appendix E: Stream Data at Nominal Load

The flue gas composition and flow were calculated from the nominal waste 2020. The original calculation of kg/ton waste for each compound given by Sysav is shown in Table E-1. This was then calculated to the total flow by multiplying with the nominal load 32.3 ton/h. Some compounds were neglected in the Aspen simulation model which is shown in the column ”Simplified”. The mass fractions were calculated, and the water content was modified to make the stream reach the saturation point. The column “After modifying water content” is the input which was implemented in Aspen Plus. N_2 was used to balance the total flow.

Table E-1. Flue gas flow and composition calculated from nominal waste at Sysav. Some compounds are neglected and the water content is modified to be appropriate for the Aspen Plus simulation model.

Flue gas after ESP	**From nominal waste composition [kg/ton waste]**	**Total at 32.3 ton load [kg/h]**	**Simplified [kg/h]**	**Mass fraction [kg/kg]**	**After modifying water content [kg/kg]**
Mass flow (excl. particulates)	7 093	229104	229104	1	1
Mass flow, H2O	661	21350	21350	0.093190	0.15
Mass flow, CO2	1 019	32914	32914	0.14366	0.14366
Volume flow, O2	411.22	13282	0	0	0
Mass flow O2	555.15	17931	17931	0.078267	0.078267
Particles	0.01	0.323	0		
NOx	1.89	61.047	61.047	0.00026646	0.00026646
CO	0.18	5.814	0		
HCl	4.81	155.36	155.36	0.00067813	0.00067813
SO2	1.35	43.605	43.605	0.00019033	0,00019033

HF	0	0	0	0	0
NH3	0	0	0	0	0
N2			156649	0.68375	0.62694
Volume flow	5 587 Nm^3/ton	180460 Nm^3/h			

Appendix F: Input to Aspen Plus – Base Case

The following is obtained from Aspen Plus report on input data to the simulation model of the base case for the simulation model of G1 and LDS1. The flows were varied somewhat for the other cases tested and sensitivity analyzes as explained in the Methodology section. However, the conditions and specifications for the units remained unchanged, as summarized in the report below. The model of G2 and LDS2 had the same specifications for the unit operation blocks, physical properties and chemistry.

```
;
;Input Summary created by Aspen Plus Rel. 36.0 at 08:35:33 Thu Nov 18, 2021
;Directory H:\Documents\AspenTech\Aspen Plus V10.0\Exjobb\Case results\slutfiler v2 Filename C:\Users\SA5656~1\AppData\Local\Temp\~ap60f7.txt
;


DYNAMICS
    DYNAMICS RESULTS=ON

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar SHORT-LENGTH=mm

DEF-STREAMS MIXCISLD ALL

MODEL-OPTION

DESCRIPTION "
    Electrolytes Simulation with Metric Units :
    C, bar, kg/hr, kmol/hr, Gcal/hr, cum/hr.

    Property Method: ELECNRTL
```

```
   Flow basis for input: Mass

   Stream report composition: Mass flow
   "

DATABANKS 'APV100 ASPENPCD' / 'APV100 AQUEOUS' / 'APV100 SOLIDS' &
      / 'APV100 INORGANIC' / 'APV100 PURE36'

PROP-SOURCES 'APV100 ASPENPCD' / 'APV100 AQUEOUS' /  &
      'APV100 SOLIDS' / 'APV100 INORGANIC' / 'APV100 PURE36'

COMPONENTS
   H2O H2O /
   O2 O2 /
   CO2 CO2 /
   HCL HCL /
   SO2 O2S /
   NO2 NO2 /
   N2 N2 /
   CaCO3 CaCO3 /
   CA++ CA+2 /
   CAOH+ CAOH+ /
   H3O+ H3O+ /
   OH- OH- /
   HSO3- HSO3- /
   HCO3- HCO3- /
   CL- CL- /
   SO3-- SO3-2 /
   CO3-- CO3-2 /
   "CaSO3(S)" "CaSO3*1:2W" /
   "CASO4(S)" "CaSO4*2H2O" /
   CaSO3 "CaSO3*1:2W" /
   CaSO4 "CaSO4*2H2O" /
```

```
    H2SO4 H2SO4 /
    HSO4- HSO4- /
    SO4-- SO4-2 /
    "CaCO3(S)" CaCO3 /
    "CALCI(S)" "CA(OH)2" /
    "CACL2(S)" CACL2 /
    SALT1 "CACL2*W" /
    SALT2 "CACL2*6W" /
    SALT3 "CACL2*4W" /
    SALT4 "CACL2*2W" /
    SALT5 CaSO3 /
    SALT6 CaSO4 /
    SALT7 "CASO4*1:2W:A"

CISOLID-COMPS "CaSO3(S)" "CASO4(S)" "CaCO3(S)" "CALCI(S)"  &
        "CACL2(S)" SALT1 SALT2 SALT3 SALT4 SALT5 SALT6 SALT7

HENRY-COMPS GLOBAL CO2 SO2 HCL O2 N2

SOLVE
    RUN-MODE MODE=SIM

CHEMISTRY C-1
    SALT "CaSO3(S)" CA++ 1. / SO3-- 1. / H2O 0.5
    SALT "CASO4(S)" CA++ 1. / SO4-- 1. / H2O 2.

CHEMISTRY GLOBAL
    PARAM GAMMA-BASIS=UNSYMMETRIC
    DISS CaCO3 CO3-- 1 / CA++ 1
    DISS CaSO3 H2O 0.5 / CA++ 1 / SO3-- 1
    DISS CaSO4 CA++ 1 / SO4-- 1 / H2O 2
    STOIC 1 H2O -1 / HSO3- -1 / H3O+ 1 / SO3-- 1
    STOIC 2 H2O -2 / SO2 -1 / H3O+ 1 / HSO3- 1
    STOIC 3 CAOH+ -1 / CA++ 1 / OH- 1
```

```
    STOIC 4 HCL -1 / H2O -1 / CL- 1 / H3O+ 1
    STOIC 5 H2O -1 / HSO4- -1 / H3O+ 1 / SO4-- 1
    STOIC 6 H2SO4 -1 / H2O -1 / H3O+ 1 / HSO4- 1
    STOIC 7 H2O -1 / HCO3- -1 / CO3-- 1 / H3O+ 1
    STOIC 8 H2O -2 / CO2 -1 / HCO3- 1 / H3O+ 1
    STOIC 9 H2O -2 / OH- 1 / H3O+ 1
    K-STOIC 1 A=-25.290564 B=1333.400024 C=0 D=0
    K-STOIC 2 A=-5.978673 B=637.395996 C=0 D=-0.015134
    K-STOIC 7 A=216.050446 B=-12431.700195 C=-35.481899 D=0
    K-STOIC 8 A=231.465439 B=-12092.099609 C=-36.781601 D=0
    K-STOIC 9 A=132.89888 B=-13445.900391 C=-22.477301 D=0

CHEMISTRY SALTSION
    PARAM GAMMA-BASIS=UNSYMMETRIC
    DISS CaCO3 CO3-- 1 / CA++ 1
    DISS CaSO4 CA++ 1 / SO4-- 1 / H2O 2
    DISS CaSO3 H2O 0.5 / CA++ 1 / SO3-- 1
    STOIC 1 H2O -1 / HSO3- -1 / H3O+ 1 / SO3-- 1
    STOIC 2 H2O -2 / SO2 -1 / H3O+ 1 / HSO3- 1
    STOIC 3 CAOH+ -1 / CA++ 1 / OH- 1
    STOIC 4 HCL -1 / H2O -1 / CL- 1 / H3O+ 1
    STOIC 5 H2O -1 / HSO4- -1 / H3O+ 1 / SO4-- 1
    STOIC 6 H2SO4 -1 / H2O -1 / H3O+ 1 / HSO4- 1
    STOIC 7 H2O -1 / HCO3- -1 / CO3-- 1 / H3O+ 1
    STOIC 8 H2O -2 / CO2 -1 / HCO3- 1 / H3O+ 1
    STOIC 9 H2O -2 / OH- 1 / H3O+ 1
    K-STOIC 1 A=-25.290564 B=1333.400024 C=0 D=0
    K-STOIC 2 A=-5.978673 B=637.395996 C=0 D=-0.015134
    K-STOIC 7 A=216.050446 B=-12431.700195 C=-35.481899 D=0
    K-STOIC 8 A=231.465439 B=-12092.099609 C=-36.781601 D=0
    K-STOIC 9 A=132.89888 B=-13445.900391 C=-22.477301 D=0
    SALT "CASO4(S)" CA++ 1 / SO4-- 1 / H2O 2
    SALT SALT7 H2O 0.5 / CA++ 1 / SO4-- 1
    SALT "CaSO3(S)" H2O 0.5 / CA++ 1 / SO3-- 1
```

```
  SALT SALT6 CA++ 1 / SO4-- 1
  SALT SALT5 CA++ 1 / SO3-- 1
  SALT SALT4 CA++ 1 / H2O 2 / CL- 2
  SALT SALT3 CA++ 1 / CL- 2 / H2O 4
  SALT SALT2 CA++ 1 / CL- 2 / H2O 6
  SALT SALT1 H2O 1 / CA++ 1 / CL- 2
  SALT "CACL2(S)" CA++ 1 / CL- 2
  SALT "CALCI(S)" CAOH+ 1 / OH- 1
  SALT "CaCO3(S)" CO3-- 1 / CA++ 1
  K-SALT "CASO4(S)" A=354.905609 B=-14056.379883 C=-59.450218  &
    D=0.042882
  K-SALT SALT4 A=-1504.261475 B=44596.003906 C=257.013245  &
    D=-0.376
  K-SALT SALT3 A=42.359161 B=0 C=-10.991856 D=0.049194
  K-SALT SALT2 A=1397.392578 B=-31788.371094 C=-255.455246  &
    D=0.526739
  K-SALT SALT1 A=5.952156 B=0 C=0 D=-0.01806

FLOWSHEET
  BLOCK G1 IN=FLUE PUMPSTR OUT=S-1 SLURRYOU
  BLOCK MIX IN=SLURRY CaCO3 RECIRK OUT=PUMPSTR
  BLOCK SPLIT IN=SLURRYOU OUT=RECIRK S-2
  BLOCK DROPSEP IN=DROPLETS FLUEOUT OUT=SCALE GAS
  BLOCK SEP IN=S-1 OUT=O2 FLUEOUT
  BLOCK B-1 IN=S-2 OUT=PURGE DROPLETS

PROPERTIES ELECNRTL HENRY-COMPS=GLOBAL CHEMISTRY=SALTSION  &
    TRUE-COMPS=YES

PROP-DATA HENRY-1
  IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
    HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
    VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
    MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
```

```
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar SHORT-LENGTH=mm
    PROP-LIST HENRY
    BPVAL O2 H2O 144.4080745 -7775.060000 -18.39740000  &
        -9.4435400E-3 .8500000000 74.85000000 0.0
    BPVAL CO2 H2O 159.1996745 -8477.711000 -21.95743000  &
        5.78074800E-3 -.1500000000 226.8500000 0.0
    BPVAL HCL H2O 46.94003454 -7762.832000 0.0 0.0  &
        -.1500000000 126.8500000 0.0
    BPVAL SO2 H2O 72.44767454 -5578.800000 -8.761520000 0.0  &
        -.1500000000 99.85000000 0.0
    BPVAL N2 H2O 164.9940745 -8432.770000 -21.55800000  &
        -8.4362400E-3 -.1500000000 72.85000000 0.0

PROP-DATA NRTL-1
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar SHORT-LENGTH=mm
    PROP-LIST NRTL
    BPVAL H2O CO2 10.06400000 -3268.135000 .2000000000 0.0 0.0  &
        0.0 0.0 200.0000000
    BPVAL CO2 H2O 10.06400000 -3268.135000 .2000000000 0.0 0.0  &
        0.0 0.0 200.0000000

PROP-DATA VLCLK-1
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar SHORT-LENGTH=mm
```

```
    PROP-LIST VLCLK
    BPVAL H3O+ CL- 34.55111000 13.36581000
    BPVAL H3O+ HSO4- 54.80395000 20.24347000

PROP-DATA GMELCC-1
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar SHORT-LENGTH=mm
    PROP-LIST GMELCC
    PPVAL H2O ( CA++ CL- ) 10.47200000
    PPVAL ( CA++ CL- ) H2O -5.060000000
    PPVAL H2O ( H3O+ OH- ) 8.045000000
    PPVAL ( H3O+ OH- ) H2O -4.072000000
    PPVAL H2O ( H3O+ HCO3- ) 8.045000000
    PPVAL ( H3O+ HCO3- ) H2O -4.072000000
    PPVAL H2O ( H3O+ CL- ) 4.110129000
    PPVAL ( H3O+ CL- ) H2O -3.344103000
    PPVAL H2O ( H3O+ CO3-- ) 8.045000000
    PPVAL ( H3O+ CO3-- ) H2O -4.072000000
    PPVAL CO2 ( H3O+ OH- ) 15.00000000
    PPVAL ( H3O+ OH- ) CO2 -8.000000000
    PPVAL CO2 ( H3O+ HCO3- ) 15.00000000
    PPVAL ( H3O+ HCO3- ) CO2 -8.000000000
    PPVAL CO2 ( H3O+ CO3-- ) 15.00000000
    PPVAL ( H3O+ CO3-- ) CO2 -8.000000000
    PPVAL HCL ( H3O+ OH- ) 15.00000000
    PPVAL ( H3O+ OH- ) HCL -8.000000000
    PPVAL HCL ( H3O+ CL- ) 12.00000000
    PPVAL ( H3O+ CL- ) HCL -1.0000000E-3
    PPVAL H2O ( H3O+ HSO4- ) 6.362000000
    PPVAL ( H3O+ HSO4- ) H2O -3.749000000
```

```
    PPVAL H2O ( H3O+ SO4-- ) 8.000000000
    PPVAL ( H3O+ SO4-- ) H2O -4.000000000
    PPVAL HCL ( H3O+ HSO4- ) 10.00000000
    PPVAL ( H3O+ HSO4- ) HCL -2.000000000
    PPVAL HCL ( H3O+ SO4-- ) 15.00000000
    PPVAL ( H3O+ SO4-- ) HCL -8.000000000
    PPVAL H2SO4 ( H3O+ CL- ) 10.00000000
    PPVAL ( H3O+ CL- ) H2SO4 -2.000000000
    PPVAL H2SO4 ( H3O+ HSO4- ) 12.99200000
    PPVAL ( H3O+ HSO4- ) H2SO4 -2.981000000
    PPVAL H2SO4 ( H3O+ SO4-- ) 8.000000000
    PPVAL ( H3O+ SO4-- ) H2SO4 -4.000000000
    PPVAL ( H3O+ CL- ) ( H3O+ HSO4- ) .9536271000
    PPVAL ( H3O+ HSO4- ) ( H3O+ CL- ) 0.0

PROP-DATA GMELCD-1
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar SHORT-LENGTH=mm
    PROP-LIST GMELCD
    PPVAL H2O ( H3O+ CL- ) 2306.642000
    PPVAL ( H3O+ CL- ) H2O -653.5391000
    PPVAL CO2 ( H3O+ OH- ) 0.0
    PPVAL ( H3O+ OH- ) CO2 0.0
    PPVAL CO2 ( H3O+ HCO3- ) 0.0
    PPVAL ( H3O+ HCO3- ) CO2 0.0
    PPVAL CO2 ( H3O+ CO3-- ) 0.0
    PPVAL ( H3O+ CO3-- ) CO2 0.0
    PPVAL HCL ( H3O+ OH- ) 0.0
    PPVAL ( H3O+ OH- ) HCL 0.0
    PPVAL HCL ( H3O+ CL- ) 0.0
```

```
    PPVAL ( H3O+ CL- ) HCL 0.0
    PPVAL H2O ( H3O+ HSO4- ) 1958.200000
    PPVAL ( H3O+ HSO4- ) H2O -583.2000000
    PPVAL H2O ( H3O+ SO4-- ) 0.0
    PPVAL ( H3O+ SO4-- ) H2O 0.0
    PPVAL HCL ( H3O+ HSO4- ) 0.0
    PPVAL ( H3O+ HSO4- ) HCL 0.0
    PPVAL HCL ( H3O+ SO4-- ) 0.0
    PPVAL ( H3O+ SO4-- ) HCL 0.0
    PPVAL H2SO4 ( H3O+ HSO4- ) -1732.900000
    PPVAL ( H3O+ HSO4- ) H2SO4 -162.3000000
    PPVAL H2SO4 ( H3O+ SO4-- ) 0.0
    PPVAL ( H3O+ SO4-- ) H2SO4 0.0
    PPVAL ( H3O+ CL- ) ( H3O+ HSO4- ) -201.7466000
    PPVAL ( H3O+ HSO4- ) ( H3O+ CL- ) 0.0

PROP-DATA GMELCE-1
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar SHORT-LENGTH=mm
    PROP-LIST GMELCE
    PPVAL H2O ( H3O+ CL- ) .3417959000
    PPVAL ( H3O+ CL- ) H2O 2.121453000
    PPVAL CO2 ( H3O+ OH- ) 0.0
    PPVAL ( H3O+ OH- ) CO2 0.0
    PPVAL CO2 ( H3O+ HCO3- ) 0.0
    PPVAL ( H3O+ HCO3- ) CO2 0.0
    PPVAL CO2 ( H3O+ CO3-- ) 0.0
    PPVAL ( H3O+ CO3-- ) CO2 0.0
    PPVAL HCL ( H3O+ OH- ) 0.0
    PPVAL ( H3O+ OH- ) HCL 0.0
```

```
    PPVAL HCL ( H3O+ CL- ) 0.0
    PPVAL ( H3O+ CL- ) HCL 0.0
    PPVAL H2O ( H3O+ HSO4- ) -4.599000000
    PPVAL ( H3O+ HSO4- ) H2O 4.472000000
    PPVAL HCL ( H3O+ SO4-- ) 0.0
    PPVAL ( H3O+ SO4-- ) HCL 0.0
    PPVAL H2SO4 ( H3O+ HSO4- ) -30.12600000
    PPVAL ( H3O+ HSO4- ) H2SO4 .8060000000

PROP-DATA GMELCN-1
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar SHORT-LENGTH=mm
    PROP-LIST GMELCN
    PPVAL CO2 ( H3O+ OH- ) .1000000000
    PPVAL CO2 ( H3O+ HCO3- ) .1000000000
    PPVAL CO2 ( H3O+ CO3-- ) .1000000000
    PPVAL HCL ( H3O+ OH- ) .1000000000
    PPVAL H2O ( H3O+ HSO4- ) .2000000000
    PPVAL HCL ( H3O+ SO4-- ) .1000000000
    PPVAL H2SO4 ( H3O+ HSO4- ) .2000000000

DEF-STREAMS MIXCISLD SLURRYOU S-1 S-2

PROP-SET PH PH SUBSTREAM=MIXED PHASE=L
;  "pH at current temperature"


STREAM CaCO3
    SUBSTREAM MIXED TEMP=60. PRES=1. <atm> MASS-FLOW=560.
    MASS-FRAC H2O 0.7 / CaCO3 0.3
```

```
STREAM FLUE
    SUBSTREAM MIXED TEMP=60. PRES=1. <atm> MASS-FLOW=229103.9
    MASS-FRAC H2O 0.15 / O2 0.078266788 / CO2 0.143662766 /  &
        HCL 0.000678133 / SO2 0.000190328 / NO2 0.00026646 /  &
        N2 0.626935524

STREAM SLURRY
    SUBSTREAM MIXED TEMP=60. PRES=1. <atm> MASS-FLOW=9872.9
    MASS-FRAC H2O 1. / CaCO3 0.

BLOCK MIX MIXER
    PARAM
    PROPERTIES ELECNRTL HENRY-COMPS=GLOBAL CHEMISTRY=GLOBAL  &
        FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES

BLOCK B-1 FSPLIT
    MASS-FLOW DROPLETS 8000.

BLOCK SPLIT FSPLIT
    FRAC S-2 0.0143
    PROPERTIES ELECNRTL HENRY-COMPS=GLOBAL CHEMISTRY=GLOBAL  &
        FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES

BLOCK SEP SEP
    PARAM
    MASS-FLOW STREAM=O2 SUBSTREAM=MIXED COMPS=O2 FLOWS=0.

BLOCK G1 RADFRAC
    PARAM NSTAGE=10 ALGORITHM=STANDARD ABSORBER=YES HYDRAULIC=NO  &
        MAXOL=100 DAMPING=NONE
    PARAM2 STATIC-DP=YES
    COL-CONFIG CONDENSER=NONE REBOILER=NONE CA-CONFIG=INT-1
    FEEDS FLUE 10 ON-STAGE / PUMPSTR 1
```

```
    PRODUCTS SLURRYOU 10 L / S-1 1 V
    P-SPEC 1 1. <atm>
    COL-SPECS
    T-EST 1 60. / 2 60. / 3 60. / 4 60. / 5 60. / 6  &
        60. / 7 60. / 8 60. / 9 60. / 10 60.
    TRAY-REPORT PROPERTIES=PH
    PROPERTIES ELECNRTL HENRY-COMPS=GLOBAL CHEMISTRY=GLOBAL  &
        FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES
    REPORT NOHYDRAULIC

BLOCK DROPSEP RCSTR
    PARAM TEMP=60. PRES=1. <atm> NPHASE=2 RES-TIME=0.25
    PRODUCTS SCALE L / GAS V
    BLOCK-OPTION FREE-WATER=NO
    REACTIONS RXN-IDS=R-1 OXIDIZE

EO-CONV-OPTI

CONV-OPTIONS
    PARAM TEAR-METHOD=BROYDEN

STREAM-REPOR MOLEFLOW MASSFLOW

REACTIONS OXIDIZE POWERLAW
    REAC-DATA 1 KINETIC
    RATE-CON 1 PRE-EXP=616644. ACT-ENERGY=86000. <kJ/kmol>
    STOIC 1 MIXED HSO3- -1. / O2 -0.5 / H2O -1. / SO4--  &
        1. / H3O+ 1.
    POWLAW-EXP 1 MIXED HSO3- 1.5 / MIXED O2 0.

REACTIONS R-1 POWERLAW
    REAC-DATA 1 EQUIL
    REAC-DATA 3 EQUIL
    REAC-DATA 2 EQUIL
```

```
    REAC-DATA 4 EQUIL
    STOIC 1 MIXED CA++ -1. / SO3-- -1. / H2O -0.5 / CaSO3  &
       1.
    STOIC 3 MIXED CA++ -1. / SO4-- -1. / H2O -2. / CaSO4  &
       1.
    STOIC 2 MIXED CaSO3 -1. / CISOLID "CaSO3(S)" 1.
    STOIC 4 MIXED CaSO4 -1. / CISOLID "CASO4(S)" 1.
;
;
;
;
;
```

