Post-treatment of precipitated calcium carbonate (PCC) produced from steel converter slag

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Abstract

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Carbon dioxide released from burning fossil fuels is one of the largest contributors to global warming. Minimizing industrial emissions is essential for the wellbeing of our planet. Completely cutting off the fossil fuel consumption is not a realistic option; however, there is an alternative called carbon capture and storage (CCS).

This thesis is a part of a CCS study of mineral carbonation using ammonium chloride (NH_4Cl) as a solvent salt in water, to produce precipitated calcium carbonate (PCC) from steel converter slag. A fraction of the solvent is left in the PCC end product and in the slag residue. The NH_4Cl solvent salt needs to be removed from the product and slag residue to be later reused in the PCC production process.

The solvent recovery process uses water to dissolve the solvent and remove it with the filtrate in a continuous batch filtration. The water in the filtrate can then be e.g. evaporated to recover the solvent salt. Two batch filtration setups, a countercurrent and a crosscurrent, were tested to study the efficiencies of the cleaning processes.

An easy and fast method for measuring the NH_4Cl fraction in PCC was developed to assist the study. The method can at the same time be used to determine the structural form of the PCC crystals.

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Koldioxidutsläpp från förbränning av fossila bränslen är ett av de största bidragen till den globala uppvärmningen. Att minimera industriella utsläpp är en nödvändighet för vår planets välbefinnande. Att totalt sluta använda fossila bränslen är dock inte ett realistiskt alternativ. Det finns däremot en möjlighet som kallas koldioxidinfångning- och lagring (på engelska: CCS).

Detta diplomarbete är en del av en koldioxidinfångnings- och lagringsstudie inom mineralkarbonatisering med ammoniumklorid (NH_4Cl) som lösningsmedel i vatten, för att tillverka utfällt kalciumkarbonat från stålslagg. En liten del av lösningsmedlet lämnar kvar i det utfällda kalciumkarbonatet och i slaggöverskottet. Lösningsmedlet ska avlägsnas från produkten och slaggöverskottet för att sedan användas på nytt för att extrahera mera kalcium från stålslagg.

Separationen av lösningsmedlet från det utfällda kalciumkarbonatet och slaggöverskottet sker genom att lösa upp det i vatten och sedan avlägsna filtratet genom en kontinuerlig satsfiltrering. Vattnet i filtratet kan till exempel avdunstas bort för att återvinna lösningsmedelssaltet. Två satsfiltreringsuppsättningar testades, ett motströms och ett korsströms, för att studera reningsprocessernas effektivitet.

En lätt och snabb metod för att mäta NH_4Cl-halten i utfällt kalciumkarbonat utvecklades i samband med arbetet. Metoden kan även användas för att bestämma den strukturella formen på kalciumkarbonatkristallerna.

Preface

This Master's Thesis was carried out for the Carbon Capture and Storage Program (CCSP) coordinated by CLEEN Ltd. The study was performed at the Thermal and Flow Engineering Laboratory at the Department of Chemical Engineering at Åbo Akademi University.

I would like to sincerely thank: Professor Ron Zevenhoven and M.Sc. Hannu-Petteri Mattila, my supervisors who have encouraged and assisted me along the work and given me the opportunity to do this study. I would also like to thank Runar Bäckströms Stiftelsen for the financial help that enabled me to do this study and CLEEN Ltd. for the opportunity to be a part of their world-class research.

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Turku, February 2014

Hannes Hudd

Swedish Summary

Svensk sammanfattning

Efterbehandling av utfällt kalciumkarbonat (PCC) framställt av stålslagg

Problemen med den globala uppvärmningen har varit ett av 2000-talets hetaste debattämnen. Ett av problemen består av koldioxidutsläppen som produceras genom förbränning av fossila bränslen. Koldioxid (CO_2) är en så kallad växthusgas vilken genom fossil förbränning förflyttas till atmosfären där den förstärker växthuseffekten och bidrar till den globala uppvärmningen. Den i sin tur förorsakar allt från smältande glaciärer till förändringar i odlingssäsonger i olika delar av världen. Därför måste de fossila CO_2-utsläppen minska.

