Master in Chemical Engineering

Flue gas desulphurization through wet limestone process – adding acids and bases to the limestone suspension

Master Thesis

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July 2010
Acknowledgments

The realization of this thesis was made possible due to all the individuals that supported me during my academic life, who confided in my personal capacities and motivated me.

First of all I would like to thank Pavel Machač for his orientation, accessibility, support and motivation provided during the last five months. I would also like to thank my laboratory partner, Tomáš Hásl, for all the help and collaboration he provided and for creating a friendly work environment.

To all my friends, especially during these last five months; a very special thank-you for the way you supported and stood by me throughout the good and bad moments.

I would also like to acknowledge the friends I created during these five months, who were able to, despite the distance, make me feel at home and helped me to overcome all the obstacles that arose during my stay in Prague.

A very special thank-you to André Maia, for all the support, patience and unconditional friendship and for always repeating the phrase: “You can do it.”

To my family, who always supported my decisions, gave me strength and lifted my spirit, as well as, for being patient. A very warm thank-you for the feelings they transmitted, and for always being by my side during the most complicated moments.
Abstract

Wet limestone is the most efficient and used method in the desulphurization process of combustible flue gas. Although, this process attains high levels of efficiency and/or minor rates of wasted limestone through the addition of certain substances in small quantities.

In this case, the principal aim of this project is to analyse and compare the desulphurization performance of a gaseous current after the addition of various organic acids and bases to limestone suspension. Such work is just a laboratorial experience and it is not supposed to implement in a larger scale.

The acids which were analysed during this project were adipic acid, maleic acid and glutaric acid, each with a concentration of 4.3mmol/L according to experimental experiences previously realised at ICT Prague under supervision of Pavel Machač. On the other hand, the addition of bases, such as, calcium oxide and Maalox (syrup used to treat stomach acid) were studied.

The obtained results were compared in view of the limestone conversion, as well as, the efficiency of the process confirmed for the gas volume in which the suspension was not saturated with SO$_2$ and for the other volume where some saturation was registered.

In conclusion, after all the results were analysed, the efficiency of the process attained levels superior to 99% and the conversion of limestone confirmed was 100% and 93% respectively, after the addition of 4.3mmol/L of adipic acid or the addition of Maalox with 4.3mmol of Mg(OH)$_2$ per litre of suspension. On the other hand, it was possible to confirm that the choice of one in detriment of the other is related to the proposed objectives of the desulphurization process (volume of gas to be considered, advantages/ wasted limestone).

Keywords: Wet flue gas desulphurization, limestone absorption, testing additives
Flue gas desulphurization through Wet Limestone Process – adding acids and bases to the limestone suspension

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Notation and Glossary

L  Liquid
G  Gas
SO₂  Sulphur dioxide
CaO  Calcium oxide
CaCO₃  Calcium carbonate/Limestone
H₂O  Water
O₂  Oxygen
CaSO₄.2H₂O  Calcium sulphate di-hydrate
CO₂  Carbon dioxide
H₂SO₃  Sulfurous acid
H⁺  Hydron
HSO₃⁻  Hydrogen sulfite
SO₃²⁻  Sulfite
Ca²⁺  Calcium
CO₃²⁻  Carbonate
HCO₃⁻  Bicarbonate
CaSO₃  Calcium sulfite
Ca(HSO₃)₂  Calcium hydrogen sulfite
Al(OH)₃  Aluminium hydroxide
Al(OH)₄⁻  Aluminate
C₅O₂  SO₂ concentration  mg/dm³
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{SO_2}$</td>
<td>Molar weight of SO$_2$</td>
<td>g/mol</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Efficiency</td>
<td>%</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Limestone conversion</td>
<td>%</td>
</tr>
</tbody>
</table>

**List of Abbreviations**

FGD – Flue Gas Desulphurization

WFGD – Wet Flue Gas Desulphurization
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1 Introduction

The economic progress has been accompanied by a growing energy demand. Such demand means more gaseous emissions, harmful to the environment, resulting from combustion.

Industries based on the use of coal need to control SO$_2$ emissions, because this kind of fuel presents a high level of sulphur. SO$_2$ is one of the principal gaseous pollutants emitted by human activity. It can be a hazard to human health and damages both the natural and built environments. High levels of SO$_2$ can cause respiratory illness and its presence in the environment causes acid rain that damages both vegetation and buildings. The need of controlling and reducing SO$_2$ emissions has therefore been recognized as important since the mid-19th century; many countries now set limits on the amount and concentration of sulphur compounds emitted from the stacks of industrial plants.

Emissions of SO$_2$ can be controlled in several ways: switch to a fuel that has lower sulphur content, or improve the efficiency of the industrial process so that less fuel is required. The sulphur in the fuel can in principle be removed before use; however, in practice, it is uneconomic to remove more than a small percentage of the sulphur. In many applications, the most efficient means of controlling SO$_2$ emissions is to remove the SO$_2$ from the flue gases before they are released to the atmosphere.

Several different flue gas desulphurization (FGD) technologies have been developed for this aim.\textsuperscript{(1)} Among this processes, due to its high efficiency, notice the wet limestone flue gas desulphurization process. This process is based on the reaction between a limestone suspension and the flue gases to promote maximum gas-liquid surface area in order to perform high removal efficiencies (up to 90%), remove the SO$_2$ and neutralize it.

This process is realized after combustion, or in other words, the sulphur is removed from the resulting combustion gases and not directly from the fuel. The
sulphur dioxide present in the flue gas passes through a chamber that exposes it to slurry of finely divided limestone. The slurry absorbs the SO$_2$ and the calcium existent in the limestone reacts with the SO$_2$ to form a mixture of calcium sulphite and calcium sulphate.

Nevertheless, this process is very complex due a straight relationship between the gases dissolution and the reactions stage: a good dissolution performance implies a high reaction rate (with sufficient limestone in the suspension), and vice versa.

The success of this relationship will determinate the removal efficiency level. High efficiency can be achieved if a high dissolution rate was verified, but obviously with optimal conditions for a good reaction performance. However, there is a strong dependence between these processes (dissolution and reaction) and several parameters. For instance, high pH levels promote a better SO$_2$ absorption in the liquid phase but low pH level increases the limestone dissolution.

There are many parameters with influence in the process and such parameters are related each other. So, the optimization is difficult to achieve because there is no theoretical model. Therefore, another way to reach high efficiency can be performed through the addition of some substances in small quantities – additives.

Thus, this work focuses on the test of several compounds as additives. Such compounds are organic acids (adipic, glutaric and maleic acids) and some basis (CaO and Maalox). Testing will consider the performance of each additive through the limestone conversion utilization and the desulphurization efficiency.

This work is organized as follows: chapter 2 will include a theoretical part where this type of FGD is classified, with a description of the wet limestone process fundamentals; in chapter 3, the instruments, samples of media, experimental installation and the procedure used during this work will be explained and characterized; chapter 4 will show the results obtained and the respective discussion; chapter 5 will contain concluding remarks and finally, in chapter 6 a project assessment will be made.
2 State of Art

Methods for removing sulphur dioxide from flues gases have been studied for over 150 years. Early concepts useful for FGD appear to have germinated in 1850 in England.