Appendix G: Results report from Aspen Plus – Base Case

The results report generated from Aspen Plus is displayed here for the base case model for the file containing G1 and LDS1.

```
+ + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + +
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+ +                                            + +
+ +                ASPEN PLUS CALCULATION REPORT                + +
+ +                                            + +
+ + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + + +
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ASPEN TECHNOLOGY, INC.               U.S.A. 888/996-7100
781/221-6400                     EUROPE (44) 1189-226555


PLATFORM: WINDOWS                              NOVEMBER 18, 2021
VERSION: 36.0   Build 249                       THURSDAY
INSTALLATION:                                  8:09:02 A.M.


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                    RUN CONTROL SECTION


RUN CONTROL INFORMATION
----------------------


THIS COPY OF ASPEN PLUS LICENSED TO LUND UNIVERSITY


TYPE OF RUN: EDIT


INPUT FILE NAME: _2447lfh.inm


INPUT PROBLEM DATA FILE NAME : _2447lfh
OUTPUT PROBLEM DATA FILE NAME: _0856qww
LOCATED IN:



PDF SIZE USED FOR INPUT TRANSLATION:
  NUMBER OF FILE RECORDS (PSIZE) =     0
  NUMBER OF IN-CORE RECORDS      =   256
PSIZE NEEDED FOR SIMULATION    =     1


CALLING PROGRAM NAME:          apmain
LOCATED IN: C:\Program Files (x86)\AspenTech\Aspen Plus V10.0\Engine\\xeq
```

```
SIMULATION REQUESTED FOR ENTIRE FLOWSHEET


DESCRIPTION
-----------


     Electrolytes Simulation with Metric Units : C, bar, kg/hr,
     kmol/hr, Gcal/hr, cum/hr. Property Method: ELECNRTL Flow basis
     for input: Mass Stream report composition: Mass flow
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                        FLOWSHEET SECTION


FLOWSHEET CONNECTIVITY BY STREAMS
---------------------------------


  STREAM     SOURCE     DEST          STREAM     SOURCE     DEST
  FLUE       ----       G1            CaCO3      ----       MIX
  SLURRY     ----       MIX           S-1        G1         SEP
  SLURRYOU   G1         SPLIT         PUMPSTR    MIX        G1
  PURGE      B-1        ----          RECIRK     SPLIT      MIX
  DROPLETS   B-1        DROPSEP       SCALE      DROPSEP    ----
  GAS        DROPSEP    ----          O2         SEP        ----
  FLUEOUT    SEP        DROPSEP       S-2        SPLIT      B-1


FLOWSHEET CONNECTIVITY BY BLOCKS
```

```
--------------------------------


   BLOCK      INLETS                    OUTLETS

   G1         FLUE PUMPSTR              S-1 SLURRYOU

   MIX        SLURRY CaCO3 RECIRK       PUMPSTR

   SPLIT      SLURRYOU                  RECIRK S-2

   DROPSEP    DROPLETS FLUEOUT          SCALE GAS

   SEP        S-1                       O2 FLUEOUT

   B-1        S-2                       PURGE DROPLETS


CONVERGENCE STATUS SUMMARY

--------------------------


   TEAR STREAM SUMMARY

   ==================



   STREAM    VARIABLE        MAXIMUM      MAX. ERR.    ABSOLUTE        CONV

   ID        ID              ERR/TOL      RELATIVE     ERROR      STAT  BLOCK

   ------    --------        --------     -------      ---------   ----  -----

   PUMPSTR  NO2 MOLEFLOW      0.44488     -0.44488E-04  0.22060E-07  #    $OLVER19


   #  = CONVERGED

   *  = NOT CONVERGED


CONVERGENCE BLOCK:  $OLVER19
```

```
---------------------------

    Tear Stream  :  PUMPSTR

    Tolerance used:  0.100D-03

    Trace molefrac:  0.100D-05

    Trace substr-2:  0.100D-05


    MAXIT =   30 WAIT =   2

    METHOD: BROYDEN       STATUS: CONVERGED

    TOTAL NUMBER OF ITERATIONS:    19

    NUMBER OF ITERATIONS ON LAST OUTER LOOP:     0


                    *** FINAL VALUES ***


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                         FLOWSHEET SECTION


CONVERGENCE BLOCK:  $OLVER19 (CONTINUED)

VAR#    TEAR  STREAM  VAR    STREAM     SUBSTREA  COMPONEN  ATTRIBUT
ELEMENT     UNIT        VALUE      PREV VALUE      ERR/TOL

----  --------------  -------- -------- -------- -------- -------- ----------- ------------   ------------   -------
-----

   1  TOTAL MOLEFLOW   PUMPSTR  MIXED                        KMOL/HR     6.4647+04
6.4647+04     -4.3594-03

   2  TOTAL MOLEFLOW   PUMPSTR  CISOLID                           KMOL/HR         0.0
0.0           0.0

   3  MOLE-FLOW       PUMPSTR  MIXED    H2O                  KMOL/HR     6.4171+04
6.4171+04     -4.3207-03
```

```
  4  MOLE-FLOW       PUMPSTR  MIXED    O2                     KMOL/HR      6.5011-02
6.5011-02    -1.4086-02

  5  MOLE-FLOW       PUMPSTR  MIXED    CO2                    KMOL/HR         3.3215
3.3215    -9.4518-03

  6  MOLE-FLOW       PUMPSTR  MIXED    HCL                    KMOL/HR      5.1278-09
5.1285-09       -1.3464    T

  7  MOLE-FLOW       PUMPSTR  MIXED    SO2                    KMOL/HR      4.0309-02
4.0309-02    -1.9277-02

  8  MOLE-FLOW       PUMPSTR  MIXED    NO2                    KMOL/HR         1.7850
1.7851       -0.4449

  9  MOLE-FLOW       PUMPSTR  MIXED    N2                     KMOL/HR         0.3300
0.3300    -1.2672-02

 10  MOLE-FLOW       PUMPSTR  MIXED    CaCO3                  KMOL/HR            0.0
0.0          0.0

 11  MOLE-FLOW       PUMPSTR  MIXED    CA++                   KMOL/HR       117.3855
117.3856    -6.5879-03

 12  MOLE-FLOW       PUMPSTR  MIXED    CAOH+                  KMOL/HR       3.1483-
09     3.1482-09        0.2069

 13  MOLE-FLOW       PUMPSTR  MIXED    H3O+                   KMOL/HR        58.9395
58.9395    -8.1469-03

 14  MOLE-FLOW       PUMPSTR  MIXED    OH-                    KMOL/HR      5.8404-09
5.8403-09        0.1928

 15  MOLE-FLOW       PUMPSTR  MIXED    HSO3-                  KMOL/HR      1.4803-02
1.4803-02    -5.4101-02

 16  MOLE-FLOW       PUMPSTR  MIXED    HCO3-                  KMOL/HR      1.0084-04
1.0084-04    1.7259-02

 17  MOLE-FLOW       PUMPSTR  MIXED    CL-                    KMOL/HR       293.6986
293.6989    -8.4120-03

 18  MOLE-FLOW       PUMPSTR  MIXED    SO3--                  KMOL/HR      6.1464-08
6.1464-08    -5.1354-02

 19  MOLE-FLOW       PUMPSTR  MIXED    CO3--                  KMOL/HR      9.5474-13
9.5473-13    7.6541-02

 20  MOLE-FLOW       PUMPSTR  MIXED    CaSO3(S)               KMOL/HR            0.0
0.0          0.0
```

```
  21  MOLE-FLOW       PUMPSTR  MIXED    CASO4(S)              KMOL/HR          0.0
0.0           0.0

  22  MOLE-FLOW       PUMPSTR  MIXED    CaSO3                 KMOL/HR          0.0
0.0           0.0

  23  MOLE-FLOW       PUMPSTR  MIXED    CaSO4                 KMOL/HR          0.0
0.0           0.0

  24  MOLE-FLOW       PUMPSTR  MIXED    H2SO4                 KMOL/HR          0.0
0.0           0.0

  25  MOLE-FLOW       PUMPSTR  MIXED    HSO4-                 KMOL/HR          0.0
0.0           0.0

  26  MOLE-FLOW       PUMPSTR  MIXED    SO4--                 KMOL/HR          0.0
0.0           0.0

  27  MOLE-FLOW       PUMPSTR  MIXED    CaCO3(S)              KMOL/HR          0.0
0.0           0.0

  28  MOLE-FLOW       PUMPSTR  MIXED    CALCI(S)              KMOL/HR          0.0
0.0           0.0

  29  MOLE-FLOW       PUMPSTR  MIXED    CACL2(S)              KMOL/HR          0.0
0.0           0.0

  30  MOLE-FLOW       PUMPSTR  MIXED    SALT1                 KMOL/HR          0.0
0.0           0.0

  31  MOLE-FLOW       PUMPSTR  MIXED    SALT2                 KMOL/HR          0.0
0.0           0.0

  32  MOLE-FLOW       PUMPSTR  MIXED    SALT3                 KMOL/HR          0.0
0.0           0.0

  33  MOLE-FLOW       PUMPSTR  MIXED    SALT4                 KMOL/HR          0.0
0.0           0.0

  34  MOLE-FLOW       PUMPSTR  MIXED    SALT5                 KMOL/HR          0.0
0.0           0.0

  35  MOLE-FLOW       PUMPSTR  MIXED    SALT6                 KMOL/HR          0.0
0.0           0.0

  36  MOLE-FLOW       PUMPSTR  MIXED    SALT7                 KMOL/HR          0.0
0.0           0.0

  37  PRESSURE      PUMPSTR  MIXED                      BAR         1.0133       1.0133
0.0
```