Det finns flera sätt att minska på CO_2-utsläppen varav ett är koldioxidinfångning, användning och lagring (CCUS), som är en utvidgning av det tidigare konceptet koldioxidinfångning och lagring (CCS). Inom dessa koncept finns mineralkarbonatisering, där slutprodukten till exempel kan vara utfällt kalciumkarbonat. I och med att stålindustrin står för ca 6,7 % (år 2010) av de globala koldioxidutsläppen finns det all anledning för den att minska på sina utsläpp. Slaggavfall från järn- och stålindustrin innehåller rikligt med kalcium, vilket kan användas för att mineralisera CO_2. Kalcium kan extraheras från stålslagg med ammoniumklorid (NH_4Cl), varefter CO_2 tillförs för att fälla ut kalciumkarbonatet ($CaCO_3$).

Utfällt kalciumkarbonat (PCC) är ett vitt pulver som används bland annat inom plast- gummi- och färgindustrin, men framför allt inom pappersindustrin. Vitt papper kan till exempel bestå av upp till 30 % kalciumkarbonat både som fyllningsmedel och som bestrykningsmedel. Om järn- och stålindustrin börjar mineralisera CO_2, minskar CO_2-utsläppen och slaggavfallet, och i samband med detta tillverkas en eftertraktad produkt.

Tidigare forskning har visat att en kontinuerlig mineralkarbonatiseringsprocess med stålslagg och NH_4Cl för att tillverka utfällt kalciumkarbonat fungerar i laboratorieskala. En liten del av lösningsmedlet (NH_4Cl) lämnar kvar i det utfällda

kalciumkarbonatet och i slaggöverskottet. Detta ska avlägsnas från kalciumkarbonatprodukten och slaggöverskottet för att sedan användas på nytt i kalciumkarbonatproduktionen.

För att lätt och snabbt kunna mäta mängden av NH_4Cl i kalciumkarbonatprodukten utvecklades en metod som med hjälp av pH och temperatur får ut viktprocenten av lösningsmedlet i slutprodukten. Metoden borde också kunna bestämma den strukturella formen på kalciumkarbonatkristallen. Dock testades endast den strukturella formen på rombohedrisk kalcit.

Separationen av lösningsmedlet från det utfällda kalciumkarbonatet och slaggöverskottet sker genom att lösa upp lösningsmedlet i vatten och sedan avlägsna filtratet genom en kontinuerlig satsfiltrering. Två satsfiltreringsuppsättningar testades, en motströms och en korsströms, för att studera reningsprocessernas effektivitet. Det visade sig att motströmssatsfiltrering var effektivare då en vattenmängd som var tio gånger mera än $CaCO_3$-NH_4Cl-blandningen, som innehöll 1,00 viktprocent NH_4Cl, testades med båda filtreringstyperna. Motströmssatsfiltreringen gav 0,0019 viktprocent och korsströmsfiltreringen gav 0,0296 viktprocent NH_4Cl i slutprodukten.

När separationsprocesserna testades experimentellt visade det sig att lösningsmedlet var svårare att avlägsna från kalciumkarbonatet vid lägre koncentrationer av NH_4Cl. Detta beror på adsorption av vatten till kalciumkarbonatet. I det adsorberade vattnet finns en liten del av det upplösta lösningsmedlet som är svår att avlägsna. I och med detta kommer jämviktskonstanten (K) att vara olinjär vid separationen. En formel för den olinjära jämviktskonstanten erhölls från experimentell data. Ett matematiskt simuleringsprogram i Matlab gjordes i samband med denna studie för att simulera de experiment som gjordes. Simuleringen ger data på hur mycket vatten som behövs för att minska NH_4Cl-halten i kalciumkarbonatprodukten. Exempelvis krävs det 5,2 gånger mera vatten (i gram) än vikten av $CaCO_3$-NH_4Cl-blandningen för att minska halten av NH_4Cl i en $CaCO_3$-NH_4Cl-blandning från 1,00 viktprocent till 0,01 viktprocent.

Experiment och matematiska simuleringar gjordes också för separationen av NH_4Cl från stålslaggsöverskottet. Även för slaggöverskottet visade det sig svårt att separera NH_4Cl från de fasta partiklarna vid låga NH_4Cl-koncentrationer. Därför gjordes också en ekvation för jämviktskonstanten (K) för separation av NH_4Cl från NH_4Cl-slaggsöverskottblandningar. Det visade sig vara mycket svårare att separera NH_4Cl från slaggöverskottet än från det utfällda kalciumkarbonatet. Exempelvis krävdes det 3,4 gånger mera vatten än vikten av slaggöverskott-NH_4Cl-blandningen för att minska halten av NH_4Cl i en slaggöverskott-NH_4Cl-blandning från 1,00 viktprocent till så högt värde som 0,1 viktprocent. Det motsvarar 11,0 gånger större mängd vatten (i gram) än vikten av kalciumkarbonatprodukten.