With the construction of large-scale power plants in England in the 1920s, the problems associated with large volumes of SO₂ emissions began to concern the public. The problem did not receive much attention until 1929, when the British government upheld the claim of a landowner against the Barton Electricity Works for damages to his land resulting from SO₂ emissions. Shortly thereafter a press campaign was launched against the increase of power plants within the confines of London. This led to the imposition of SO₂ controls on all such power plants. (2)

During this period, major FGD installations went into operation in England within three power plants. The first one began operation at the Battersea Station in London in 1931. In 1935, the second went into service at the Swansea Power Station. The third was installed in 1938 at the Fulham Power Station. All three installations were abandoned during World War II.

Large-scale FGD units did not reappear in commercial operation until the 1970’s, and most of the activity occurred in the United States and Japan. (2) As of June 1973, there were 42 FGD units, treating gases from power plants in size from 5 to 250 MW, in operation: 36 in Japan and 6 in the United States. (3)

As of about 1999/2000, there were 678 FGD units operating worldwide (in 27 countries) corresponding to a total of about 229 GW of energy produced in the respective power plants. About 45% of that FGD capacity was in the United States, 24% in Germany, 11% in Japan and 20% in other countries. Approximately 79% of the units, representing about 199 GW of capacity, were using lime or limestone wet scrubbing. About 18% (or 25 GW) utilized spray-dry scrubbers or dry sorbent injection systems. (4) (5) (6)
2.1 Flue Gas Desulphurization (FGD)

There are several technologies in order to remove the sulphur presented in the fuels used in many industries, like in power plants. This work focuses on a process where such removal is realized after combustion, i.e. the sulphur is removed from the resulting combustion gases and not directly from the fuel.

The FGD typically uses calcium or sodium based alkaline reagents. The reagent is injected in the flue gas in a spray tower or directly into the duct. The SO$_2$ is absorbed, neutralized and/or oxidized by the alkaline reagent into a solid compound, either calcium or sodium sulphate.\(^{(7)}\)

This process can be classified as non-renewable or renewable. In the first case, the reagent in the scrubber is consumed in order to directly generate a by-product containing the sulphur, such as gypsum. In the other case, the spent reagent is regenerated in a separate step to renew the reagent material for further use and to produce a separate by-product, such as elemental sulphur.\(^{(8)}\)

Both types of systems can be further categorized as dry, semi-dry or wet.\(^{(9)}\)

- **Dry-Process** (Furnace desulphurization process): The furnace desulphurization process is used for fluidized-bed boilers. Limestone to be used for desulphurization is mixed and combusted with the coal, causing the following reaction to remove SO$_2$ at a furnace temperature of 760-860 ºC:\(^{(9)}\)

\[
CaCO_3(s) \rightarrow CaO(aq) + CO_2(g) \quad (1)
\]
\[
CaO(aq) + SO_2(g) \rightarrow CaSO_3(aq) \quad (2)
\]

- **Spray Dryer Process** (Semi-Dry Process): The spray dryer process is a so-called "semi-dry process," where water is added to burned lime (CaO) to
Flue gas desulphurization through Wet Limestone Process – adding acids and bases to the limestone suspension

make a slack lime (Ca(OH)$_2$) slurry, which is sprayed into a spray dryer, causing the SO$_2$ in the flue gas to react with Ca(OH)$_2$, and to be removed. Within the dryer, the desulphurization reaction and limestone drying take place simultaneously, giving a particle mixture of gypsum (CaSO$_4$-H$_2$O) and calcium sulphite (CaSO$_3$-$\frac{1}{2}$H$_2$O). These particles are recovered at a down-stream precipitator. Since this process is not adequate for good-quality gypsum and, moreover, ash remains in the mix, desulphurized particles are disposed of as waste. (9)

- **Wet Process:** Wet FGD is the process of removing sulphur oxides, primarily SO$_2$ from combustion gases. In wet process FGD Systems, flue gases are in contact with an absorbent in the vessel called either an absorber or a scrubber. The SO$_2$ reacts with the absorbent or dissolves into the solution to produce slurry or liquid that contains dissolved or solidified sulphur compounds. Amongst the wet FGD system used in industries, the lime and limestone scrubbing are most commonly used. (10)

The Wet Flue Gas Desulphurization is the most commonly used method and the most efficient as shown in the table below:

<table>
<thead>
<tr>
<th>Desulphurization methods</th>
<th>The effectiveness of flue gas desulphurization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry fluidized bed combustion technology</td>
<td>80-90</td>
</tr>
<tr>
<td>Semi dry limestone method</td>
<td>60-90</td>
</tr>
<tr>
<td>Wet limestone method</td>
<td>≥96</td>
</tr>
</tbody>
</table>

Table 1: Relation between the different methods and efficiency of flue gas desulphurization (11)
2.2 Wet limestone method

Wet limestone flue gas desulphurization systems remove the sulphur dioxide from the flue gas by passing the flue gas through a chamber that exposes the flue gas to slurry of finely ground limestone. The slurry absorbs the SO\(_2\) from the flue gas and the calcium in the limestone reacts with the SO\(_2\) to form a mixture of calcium sulphite and calcium sulphate.\(^{(12)}\) The overall reaction of this process appears below and the operation conditions are T=60ºC and pH=5.

\[
\text{CaCO}_3 + \text{SO}_2 + 2\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} + \text{CO}_2
\]  

(3)

The reaction system is very complex. Many different processes take place inside the absorber and in the reaction vessel. There are two basic processes: mainly the physical absorption of SO\(_2/\)CO\(_2/\)O\(_2\) and some chemical reactions. One way to express these chemical processes is by means of equations (4)-(14):\(^{(13)}\)

- **Gas diffusion/dissolution:**
  \[
  \text{SO}_2(\text{g}) \leftrightarrow \text{SO}_2(\text{aq}) \quad (4)
  \]
  \[
  \text{SO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_2\text{SO}_3(\text{aq}) \quad (5)
  \]
  \[
  \text{H}_2\text{SO}_3(\text{aq}) \leftrightarrow \text{H}^+(\text{aq}) + \text{HSO}_3^-(\text{aq}) \quad (6)
  \]
  \[
  \text{HSO}_3^-(\text{aq}) \leftrightarrow \text{H}^+(\text{aq}) + \text{SO}_3^{2-}(\text{aq}) \quad (7)
  \]

- **Solid diffusion/dissolution:**
  \[
  \text{CaCO}_3(\text{s}) \leftrightarrow \text{CaCO}_3(\text{aq}) \quad (8)
  \]
  \[
  \text{CaCO}_3(\text{aq}) \leftrightarrow \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \quad (9)
  \]