38 MASS ENTHALPY PUMPSTR MIXED KCAL/KG -3731.2369 -3731.2369 -1.4352-04

39 MOLE-FLOW PUMPSTR CISOLID H2O KMOL/HR 0.0 0.0 0.0

40 MOLE-FLOW PUMPSTR CISOLID O2 KMOL/HR 0.0 0.0 0.0

41 MOLE-FLOW PUMPSTR CISOLID CO2 KMOL/HR 0.0 0.0 0.0

42 MOLE-FLOW PUMPSTR CISOLID HCL KMOL/HR 0.0 0.0 0.0

43 MOLE-FLOW PUMPSTR CISOLID SO_2 KMOL/HR 0.0 0.0 0.0

44 MOLE-FLOW PUMPSTR CISOLID NO2 KMOL/HR 0.0 0.0 0.0

45 MOLE-FLOW PUMPSTR CISOLID N_2 KMOL/HR 0.0 0.0 0.0

46 MOLE-FLOW PUMPSTR CISOLID $CaCO_3$ KMOL/HR 0.0 0.0 0.0

47 MOLE-FLOW PUMPSTR CISOLID CA++ KMOL/HR 0.0 0.0 0.0

48 MOLE-FLOW PUMPSTR CISOLID CAOH+ KMOL/HR 0.0 0.0 0.0

49 MOLE-FLOW PUMPSTR CISOLID H3O+ KMOL/HR 0.0 0.0 0.0

50 MOLE-FLOW PUMPSTR CISOLID OH- KMOL/HR 0.0 0.0 0.0

51 MOLE-FLOW PUMPSTR CISOLID HSO3- KMOL/HR 0.0 0.0 0.0

52 MOLE-FLOW PUMPSTR CISOLID HCO3- KMOL/HR 0.0 0.0 0.0

53 MOLE-FLOW PUMPSTR CISOLID CL- KMOL/HR 0.0 0.0 0.0

54 MOLE-FLOW PUMPSTR CISOLID SO3-- KMOL/HR 0.0 0.0 0.0

```
  55  MOLE-FLOW        PUMPSTR  CISOLID  CO3--                    KMOL/HR          0.0
0.0           0.0

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                         FLOWSHEET SECTION


CONVERGENCE BLOCK:  $OLVER19 (CONTINUED)

  56  MOLE-FLOW        PUMPSTR  CISOLID  CaSO3(S)                 KMOL/HR          0.0
0.0           0.0

  57  MOLE-FLOW        PUMPSTR  CISOLID  CASO4(S)                 KMOL/HR          0.0
0.0           0.0

  58  MOLE-FLOW        PUMPSTR  CISOLID  CaSO3                    KMOL/HR          0.0
0.0           0.0

  59  MOLE-FLOW        PUMPSTR  CISOLID  CaSO4                    KMOL/HR          0.0
0.0           0.0

  60  MOLE-FLOW        PUMPSTR  CISOLID  H2SO4                    KMOL/HR          0.0
0.0           0.0

  61  MOLE-FLOW        PUMPSTR  CISOLID  HSO4-                    KMOL/HR          0.0
0.0           0.0

  62  MOLE-FLOW        PUMPSTR  CISOLID  SO4--                    KMOL/HR          0.0
0.0           0.0

  63  MOLE-FLOW        PUMPSTR  CISOLID  CaCO3(S)                 KMOL/HR          0.0
0.0           0.0

  64  MOLE-FLOW        PUMPSTR  CISOLID  CALCI(S)                 KMOL/HR          0.0
0.0           0.0

  65  MOLE-FLOW        PUMPSTR  CISOLID  CACL2(S)                 KMOL/HR          0.0
0.0           0.0

  66  MOLE-FLOW        PUMPSTR  CISOLID  SALT1                    KMOL/HR          0.0
0.0           0.0

  67  MOLE-FLOW        PUMPSTR  CISOLID  SALT2                    KMOL/HR          0.0
0.0           0.0

  68  MOLE-FLOW        PUMPSTR  CISOLID  SALT3                    KMOL/HR          0.0
0.0           0.0
```

```
  69  MOLE-FLOW        PUMPSTR  CISOLID  SALT4                 KMOL/HR         0.0
0.0           0.0

  70  MOLE-FLOW        PUMPSTR  CISOLID  SALT5                 KMOL/HR         0.0
0.0           0.0

  71  MOLE-FLOW        PUMPSTR  CISOLID  SALT6                 KMOL/HR         0.0
0.0           0.0

  72  MOLE-FLOW        PUMPSTR  CISOLID  SALT7                 KMOL/HR         0.0
0.0           0.0

  73  PRESSURE        PUMPSTR  CISOLID                   BAR           1.0133        1.0133
0.0

  74  MASS ENTHALPY    PUMPSTR  CISOLID                     KCAL/KG       MISSING
MISSING         0.0


    T - SIGNIFIES COMPONENT IS A TRACE COMPONENT


                      *** ITERATION HISTORY ***


    TEAR STREAMS AND TEAR VARIABLES:


    ITERATION    MAX-ERR/TOL VAR#  STREAM ID       VARIABLE          SUBSTREA
COMPONEN ATTRIBUT ELEMENT

    ---------    ----------- ----  ---------      ---------------- -------- -------- -------- -------

        1      -71.83        13  PUMPSTR       MOLE-FLOW       MIXED    H3O+

        2       283.3        13  PUMPSTR       MOLE-FLOW       MIXED    H3O+

        3       43.09         8  PUMPSTR       MOLE-FLOW       MIXED    NO2

        4      -7.966         8  PUMPSTR       MOLE-FLOW       MIXED    NO2

        5      -5.631         8  PUMPSTR       MOLE-FLOW       MIXED    NO2

        6      -2.269         8  PUMPSTR       MOLE-FLOW       MIXED    NO2

        7     -0.4449         8  PUMPSTR       MOLE-FLOW       MIXED    NO2
```

```
COMPUTATIONAL SEQUENCE
----------------------

SEQUENCE USED WAS:
  $OLVER19 G1 SPLIT MIX
  (RETURN $OLVER19)
  *SEP B-1 DROPSEP

OVERALL FLOWSHEET BALANCE
-------------------------
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                    FLOWSHEET SECTION

OVERALL FLOWSHEET BALANCE (CONTINUED)

              ***  MASS AND ENERGY BALANCE  ***
                      IN           OUT        RELATIVE DIFF.
  CONVENTIONAL COMPONENTS (KMOL/HR )
    H2O              2473.10       2478.17      -0.204611E-02
    O2               560.372       560.372       0.107621E-08
    CO2              747.872       749.551      -0.223939E-02
    HCL             0.135814E-01  0.654563E-03   0.951804
    SO2             0.680629      0.680442       0.273533E-03
    NO2              1.32695       1.32703      -0.598425E-04
    N2               5127.29       5127.29       0.115807E-08
```

$CaCO_3$	0.00000	0.00000	0.00000
CA++	1.66236	1.67861	-0.968105E-02
CAOH+	0.161734E-01	0.410600E-10	1.00000
H3O+	4.24754	0.903630	0.787258
OH-	0.441336E-02	0.760774E-10	1.00000
HSO3-	0.868973E-05	0.195020E-03	-0.955442
HCO3-	0.205834E-01	0.652755E-06	0.999968
CL-	4.24753	4.26071	-0.309194E-02
SO3--	0.459379E-11	0.422243E-09	-0.989121
CO3--	1.65795	0.577481E-14	1.00000
$CaSO_3$(S)	0.00000	0.381273E-09	-1.00000
CASO4(S)	0.00000	0.360147E-13	-1.00000
$CaSO_3$	0.00000	0.00000	0.00000
$CaSO_4$	0.00000	0.00000	0.00000
H2SO4	0.00000	0.137571E-19	0.00000
HSO4-	0.00000	0.248480E-10	-1.00000
SO4--	0.00000	0.901349E-13	-1.00000
$CaCO_3$(S)	0.00000	0.00000	0.00000
CALCI(S)	0.00000	0.00000	0.00000
CACL2(S)	0.00000	0.00000	0.00000
SALT1	0.00000	0.00000	0.00000
SALT2	0.00000	0.00000	0.00000
SALT3	0.00000	0.00000	0.00000
SALT4	0.00000	0.00000	0.00000
SALT5	0.00000	0.00000	0.00000
SALT6	0.00000	0.00000	0.00000

```
    SALT7                  0.00000        0.00000        0.00000
  TOTAL BALANCE
    MOLE(KMOL/HR )           8922.52        8924.24      -0.193035E-03
    MASS(KG/HR   )          239537.        239537.      -0.215333E-05
    ENTHALPY(GCAL/HR )      -221.323       -221.051      -0.122994E-02

              ***  CO2 EQUIVALENT SUMMARY ***
  FEED STREAMS CO2E            32913.7      KG/HR
  PRODUCT STREAMS CO2E          32987.6      KG/HR
  NET STREAMS CO2E PRODUCTION   73.8721      KG/HR
  UTILITIES CO2E PRODUCTION     0.00000      KG/HR
  TOTAL CO2E PRODUCTION         73.8721      KG/HR
ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                11/18/2021  PAGE 6

                   PHYSICAL PROPERTIES SECTION

COMPONENTS
----------

 ID      TYPE  ALIAS         NAME
  H2O      C     H2O           WATER
  O2       C     O2           OXYGEN
  CO2      C     CO2           CARBON-DIOXIDE
  HCL      C     HCL           HYDROGEN-CHLORIDE
  SO₂      C     O2S           SULFUR-DIOXIDE
  NO2      C     NO2           NITROGEN-DIOXIDE
```