Processvatten från kalciumkarbonatproduktionen kunde i princip användas till separationsprocessen av NH_4Cl från både slaggöverskottet och kalciumkarbonatprodukten. Det visade sig dock att mängden processvatten som behövdes för separationsprocessen blev alldeles för stor och skillnaden i den rena slutprodukten med och utan processvatten blev försummande liten. Exempelvis så minskade vattenbehovet från 11,0 gånger massan av kalciumkarbonatprodukten till 10,7 för en reducering av NH_4Cl-halten i en slaggöverskott-NH_4Cl-blandning från 1,00 viktprocent till 0,1. Men processvattenmängden blev dock 32,1 gånger större än kalciumkarbonatprodukten, vilket inte är ett hållbart alternativ.

Värme kan användas för att separera NH_4Cl från filtratet genom att avdunsta vattnet. Energibehovet skulle då bli mycket högt. Ett förslag på hur en separationsprocess för att avlägsna NH_4Cl från filtrat kunde se ut gavs och för den processen gjordes också en matematisk simulering i Matlab. Som ett typiskt exempel krävdes det 0,88 $\frac{\mathrm{kJ}}{\mathrm{g\ CaCO_3}}$, vid en temperatur mellan 120 °C och 150 °C, för att separera NH_4Cl från filtratet då halten av NH_4Cl i en $CaCO_3$-NH_4Cl-blandning reducerades från 1,00 viktprocent till 0,01, med temperaturen 25 °C både i kalciumkarbonatproduktionen och i NH_4Cl-separationsprocessen.

Energibehovet för att separera NH_4Cl från slaggöverskottsfiltratet blir mycket högre än för NH_4Cl separationen från kalciumkarbonatfiltratet. Detta beror inte bara på det att det finns 3,2 gånger mera slaggöverskott än kalciumkarbonatprodukt utan också på det att jämviktskonstanten är mycket sämre. Exempelvis krävdes det 2,31 $\frac{\mathrm{kJ}}{\mathrm{g\ slaggöverskott}}$, som motsvarar 7,40 $\frac{\mathrm{kJ}}{\mathrm{g\ CaCO_3}}$, vid en temperatur mellan 120 °C och 150 °C, för att separera NH_4Cl från filtratet då halten av NH_4Cl i en slaggöverskott-NH_4Cl-blandning reducerades från 1,00 viktprocent till 0,1, med temperaturen 25 °C både i kalciumkarbonatproduktionen och i NH_4Cl-separationsprocessen.

Eftersom energibehovet för avdunstningen är så högt blir energikostnaderna också höga. Den summa som sparas in från att få tillbaka lösningsmedlet täcker inte energikostnaderna. Däremot finns det en möjlighet att inte ta tillbaka allt lösningsmedel. Genom att optimera vatten-, energi- och NH_4Cl-kostnaderna kunde man få ett mera ekonomiskt alternativ till separationsprocessen. Detta beror dock på miljölagstiftningen angående, NH_4Cl-mängder som är tillåtna att släppa ut i miljön. Detta studerades inte och därför antogs det att inget NH_4Cl ska släppas ut i miljön. Mängden av NH_4Cl i slutprodukterna (både i $CaCO_3$ och i slaggöverskottet) blir en senare fråga för kunden.

Eftersom energikostnaderna blir höga på grund av avdunstningsprocessen, borde fortsatta studier se på alternativa separationsprocesser. Membranseparation kunde vara en lösning, och därför rekommenderar skribenten att fortsatta studier bör rikta in sig på membraner som kan separera NH_4Cl från vatten på ett kostnadseffektivt sätt.

List of symbols and abbreviations

(s)	Solid
(g)	Gas
(l)	Liquid
(aq)	Dissolved in water
CCS	Carbon Capture and Storage
CCUS	Carbon Capture Utilization and Storage
GCC	Ground Calcium Carbonate
PCC	Precipitated Calcium Carbonate
ppm	Parts per million
SEM	Scanning Electron Microscope
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
CO_2	Carbon dioxide
$(NH_4)_2CO_3$	Ammonium carbonate
NH_4Cl	Ammonium chloride
NH_4OH	Ammonium hydroxide
ΔH	Reaction enthalpy
m	Mass
$\dot{m}$	Mass flow
K_a	Acid dissociation constant
K_b	Base dissociation constant
K_s	Solubility constant
K_w	Water dissociation constant
$\dot{Q}$	Heat flow
R^2	Correlation coefficient
T	Temperature

Table of Contents

1 Introduction

Global warming is one of the hot topics of debate in the 21st century. One of its causes is the carbon dioxide (CO_2) emitted by humans when burning fossil fuels, contributing to the greenhouse effect. The impacts of global warming are severe, ranging from melting glaciers and rising water levels to changing crop seasons for farmers around the world.