- **Reactions:**
  \[
  \text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \leftrightarrow \text{HCO}_3^-(\text{aq}) \quad (10)
  \]
  \[
  \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \leftrightarrow \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \quad (11)
  \]
  \[
  \text{SO}_2(\text{aq}) + \text{HCO}_3^-(\text{aq}) \leftrightarrow \text{HSO}_3^-(\text{aq}) + \text{CO}_2(\text{aq}) \quad (12)
  \]
  \[
  \text{SO}_2(\text{aq}) + \text{SO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow 2\text{HSO}_3^-(\text{aq}) \quad (13)
  \]
  \[
  \text{CO}_3^{2-}(\text{aq}) + \text{HSO}_3^-(\text{aq}) \leftrightarrow \text{HCO}_3^-(\text{aq}) + \text{SO}_3^{2-}(\text{aq}) \quad (14)
  \]
Expressing in a non-ion way, an overall view about the process can be synthesized by the equations (15)-(20):

\[
\begin{align*}
\text{SO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) & \rightarrow \text{H}_2\text{SO}_3(\text{aq}) \quad (15) \\
\text{CaCO}_3(\text{aq}) + \text{H}_2\text{SO}_3(\text{aq}) & \rightarrow \text{CaSO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{aq}) \quad (16) \\
\text{CaCO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{SO}_2(\text{aq}) & \rightarrow \text{Ca(HSO}_3)_2(\text{aq}) + \text{CO}_2(\text{aq}) \quad (17) \\
\text{Ca(HSO}_3)_2(\text{aq}) + \text{CaCO}_3(\text{aq}) & \rightarrow 2\text{CaSO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{aq}) \quad (18) \\
\text{CaSO}_3(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(\text{aq}) & \rightarrow \text{CaSO}_4.2\text{H}_2\text{O (aq)} \quad (19) \\
\text{Ca(HSO}_3)_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(\text{aq}) & \rightarrow \text{CaSO}_4.2\text{H}_2\text{O (aq)} + \text{SO}_2(\text{aq}) \quad (20)
\end{align*}
\]

However, throughout the process, there is a critical step that is the resistance against SO₂ diffusion in the liquid phase, and in this way the dissolution rate of limestone. The relationship between dissolutions and reactions affects the global efficiency of the process. Furthermore, this relationship may be affected by several parameters, seen below, as demonstrated by Jerzy Warych and Marek Szymanowski. (14)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Range of parameter value</th>
<th>Min and max efficiency value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry pH</td>
<td></td>
<td>5.2-5.8</td>
<td>86.4-93.5</td>
</tr>
<tr>
<td>Drop diameter</td>
<td>μm</td>
<td>2000-3000</td>
<td>74.5-99.3</td>
</tr>
<tr>
<td>Height of the absorption section</td>
<td>m</td>
<td>6-18</td>
<td>66.5-99.7</td>
</tr>
<tr>
<td>Magnesium concentration</td>
<td>kmol/m³</td>
<td>0.03-0.13</td>
<td>66.4-95.0</td>
</tr>
<tr>
<td>Chloride concentration</td>
<td>kmol/m³</td>
<td>0.1-0.3</td>
<td>83.6-93.4</td>
</tr>
<tr>
<td>Inlet SO₂ concentration</td>
<td>ppm</td>
<td>1500-5000</td>
<td>73.4-97.0</td>
</tr>
<tr>
<td>Gas velocity</td>
<td>m/s</td>
<td>2-4</td>
<td>90.0-98.9</td>
</tr>
<tr>
<td>L/G ratio</td>
<td>dm³/m³</td>
<td>8-15</td>
<td>68.3-97.7</td>
</tr>
</tbody>
</table>
In order to achieve the best efficiency of the process, there are two possible ways:

- Achieving the optimum values for each parameter by a optimization strategic technique;
- Add more substances to the process – additives.

However, the first case is a difficult way because there is a strong dependence between the various parameters. For example, changing the size of particles, is already affecting the interface L/G. In addition, there is no model known for this case.

Therefore, this work focuses on additive action alternative, since through the addition of substances in small concentrations, it’s possible to increase the overall process efficiency and thus reduce investment and operating costs.

This efficiency could be improved if, on one hand the SO\textsubscript{2} transfer rate from the gas phase to the liquid phase increases, and/or on the other hand the limestone dissolution is promoted.

Being absorbed in the liquid phase, SO\textsubscript{2} originates the sulphite ion, SO\textsubscript{3}\textsuperscript{2-}, which is continually neutralized by Ca\textsuperscript{2+} ion derived from limestone dissolution. So, by increasing the Ca\textsuperscript{2+} concentration, the absorbed SO\textsubscript{2} neutralization becomes faster, and consequently, the gas absorption becomes faster too.

Thus, for this reason, the addition of alkaline ions, like Na\textsuperscript{+}, Mg\textsuperscript{2+} or Ca\textsuperscript{2+}, is a hypothesis to improve the SO\textsubscript{2} absorption efficiency.

In addition, organic acids can be seen as a vapour-liquid mass transfer enhancing effect. For instance, once the interface G/L becomes saturated with SO\textsubscript{2}, no more SO\textsubscript{2} can be dissolved, even if the bulk liquid has not yet reached saturation levels. So, the dissolving stage can continue as SO\textsubscript{2} diffuses away from the surface into the bulk liquid (too slow), or if the concentration of SO\textsubscript{2} at the surface of the liquid can be minimized in other ways, such as through chemical reactions (relatively fast compared with SO\textsubscript{2} diffusion). This can be accomplished by the buffer effect of the
added acid, which consumes the acidity generated by SO₂ as it dissolves, converting SO₂ into sulphite salts.

Organic acids can also be seen as solid-liquid mass transfer enhanced factor. It allows the operation of the scrubber at a lower pH than would otherwise be possible. (15)

As seen above, high pH is desirable for maximum SO₂ absorption (better acidity neutralization), but, as shown below in figure 1 low pH is desirable for a maximum rate of limestone dissolution.

![Figure 1: Limestone dissolution speed at various pH and CO₂ out pressure [atm] (16)](image)

Thus, this work focuses on testing the addition of three organic acids as adipic, glutaric and maleic acids and two bases as Maalox and CaO.
3 Experimental Framework

The principal aim of this experimental work was the improvement of the flue gas desulphurization by wet limestone process through lab-scale research. Several measurements were made in order to find the best additives that enhance the process efficiency – higher SO₂ absorption.

In this chapter the equipments and the samples used, as well as, information that characterizes the samples will be addressed.

On the other hand, a description of the experimental procedure and a demonstration of the used experimental facility will be provided.

3.1 Analytical methods and devices used

Subsequently, it is described all the equipments and technical data used during the experiments performed. (17) (18) (19) (20) (21)

3.1.1 Servomex Xentra 4900 - SO₂ analyser

This analyzer consists of two channels that measure the concentrations of SO₂, which operate based on infrared absorption spectrometry and uses a gas filter correlation. This instrument has a measuring range of 0-3300 ppm of SO₂, with an error of ± 1%.
3.1.2 Cooling Module 407

This device has three independent non-corrosive paths, as a cooling source is used compressor type of refrigerator, switched on by temperature regulator, together with the peristaltic pump of condensate exhaust. Maximum temperature of the input gas is 80 °C and a maximum gas flow of 200 l/hr.