N_2	C	N_2	NITROGEN
$CaCO_3$	C	$CaCO_3$	CALCIUM-CARBONATE-CALCITE
CA++	C	CA+2	CA++
CAOH+	C	CAOH+	CAOH+
H3O+	C	H3O+	H3O+
OH-	C	OH-	OH-
HSO3-	C	HSO3-	HSO3-
HCO3-	C	HCO3-	HCO3-
CL-	C	CL-	CL-
SO3--	C	SO3-2	SO3--
CO3--	C	CO3-2	CO3--
$CaSO_3$(S)	C	$CaSO_3$*1:2W	CALCIUM-SULFITE-HEMIHYDRATE
CASO4(S)	C	$CaSO_4$*$2H_2O$	CALCIUM-SULFATE-DIHYDRATE-GYPSUM
$CaSO_3$	C	$CaSO_3$*1:2W	CALCIUM-SULFITE-HEMIHYDRATE
$CaSO_4$	C	$CaSO_4$*$2H_2O$	CALCIUM-SULFATE-DIHYDRATE-GYPSUM
H2SO4	C	H2SO4	SULFURIC-ACID
HSO4-	C	HSO4-	HSO4-
SO4--	C	SO4-2	SO4--
$CaCO_3$(S)	C	$CaCO_3$	CALCIUM-CARBONATE-CALCITE
CALCI(S)	C	CA(OH)2	CALCIUM-HYDROXIDE
CACL2(S)	C	CACL2	CALCIUM-CHLORIDE
SALT1	C	CACL2*W	CACL2*H2O
SALT2	C	CACL2*6W	CACL2*6H2O
SALT3	C	CACL2*4W	CACL2*4H2O
SALT4	C	CACL2*2W	CACL2*2H2O
SALT5	C	$CaSO_3$	CALCIUM-SULFITE

```
  SALT6    C    CaSO4        CALCIUM-SULFATE
  SALT7    C    CASO4*1:2W:A   CALCIUM-SULFATE-HEMIHYDRATE:S-A


 LISTID        SUPERCRITICAL COMPONENT LIST
  GLOBAL        CO2 SO2 HCL O2 N2
ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                 11/18/2021  PAGE 7


                      REACTION SECTION


REACTION:   OXIDIZE   TYPE: POWERLAW
-----------------------------------


    Unit operations referencing this reaction model:


    Reactor Name: DROPSEP      Block Type: RCSTR


REACTION:   R-1      TYPE: POWERLAW
-----------------------------------


    Unit operations referencing this reaction model:


    Reactor Name: DROPSEP      Block Type: RCSTR
ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                 11/18/2021  PAGE 8


                     U-O-S BLOCK SECTION
```

```
BLOCK:  B-1     MODEL: FSPLIT
------------------------------
   INLETSTREAM:          S-2
   OUTLET STREAMS:       PURGE      DROPLETS
   PROPERTY OPTION SET:   ELECNRTL  ELECTROLYTE NRTL / REDLICH-KWONG
   HENRY-COMPS ID:       GLOBAL
   CHEMISTRY ID:         SALTSION - TRUE SPECIES


                  ***  MASS AND ENERGY BALANCE  ***
                               IN             OUT       RELATIVE DIFF.
    TOTAL BALANCE
       MOLE(KMOL/HR )           929.521        929.521       0.391382E-13
       MASS(KG/HR   )          16859.3        16859.3        0.00000
       ENTHALPY(GCAL/HR )      -62.9041       -62.9041      -0.756577E-09


                  ***  CO2 EQUIVALENT SUMMARY ***
    FEED STREAMS CO2E            1.04899      KG/HR
    PRODUCT STREAMS CO2E         1.04899      KG/HR
    NET STREAMS CO2E PRODUCTION   0.00000      KG/HR
    UTILITIES CO2E PRODUCTION     0.00000      KG/HR
    TOTAL CO2E PRODUCTION         0.00000      KG/HR


                      ***  INPUT DATA  ***


  MASS-FLOW  (KG/HR   )          STRM=DROPLETS FLOW=     8,000.00       KEY= 0
```

```
                    ***  RESULTS  ***

  STREAM= PURGE       SPLIT=       0.52548    KEY=  0    STREAM-ORDER=   2
        DROPLETS                  0.47452         0                1

BLOCK:  DROPSEP  MODEL: RCSTR
----------------------------
   INLET STREAMS:        DROPLETS    FLUEOUT
   OUTLET STREAMS:        SCALE      GAS
   PROPERTY OPTION SET:   ELECNRTL  ELECTROLYTE NRTL / REDLICH-KWONG
   HENRY-COMPS ID:       GLOBAL
   CHEMISTRY ID:         SALTSION - TRUE SPECIES

                  ***  MASS AND ENERGY BALANCE  ***
                       IN          OUT       GENERATION   RELATIVE DIFF.
ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                11/18/2021  PAGE 9

                       U-O-S BLOCK SECTION

BLOCK:  DROPSEP  MODEL: RCSTR (CONTINUED)
   TOTAL BALANCE
   MOLE(KMOL/HR )        8435.79      8435.79      0.104238E-04  0.123578E-08
   MASS(KG/HR   )        230678.      230678.                   0.123958E-08
   ENTHALPY(GCAL/HR )    -188.270     -187.996                  -0.145633E-02

                  ***  CO2 EQUIVALENT SUMMARY ***
```

```
FEED STREAMS CO2E           32987.0     KG/HR

PRODUCT STREAMS CO2E         32987.0     KG/HR

NET STREAMS CO2E PRODUCTION -0.395160E-04  KG/HR

UTILITIES CO2E PRODUCTION    0.00000     KG/HR

TOTAL CO2E PRODUCTION       -0.395160E-04  KG/HR


                 ***  INPUT DATA  ***


REACTOR TYPE: TEMP SPEC TWO    PHASE REACTOR


RESIDENCE TIME                 HR                  0.25000

REACTOR TEMPERATURE              C                     60.000

REACTOR PRESSURE                BAR                  1.0132


REACTION PARAGRAPH          ID:  R-1          TYPE:  POWERLAW

GLOBAL BASES:

KBASIS                              MOLE-GAMMA

CBASIS                              MOLARITY

SBASIS                              GLOBAL


STOICHIOMETRY:


REACTION NUMBER:          1

  SUBSTREAM:  MIXED

    H2O      -0.50000     CA++      -1.0000     SO3--     -1.0000     CaSO3      1.0000
```

```
   REACTION NUMBER:          2
     SUBSTREAM:  MIXED
       CaSO3      -1.0000
     SUBSTREAM:  CISOLID
       CaSO3(S)    1.0000


   REACTION NUMBER:          3
     SUBSTREAM:  MIXED
       H2O       -2.0000      CA++       -1.0000      CaSO4       1.0000      SO4--      -1.0000


   REACTION NUMBER:          4
     SUBSTREAM:  MIXED
       CaSO4      -1.0000
     SUBSTREAM:  CISOLID
       CASO4(S)    1.0000
ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                11/18/2021  PAGE 10


                       U-O-S BLOCK SECTION


BLOCK:  DROPSEP  MODEL: RCSTR (CONTINUED)


   REAC-DATA ENTRIES:


     REACTION NO    TYPE     PHASE       DELT            BASIS
                                C
```

```
     1     EQUIL     L     0.0000       MOLE-GAMMA

     2     EQUIL     L     0.0000       MOLE-GAMMA

     3     EQUIL     L     0.0000       MOLE-GAMMA

     4     EQUIL     L     0.0000       MOLE-GAMMA


  REACTION NO    SOLID BASIS    LIQ. PHASE BASIS    SOL. PHASE BASIS


     1         GLOBAL          L              S

     2         GLOBAL          L              S

     3         GLOBAL          L              S

     4         GLOBAL          L              S



 REACTION PARAGRAPH          ID:  OXIDIZE        TYPE:  POWERLAW

 GLOBAL BASES:

 KBASIS                                  MOLE-GAMMA

 CBASIS                                  MOLARITY

 SBASIS                                  GLOBAL


 STOICHIOMETRY:


 REACTION NUMBER:          1

   SUBSTREAM:  MIXED

     H2O       -1.0000     O2       -0.50000     H3O+       1.0000     HSO3-      -1.0000

SO4--      1.0000
```

```
   REAC-DATA ENTRIES:


     REACTION NO    TYPE     PHASE       DELT           BASIS
                                          C


         1       KINETIC      L       0.0000          MOLARITY


     REACTION NO    SOLID BASIS    LIQ. PHASE BASIS    SOL. PHASE BASIS


         1           GLOBAL            L                  S



   RATE PARAMETERS:


     REACTION NO    PREEXP. FACTOR    ACT. ENERGY    TEMP. EXPONENT    REF.
TEMP
                                      KCAL/MOL                    C


         1          0.61664E+06      20.541        0.0000
ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                 11/18/2021  PAGE 11


                              U-O-S BLOCK SECTION


BLOCK:  DROPSEP  MODEL: RCSTR (CONTINUED)


   POWERLAW EXPONENTS:
```

```
  REACTION NUMBER:         1
    SUBSTREAM:  MIXED
      HSO3-      1.5000


                    ***  RESULTS  ***


  REACTOR HEAT DUTY               GCAL/HR              0.27418
  REACTOR VOLUME                  CUM                  54724.
  VAPOR PHASE VOLUME FRACTION                          0.99997
  VAPOR PHASE VOLUME              CUM                  54722.
  LIQUID PHASE VOLUME             CUM                  1.8984



BLOCK:  G1      MODEL: RADFRAC
------------------------------
  INLETS   - FLUE     STAGE  10
             PUMPSTR  STAGE   1
  OUTLETS  - S-1      STAGE   1
             SLURRYOU STAGE  10
  PROPERTY OPTION SET:   ELECNRTL  ELECTROLYTE NRTL / REDLICH-KWONG
  HENRY-COMPS ID:        GLOBAL
  CHEMISTRY ID:          GLOBAL   - TRUE SPECIES


                ***  MASS AND ENERGY BALANCE  ***
                     IN         OUT      GENERATION   RELATIVE DIFF.
  TOTAL BALANCE
```

```
    MOLE(KMOL/HR )        72996.2       72996.2      0.497876E-03  0.344879E-13
    MASS(KG/HR   )      0.140165E+07  0.140165E+07                 0.182723E-14
    ENTHALPY(GCAL/HR )    -4557.31      -4557.31                   0.955889E-09

                  ***  CO2 EQUIVALENT SUMMARY ***
     FEED STREAMS CO2E             33059.9      KG/HR
     PRODUCT STREAMS CO2E          33059.9      KG/HR
     NET STREAMS CO2E PRODUCTION  0.233419E-02  KG/HR
     UTILITIES CO2E PRODUCTION     0.00000      KG/HR
     TOTAL CO2E PRODUCTION        0.233419E-02  KG/HR
 ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                11/18/2021  PAGE 12

                         U-O-S BLOCK SECTION

 BLOCK:  G1       MODEL: RADFRAC (CONTINUED)



                       **********************
                       ****  INPUT DATA  ****
                       **********************

    ****   INPUT PARAMETERS   ****

     NUMBER OF STAGES                                10
     ALGORITHM OPTION                              STANDARD
```

```
 INITIALIZATION OPTION                          STANDARD
 HYDRAULIC PARAMETER CALCULATIONS                   NO
 INSIDE LOOP CONVERGENCE METHOD                   NEWTON
 DESIGN SPECIFICATION METHOD                    NESTED
 MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS              100
 MAXIMUM NO. OF INSIDE LOOP ITERATIONS               10
 MAXIMUM NUMBER OF FLASH ITERATIONS                  30
 FLASH TOLERANCE                                0.000100000
 OUTSIDE LOOP CONVERGENCE TOLERANCE                  0.000100000

****   COL-SPECS   ****

 MOLAR VAPOR DIST / TOTAL DIST                      1.00000
 CONDENSER DUTY (W/O SUBCOOL)   GCAL/HR              0.0
 REBOILER DUTY                GCAL/HR               0.0

**** REAC-STAGES SPECIFICATIONS ****

 STAGE  TO  STAGE          REACTIONS/CHEMISTRY ID
   1        10                  GLOBAL



     *****  CHEMISTRY PARAGRAPH GLOBAL  *****
ASPEN PLUS   PLAT: WINDOWS   VER: 36.0               11/18/2021  PAGE 13

                         U-O-S BLOCK SECTION
```

```
BLOCK:  G1      MODEL: RADFRAC (CONTINUED)


      ****  REACTION PARAMETERS  ****


  RXN NO. TYPE        PHASE      CONC.     TEMP APP TO EQUIL    CONVERSION
                     BASIS           C
    1    EQUILIBRIUM  LIQUID    MOLE-GAMMA      0.0000
    2    EQUILIBRIUM  LIQUID    MOLE-GAMMA      0.0000
    3    EQUILIBRIUM  LIQUID    MOLE-GAMMA      0.0000
    4    EQUILIBRIUM  LIQUID    MOLE-GAMMA      0.0000
    5    EQUILIBRIUM  LIQUID    MOLE-GAMMA      0.0000
    6    EQUILIBRIUM  LIQUID    MOLE-GAMMA      0.0000
    7    EQUILIBRIUM  LIQUID    MOLE-GAMMA      0.0000
    8    EQUILIBRIUM  LIQUID    MOLE-GAMMA      0.0000
    9    EQUILIBRIUM  LIQUID    MOLE-GAMMA      0.0000


     **  STOICHIOMETRIC COEFFICIENTS  **


  RXN NO.    H2O        O2         CO2        HCL        SO2
    1      -1.000     0.000      0.000      0.000      0.000
    2      -2.000     0.000      0.000      0.000     -1.000
    3       0.000     0.000      0.000      0.000      0.000
    4      -1.000     0.000      0.000     -1.000      0.000
    5      -1.000     0.000      0.000      0.000      0.000
```

6	-1.000	0.000	0.000	0.000	0.000
7	-1.000	0.000	0.000	0.000	0.000
8	-2.000	0.000	-1.000	0.000	0.000
9	-2.000	0.000	0.000	0.000	0.000

RXN NO.	NO2	N_2	CA++	CAOH+	H3O+
1	0.000	0.000	0.000	0.000	1.000
2	0.000	0.000	0.000	0.000	1.000
3	0.000	0.000	1.000	-1.000	0.000
4	0.000	0.000	0.000	0.000	1.000
5	0.000	0.000	0.000	0.000	1.000
6	0.000	0.000	0.000	0.000	1.000
7	0.000	0.000	0.000	0.000	1.000
8	0.000	0.000	0.000	0.000	1.000
9	0.000	0.000	0.000	0.000	1.000