The steel industry is one of the largest CO_2 producers globally. In 2010 alone it produced 6.7 % of the total world CO_2 emissions [1]. In Finland Ruukki Metals produced about 4 Mt CO_2 in recent years [2], and in 2012 the company decreased their CO_2 emissions with 600 000 ton by recycling metals and minerals [3]. Because of the large emissions, it is important to focus on future emission reduction in the iron- and steel industry.

CO_2 emissions can be reduced in several ways, one of them is CCUS (Carbon Capture Utilization and Storage) an extension of the earlier concept CCS (Carbon Capture and Storage) where for example mineral carbonation is used. This CCS/CCUS is still far too expensive for commercial use due to the low costs of CO_2 emissions defined by the European Union, currently about 7 €/ton (5.3.2014) [4] and the cost of different mineral carbonation technologies is nowadays more than 20 €/ton [2] [5]. Due to the high price of implementing CCS/CCUS there is a need for more economical ways of reducing the CO_2 emissions.

Slag2PCC is a mineral carbonation procedure where slag from the iron and steel industry is used to produce PCC (Precipitated Calcium Carbonate) [6]. The iron and steelmaking slag is rich in calcium and due to the fact that the iron and steel industry produces significant amounts of CO_2 there is a potential for PCC manufacturing within that industry [7]. The slag from the iron and steel industry is seen as a by-product that eventually becomes a waste material according to the European legislation and it is often disposed of in e.g. landfill, as there is barely any economic value in the slag business. Slag2PCC on the other hand will turn the iron and steel slag from a waste into a byproduct with a higher economic value [6]. PCC is mainly used in the paper industry as a filler in the pulp and for the coating of the paper itself, but it can also be utilized in plastics, paint, pharmaceuticals etc. [8]

PCC production from steel slag to reduce CO_2 emissions using the Finnish “Slag2PCC” concept has been successfully accomplished on a lab-scale and is being developed on a commercial scale. In previous research, separation of calcium from the steel or iron slags has been done using different ammonium salts [6]. In this thesis ammonium chloride, NH_4Cl, will be used because it is the safest and most economical ammonium salt for this application [9].

In previous research [2] [10] [11] a laboratory scale process setup has been built for production of PCC from steel converter slag using ammonium chloride. The product is not as pure as the commercial qualities, due to a small content of ammonium chloride left in the PCC. This thesis will deal with this process and specifically a part where the PCC is washed and dried to the quality the customers require, while recovering the NH_4Cl salt for re-use.

2 Background

2.1 Industrial fossil fuel emissions and their impact on the carbon cycle

Carbon dioxide (CO_2) in the atmosphere is a part of the global carbon cycle. From the atmosphere the CO_2 goes through photosynthesis to organic carbon chains and after a while the carbon chains decompose and are released back to the atmosphere. The oceans are an important factor in the carbon cycle, not only because of the photosynthesis done by organisms, but also due to their capability to store CO_2. The oceans contain about 50 times more CO_2 than the atmosphere and in deep waters the CO_2 can stay dissolved for thousands of years before it returns to the cycle [12]. The problem accrues when carbon stored a long time ago returns to the carbon cycle in a short period of time, during combustion of fossil fuels. This disturbs the carbon cycle by adding too much CO_2 to the atmosphere. It is claimed that the ocean and land ecosystems absorb half of the emissions created from fossil fuels [13]. The other half of the CO_2 emissions released stays in the atmosphere. When the CO_2 emissions increase year after year it will eventually affect the climate on our planet.

The CO_2 level in the atmosphere is currently about 394 ppm (2014) [14] and is increasing. It is estimated that during this century the CO_2 levels in the atmosphere will reach 450-600 ppm [15]. Atmospheric CO_2 works as a greenhouse gas and contributes to global warming through the greenhouse effect. The greenhouse effect prevents some of the solar radiation from being reflected back into space and keeps the earth warm. Even though the greenhouse effect is essential for the temperature level of our earth, the CO_2 from fossil fuels intensifies it and creates a warmer climate. A climate change may cause for example dry seasons and lesser rainfalls in certain areas of the world and a sea level rise leading to flooding in lowlands. Altogether, millions of environmental refugees may have to abandon their homes [9] [15] [16].