![Figure 3: Servomex and Cooling Module 407](image)

3.1.3 Gas meter

This instrument performs precise measurements of the gas volume used during all the process, however, the pressure upper limit of the gas meter is 1200 kPa. First, it was necessary to calibrate it in order to determine the correction factor of gas volume measured.

In the follow figure, a photograph of the used gas meter is shown.

![Figure 4: Gas meter](image)
3.1.4 pH Meter 340

Through this device, it is possible to measure the temperature and the pH level of the solution inside the reactor. Such measurement is realized through one sounding-line that when not in use, must be maintained in an aqueous environment to not be damaged.

Figure 5 shows a photograph of the pH meter used.

![Figure 5: pH Meter 340](image)

3.2 Limestone and pure calcium carbonate - samples and their characteristics

With a basic standard to carry out the suspension preparation, Devon-Barrandian - Čerstový Schody limestone was chosen due to its elevated level of purity that is adequate for environmental functions. This material was provided by Melnik, whereby it is used as raw material in the WFGD process.

By means of comparison, pure calcium carbonate (prepared by precipitation), fabricated by Lachema Neratovice was chosen.

In the following figures, frequency distribution is represented where (1) and (2) show the cumulative frequency and density distribution, respectively.
Flue gas desulphurization through Wet Limestone Process – adding acids and bases to the limestone suspension

The most important reading and the statistical analysis of the data are represented in the chart below:

Table 3: Frequency distribution of limestone and pure CaCO$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Part of sample certain size in [%]</th>
<th>Average [μm]</th>
<th>Mode [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Čerstovy Schody Limestone</td>
<td>5 &lt;10μm 91.5 &lt;20μm &lt;40μm &lt;100μm</td>
<td>4.56</td>
<td>15.49</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>3.3 14.5 54.1 98.3</td>
<td>37.34</td>
<td>34.1</td>
</tr>
</tbody>
</table>

As shown in table 3, the size of the majority of the Čerstovy Schody limestone particles is less than 40 μm, while pure CaCO$_3$ is less than 100 μm. In order to reach comparable parameters, the calcium carbonate was grinded in the same manner as the limestone, as shown in the figure below and the tables that follow.
Flue gas desulphurization through Wet Limestone Process – adding acids and bases to the limestone suspension

**Experimental Framework**

Table 4: Frequency distribution from grinded pure CaCO$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Part of sample certain size in [%]</th>
<th>Average [μm]</th>
<th>Mode [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulverized CaCO$_3$</td>
<td>&lt;10μm 97.8 99.9 100</td>
<td>3.48</td>
<td>5.13</td>
</tr>
</tbody>
</table>

The table below shows the surface area values (BET) and the pore volume of the samples.

Table 5: Samples BET surface and pores volume

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface [m$^2$.g]</th>
<th>Pore volume [ml.g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Čerstovy Schody Limestone</td>
<td>2.061</td>
<td>0.0092</td>
</tr>
<tr>
<td>Pure CaCO$_3$</td>
<td>0.063</td>
<td>0.0022</td>
</tr>
</tbody>
</table>

Through the analysis of table 5, we can verify the major difference in the surface area of both samples. Therefore, the sample which is more adequate is Čerstovy Schody Limestone since it shows a greater surface area and consequently potentially greater absorption than SO$_2$.

Table 6 summarizes the principle components existent in both samples.
3.3 The additives

As previously stated, additives are additional substances in small quantities with the objective of improving the efficiency of the process. In this work, two types of additives were used: organic acids (adipic acid, glutaric acid and maleic acid) and bases (Maalox and CaO).

3.3.1 Organic acids

The choice on the organic acids to be studied was based on cost, low volatility and elevated stability during the desulphurization process.

Thus, the three acids chosen (adipic, maleic and glutaric), comply with these requisites and their properties are shown in the table below:

<table>
<thead>
<tr>
<th>Acid</th>
<th>Molecular Formula</th>
<th>Molar Mass (g/mol)</th>
<th>Dissociation constant pKa (T=25°C)</th>
<th>pKα₁</th>
<th>pKα₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adipic</td>
<td>C₆H₁₀O₄</td>
<td>146.14</td>
<td></td>
<td>4.41</td>
<td>5.41</td>
</tr>
<tr>
<td>Glutaric</td>
<td>C₅H₈O₄</td>
<td>132.12</td>
<td></td>
<td>4.32</td>
<td>5.41</td>
</tr>
<tr>
<td>Maleic</td>
<td>C₄H₄O₄</td>
<td>116.07</td>
<td></td>
<td>1.91</td>
<td>6.33</td>
</tr>
</tbody>
</table>
According to Frandsen \(^{(24)}\), the greater the value of pKa, the greater the absorption efficiency of SO\(_2\). Therefore, while analyzing pKa values, it is expected to have an identical buffer effect verified in the three cases. On one hand, the dissociation constants of the adipic and glutaric acids are practically the same; on the other hand, despite the fact that the maleic acid presents more elevated pKa\(_2\), it also presents a lower pka1 value.

### 3.3.2 Bases

Another possibility tested in this work, was the addition of bases with the intent of increasing pH and therefore favour the dissolution of calcium.

First we tested the influence of syrup used to combat human stomach acid – Maalox with magnesium hydroxide, strong base, and aluminium hydroxide, which despite the fact that it presents an anphoteric character, is dissolvable in strong bases. Therefore, Al(OH)\(_3\) forms a Al(OH)\(_4^-\) ion, leaving the magnesium ion “free” to react with the sulphite ion existent in the G/L interface promoting better absorption of SO\(_2\). Due this reaction and to the buffering effect, were several experiments realized with Maalox addition. In this syrup, in 100 ml, there are 3.5 g of Al(OH)\(_3\) and 4 g of Mg(OH)\(_2\).

On the other hand, the addition of calcium oxide, CaO, was also tested, and besides producing a more basic character to the solution, could imply less consumption of limestone, since it already contains calcium ions.

### 3.4 Experimental Procedures

Before each experiment, the thermostatic bath was fixed at 60ºC because the reaction occurs at this temperature. Cleansing of the SO\(_2\) residual system was also carried out through a cleaning process using atmospheric air.
Meanwhile, for the suspension preparation, two grams of the sample were weighed with an analytical scale and these were placed in the reactor with 100ml of distilled water. The additives used were also prepared considering their analytical weight, with the necessary quantities previously calculated. Next, the reactor was placed in the solution and the gas valve was opened, whereby the acquisition of data began.

During each experimental activity, in intervals of 5 minutes, the concentration values of SO$_2$, pH, temperature and gas volume were read through the equipment’s display unit, and registered.