RXN NO.	OH-	HSO3-	HCO3-	CL-	SO3--
1	0.000	-1.000	0.000	0.000	1.000
2	0.000	1.000	0.000	0.000	0.000
3	1.000	0.000	0.000	0.000	0.000
4	0.000	0.000	0.000	1.000	0.000
5	0.000	0.000	0.000	0.000	0.000
6	0.000	0.000	0.000	0.000	0.000
7	0.000	0.000	-1.000	0.000	0.000
8	0.000	0.000	1.000	0.000	0.000
9	1.000	0.000	0.000	0.000	0.000

```
                        U-O-S BLOCK SECTION

BLOCK:  G1       MODEL: RADFRAC (CONTINUED)

  RXN NO.    CO3--
     1       0.000
     2       0.000
     3       0.000
     4       0.000
     5       0.000
     6       0.000
     7       1.000
     8       0.000
     9       0.000

      **  COEFFICIENTS OF EQUILIBRIUM CONSTANT EXPRESSION  **

  RXN NO.     A            B            C            D            E
     1    -25.291       1333.4       0.0000       0.0000       0.0000
     2    -5.9787       637.40       0.0000     -0.15134E-01    0.0000
     7     216.05      -12432.      -35.482       0.0000       0.0000
     8     231.47      -12092.      -36.782       0.0000       0.0000
     9     132.90      -13446.      -22.477       0.0000       0.0000
```

```
****    PROFILES   ****


 P-SPEC         STAGE   1  PRES, BAR                  1.01325


 TEMP-EST        STAGE   1  TEMP, C                   60.0000
                       2                     60.0000
                       3                     60.0000
                       4                     60.0000
                       5                     60.0000
                       6                     60.0000
                       7                     60.0000
                       8                     60.0000
                       9                     60.0000
                      10                      60.0000

                      *******************
                      ****  RESULTS  ****
                      *******************



***   COMPONENT SPLIT FRACTIONS   ***


                       OUTLET STREAMS
                       --------------
                  S-1         SLURRYOU
 COMPONENT:
```

```
  H2O        .23542E-01   .97646

  O2         .99988       .11768E-03

  CO2        .99778       .22189E-02

  HCL        1.0000       .43774E-09

  SO2        .94241       .57590E-01

  NO2        .41810       .58190

  N2         .99993       .65298E-04

  CA++       0.0000       1.0000
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                        U-O-S BLOCK SECTION


BLOCK:  G1       MODEL: RADFRAC (CONTINUED)


  ***   COMPONENT SPLIT FRACTIONS   ***


                       OUTLET STREAMS

                       --------------

               S-1         SLURRYOU

  COMPONENT:

  CAOH+       0.0000       1.0000

  H3O+        0.0000       1.0000

  OH-         0.0000       1.0000

  HSO3-       0.0000       1.0000

  HCO3-       0.0000       1.0000

  CL-         0.0000       1.0000
```

```
   SO3--       0.0000       1.0000

   CO3--       MISSING      MISSING



  ***    SUMMARY OF KEY RESULTS    ***


   TOP STAGE TEMPERATURE          C                      59.7128

   BOTTOM STAGE TEMPERATURE       C                      59.7145

   TOP STAGE LIQUID FLOW          KMOL/HR             64,644.7

   BOTTOM STAGE LIQUID FLOW       KMOL/HR             65,001.5

   TOP STAGE VAPOR FLOW           KMOL/HR              7,994.72

   BOILUP VAPOR FLOW              KMOL/HR              7,992.68

   CONDENSER DUTY (W/O SUBCOOL)   GCAL/HR                  0.0

   REBOILER DUTY                  GCAL/HR                  0.0


  ****   MAXIMUM FINAL RELATIVE ERRORS   ****


   BUBBLE POINT                   0.84381E-07  STAGE=  5

   COMPONENT MASS BALANCE         0.34106E-06  STAGE=  1 COMP=HSO3-

   ENERGY BALANCE                 0.60755E-08  STAGE=  1


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                          U-O-S BLOCK SECTION


BLOCK:  G1       MODEL: RADFRAC (CONTINUED)
```

```
  ****    PROFILES   ****


  **NOTE** REPORTED VALUES FOR STAGE LIQUID AND VAPOR RATES ARE THE
FLOWS

         FROM THE STAGE INCLUDING ANY SIDE PRODUCT.


                                 ENTHALPY

STAGE TEMPERATURE   PRESSURE          KCAL/MOL          HEAT DUTY

     C           BAR          LIQUID      VAPOR       GCAL/HR


  1   59.713        1.0132       -67.675      -19.816

  2   59.713        1.0132       -67.675      -19.798

  3   59.713        1.0132       -67.675      -19.798

  4   59.713        1.0132       -67.675      -19.798

  9   59.713        1.0132       -67.675      -19.798

 10   59.715        1.0132       -67.674      -19.798


STAGE     FLOW RATE               FEED RATE             PRODUCT RATE

         KMOL/HR                KMOL/HR               KMOL/HR

     LIQUID     VAPOR       LIQUID    VAPOR    MIXED      LIQUID    VAPOR

  1 0.6464E+05  7995.      .64647+05 .75832-01                 7994.7187

  2 0.6464E+05  7993.

  3 0.6464E+05  7993.

  4 0.6464E+05  7993.

  9 0.6464E+05  7993.

 10 0.6500E+05  7993.                  8349.3873  .65001+05
```

```
    ****  MASS FLOW PROFILES  ****


STAGE     FLOW RATE                FEED RATE              PRODUCT RATE

          KG/HR                  KG/HR                 KG/HR

      LIQUID     VAPOR       LIQUID    VAPOR    MIXED      LIQUID    VAPOR

   1 0.1172E+07 0.2227E+06  .11725+07    2.2228                    .22268+06

   2 0.1172E+07 0.2226E+06

   3 0.1172E+07 0.2226E+06

   4 0.1172E+07 0.2226E+06

   9 0.1172E+07 0.2226E+06

  10 0.1179E+07 0.2226E+06                    .22910+06  .11790+07


                   ****   MOLE-X-PROFILE     ****

   STAGE     H2O          O2           CO2          HCL          SO2

      1    0.99267       0.10153E-05   0.25713E-04   0.33941E-17   0.63822E-06

      2    0.99267       0.10156E-05   0.25663E-04   0.33941E-17   0.63961E-06

      3    0.99267       0.10156E-05   0.25663E-04   0.33941E-17   0.63973E-06

      4    0.99267       0.10156E-05   0.25663E-04   0.33941E-17   0.63974E-06

      9    0.99267       0.10156E-05   0.25663E-04   0.33941E-17   0.63973E-06

     10     0.99258       0.10147E-05   0.25643E-04   0.36361E-17   0.63913E-06

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                        U-O-S BLOCK SECTION


BLOCK:  G1       MODEL: RADFRAC (CONTINUED)
```

```
                **** MOLE-X-PROFILE ****
STAGE   NO2         N2          CA++        CAOH+       H3O+
  1   0.27613E-04  0.51544E-05  0.18159E-02  0.48671E-13  0.91175E-03
  2   0.27620E-04  0.51557E-05  0.18159E-02  0.48671E-13  0.91175E-03
  3   0.27628E-04  0.51557E-05  0.18159E-02  0.48672E-13  0.91175E-03
  4   0.27640E-04  0.51557E-05  0.18159E-02  0.48672E-13  0.91175E-03
  9   0.27808E-04  0.51557E-05  0.18159E-02  0.48672E-13  0.91175E-03
 10    0.27859E-04  0.51510E-05  0.18059E-02  0.45336E-13  0.97228E-03

                **** MOLE-X-PROFILE ****
STAGE   OH-         HSO3-       HCO3-       CL-         SO3--
  1   0.90334E-13  0.23455E-06  0.78431E-09  0.45433E-02  0.97431E-12
  2   0.90335E-13  0.23506E-06  0.78278E-09  0.45433E-02  0.97644E-12
  3   0.90335E-13  0.23510E-06  0.78277E-09  0.45433E-02  0.97661E-12
  4   0.90335E-13  0.23510E-06  0.78277E-09  0.45433E-02  0.97662E-12
  9   0.90335E-13  0.23510E-06  0.78277E-09  0.45433E-02  0.97661E-12
 10    0.84929E-13  0.22102E-06  0.73584E-09  0.45839E-02  0.86442E-12

                **** MOLE-X-PROFILE ****
STAGE   CO3--
  1   0.74277E-17
  2   0.74132E-17
  3   0.74132E-17
  4   0.74131E-17
  9   0.74131E-17
```

```
  10    0.65605E-17


                     ****   MOLE-Y-PROFILE     ****

 STAGE     H2O          O2           CO2          HCL          SO2

   1    0.19457       0.70093E-01   0.93753E-01   0.67536E-07   0.85036E-04

   2    0.19457       0.70111E-01   0.93569E-01   0.67536E-07   0.85221E-04

   3    0.19457       0.70111E-01   0.93569E-01   0.67537E-07   0.85237E-04

   4    0.19457       0.70111E-01   0.93569E-01   0.67537E-07   0.85238E-04

   9    0.19457       0.70111E-01   0.93569E-01   0.67538E-07   0.85238E-04

  10    0.19457       0.70111E-01   0.93569E-01   0.72470E-07   0.85238E-04


                     ****   MOLE-Y-PROFILE     ****

 STAGE     NO2          N2           CA++         CAOH+        H3O+

   1    0.16275E-03   0.64133       0.0000       0.0000       0.0000

   2    0.16279E-03   0.64150       0.0000       0.0000       0.0000

   3    0.16284E-03   0.64150       0.0000       0.0000       0.0000

   4    0.16291E-03   0.64150       0.0000       0.0000       0.0000

   9    0.16390E-03   0.64150       0.0000       0.0000       0.0000

  10    0.16436E-03   0.64150       0.0000       0.0000       0.0000


                     ****   MOLE-Y-PROFILE     ****

 STAGE     OH-          HSO3-        HCO3-        CL-          SO3--

   1     0.0000       0.0000       0.0000       0.0000       0.0000

   2     0.0000       0.0000       0.0000       0.0000       0.0000

   3     0.0000       0.0000       0.0000       0.0000       0.0000

   4     0.0000       0.0000       0.0000       0.0000       0.0000
```

```
    9     0.0000        0.0000        0.0000        0.0000        0.0000
   10     0.0000        0.0000        0.0000        0.0000        0.0000
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                         U-O-S BLOCK SECTION


BLOCK:  G1       MODEL: RADFRAC (CONTINUED)


                     ****   MOLE-Y-PROFILE     ****
  STAGE     CO3--
    1     0.0000
    2     0.0000
    3     0.0000
    4     0.0000
    9     0.0000
   10     0.0000


                     ****   K-VALUES           ****
  STAGE     H2O          O2          CO2          HCL          SO2
    1    0.19601       69035.       3646.1       0.19898E+11    133.24
    2    0.19601       69035.       3646.1       0.19898E+11    133.24
    3    0.19601       69035.       3646.1       0.19898E+11    133.24
    4    0.19601       69035.       3646.1       0.19898E+11    133.24
    9    0.19601       69035.       3646.1       0.19899E+11    133.24
   10    0.19603       69098.       3648.9       0.19931E+11    133.37
```

```
              ****  K-VALUES       ****

STAGE    NO2        N2         CA++        CAOH+       H3O+

  1    5.8939     0.12443E+06   0.0000      0.0000      0.0000

  2    5.8939     0.12443E+06   0.0000      0.0000      0.0000

  3    5.8939     0.12443E+06   0.0000      0.0000      0.0000

  4    5.8939     0.12443E+06   0.0000      0.0000      0.0000

  9    5.8939     0.12443E+06   0.0000      0.0000      0.0000

 10     5.8996     0.12454E+06   0.0000      0.0000      0.0000


              ****  K-VALUES       ****

STAGE    OH-        HSO3-      HCO3-      CL-        SO3--

  1    0.0000      0.0000      0.0000      0.0000      0.0000

  2    0.0000      0.0000      0.0000      0.0000      0.0000

  3    0.0000      0.0000      0.0000      0.0000      0.0000

  4    0.0000      0.0000      0.0000      0.0000      0.0000

  9    0.0000      0.0000      0.0000      0.0000      0.0000

 10     0.0000      0.0000      0.0000      0.0000      0.0000


              ****  K-VALUES       ****

STAGE    CO3--

  1    0.0000

  2    0.0000

  3    0.0000

  4    0.0000

  9    0.0000

 10     0.0000
```

```
              ****    RATES OF GENERATION     ****
                      KMOL/HR
  STAGE    H2O       O2        CO2       HCL       SO2       NO2
     1   -.6184E-03   0.000     0.5014E-04  0.1333E-06  -.3594E-03   0.000
     2   -.6597E-04   0.000     0.9924E-07  -.1445E-08  -.3308E-04   0.000
     3   -.5452E-05   0.000     0.2485E-09  -.1836E-08  -.2725E-05   0.000
     4   -.3948E-06   0.000     0.5773E-10  -.1966E-08  -.1965E-06   0.000
     9   -.3933E-04   0.000     0.1346E-09  -.3942E-04  0.4762E-07   0.000
    10   -.1132E-01   0.000     0.2800E-05  -.1300E-01  0.8400E-03   0.000
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                     U-O-S BLOCK SECTION

BLOCK:  G1      MODEL: RADFRAC (CONTINUED)

              ****    RATES OF GENERATION     ****
                      KMOL/HR
  STAGE    N2        CA++       CAOH+      H3O+       OH-        HSO3-
     1    0.000     0.1946E-11  -.1946E-11  0.3091E-03  -.7776E-12  0.3594E-03
     2    0.000     -.5652E-15  0.5652E-15  0.3299E-04  0.3953E-14  0.3308E-04
     3    0.000     -.6469E-14  0.6469E-14  0.2727E-05  0.8666E-14  0.2725E-05
     4    0.000     -.7097E-14  0.7097E-14  0.1984E-06  0.9253E-14  0.1965E-06
     9    0.000     -.1564E-15  0.1564E-15  0.3937E-04  -.7441E-14  -.4762E-07
    10    0.000     0.1995E-09  -.1995E-09  0.1216E-01  -.3226E-09  -.8400E-03
```

```
              ****    RATES OF GENERATION     ****

                       KMOL/HR

STAGE    HCO3-      CL-        SO3--      CO3--

  1   -.5014E-04  -.1333E-06  0.1520E-08  -.4746E-12

  2   -.9924E-07  0.1445E-08  0.1374E-09  -.9397E-15

  3   -.2485E-09  0.1836E-08  0.1129E-10  -.2356E-17

  4   -.5773E-10  0.1966E-08  0.7829E-12  -.5176E-18

  9   -.1346E-09  0.3942E-04  -.3150E-12  -.2725E-17

 10   -.2800E-05  0.1300E-01  -.6949E-08  -.5281E-13


               ****   MASS-X-PROFILE    ****

STAGE    H2O          O2           CO2          HCL          SO2

  1    0.98600      0.17913E-05   0.62394E-04   0.68231E-17   0.22544E-05

  2    0.98600      0.17918E-05   0.62272E-04   0.68231E-17   0.22593E-05

  3    0.98600      0.17918E-05   0.62271E-04   0.68231E-17   0.22597E-05

  4    0.98600      0.17918E-05   0.62271E-04   0.68231E-17   0.22597E-05

  9    0.98600      0.17918E-05   0.62271E-04   0.68231E-17   0.22597E-05

 10    0.98588      0.17901E-05   0.62221E-04   0.73094E-17   0.22575E-05


               ****   MASS-X-PROFILE    ****

STAGE    NO2          N2           CA++         CAOH+        H3O+

  1    0.70042E-04   0.79612E-05   0.40124E-02   0.15319E-12   0.95627E-03

  2    0.70058E-04   0.79632E-05   0.40124E-02   0.15319E-12   0.95627E-03

  3    0.70080E-04   0.79632E-05   0.40124E-02   0.15319E-12   0.95627E-03

  4    0.70110E-04   0.79632E-05   0.40124E-02   0.15319E-12   0.95627E-03

  9    0.70536E-04   0.79632E-05   0.40124E-02   0.15319E-12   0.95627E-03
```

```
   10   0.70665E-04  0.79557E-05  0.39903E-02  0.14269E-12  0.10197E-02


                 ****   MASS-X-PROFILE    ****

  STAGE    OH-         HSO3-       HCO3-       CL-         SO3--

    1   0.84711E-13  0.10484E-05  0.26386E-08  0.88809E-02  0.43011E-11

    2   0.84711E-13  0.10507E-05  0.26335E-08  0.88809E-02  0.43105E-11

    3   0.84711E-13  0.10509E-05  0.26335E-08  0.88809E-02  0.43112E-11

    4   0.84711E-13  0.10509E-05  0.26335E-08  0.88809E-02  0.43113E-11

    9   0.84711E-13  0.10509E-05  0.26334E-08  0.88809E-02  0.43112E-11

   10   0.79639E-13  0.98794E-06  0.24755E-08  0.89601E-02  0.38158E-11
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                     U-O-S BLOCK SECTION


BLOCK:  G1      MODEL: RADFRAC (CONTINUED)


                 ****   MASS-X-PROFILE    ****

  STAGE    CO3--

    1   0.24576E-16

    2   0.24528E-16

    3   0.24528E-16

    4   0.24528E-16

    9   0.24528E-16

   10   0.21706E-16


                 ****   MASS-Y-PROFILE    ****
```

```
STAGE    H2O          O2           CO2          HCL          SO2
   1   0.12585      0.80525E-01  0.14814      0.88407E-07  0.19559E-03
   2   0.12586      0.80554E-01  0.14786      0.88416E-07  0.19604E-03
   3   0.12586      0.80554E-01  0.14786      0.88417E-07  0.19607E-03
   4   0.12586      0.80554E-01  0.14786      0.88417E-07  0.19608E-03
   9   0.12586      0.80554E-01  0.14786      0.88418E-07  0.19608E-03
  10   0.12586      0.80554E-01  0.14786      0.94876E-07  0.19608E-03
```

```
                 ****   MASS-Y-PROFILE    ****
STAGE    NO2          N2           CA++         CAOH+        H3O+
   1   0.26882E-03  0.64503      0.0000       0.0000       0.0000
   2   0.26890E-03  0.64526      0.0000       0.0000       0.0000
   3   0.26899E-03  0.64526      0.0000       0.0000       0.0000
   4   0.26911E-03  0.64526      0.0000       0.0000       0.0000
   9   0.27074E-03  0.64526      0.0000       0.0000       0.0000
  10   0.27150E-03  0.64526      0.0000       0.0000       0.0000
```

```
                 ****   MASS-Y-PROFILE    ****
STAGE    OH-          HSO3-        HCO3-        CL-          SO3--
   1    0.0000       0.0000       0.0000       0.0000       0.0000
   2    0.0000       0.0000       0.0000       0.0000       0.0000
   3    0.0000       0.0000       0.0000       0.0000       0.0000
   4    0.0000       0.0000       0.0000       0.0000       0.0000
   9    0.0000       0.0000       0.0000       0.0000       0.0000
  10    0.0000       0.0000       0.0000       0.0000       0.0000
```

```
                  ****   MASS-Y-PROFILE     ****

  STAGE     CO3--

     1     0.0000

     2     0.0000

     3     0.0000

     4     0.0000

     9     0.0000

    10     0.0000


   STAGE        PH

             LIQUID






      1         1.5218

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                          U-O-S BLOCK SECTION


BLOCK:  G1       MODEL: RADFRAC (CONTINUED)


   STAGE        PH

             LIQUID
```

```
      2       1.5218
      3       1.5218
      4       1.5218
      9       1.5218
     10       1.4945

BLOCK:  MIX     MODEL: MIXER
-----------------------------
   INLET STREAMS:        SLURRY     CaCO3      RECIRK
   OUTLET STREAM:        PUMPSTR
   PROPERTY OPTION SET:  ELECNRTL  ELECTROLYTE NRTL / REDLICH-KWONG
   HENRY-COMPS ID:       GLOBAL
   CHEMISTRY ID:         GLOBAL   - TRUE SPECIES

                 ***  MASS AND ENERGY BALANCE  ***
                           IN            OUT       RELATIVE DIFF.
    TOTAL BALANCE
       MOLE(KMOL/HR )          64645.1        64646.8       -0.266401E-04
       MASS(KG/HR   )        0.117254E+07    0.117254E+07   -0.440144E-06
       ENTHALPY(GCAL/HR )      -4375.04       -4375.04       0.449247E-06

                 ***  CO2 EQUIVALENT SUMMARY ***
```

```
    FEED STREAMS CO2E            72.3073      KG/HR
    PRODUCT STREAMS CO2E         146.177      KG/HR
    NET STREAMS CO2E PRODUCTION   73.8698      KG/HR
    UTILITIES CO2E PRODUCTION     0.00000      KG/HR
    TOTAL CO2E PRODUCTION        73.8698      KG/HR


                          ***  INPUT DATA  ***
   TWO    PHASE      FLASH
   MAXIMUM NO. ITERATIONS                              30
   CONVERGENCE TOLERANCE                                  0.000100000
   OUTLET PRESSURE:  MINIMUM OF INLET STREAM PRESSURES
 ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                  11/18/2021  PAGE 22


                              U-O-S BLOCK SECTION


 BLOCK:  SEP      MODEL: SEP
 --------------------------
   INLET STREAM:          S-1
   OUTLET STREAMS:        O2         FLUEOUT
   PROPERTY OPTION SET:   ELECNRTL  ELECTROLYTE NRTL / REDLICH-KWONG
   HENRY-COMPS ID:        GLOBAL
   CHEMISTRY ID:          SALTSION - TRUE SPECIES



     ***********************************************************************
     *                                               *
```

```
 *    OUTLET STREAM HAS ZERO FLOW.                              *
 *                                               *
 ********************************************************************



                ***  MASS AND ENERGY BALANCE  ***
                             IN             OUT        RELATIVE DIFF.
TOTAL BALANCE
   MOLE(KMOL/HR )           7994.72         7994.72         0.00000
   MASS(KG/HR   )           222678.         222678.         0.00000
   ENTHALPY(GCAL/HR )       -158.421        -158.421        0.00000

                ***  CO2 EQUIVALENT SUMMARY ***
FEED STREAMS CO2E             32986.5      KG/HR
PRODUCT STREAMS CO2E          32986.5      KG/HR
NET STREAMS CO2E PRODUCTION   0.00000      KG/HR
UTILITIES CO2E PRODUCTION     0.00000      KG/HR
TOTAL CO2E PRODUCTION         0.00000      KG/HR



                    ***  INPUT DATA  ***


FLASH SPECS FOR STREAM O2
TWO    PHASE  TP  FLASH
PRESSURE DROP         BAR                          0.0
MAXIMUM NO. ITERATIONS                               30
```

```
   CONVERGENCE TOLERANCE                        0.000100000
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                              U-O-S BLOCK SECTION

BLOCK:  SEP      MODEL: SEP (CONTINUED)

   FLASH SPECS FOR STREAM FLUEOUT
   TWO    PHASE  TP  FLASH
   PRESSURE DROP        BAR                        0.0
   MAXIMUM NO. ITERATIONS                             30
   CONVERGENCE TOLERANCE                        0.000100000

   MASS FLOW (KG/HR   )
     SUBSTREAM= MIXED
       STREAM= O2       CPT= O2       FLOW=            0.0


                           ***  RESULTS  ***

   HEAT DUTY            GCAL/HR                     0.0000

  COMPONENT = H2O
    STREAM     SUBSTREAM    SPLIT FRACTION
    FLUEOUT    MIXED              1.00000
```

```
 COMPONENT = O2
   STREAM     SUBSTREAM    SPLIT FRACTION
   FLUEOUT    MIXED             1.00000

 COMPONENT = CO2
   STREAM     SUBSTREAM    SPLIT FRACTION
   FLUEOUT    MIXED             1.00000

 COMPONENT = HCL
   STREAM     SUBSTREAM    SPLIT FRACTION
   FLUEOUT    MIXED             1.00000

 COMPONENT = SO2
   STREAM     SUBSTREAM    SPLIT FRACTION
   FLUEOUT    MIXED             1.00000

 COMPONENT = NO2
   STREAM     SUBSTREAM    SPLIT FRACTION
   FLUEOUT    MIXED             1.00000

 COMPONENT = N2
   STREAM     SUBSTREAM    SPLIT FRACTION
   FLUEOUT    MIXED             1.00000
ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                 11/18/2021  PAGE 24

                          U-O-S BLOCK SECTION
```

```
BLOCK:  SPLIT    MODEL: FSPLIT
------------------------------
   INLET STREAM:          SLURRYOU
   OUTLET STREAMS:        RECIRK      S-2
   PROPERTY OPTION SET:   ELECNRTL  ELECTROLYTE NRTL / REDLICH-KWONG
   HENRY-COMPS ID:        GLOBAL
   CHEMISTRY ID:          GLOBAL   - TRUE SPECIES

                   ***  MASS AND ENERGY BALANCE  ***
                                 IN            OUT        RELATIVE DIFF.
    TOTAL BALANCE
       MOLE(KMOL/HR )          65001.5         65001.5         0.00000
       MASS(KG/HR   )       0.117897E+07    0.117897E+07     0.00000
       ENTHALPY(GCAL/HR )      -4398.89        -4398.89        0.00000

                   ***  CO2 EQUIVALENT SUMMARY ***
    FEED STREAMS CO2E            73.3563      KG/HR
    PRODUCT STREAMS CO2E         73.3563      KG/HR
    NET STREAMS CO2E PRODUCTION   0.00000      KG/HR
    UTILITIES CO2E PRODUCTION     0.00000      KG/HR
    TOTAL CO2E PRODUCTION         0.00000      KG/HR

                      ***  INPUT DATA  ***

  FRACTION OF FLOW               STRM=S-2      FRAC=         0.014300
```

```
               *** RESULTS ***


 STREAM= RECIRK      SPLIT=      0.98570    KEY= 0   STREAM-ORDER=  2

     S-2                0.014300      0             1

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                  STREAM SECTION


CaCO3 DROPLETS FLUE FLUEOUT GAS

------------------------------


STREAM ID          CaCO3    DROPLETS  FLUE     FLUEOUT   GAS

FROM :              ----     B-1      ----     SEP      DROPSEP

TO   :            MIX      DROPSEP   G1      DROPSEP   ----

CLASS:              MIXCISLD  MIXCISLD  MIXCISLD  MIXCISLD  MIXCISLD

TOTAL STREAM:

  KG/HR             560.0000  8000.0000  2.2910+05  2.2268+05  2.2313+05

  GCAL/HR             -1.9600   -29.8490  -182.2715  -158.4210  -159.8484

SUBSTREAM: MIXED

PHASE:              LIQUID    LIQUID    MIXED     VAPOR     VAPOR

COMPONENTS: KMOL/HR

  H2O               21.7387   437.7990  1903.3323  1555.5494  1580.6560

  O2               0.0    4.4753-04   560.3718   560.3709   560.3709

  CO2             1.6775-07  1.1310-02   747.8721   749.5268   749.5275

  HCL               0.0    1.6038-15  1.3581-02  5.3993-04  6.5456-04
```