Teir et al. [5] studied the potential of carbon capture in the Nordic countries and listed the 277 most CO_2 intensive facilities. 51 % of the CO_2 produced (113 Mt, 2007) by the facilities originated from fossil fuels. In total, the global CO_2 emissions from fossil fuels were 29 728 Mt in the same year [17]. In the Nordic countries, heat and power facilities are the largest consumers of fossil fuels, oil and gas activities come second while the iron and steel industry is on the third place. The major CO_2 producers in the Nordic countries are shown in Figure 2.1.1. This thesis will focus on the iron and steel industry's CO_2 emissions and the utilization possibilities of the CO_2 emissions. The biogenic fuels used by, for example, the pulp and paper industry, are CO_2 neutral because the fuel is taken directly from the carbon cycle and does not add any extra CO_2 to the atmosphere when burnt. In fact, if CO_2 emissions from biogenic fuels are captured and stored, the overall system becomes CO_2 negative and it would be possible to sell CO_2 rights to other industries.

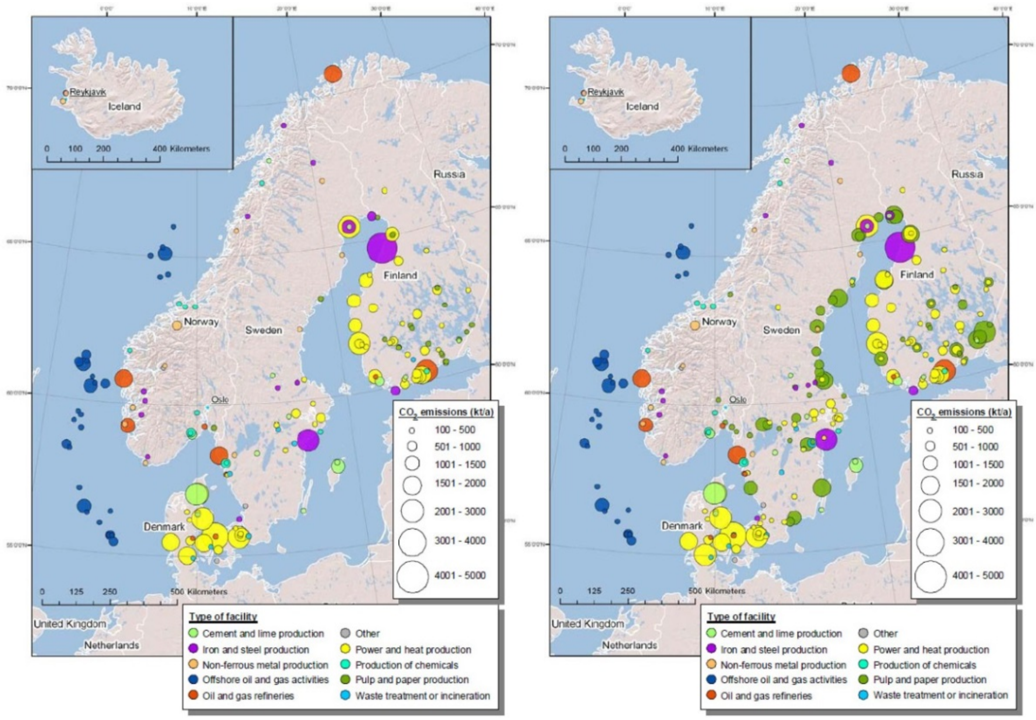


Figure 2.1.1 (Left) Map of facilities with CO_2 emissions > 0.1 Mt CO_2/year in 2007 – only fossil CO_2 emissions visible. (Right) Map of facilities with CO_2 emissions > 0.1 Mt CO_2/year in 2007 – both fossil and biogenic CO_2 emissions visible [5].

The steel industry produces more than 1.4 billion tons of steel per year globally and the numbers are increasing year after year (see Figure 2.1.3). Steel is mainly used in construction, and therefore steel production in developing countries is increasing rapidly at the same time as it decreases in developed countries [1]. The trend shows that more steel will be produced, and hand in hand with that, more CO_2 emissions will be emitted by the same industry.