### 3.5 Experimental set-up

During this experiment the mechanisms used were always the same, composed of a variety of processing apparatus/units, with the following schematic representation (figure 9):

![Diagram apparatus to measure SO2 absorption.](image)

The gaseous mixture containing SO$_2$, found in the cylinder, is divided in two paths: the first is through a manostat in order to maintain the pressure monitored; the second path is through tubing in the interior of the reactor.
In the reactor, the gas passes through an absorbing suspension from the base to the top in a manner that guarantees a good mixture of the solution, since the reactor presents a conic form. The reactor is equipped with a pH measurer, which also provides information about the temperature of the suspension. In the following figures it is possible to observe the reactor used, as well as, the necessary suspension for the absorption of SO₂.

![Figure 10: Mixing suspension detail](image1)
![Figure 11: Detail of the reactor](image2)

During the reaction a wet gas containing CO₂ and H₂O, as a result of vaporization, was formed and the SO₂ that was not absorbed did not react. This gas is driven to a condenser with the objective of drying it by condensing the water vapour. This water vapour returns to the reactor while the dry gas is directed to the analyser (Servomex Xentra 4900) in a manner which allows the concentration of SO₂ to be measured.

The volume of gas that comes from the reactor is measured through a gas meter. Therefore, once the reaction occurs with low pH, it will be necessary to protect this equipment from the corrosion provoked by the acid (resulting from unreacted SO₂), which is why two washers containing hydrogen peroxide were included.
4 Results and Discussion

In order to analyse the data obtained from the measurements taken, Microsoft Excel™ was used.

The results will be presented in graph and table formats, and concentration will always be expressed in mg/dm³. Therefore, since the concentration of SO₂, measured by Servomex, at the entry and exit points is expressed in ppm, it is necessary to convert these values to mg/dm³. This conversion is done through the following equation (21), considering that molarities of gas occupy, through the law of ideal gases, 24.05 dm³, and laboratory conditions, temperature and pressure are constant at 20ºC and 1 atm respectively.

\[
C_\text{SO}_2 \text{[mg/dm}^3\text{]} = \frac{C_\text{SO}_2 \text{[ppm]} \times M_{\text{SO}_2 } \text{[g/mol]}}{24.05 \text{[dm}^3\text{/mol]} \times 10^3}
\]  \hspace{1cm} (21)

Thus, after reading these values of concentration at the entrance and exit of the reactor, through Servomex, it is easily converted to a more convenient unit mg/dm³.

To calculate the mass of SO₂ that reacts, it is necessary to know the mass of SO₂ present at the entrance and exit of the reactor, once the mass balance has been applied to this, the difference between the quantity of SO₂ that enters and the quantity that leaves the system is the quantity of SO₂ that reacted.

In each experiment, the reactor is always exposed to the same concentration of SO₂. Therefore, through the product between the concentration of SO₂ in the feeder and the total volume of gas fed through the system (measured by the gas meter) the total mass of SO₂ that entered the reactor during the reaction time is determined.

However, at the exit point, the concentration varies (increasing) since initially, practically all the SO₂ that enters is absorbed through the suspension; then, as the suspension becomes saturated, the greater is the quantity of SO₂ that exits the system.
without reacting. Either in this example, either during all realizations made along this work, the desulphurization process was stopped when the outlet SO\textsubscript{2} concentration reached 100 ppm.

This situation is demonstrated by figure 11, where an experiment was carried out only through the use of one suspension containing 2g of limestone and without any additives.

![Figure 12: Details of the Breakthrough curve and area of unreacted SO\textsubscript{2}](image)

Therefore it is necessary to use the concept of cumulative mass, in order to determine the quantity of SO\textsubscript{2} that did not react and left the system.

Thus, through the integral resolution of the descriptive curve in the above graph, in other words, by determining the area “below” the curve, the mass of SO\textsubscript{2} that left the reactor is determined.

As mentioned above, the difference between the mass of SO\textsubscript{2} that entered the reactor and the mass that exits the reactor is the mass that reacted, in other words, the quantity of SO\textsubscript{2} removed from the gaseous current through desulphurization.

Knowing the concentration at the exit point and the mass of SO\textsubscript{2} that was removed, it is possible to evaluate the efficiency of the process in two ways: efficiency (\(\eta\)) and the limestone conversion. Efficiency indicates the percentage of SO\textsubscript{2} removed
verified at a certain point. On the other hand, the limestone conversion points to the quantity of limestone used.

Thus, the efficiency verified at a certain point is calculated through the difference between the concentrations at the entrance and exit points and the concentration at the point of entry $SO_2$ – equation (22).

$$\eta = \frac{c_{SO_2, in} - c_{SO_2, out}}{c_{SO_2, in}} \times 100$$  \hspace{1cm} (22)

For example, in the experiment described above (figure 11), two points were chosen to show the logic of what occurred: after the addition of 100 and 120 dm$^3$ of gas. This decision was made in a manner that allowed the analysis of when the absorption rates are elevated and another in which the verification of the suspension saturation starts.

The graph indicates that for 100 dm$^3$ the concentration of $SO_2$ at the exit point is 34.8 ppm (0.093 mg/dm$^3$) and that for 120 dm$^3$ it is 78.1 ppm (0.28 mg/dm$^3$). The $SO_2$ concentration of at the entrance point is constant, 3000 ppm (8.0 mg/dm$^3$).

Thus, the efficiency for these two points is given by the following:

$$\eta_{100 \text{ dm}^3} = \frac{8.0 - 0.093}{8.0} \times 100 = 98.8\%$$

$$\eta_{200 \text{ dm}^3} = \frac{8.0 - 0.28}{8.0} \times 100 = 97.4\%$$

On the other hand, knowing the amount of $SO_2$ that was removed, it is possible to calculate the quantity of CaCO$_3$ that reacted, by resorting to the stoichiometry of the reaction, 1:1 (equation 3). This value is calculated by multiplying the mass of $SO_2$ absorbed through the mass mole of calcium carbonate and the Sulphur Dioxide.

Through the calculation of the area below the curve, the $SO_2$ mass that did not react can be determined as 7.9 mg. Considering that 127 dm$^3$ of gas with 8 mg of $SO_2$ entered the reactor per dm$^3$, the total mass of $SO_2$ that entered the reactor was 1016 mg. Therefore, a total of 1008.1 mg of $SO_2$ was removed.
The other method of analysing the efficiency process is through the limestone conversion – equation (23) – given through the CaCO$_3$ that reacted and the limestone mass introduced in the reactor.

\[
\chi = \frac{m_{\text{CaCO}_3 \text{ reacted}}}{m_{\text{limestone inlet}}} \times 100
\]  

(23)

As already mentioned, for the example described above, 1008.1 mg of SO$_2$ were removed, which corresponds to the mass of 1573.4 mg of CaCO$_3$ that reacted. Therefore, the limestone conversion is given by:

\[
\chi = \frac{1573.4}{2000} \times 100 = 78.7\%
\]

(24)

From this point forward, all the results will be presented will follow this logic. As a result, no more calculations will be presented, only the results obtained and their respective analysis.
4.1 Organic acids addition

In order to evaluate the effects of the organic acids in the efficiency process, various experiments were carried out, adding acid in order to the resulting concentration inside the reactor were 4.3 mmol of each acid per litre of calcium carbonate suspension.