SO_2	0.0	2.8190-04	0.6806	0.6798	0.6799
NO2	0.0	1.2288-02	1.3269	1.3011	1.3022
N_2	0.0	2.2720-03	5127.2949	5127.2901	5127.2903
$CaCO_3$	0.0	0.0	0.0	0.0	0.0
CA++	1.6624	0.7965	0.0	0.0	0.0
CAOH+	1.6173-02	1.9997-11	0.0	0.0	0.0
H3O+	1.1683-11	0.4288	4.2475	0.0	0.0
OH-	4.4103-03	3.7460-11	3.3662-12	0.0	0.0
HSO3-	0.0	9.7487-05	8.6897-06	0.0	0.0
HCO3-	2.0583-02	3.2456-07	2.8582-08	0.0	0.0
CL-	0.0	2.0218	4.2475	0.0	0.0
SO3--	0.0	3.8127-10	4.5938-12	0.0	0.0
CO3--	1.6580	2.8936-15	3.3896-17	0.0	0.0
$CaSO_3$(S)	0.0	0.0	0.0	0.0	0.0
CASO4(S)	0.0	0.0	0.0	0.0	0.0
$CaSO_3$	0.0	0.0	0.0	0.0	0.0
$CaSO_4$	0.0	0.0	0.0	0.0	0.0
H2SO4	0.0	0.0	0.0	0.0	4.3696-25
HSO4-	0.0	0.0	0.0	0.0	0.0
SO4--	0.0	0.0	0.0	0.0	0.0
$CaCO_3$(S)	0.0	0.0	0.0	0.0	0.0
CALCI(S)	0.0	0.0	0.0	0.0	0.0
CACL2(S)	0.0	0.0	0.0	0.0	0.0
SALT1	0.0	0.0	0.0	0.0	0.0
SALT2	0.0	0.0	0.0	0.0	0.0
SALT3	0.0	0.0	0.0	0.0	0.0

```
  SALT4              0.0      0.0      0.0      0.0      0.0
  SALT5              0.0      0.0      0.0      0.0      0.0
  SALT6              0.0      0.0      0.0      0.0      0.0
  SALT7              0.0      0.0      0.0      0.0      0.0
COMPONENTS: KG/HR
  H2O            391.6292  7887.0723  3.4289+04  2.8024+04  2.8476+04
  O2             0.0     1.4321-02  1.7931+04  1.7931+04  1.7931+04
  CO2           7.3825-06     0.4978  3.2914+04  3.2987+04  3.2987+04
  HCL              0.0     5.8475-14     0.4952  1.9686-02  2.3866-02
  SO2             0.0     1.8060-02    43.6043    43.5537    43.5557
  NO2              0.0       0.5653    61.0470    59.8593    59.9066
  N2             0.0     6.3645-02  1.4363+05  1.4363+05  1.4363+05
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                       STREAM SECTION

CaCO3 DROPLETS FLUE FLUEOUT GAS (CONTINUED)

STREAM ID            CaCO3     DROPLETS   FLUE      FLUEOUT    GAS

  CaCO3              0.0      0.0      0.0      0.0      0.0
  CA++             66.6224    31.9224    0.0      0.0      0.0
  CAOH+              0.9233  1.1415-09    0.0      0.0      0.0
  H3O+           2.2225-10     8.1578    80.7996    0.0      0.0
  OH-           7.5010-02  6.3711-10  5.7253-11    0.0      0.0
  HSO3-              0.0     7.9035-03  7.0450-04    0.0      0.0
```

```
  HCO3-            1.2560  1.9804-05  1.7440-06    0.0       0.0
  CL-           0.0       71.6804   150.5888    0.0       0.0
  SO3--           0.0     3.0527-08  3.6780-10    0.0       0.0
  CO3--           99.4942  1.7365-13  2.0341-15    0.0       0.0
  CaSO3(S)           0.0       0.0       0.0       0.0       0.0
  CASO4(S)            0.0       0.0       0.0       0.0       0.0
  CaSO3            0.0       0.0       0.0       0.0       0.0
  CaSO4            0.0       0.0       0.0       0.0       0.0
  H2SO4             0.0       0.0       0.0       0.0    4.2856-23
  HSO4-            0.0       0.0       0.0       0.0       0.0
  SO4--           0.0       0.0       0.0       0.0       0.0
  CaCO3(S)           0.0       0.0       0.0       0.0       0.0
  CALCI(S)            0.0       0.0       0.0       0.0       0.0
  CACL2(S)            0.0       0.0       0.0       0.0       0.0
  SALT1             0.0       0.0       0.0       0.0       0.0
  SALT2             0.0       0.0       0.0       0.0       0.0
  SALT3             0.0       0.0       0.0       0.0       0.0
  SALT4             0.0       0.0       0.0       0.0       0.0
  SALT5             0.0       0.0       0.0       0.0       0.0
  SALT6             0.0       0.0       0.0       0.0       0.0
  SALT7             0.0       0.0       0.0       0.0       0.0
TOTAL FLOW:
  KMOL/HR             25.1002   441.0729  8349.3874  7994.7187  8019.8274
  KG/HR            560.0000  8000.0000  2.2910+05  2.2268+05  2.2313+05
  CUM/HR              0.3400     8.0525  2.1812+05  2.1802+05  2.1889+05
STATE VARIABLES:
```

```
  TEMP   C           60.0000    59.7145    60.0000    59.7128    60.0000
  PRES   BAR           1.0133     1.0133     1.0133     1.0133     1.0133
  VFRAC               0.0        0.0        0.9571     1.0000     1.0000
  LFRAC              1.0000     1.0000  4.2902-02     0.0        0.0
  SFRAC              0.0        0.0        0.0        0.0        0.0
ENTHALPY:
  KCAL/MOL           -78.0854   -67.6737   -21.8305   -19.8157   -19.9317
  KCAL/KG          -3499.9267 -3731.1301  -795.5846  -711.4353  -716.3900
  GCAL/HR            -1.9600   -29.8490  -182.2715  -158.4210  -159.8484
ENTROPY:
  CAL/MOL-K          -38.5047   -36.8303    -0.7890     0.8205     0.8040
  CAL/GM-K           -1.7259    -2.0306 -2.8754-02  2.9459-02  2.8899-02
DENSITY:
  KMOL/CUM            73.8335    54.7746  3.8280-02  3.6670-02  3.6639-02
  KG/CUM           1647.2675   993.4800     1.0504     1.0214     1.0194
AVG MW               22.3106    18.1376    27.4396    27.8531    27.8223
ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                 11/18/2021  PAGE 27


                      STREAM SECTION


O2 PUMPSTR PURGE RECIRK S-1
---------------------------


STREAM ID            O2        PUMPSTR    PURGE      RECIRK     S-1
FROM :              SEP       MIX       B-1       SPLIT      G1
TO   :             ----      G1        ----      MIX       SEP
```

```
CLASS:            MIXCISLD  MIXCISLD  MIXCISLD  MIXCISLD  MIXCISLD

CONV. MAX. REL. ERR:   0.0   -4.4488-05   0.0      0.0      0.0
TOTAL STREAM:
  KG/HR             0.0    1.1725+06  8859.2659  1.1621+06  2.2268+05
  GCAL/HR           0.0   -4375.0386   -33.0551 -4335.9850  -158.4210
SUBSTREAM: MIXED
PHASE:            MISSING   MIXED     LIQUID     LIQUID     VAPOR
COMPONENTS: KMOL/HR
  H2O               0.0    6.4171+04   484.8223  6.3596+04  1555.5494
  O2                0.0    6.5011-02  4.9560-04  6.5011-02   560.3709
  CO2               0.0       3.3215  1.2525-02     1.6430   749.5268
  HCL               0.0    5.1285-09  1.7760-15  2.3297-13  5.3993-04
  SO2               0.0    4.0309-02  3.1218-04  4.0950-02     0.6798
  NO2               0.0       1.7851  1.3608-02     1.7850     1.3011
  N2                0.0       0.3300  2.5160-03     0.3300  5127.2901
  CaCO3             0.0       0.0        0.0        0.0        0.0
  CA++              0.0     117.3856     0.8821   115.7070     0.0
  CAOH+             0.0    3.1482-09  2.2144-11  2.9048-09     0.0
  H3O+              0.0      58.9395     0.4749    62.2959     0.0
  OH-               0.0    5.8403-09  4.1483-11  5.4415-09     0.0
  HSO3-             0.0    1.4803-02  1.0796-04  1.4161-02     0.0
  HCO3-             0.0    1.0084-04  3.5942-07  4.7147-05     0.0
  CL-               0.0     293.6989     2.2390   293.6986     0.0
  SO3--             0.0    6.1464-08  4.2222-10  5.5385-08     0.0
  CO3--             0.0    9.5473-13  3.2044-15  4.2034-13     0.0
```

```
   CaSO3(S)          0.0       0.0       0.0       0.0       0.0
   CASO4(S)          0.0       0.0       0.0       0.0       0.0
   CaSO3             0.0       0.0       0.0       0.0       0.0
   CaSO4             0.0       0.0       0.0       0.0       0.0
   H2SO4             0.0       0.0       0.0       0.0       0.0
   HSO4-             0.0       0.0       0.0       0.0       0.0
   SO4--             0.0       0.0       0.0       0.0       0.0
   CaCO3(S)          0.0       0.0       0.0       0.0       0.0
   CALCI(S)          0.0       0.0       0.0       0.0       0.0
   CACL2(S)          0.0       0.0       0.0       0.0       0.0
   SALT1             0.0       0.0       0.0       0.0       0.0
   SALT2             0.0       0.0       0.0       0.0       0.0
   SALT3             0.0       0.0       0.0       0.0       0.0
   SALT4             0.0       0.0       0.0       0.0       0.0
   SALT5             0.0       0.0       0.0       0.0       0.0
   SALT6             0.0       0.0       0.0       0.0       0.0
   SALT7             0.0       0.0       0.0       0.0       0.0
 COMPONENTS: KG/HR
   H2O               0.0     1.1561+06  8734.2088  1.1457+06  2.8024+04
   O2                0.0       2.0803  1.5859-02     2.0803  1.7931+04
   CO2               0.0     146.1771     0.5512    72.3073  3.2987+04
   HCL               0.0     1.8699-07  6.4756-14  8.4944-12  1.9686-02
   SO2               0.0       2.5824  2.0000-02     2.6235    43.5537
 ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                   11/18/2021  PAGE 28

                     STREAM SECTION
```

O2 PUMPSTR PURGE RECIRK S-1 (CONTINUED)

STREAM ID	O2	PUMPSTR	PURGE	RECIRK	S-1
NO2	0.0	82.1237	0.6260	82.1200	59.8593
N_2	0.0	9.2454	7.0481-02	9.2454	1.4363+05
$CaCO_3$	0.0	0.0	0.0	0.0	0.0
CA++	0.0	4704.4497	35.3512	4637.1761	0.0
CAOH+	0.0	1.7972-07	1.2641-09	1.6582-07	0.0
H3O+	0.0	1121.1875	9.0340	1185.0339	0.0
OH-	0.0	9.9331-08	7.0554-10	9.2549-08	0.0
HSO3-	0.0	1.2001	8.7524-03	1.1481	0.0
HCO3-	0.0	6.1530-03	2.1931-05	2.8768-03	0.0
CL-	0.0	1.0413+04	79.3795	1.0413+04	0.0
SO3--	0.0	4.9212-06	3.3806-08	4.4344-06	0.0
CO3--	0.0	5.7294-11	1.9230-13	2.5225-11	0.0
$CaSO_3$(S)	0.0	0.0	0.0	0.0	0.0
CASO4(S)	0.0	0.0	0.0	0.0	0.0
$CaSO_3$	0.0	0.0	0.0	0.0	0.0
$CaSO_4$	0.0	0.0	0.0	0.0	0.0
H2SO4	0.0	0.0	0.0	0.0	0.0
HSO4-	0.0	0.0	0.0	0.0	0.0
SO4--	0.0	0.0	0.0	0.0	0.0
$CaCO_3$(S)	0.0	0.0	0.0	0.0	0.0
CALCI(S)	0.0	0.0	0.0	0.0	0.0

```
  CACL2(S)           0.0       0.0       0.0       0.0       0.0
  SALT1             0.0       0.0       0.0       0.0       0.0
  SALT2             0.0       0.0       0.0       0.0       0.0
  SALT3             0.0       0.0       0.0       0.0       0.0
  SALT4             0.0       0.0       0.0       0.0       0.0
  SALT5             0.0       0.0       0.0       0.0       0.0
  SALT6             0.0       0.0       0.0       0.0       0.0
  SALT7             0.0       0.0       0.0       0.0       0.0
TOTAL FLOW:
  KMOL/HR            0.0     6.4647+04   488.4478  6.4072+04  7994.7187
  KG/HR             0.0     1.1725+06  8859.2659  1.1621+06  2.2268+05
  CUM/HR             0.0     1182.3584     8.9174  1169.7370  2.1802+05
STATE VARIABLES:
  TEMP   C          MISSING    59.7212    59.7145    59.7145    59.7128
  PRES   BAR          MISSING     1.0133     1.0133     1.0133     1.0133
  VFRAC             MISSING  1.1730-06     0.0       0.0       1.0000
  LFRAC             MISSING     1.0000     1.0000     1.0000     0.0
  SFRAC             MISSING     0.0       0.0       0.0       0.0
ENTHALPY:
  KCAL/MOL            MISSING   -67.6760   -67.6737   -67.6737   -19.8157
  KCAL/KG           MISSING -3731.2369 -3731.1301 -3731.1301  -711.4353
  GCAL/HR           MISSING -4375.0386   -33.0551 -4335.9850  -158.4210
ENTROPY:
  CAL/MOL-K           MISSING   -36.8293   -36.8303   -36.8303     0.8205
  CAL/GM-K           MISSING    -2.0305    -2.0306    -2.0306  2.9459-02
DENSITY:
```

```
  KMOL/CUM          MISSING   54.6761   54.7746   54.7746  3.6670-02
  KG/CUM          MISSING  991.6991  993.4800  993.4800    1.0214
AVG MW            MISSING   18.1377   18.1376   18.1376   27.8531
ASPEN PLUS  PLAT: WINDOWS  VER: 36.0              11/18/2021  PAGE 29


                      STREAM SECTION


S-2 SCALE SLURRY SLURRYOU
-------------------------


STREAM ID            S-2      SCALE     SLURRY    SLURRYOU
FROM :              SPLIT     DROPSEP    ----      G1
TO   :             B-1       ----      MIX       SPLIT
CLASS:              MIXCISLD  MIXCISLD  MIXCISLD  MIXCISLD
TOTAL STREAM:
  KG/HR            1.6859+04  7547.6063  9872.9000  1.1790+06
  GCAL/HR            -62.9041   -28.1475   -37.0917 -4398.8891
SUBSTREAM: MIXED
PHASE:              LIQUID    LIQUID    LIQUID    LIQUID
COMPONENTS: KMOL/HR
  H2O              922.6213   412.6926   548.0292  6.4519+04
  O2             9.4314-04  4.1756-04    0.0     6.5954-02
  CO2             2.3835-02  1.0560-02    0.0       1.6668
  HCL             3.3798-15  1.6592-15    0.0     2.3635-13
  SO2            5.9408-04  2.6109-04    0.0     4.1544-02
  NO2             2.5896-02  1.1261-02    0.0       1.8109
```

N_2	4.7879-03	2.1214-03	0.0	0.3348
$CaCO_3$	0.0	0.0	0.0	0.0
CA++	1.6786	0.7965	0.0	117.3856
CAOH+	4.2141-11	1.8916-11	0.0	2.9469-09
H3O+	0.9038	0.4287	3.0383-06	63.1996
OH-	7.8943-11	3.4594-11	3.0383-06	5.5205-09
HSO3-	2.0544-04	8.7062-05	0.0	1.4367-02
HCO3-	6.8398-07	2.9334-07	0.0	4.7831-05
CL-	4.2608	2.0217	0.0	297.9595
SO3--	8.0350-10	1.8800-14	0.0	5.6189-08
CO3--	6.0981-15	2.5704-15	0.0	4.2644-13
$CaSO_3$(S)	0.0	0.0	0.0	0.0
CASO4(S)	0.0	0.0	0.0	0.0
$CaSO_3$	0.0	0.0	0.0	0.0
$CaSO_4$	0.0	0.0	0.0	0.0
H2SO4	0.0	1.3757-20	0.0	0.0
HSO4-	0.0	2.4848-11	0.0	0.0
SO4--	0.0	9.0135-14	0.0	0.0
$CaCO_3$(S)	0.0	0.0	0.0	0.0
CALCI(S)	0.0	0.0	0.0	0.0
CACL2(S)	0.0	0.0	0.0	0.0
SALT1	0.0	0.0	0.0	0.0
SALT2	0.0	0.0	0.0	0.0
SALT3	0.0	0.0	0.0	0.0
SALT4	0.0	0.0	0.0	0.0
SALT5	0.0	0.0	0.0	0.0

```
  SALT6             0.0      0.0      0.0      0.0
  SALT7             0.0      0.0      0.0      0.0
COMPONENTS: KG/HR
  H2O            1.6621+04  7434.7726  9872.8999  1.1623+06
  O2            3.0179-02  1.3362-02     0.0        2.1104
  CO2              1.0490     0.4648     0.0      73.3563
  HCL            1.2323-13  6.0495-14     0.0     8.6176-12
  SO2            3.8060-02  1.6727-02     0.0        2.6615
  NO2              1.1914     0.5181     0.0      83.3114
  N2              0.1341  5.9427-02     0.0       9.3795
ASPEN PLUS   PLAT: WINDOWS   VER: 36.0              11/18/2021  PAGE 30

                      STREAM SECTION

S-2 SCALE SLURRY SLURRYOU (CONTINUED)

STREAM ID            S-2       SCALE     SLURRY    SLURRYOU

  CaCO3             0.0      0.0      0.0      0.0
  CA++             67.2736    31.9224     0.0     4704.4497
  CAOH+            2.4056-09  1.0798-09     0.0     1.6822-07
  H3O+             17.1918     8.1554  5.7796-05  1202.2257
  OH-            1.3427-09  5.8837-10  5.1674-05  9.3892-08
  HSO3-           1.6656-02  7.0584-03     0.0       1.1648
  HCO3-           4.1735-05  1.7899-05     0.0     2.9185-03
  CL-            151.0599    71.6764     0.0     1.0564+04
```

```
   SO3--            6.4332-08  1.5053-12    0.0    4.4988-06
   CO3--            3.6595-13  1.5425-13    0.0    2.5591-11
   CaSO3(S)             0.0       0.0       0.0       0.0
   CASO4(S)             0.0       0.0       0.0       0.0
   CaSO3                0.0       0.0       0.0       0.0
   CaSO4                0.0       0.0       0.0       0.0
   H2SO4                0.0    1.3492-18    0.0       0.0
   HSO4-                0.0    2.4120-09    0.0       0.0
   SO4--                0.0    8.6588-12    0.0       0.0
   CaCO3(S)             0.0       0.0       0.0       0.0
   CALCI(S)             0.0       0.0       0.0       0.0
   CACL2(S)             0.0       0.0       0.0       0.0
   SALT1                0.0       0.0       0.0       0.0
   SALT2                0.0       0.0       0.0       0.0
   SALT3                0.0       0.0       0.0       0.0
   SALT4                0.0       0.0       0.0       0.0
   SALT5                0.0       0.0       0.0       0.0
   SALT6                0.0       0.0       0.0       0.0
   SALT7                0.0       0.0       0.0       0.0
 TOTAL FLOW:
   KMOL/HR            929.5208   415.9643   548.0292  6.5001+04
   KG/HR            1.6859+04  7547.6063  9872.9000  1.1790+06
   CUM/HR              16.9699     7.5936    10.0417  1186.7069
 STATE VARIABLES:
   TEMP   C            59.7145    60.0000    60.0000    59.7145
   PRES   BAR           1.0133     1.0133     1.0133     1.0133
```

```
   VFRAC               0.0       0.0       0.0       0.0
   LFRAC              1.0000    1.0000    1.0000    1.0000
   SFRAC               0.0       0.0       0.0       0.0
ENTHALPY:
   KCAL/MOL           -67.6737   -67.6680   -67.6819   -67.6737
   KCAL/KG         -3731.1301 -3729.3228 -3756.9168 -3731.1301
   GCAL/HR            -62.9041   -28.1475   -37.0917 -4398.8891
ENTROPY:
   CAL/MOL-K          -36.8303   -36.8063   -36.9748   -36.8303
   CAL/GM-K            -2.0306    -2.0285    -2.0524    -2.0306
DENSITY:
   KMOL/CUM            54.7746    54.7781    54.5752    54.7746
   KG/CUM             993.4800   993.9402   983.1877   993.4800
AVG MW                 18.1376    18.1448    18.0153    18.1376

SUBSTREAM: CISOLID     STRUCTURE: CONVENTIONAL
COMPONENTS: KMOL/HR
   H2O                 0.0       0.0       0.0       0.0
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                         STREAM SECTION

S-2 SCALE SLURRY SLURRYOU (CONTINUED)

STREAM ID              S-2       SCALE     SLURRY    SLURRYOU
```

O2	0.0	0.0	0.0	0.0
CO2	0.0	0.0	0.0	0.0
HCL	0.0	0.0	0.0	0.0
SO_2	0.0	0.0	0.0	0.0
NO2	0.0	0.0	0.0	0.0
N_2	0.0	0.0	0.0	0.0
$CaCO_3$	0.0	0.0	0.0	0.0
CA++	0.0	0.0	0.0	0.0
CAOH+	0.0	0.0	0.0	0.0
H3O+	0.0	0.0	0.0	0.0
OH-	0.0	0.0	0.0	0.0
HSO3-	0.0	0.0	0.0	0.0
HCO3-	0.0	0.0	0.0	0.0
CL-	0.0	0.0	0.0	0.0
SO3--	0.0	0.0	0.0	0.0
CO3--	0.0	0.0	0.0	0.0
$CaSO_3$(S)	0.0	3.8127-10	0.0	0.0
CASO4(S)	0.0	3.6015-14	0.0	0.0
$CaSO_3$	0.0	0.0	0.0	0.0
$CaSO_4$	0.0	0.0	0.0	0.0
H2SO4	0.0	0.0	0.0	0.0
HSO4-	0.0	0.0	0.0	0.0
SO4--	0.0	0.0	0.0	0.0
$CaCO_3$(S)	0.0	0.0	0.0	0.0
CALCI(S)	0.0	0.0	0.0	0.0
CACL2(S)	0.0	0.0	0.0	0.0

SALT1	0.0	0.0	0.0	0.0
SALT2	0.0	0.0	0.0	0.0
SALT3	0.0	0.0	0.0	0.0
SALT4	0.0	0.0	0.0	0.0
SALT5	0.0	0.0	0.0	0.0
SALT6	0.0	0.0	0.0	0.0
SALT7	0.0	0.0	0.0	0.0

COMPONENTS: KG/HR

H2O	0.0	0.0	0.0	0.0
O2	0.0	0.0	0.0	0.0
CO2	0.0	0.0	0.0	0.0
HCL	0.0	0.0	0.0	0.0
SO_2	0.0	0.0	0.0	0.0
NO2	0.0	0.0	0.0	0.0
N_2	0.0	0.0	0.0	0.0
$CaCO_3$	0.0	0.0	0.0	0.0
CA++	0.0	0.0	0.0	0.0
CAOH+	0.0	0.0	0.0	0.0
H3O+	0.0	0.0	0.0	0.0
OH-	0.0	0.0	0.0	0.0
HSO3-	0.0	0.0	0.0	0.0
HCO3-	0.0	0.0	0.0	0.0
CL-	0.0	0.0	0.0	0.0
SO3--	0.0	0.0	0.0	0.0
CO3--	0.0	0.0	0.0	0.0
$CaSO_3$(S)	0.0	4.9241-08	0.0	0.0

```
ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                 11/18/2021  PAGE 32

                    STREAM SECTION

S-2 SCALE SLURRY SLURRYOU (CONTINUED)

STREAM ID              S-2       SCALE      SLURRY     SLURRYOU

   CASO4(S)             0.0     6.2007-12     0.0        0.0
   CaSO3              0.0        0.0        0.0        0.0
   CaSO4              0.0        0.0        0.0        0.0
   H2SO4               0.0        0.0        0.0        0.0
   HSO4-              0.0        0.0        0.0        0.0
   SO4--             0.0        0.0        0.0        0.0
   CaCO3(S)            0.0        0.0        0.0        0.0
   CALCI(S)            0.0        0.0        0.0        0.0
   CACL2(S)            0.0        0.0        0.0        0.0
   SALT1               0.0        0.0        0.0        0.0
   SALT2               0.0        0.0        0.0        0.0
   SALT3               0.0        0.0        0.0        0.0
   SALT4               0.0        0.0        0.0        0.0
   SALT5               0.0        0.0        0.0        0.0
   SALT6               0.0        0.0        0.0        0.0
   SALT7               0.0        0.0        0.0        0.0
TOTAL FLOW:
   KMOL/HR              0.0     3.8131-10     0.0        0.0
```

```
  KG/HR              0.0     4.9248-08     0.0        0.0
  CUM/HR              0.0     1.1439-11     0.0        0.0
STATE VARIABLES:
  TEMP   C          MISSING    60.0000    MISSING    MISSING
  PRES   BAR          1.0133     1.0133     1.0133     1.0133
  VFRAC             MISSING     0.0      MISSING    MISSING
  LFRAC             MISSING     0.0      MISSING    MISSING
  SFRAC             MISSING     1.0000    MISSING    MISSING
ENTHALPY:
  KCAL/MOL            MISSING  -312.3639    MISSING    MISSING
  KCAL/KG            MISSING -2418.5398    MISSING    MISSING
  GCAL/HR            MISSING -1.1911-10    MISSING    MISSING
ENTROPY:
  CAL/MOL-K           MISSING   -86.9389    MISSING    MISSING
  CAL/GM-K            MISSING    -0.6731    MISSING    MISSING
DENSITY:
  KMOL/CUM            MISSING    33.3333    MISSING    MISSING
  KG/CUM             MISSING  4305.1301    MISSING    MISSING
AVG MW              MISSING   129.1539    MISSING    MISSING
ASPEN PLUS   PLAT: WINDOWS   VER: 36.0                11/18/2021  PAGE 33


                   PROBLEM STATUS SECTION


BLOCK STATUS
------------
```

```
******************************************************************************
*

*                                                            *

* Calculations were completed with warnings                          *

*                                                            *

* The following Unit Operation blocks were                           *

* completed with warnings:                                    *

*   SEP                                                       *

*                                                            *

* All streams were FLASHed normally                                  *

*                                                            *

* All Convergence blocks were completed normally                     *

*                                                            *

******************************************************************************
*
```

Appendix H: Case Study Raw Data

The figures presented in section 6.2.1 are constructed from the numerical data according to Table H-1.

Table H-1. Case study results.

G1	**HCl removal efficiency**	**SO_2 removal efficiency**	**$CaSO_3$*1/2 H_2O [kg/h]**	**$CaSO_4$*2H_2O [kg/h]**	**$CaSO_3$*1/2 H_2O [E+07*kg/h]**	**$CaSO_4$*2H_2O [E+09*kg/h]**
Base case	0.999873	0.001175	4.92E-08	6.20074E-12	4.92E-01	0.006201
Case 1 - HCl peak	0.999807	0.001023	6.13652E-08	1.67143E-09	6.14E-01	1.671426
Case 2 - SO_2 peak	0.999832	0.001056	1.63318E-07	1.71691E-13	1.63E+00	0.000172
Case 3 - G1 high pH	0.999987	0.00274	4.64939E-07	9.64681E-10	4.65E+00	0.964681
Case 4 - G2 high pH	0.999735	0.000999	1.99764E-09	2.14411E-10	2.00E-02	0.214411

Appendix I: pH Sensitivity Analyze Raw Data

In C the numerical results are displayed for the pH sensitivity analysis.