The current of gas intended for desulphurization was composed by 7% O₂, 13% CO₂, 0.3% SO₂ (corresponding to 3000 ppm) and the remaining N₂.

Thus, for each acid being studied, adipic, glutaric and maleic, the concentrations of SO₂ was registered at the exit of the reactor considering the volume of gas used – figure 12.

By analysing figure 12, it is possible to affirm that the adipic acid and the glutaric acid present identical results for the lower volumes of gas, whereas for greater volumes a mismatch is verified. The maleic acid presents a behaviour which is very similar to the experiment that contains only limestone.

Figure 13: Comparison between organic acids addition
By calculating the area below the curves, it is possible to have a more detailed analysis of the efficiency of each additive. In the table below these results are presented:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of reacted SO₂ [mg]</th>
<th>Limestone conversion [%]</th>
<th>Efficiency η by: 100 dm³ [%]</th>
<th>120 dm³ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>1007</td>
<td>79</td>
<td>98.8</td>
<td>97.4</td>
</tr>
<tr>
<td>+ Adipic acid</td>
<td>1277</td>
<td>100</td>
<td>99.6</td>
<td>99.2</td>
</tr>
<tr>
<td>+ Glutaric acid</td>
<td>1103</td>
<td>86</td>
<td>99.6</td>
<td>98.9</td>
</tr>
<tr>
<td>+ Maleic acid</td>
<td>1053</td>
<td>82</td>
<td>98.9</td>
<td>98.1</td>
</tr>
</tbody>
</table>

For a low volume of gas (100 dm³) the efficiency of the process is the same for the adipic and the glutaric acids, which is greater than the efficiency of the maleic gas (practically equal to the efficiency process that does not contain any additives), as indicated by the graph.

For volumes that show a minor absorption (120 dm³), the difference between the efficiency of the adipic and the glutaric acids is highlighted, in which the first is more efficient, where as the maleic acid presents only slight improvements in relation to the process which used only limestone.

On the other hand, it is also verified that a greater quantity of SO₂ reacts by the addition of adipic acid, which implicates a better limestone conversion – 100%.

Figure 13 shows the behaviour of pH throughout the experiments. The solution which is initially alkaline, rapidly changes to acid. This disparity in pH is more abrupt for the maleic acid, since it presents a pKa1 value much lower than the rest, as shown in table 7.

Lower the pH greater the dissolution of limestone in the suspension. On the other hand, this presents difficulties in the transfer of mass G/L. Therefore, the
experiment which show greater efficiency was the one in which a lower disparity of pH was verified.

![Figure 14: pH behaviour during organic acids realizations](image)

In sum, in order of efficiency decline (and the limestone conversion), these tested additives are organized in the following manner: adipic acid, glutaric acid, maleic acid.

### 4.2 Maalox addition

As previously mentioned, Maalox is used in the treatment of stomach acid.

This experiment is interesting since it shows the capacity of desulphurization without the presence of calcium ions, due to the fact that Maalox is composed principally by $\text{Mg(OH)}_2$ and $\text{Al(OH)}_3$.

Therefore an experiment was carried out without limestone, only 15 ml of Maalox with the intent of testing the capacity of this syrup’s absorption. On the other hand, two experiments with Maalox as an additive to the suspension that contained 2g of limestone were also carried out.

Considering that these two components are not proportioned, two different suspensions were used: one with 2g of limestone + 2.51 ml of Maalox – which corresponds to 4.3mmol/L of $\text{Mg(OH)}_2$ and another with 2g of limestone + 3.83 ml of
Maalox – equivalent to 4.3mmol/L of Al(OH)$_3$. The results for these three experiments are presented in the following figure, as well as, the experiment which used only limestone.

![Figure 15: Comparison between different concentrations of Maalox addition](image)

Figure 15 indicates that the experiments with Maalox present a significant improvement, in comparison to the one without any additives. On the other hand, the desulphurization which used only Maalox seems to be less efficient.

Table 9 shows the efficiency values obtained for each experiment, after the calculation of the area below the curve, indicating that the experiment which indicated greater efficiency was the one in which 2.51 ml of Maalox was added to the limestone suspension.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of reacted SO$_2$ [mg]</th>
<th>Limestone conversion [%]</th>
<th>Efficiency $\eta$ by: $\frac{100 \text{ dm}^3}{%}$</th>
<th>$\frac{120 \text{ dm}^3}{%}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>1007</td>
<td>79</td>
<td>98.8</td>
<td>97.4</td>
</tr>
<tr>
<td>15 ml Maalox</td>
<td>721</td>
<td>-</td>
<td>93.3</td>
<td>82.1</td>
</tr>
<tr>
<td>2g limestone + 2.51 ml Maalox</td>
<td>1189</td>
<td>93</td>
<td>99.8</td>
<td>99.5</td>
</tr>
<tr>
<td>2g limestone + 3.83 ml Maalox</td>
<td>1102</td>
<td>86</td>
<td>99.7</td>
<td>99.1</td>
</tr>
</tbody>
</table>
The principal difference (in the efficiency and limestone conversion) between the two experiments in which Maalox was added to the limestone suspension, probably resides in the pH values registered. As previously mentioned, pH plus acid favours the dissolution of limestone, facilitating the appearance of Ca$^{2+}$ ions that will eventually react with the absorbed SO$_2$.

Despite the fact that the pH verified in both experiments with additives is slightly superior to the one verified in the standard experiment (only with limestone), the levels of efficiency presented are also slightly superior due to the induced effect of additives, essentially, magnesium ions.

By observing the graph in figure 16 that represents the evolution of pH considering the volume of gas introduced in the system, and indicates the suspension which contains additives, the one that presents greater values of pH is the one that shows more efficiency – 2 g of limestone + 2.51 ml of Maalox.

![Graph showing pH behaviour during Maalox realizations](image)

**Figure 16**: pH behaviour during Maalox realizations
4.3 CaO addition

The dissolution of calcium oxide in water originates calcium hydroxide, a strong base. Besides being a strong base, it presents calcium ions which, in theory, favour the transfer of SO$_2$ from gas to liquid.

Contrary to the other experiments carried out with additives that had a concentration of 4.3 mmol/L, the option of the following experiments was to use an additive with 2.5%; 5%; 10% and 20% of CaO to, respectively, 97.5%; 95%; 90% e 80% of limestone.

In each experiment the quantity of calcium presented in the suspension was the same, meaning that the behaviour was similar in all experiments: the concentration level of SO$_2$ that is verified at the exit of the reactor, and the pH values observed, as demonstrated in figures 17 and 18.