Table I-1. Results from pH sensitivity analysis.

pH	**HCl**	**SO2**	**pH**	CaSO$_3$	**CaSO4**
1.49449	99.99%	0.12%	1.49449	4.92E-08	6.20E-12
1.96576	100.00%	0.19%	1.96576	4.47E-07	1.10E-09
1.67114	99.99%	0.13%	1.67114	3.70E-12	1.70E-09
1.19334	99.97%	0.10%	1.19334	1.19E-08	6.20E-12
1.26903	99.98%	0.11%	1.26903	1.70E-08	4.23E-10
G2 Base case					
pH	**HCl**	**SO2**	**pH**	CaSO$_3$	**CaSO4**
5.99623	100.00%	90.33%	5.99623	4.211272	1.33E-06
6.9839	100.00%	98.06%	6.9839	70.68775	8.12E-07
6.51244	100.00%	90.01%	6.51244	51.02211	4.90E-06
5.73849	100.00%	54.31%	5.80121	25.36619	6.92E-06
5.80588	100.00%	57.92%	5.65636	21.45299	7.15E-06
5.80121	100.00%	57.60%	5.35696	13.66993	7.79E-09
5.65636	100.00%	50.19%			
5.35696	100.00%	34.06%			
G1 Case 1 HCl topp					
pH	**HCl**	**SO2**	**pH**	CaSO$_3$	**CaSO4**
1.21752	99.98%	0.10%	1.21752	6.14E-08	1.67E-09
1.28222	99.98%	0.11%	1.28222	8.31E-08	2.09E-09

1.45916	99.99%	0.12%	1.45916		
1.42259	99.99%	0.12%	1.42259	1.60E-07	3.21E-10
1.53021	99.99%	0.12%	1.53021	2.65E-07	4.90E-12
1.11033	99.97%	0.10%	1.11033	3.71E-08	3.06E-13
1.01963	99.97%	0.10%	1.01963	3.48E-09	1.04E-12
G2 Case 1 HCl topp					
pH	**HCl**	**SO2**	**pH**	$CaSO_3$	**CaSO4**
6.12609	100.00%	78.29%	5.99895	94.9519	6.79E-09
5.99895	100.00%	71.71%	6.3388	133.9746	4.70E-06
6.3388	100.00%	75.31%	6.17538	114.4531	6.19E-06
6.17538	100.00%	78.29%	5.5578	56.55313	9.14E-06
5.5578	100.00%	100.00%	5.66394	64.32252	6.59E-06
5.66394	100.00%	100.00%			
G1 Case 2 SO_2 topp					
pH	**HCl**	**SO2**	**pH**	$CaSO_3$	**CaSO4**
1.27859	99.98%	0.11%	1.27859	1.63E-07	1.72E-13
1.45461	99.99%	0.12%	1.45461	1.33E-15	1.12E-08
1.35567	99.99%	0.11%	1.35567	5.50E-07	8.05E-09
1.15515	99.98%	0.10%	1.15515	1.62E-07	3.99E-09
1.10119	99.97%	0.10%	1.10119	1.83E-10	3.32E-09
G2 Case 2 SO_2 topp					
pH	**HCl**	**SO2**	**pH**	$CaSO_3$	**CaSO4**
6.0212	100.00%	75.17%	6.0212	218.8783	8.75E-06
6.17182	100.00%	82.78%	6.17182	2.58E+02	6.91E-06
6.31642	100.00%	88.70%	6.31642	295.9792	8.47E-09
5.85716	100.00%	65.87%	5.85716	179.3701	1.02E-05

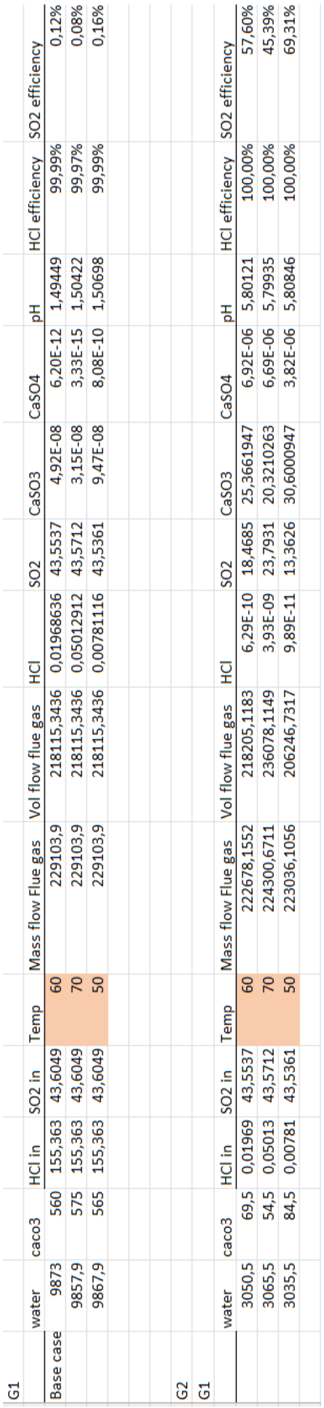
5.94176	100.00%	70.79%	5.94176	199.0579	3.30E-11
G1 Case 3 G1 pH					
pH	**HCl**	**SO2**	**pH**	$CaSO_3$	**CaSO4**
1.70825	99.99%	0.14%	1.70825	2.18E-07	6.20E-12
1.93276	100.00%	0.18%	1.93276	6.26E-07	6.13E-09
2.41111	100.00%	0.58%	2.41111	9.30E-06	3.25E-08
2.11117	100.00%	0.23%	2.20277	4.65E-07	9.65E-10
2.23944	100.00%	0.30%			
2.16901	100.00%	0.26%			
2.20277	100.00%	0.27%			
G2 Case 3 G1 pH					
pH	**HCl**	**SO2**	**pH**	$CaSO_3$	**CaSO4**
6.02048	100.00%	70.00%	6.05432	42.25738	6.11E-09
6.05432	100.00%	71.83%	6.46276	61.84519	4.94E-06
6.46276	100.00%	89.17%	6.30646	53.9728	5.60E-06
6.30646	100.00%	83.58%	5.86445	34.42579	5.73E-06
5.86445	100.00%	61.72%	5.64396	26.82015	7.33E-06
5.64396	100.00%	50.02%			
G1 Case 4 G2 pH					
pH	**HCl**	**SO2**	**pH**	$CaSO_3$	**CaSO4**
1.20862	99.97%	0.10%	1.20862	2.00E-09	2.14E-10
1.40595	99.98%	0.11%	1.40595	2.32E-08	4.25E-10
1.76327	99.99%	0.14%	1.76327	2.03E-07	8.89E-13
1.0724	99.96%	0.10%	1.0724	5.00E-09	8.81E-17
0.96862	99.95%	0.09%	0.96862	2.87E-09	9.31E-11
G2 Case 4 G2 pH					

pH	HCl	SO2	pH	$CaSO_3$	CaSO4
6.48306	100.00%	88.29%	6.43124	33.72981	4.90E-06
6.43124	100.00%	86.54%	7.67511	64.23637	1.86E-11
7.67511	100.00%	99.88%	7.06527	53.40396	2.47E-09
7.06527	100.00%	98.37%	6.14014	25.78935	0.0017
6.14014	100.00%	74.28%	5.79876	17.89023	5.74E-06
5.79876	100.00%	56.74%			

Appendix J: Temperature Sensitivity Analyze Raw Data

The results from the temperature sensitivity analysis are shown in Table J-1.

Table J-1. Results from the temperature sensitivity analysis.



G1

	water	caco3	HCl in	SO2 in	Temp	Mass flow Flue gas	Vol flow flue gas	HCl	SO2	CaSO3	CaSO4	pH	HCl efficiency	SO2 efficiency
Base case	9873	560	155,363	43,6049	60	229103,9	218115,3436	0,01968636	43,5537	4,92E-08	6,20E-12	1,49449	99,99%	0,12%
	9857,9	575	155,363	43,6049	70	229103,9	218115,3436	0,05012912	43,5712	3,15E-08	3,33E-15	1,50422	99,97%	0,08%
	9867,9	565	155,363	43,6049	50	229103,9	218115,3436	0,00781116	43,5361	9,47E-08	8,08E-10	1,50698	99,99%	0,16%

G2

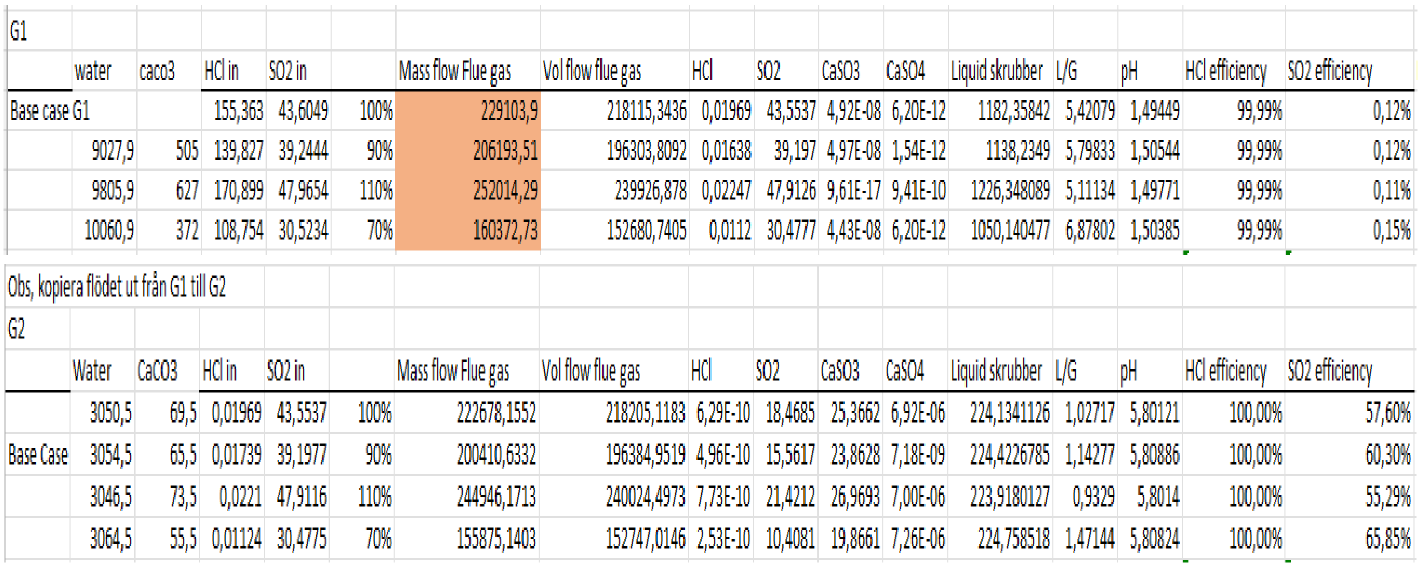
G1

	water	caco3	HCl in	SO2 in	Temp	Mass flow Flue gas	Vol flow flue gas	HCl	SO2	CaSO3	CaSO4	pH	HCl efficiency	SO2 efficiency
	3050,5	69,5	0,01969	43,5537	60	222678,1552	218205,1183	6,29E-10	18,4685	25,3661947	6,92E-06	5,80121	100,00%	57,60%
	3065,5	54,5	0,05013	43,5712	70	224300,6711	236078,1149	3,93E-09	23,7931	20,3210263	6,69E-06	5,79935	100,00%	45,39%
	3035,5	84,5	0,00781	43,5361	50	223036,1056	206246,7317	9,89E-11	13,3626	30,6000947	3,82E-06	5,80846	100,00%	69,31%

Appendix K: Load Sensitivity Analysis Raw Data

The raw data from sensitivity analyses in which the flue gas flow was varied is shown in Table K-1.

Table K-1. Results from the load sensitivity analysis.



G1															
	water	caco3	HCl in	SO2 in		Mass flow Flue gas	Vol flow flue gas	HCl	SO2	CaSO3	CaSO4	Liquid skrubber	L/G	pH	HCl efficiency	SO2 efficiency
Base case G1			155,363	43,6049	100%	229103,9	218115,3436	0,01969	43,5537	4,92E-08	6,20E-12	1182,35842	5,42079	1,49449	99,99%	0,12%
	9027,9	505	139,827	39,2444	90%	206193,51	196303,8092	0,01638	39,197	4,97E-08	1,54E-12	1138,2349	5,79833	1,50544	99,99%	0,12%
	9805,9	627	170,899	47,9654	110%	252014,29	239926,878	0,02247	47,9126	9,61E-17	9,41E-10	1226,348089	5,11134	1,49771	99,99%	0,11%
	10060,9	372	108,754	30,5234	70%	160372,73	152680,7405	0,0112	30,4777	4,43E-08	6,20E-12	1050,140477	6,87802	1,50385	99,99%	0,15%

Obs, kopiera flödet ut från G1 till G2

G2																
	Water	CaCO3	HCl in	SO2 in		Mass flow Flue gas	Vol flow flue gas	HCl	SO2	CaSO3	CaSO4	Liquid skrubber	L/G	pH	HCl efficiency	SO2 efficiency
	3050,5	69,5	0,01969	43,5537	100%	222678,1552	218205,1183	6,29E-10	18,4685	25,3662	6,92E-06	224,1341126	1,02717	5,80121	100,00%	57,60%
Base Case	3054,5	65,5	0,01739	39,1977	90%	200410,6332	196384,9519	4,96E-10	15,5617	23,8628	7,18E-09	224,4226785	1,14277	5,80886	100,00%	60,30%
	3046,5	73,5	0,0221	47,9116	110%	244946,1713	240024,4973	7,73E-10	21,4212	26,9693	7,00E-06	223,9180127	0,9329	5,8014	100,00%	55,29%
	3064,5	55,5	0,01124	30,4775	70%	155875,1403	152747,0146	2,53E-10	10,4081	19,8661	7,26E-06	224,758518	1,47144	5,80824	100,00%	65,85%

Appendix L: Recirculation Liquid Flow Sensitivity Analysis Raw Data

Results from the simulation runs with high and low recirculation liquid flow are displayed in Table L-1 and Table L-2 for G1 and G2 models respectively.

Table L-1. Results from simulations with the base case and cases 1-4 with high and low recirculation flow.

	HCl removal		**SO_2 removal efficiency**		**$CaSO_3$**		**$CaSO_4$**	
G1	**High L/G**	**Low L/G**	**High L/G**	**Low L/G**	**High L/G**	**Low L/G**	**High L/G**	**Low L/G**
Base case	99.99%	99.99%	0.12%	0.12%	4.92E-08	4.95E-08	6.2E-12	1.59E-15
Case 1 - HCl peak	99.98%	99.99%	0.10%	0.10%	6.14E-08	6.46E-08	1.67E-09	1.78E-09
Case 2 - SO_2 peak	99.98%	99.99%	0.11%	0.11%	1.63E-07	6.46E-08	1.72E-13	1.78E-09
Case 3 - G1 high pH	100.00%		0.27%		4.65E-07		9.65E-10	
Case 4 - G2 high pH	99.97%	99.98%	0.10%	0.10%	2E-09	1.11E-08	2.14E-10	3.1E-14

Table L-2. Results from simulations with the base case and cases 1-4 with high and low recirculation flow.

	HCl removal efficiency		**SO_2 removal efficiency**		**$CaSO_3$**		**$CaSO_4$**	
G2	**High L/G**	**Low L/G**	**High L/G**	**Low L/G**	**High L/G**	**Low L/G**	**High L/G**	**Low L/G**
Base case	100.0%	100.0%	0.5760	70.14%	25.37	31.43	6.918E-06	6.446E-06

Case 1 - HCl peak	100.0%	100.0%	0.7171	80.35%	94.95	108.8	6.787E-09	7.025E-06
Case 2 - SO2 peak	100.0%	100.0%	0.7517	80.92%	218.9	236.3	8.751E-06	2.661E-06
Case 3 - G1 high pH	100.0%	100.0%	0.7183	79.58%	42.26	40.94	6.114E-09	5.453E-06
Case 4 - G2 high pH	100.0%	100.0%	0.8654	89.95%	33.73	35.23	4.896E-06	8.785E-06