![Figure 17: Comparison between different quantities of limestone and CaO addition](image)

Considering this similarity in behaviour, the levels of efficiency are quite close. Therefore, as suggested by the previous graph and proven in table 10, the experiment which contains 97.5% of limestone and 2.5% of CaO presents relative improvements in comparison to the experiment which contains only limestone. There is still another
experiment which presents improved results, compared to the standard experiment – 90% limestone and 10% CaO.

**Table 10: Efficiency and limestone conversion for CaO addition**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of reacted SO$_2$ [mg]</th>
<th>Limestone conversion [%]</th>
<th>Efficiency $\eta$ by: 100 dm$^3$ [%]</th>
<th>120 dm$^3$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>1007</td>
<td>79</td>
<td>98.8</td>
<td>97.4</td>
</tr>
<tr>
<td>90% limestone + 10% wet CaO</td>
<td>1016</td>
<td>79</td>
<td>99.1</td>
<td>97.5</td>
</tr>
<tr>
<td>97.5% limestone + 2.5% wet CaO</td>
<td>1083</td>
<td>85</td>
<td>99.4</td>
<td>98.3</td>
</tr>
<tr>
<td>95% limestone + 5% wet CaO</td>
<td>974</td>
<td>76</td>
<td>98.6</td>
<td>96.8</td>
</tr>
<tr>
<td>80% limestone + 20% wet CaO</td>
<td>1002</td>
<td>78</td>
<td>98.6</td>
<td>96.8</td>
</tr>
</tbody>
</table>

**Figure 18: Comparison between different proportion of CaO and limestone addition**

The principle behavioural differences are due to the greater, or minor, resistance of Ca$^{2+}$ mass transfer, between solid and liquid; first the calcium ions introduced in calcium (hydr)oxide form react with the absorbed sulphur dioxide, and secondly react with SO$_2$ and Ca$^{2+}$ ions resulting from the limestone.

In sum, this type of additive does not provide significant improvements to the process.
4.4 Wet CaO vs dry CaO

The calcium oxide produced industrially is very hygroscopic, in other words, easily absorbs the air humidity, as well as, other impurities. Thus it is interesting to observe the differences that occur with the addition of dry “CaO” produced in a laboratory. So, the industrial calcium oxide was dried at 100°C.

Therefore, with the intent of comparing the effects provoked by the addition of “dry” and “wet” CaO, various experiments were carried out, considering the different proportions of limestone: CaO – 90% limestone + 10% CaO; 95% limestone + 5% CaO and 97.5% limestone + 2.5% CaO.

4.4.1 90% limestone + 10% CaO

The results obtained for the experiments with 90% limestone + 10% CaO, for both samples of CaO (“dry” and “wet”) are found in the graph below and in table 11.

![Graph](image-url)

*Figure 19: Comparison between 10% CaO wet and 10% CaO dry addition*
Table 11: Efficiency and limestone conversion for 90% limestone + 10% CaO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of reacted SO$_2$ [mg]</th>
<th>Limestone conversion [%]</th>
<th>Efficiency $\eta$ by:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1007</td>
<td>79</td>
<td>98.8 97.4</td>
</tr>
<tr>
<td>90% limestone + 10% wet CaO</td>
<td>1016</td>
<td>79</td>
<td>99.1 97.5</td>
</tr>
<tr>
<td>90% limestone + 10% dry CaO</td>
<td>1097</td>
<td>86</td>
<td>99.5 98.5</td>
</tr>
</tbody>
</table>

As shown above, there are only slight improvements; nevertheless, the dry limestone presents better results.

4.4.2 95% limestone + 5% CaO

As previously seen, the proportion of 95% limestone and 5% “wet” CaO does not bring any advantage in comparison to the process without additives, in addition, as shown in figure 20 and table 12, for the same proportion of “dry” calcium oxide a tenuous improvement of desulphuration is verified with low volumes of gas (100 dm$^3$); nevertheless, for elevated volumes (120 dm$^3$) the desulphuration indexes are worse than those verified in the standard experiment.
Table 12: Efficiency and limestone conversion for 95% limestone + 5% CaO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of reacted SO₂ [mg]</th>
<th>Limestone conversion [%]</th>
<th>Efficiency η by:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>100 dm³ [%]</td>
</tr>
<tr>
<td>Limestone</td>
<td>1007</td>
<td>79</td>
<td>98.8</td>
</tr>
<tr>
<td>95% limestone + 5% wet CaO</td>
<td>1016</td>
<td>76</td>
<td>98.6</td>
</tr>
<tr>
<td>95% limestone + 5% dry CaO</td>
<td>1097</td>
<td>76</td>
<td>99.0</td>
</tr>
</tbody>
</table>

4.4.3 97.5% limestone + 2.5% CaO

As observed in section 4.3, this was the proportion that presented better results, which can be compared with those obtained from the experiment with “dry” calcium oxide, as shown in the figure below and table 13.

Figure 21: Comparison between 2.5% CaO wet and 2.5% CaO dry addition
Flue gas desulphurization through Wet Limestone Process – adding acids and bases to the limestone suspension

Table 13: Efficiency and limestone conversion for 97.5% limestone + 2.5% CaO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of reacted SO₂ [mg]</th>
<th>Limestone conversion [%]</th>
<th>Efficiency η by: 100 dm³ [%]</th>
<th>120 dm³ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>1007</td>
<td>79</td>
<td>98.8</td>
<td>97.4</td>
</tr>
<tr>
<td>97.5% limestone + 2.5% raw CaO</td>
<td>1083</td>
<td>85</td>
<td>99.4</td>
<td>98.3</td>
</tr>
<tr>
<td>97.5% limestone + 2.5% dry CaO</td>
<td>1100</td>
<td>86</td>
<td>99.6</td>
<td>98.8</td>
</tr>
</tbody>
</table>

As shown in all experiments in which “dry” CaO was compared with “wet” CaO, in this case, CaO also presents greater efficiency indexes.

The levels of pH verified throughout the experiments in this section were practically the same in all cases. Therefore, the principle differences did not occur due to the effects of pH, but rather due to the “purification” provoked by the drying effect of the calcium oxide.

4.5 Maalox vs CaO

In order to decide which minor basic additive to use in the desulphurization process, we compared the addition of Maalox for each 4.3mmol/L of the principle additives with the addition of 4.3mmol/L of CaO. The results of this comparison are indicated in the following figure and table.

![Figure 22: Comparison between CaO and Maalox addition](image-url)
Table 14: Efficiency and limestone conversion for different bases

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of reacted SO₂ [mg]</th>
<th>Limestone conversion [%]</th>
<th>Efficiency η by: 100 dm³ [%]</th>
<th>120 dm³ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2g limestone + 4.3 mmol/L CaO</td>
<td>886</td>
<td>69</td>
<td>97.7</td>
<td>92.8</td>
</tr>
<tr>
<td>2g limestone + 2.51 ml Maalox</td>
<td>1189</td>
<td>93</td>
<td>99.8</td>
<td>99.5</td>
</tr>
<tr>
<td>2g limestone + 3.38 ml Maalox</td>
<td>1102</td>
<td>86</td>
<td>99.7</td>
<td>99.1</td>
</tr>
</tbody>
</table>

The experiment that shows better levels of efficiency is the one which contains 2g of limestone + 2.51ml of Maalox, in other words, 4.3mmol/L of Mg(OH)₂.

4.6 Acid vs Base

Section 4.1, demonstrated that the best acid additive was adipic acid. On the other hand, the previous section noted that the best base additive was Maalox. Thus, the results obtained from the following addition were compared: 2g of limestone, 2.51 of Maalox with 4.3mmol/L of adipic acid added.

The graph shows that for low volumes Maalox is lightly better and that for elevated volumes the adipic acid presents better results. Although, through the
calculation of efficiency for the volumes studied, 100 and 120 dm$^3$, this is not verified. Therefore, in table 15 the information of the efficiency obtained from 150 dm$^3$ of gas was added.

Table 15: Efficiency and limestone conversion for the best acid additive and the best base additive

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of reacted SO$_2$ [mg]</th>
<th>Limestone conversion [%]</th>
<th>Efficiency $\eta$ by: 100 dm$^3$ [%]</th>
<th>120 dm$^3$ [%]</th>
<th>150 dm$^3$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2g limestone + 4.3 mmol/L Adipic acid</td>
<td>1277</td>
<td>100</td>
<td>99.6</td>
<td>99.2</td>
<td>97.5</td>
</tr>
<tr>
<td>2g limestone + 2.51 ml Maalox</td>
<td>1189</td>
<td>93</td>
<td>99.8</td>
<td>99.5</td>
<td>95.4</td>
</tr>
</tbody>
</table>

Thus, the choice of the better additive resides in the parameter intended for analysis. For example, if the objective is to treat a large volume of SO$_2$, the best additive is adipic acid; for a lower volume, Maalox is more adequate.

On the other hand, by analyzing the additives’ performance, considering the mass of SO$_2$ removed to attain a concentration of 100 ppm of SO$_2$ at the exit point, the adipic acid presents better results, as well as, better limestone conversion rates.
5 Conclusions

The intention of this project was to test the addition of various compounds in order to improve the performance of the desulphurization process of gas currents through the wet limestone method. The values of efficiency confirmed for this process, without any additive, are in accordance with the values found in various studies.\(^1\)

The majority of experiments showed an improvement in the levels of efficiency and the limestone conversion.

All the organic acids added presented improvements in the performance of the desulphurization process. However, the one which presented the best results was adipic acid, with a conversion of 100% of utilized limestone and efficiency values superior to 99% for 100 and 120 dm\(^3\) of gas analysed.

Another additive which showed optimal results was Maalox, syrup used to treat stomach acid. Its performance is important when used as an additive in the suspension of limestone, since the experiment which substituted limestone with Maalox did not show interesting results. On the other hand, the experiments indicated that the addition of Maalox with 4.3 mmol/L of Mg(OH)\(_2\) produced elevated levels of efficiency, superior to 99% and with a limestone conversion of 93%.

Calcium oxide was another tested base and various experiments were carried out with different proportions of both this additive and limestone. The analysis of these experiments concluded that it is not always possible to verify improvements through the comparison of the standard experiment, and when these occur they are not very significant. Although, of all the tested proportions the one which presented greater results was the following: 97.5% limestone + 2.5% CaO.

Industrial calcium oxide presents a strong tendency in absorbing the humidity in the air (and its impurities). Therefore, the addition of “wet” CaO was compared with the addition of “dry” CaO. The resulted showed that the utilization of “dry” calcium
oxide is better than the utilization of “wet” calcium oxide, despite the fact that these improvements are only marginal.

Amongst the bases tested, we concluded that the most elevated levels of efficiency and the greatest rate of limestone conversion occurred when Maalox with 4.3 mmol/L of Mg(OH)$_2$ was added.

The choice of the best additive is subjective since it takes into account the parameter to be analysed. For example, the adipic acid is the one which presented a greater limestone conversion (100%) and the one which presented a greater efficiency when high volumes of SO$_2$ gas are used. On the other hand, Maalox is the additive which presented better efficiency in the desulphurization of low volumes.
6 Work assessment

This work focused on the test of several compounds as additives. Such compounds were organic acids (adipic, glutaric and maleic acids) and some bases (CaO and Maalox).

Generally, it can be affirm that the proposed aims were accomplished with good perspective results.

Some problems happened during the realization of this project. Sometimes, after analyzing the results obtained, it was noticed that during the experiment the gas meter was deregulated and thus, it should be calibrated again and such experiments might be repeated. In addition, in the middle of this work, the reactor was broken and it was necessary to wait for the new one.

It was realized other testes, none described in this thesis. Such rejection was indicated by the supervisor of this work. For instance, some realizations were with succinic acid; different concentration of the three studied acids and another syrup.

Nevertheless, it can be said that this project was well succeeded and opened doors to further investigation. For instance, it can be studied the addition of the tested compounds in a larger scale, in order to see if the concluding remarks maintains.

However, it is unrealistic use this kind work in industrial scale due the cost of the additives used. ~

On the other side, it should be useful focus in the modeling and optimization of the parameters that influent the process.
7 Bibliography


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21. Manual and technical information of Servomex Xentra 4900. **ARL 9400 XP+, Horiba, PG-250, Coulter SA 3100, Spectr AA 880, X’Pert PRO, Analysette 22®.**


Appendix – Concentration profile for all realizations

- **2g Limestone**

![Graph 1](image1)

- **2g limestone + 4.3mmol/L adipic acid**

![Graph 2](image2)

- **2g limestone + 4.3mmol/L glutaric acid**

![Graph 3](image3)
Flue gas desulphurization through Wet Limestone Process – adding acids and bases to the limestone suspension

• **2g limestone + 4.3mmol/L maleic acid**

![Graph showing concentration profile for 2g limestone + 4.3mmol/L maleic acid]

• **2g limestone + 4.3mmol/L CaO**

![Graph showing concentration profile for 2g limestone + 4.3mmol/L CaO]

• **15ml Maalox**

![Graph showing concentration profile for 15ml Maalox]
Flue gas desulphurization through Wet Limestone Process – adding acids and bases to the limestone suspension

- **2g limestone + 2.51ml Maalox**

- **2g limestone + 3.83ml Maalox**

- **80% limestone + 20% CaO wet**

Concentration profile for all realizations
Flue gas desulphurization through Wet Limestone Process – adding acids and bases to the limestone suspension

- **90% limestone + 10% CaO wet**

![Graph for 90% limestone + 10% CaO wet](image)

- **90% limestone + 10% CaO dry**

![Graph for 90% limestone + 10% CaO dry](image)

- **95% limestone + 5% CaO wet**

![Graph for 95% limestone + 5% CaO wet](image)
Flue gas desulphurization through Wet Limestone Process – adding acids and bases to the limestone suspension

- **95% limestone + 5% CaO dry**

- **97.5% limestone + 2.5% CaO wet**

- **97.5% limestone + 2.5% CaO dry**