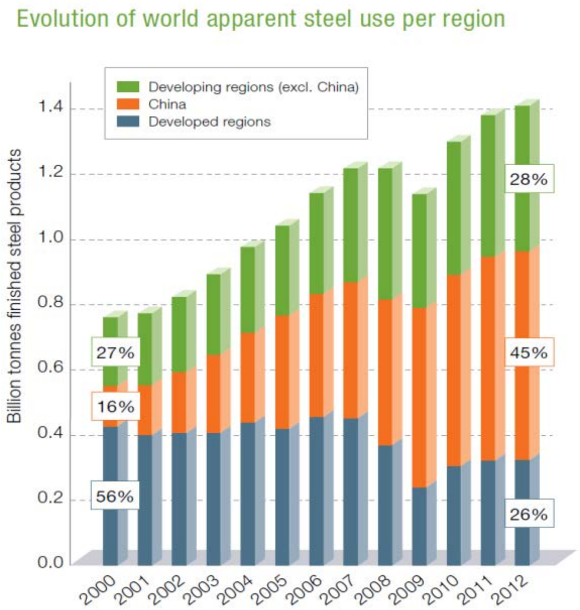


Figure 2.1.3 Evolution of world apparent steel use per region [1].

Steel manufacturing is an energy intensive process, due to high temperatures and large facilities. The manufacturing process produces a large amount of carbon dioxide, about 1.8 ton of CO_2 per ton steel produced. As earlier stated, Ruukki Metals is one of the main producers of steel, and thus also of CO_2 in Finland [3]. Ruukki Metals has therefore provided steel slag for the slag2PCC mineral carbonation project to see if it would be possible to reduce the CO_2 emissions by producing a valuable by-product from the steel slag and the CO_2. The steel converter slag contains significant amounts of calcium which makes it possible to use it for PCC manufacturing. The elemental composition of different types of iron and steel slag can be seen in Table 2.1.1.

Table 2.1.1 Various iron and steel slags and their chemical compositions [11].

Slag	CaO	Fe	SiO_2	Mn	MgO	Al_2O_3	V	Na_2O	P	S	K_2O	Ti	Cr	Rest
Blast furnace	34.5	0.2	31.2	-	16.2	12.7	-	0.7	-	2.6	0,5	1.3	-	0.1
Desulfurization	58	7	15	0.3	1.3	2.5	0.1	3.1	-	2.9	0.1	1	-	8.7
Steel converter	45.2	16.7	11.4	2.6	1.5	1.4	1.2	-	0.4	-	-	0.6	0.2	18.8
Ladle	49.4	4.4	14.1	0.7	5.8	21	0.3	-	-	0.2	-	0.7	-	3.4

2.2 Carbon dioxide Capture and Storage (CCS)

Carbon dioxide capture and storage or CCS can be applied to CO_2-intensive industrial processes where the CO_2 could be removed and then transported to long term storage [18]. Technologies for removing and storing CO_2 already exist but they are mostly meant for short term storage prior to later use [9]. The aim with CCS is to store the CO_2 for as long as possible (at least ~1000 years) to prevent global warming. The best option would be that the CO_2 never reaches the atmosphere. Today most long term storage is done in connection with producing oil or gas from underground oil/gas reservoirs. When the oil/gas reservoirs lose pressure and do not "spit out" oil/gas by itself, CO_2 can be pumped into the well forcing oil/gas up and at the same time storing the CO_2 in the reservoir. Old, mostly empty reservoirs can be used as storage places for CO_2 as well, but that does not give any economic value, rather the opposite. It is still unclear how long the CO_2 is typically able to stay in the reservoirs after storing, but models have shown that most likely 99 % of the CO_2 will stay there for around 1000 years and more [18] [19]. See Figure 2.2.1 (left) for an illustration of CO_2 storage in oil or gas reservoirs, and other geological formations.

As earlier stated, the world's oceans are the largest CO_2 natural storage places. There is therefore the possibility to store CO_2 in the oceans (see more about solubility of CO_2 in water in Chapter 3.1.2). From depths of more than 1000 m the CO_2 would not rise to the atmosphere for decades, and when it does, it gradually becomes integrated in the natural global carbon cycle. The CO_2 could be pumped via pipes from onshore and offshore facilities to the bottom of the oceans [18] (see Figure 2.2.1). However, the implementation of CO_2 storage in the ocean could disrupt the marine life and harm the ecosystem.

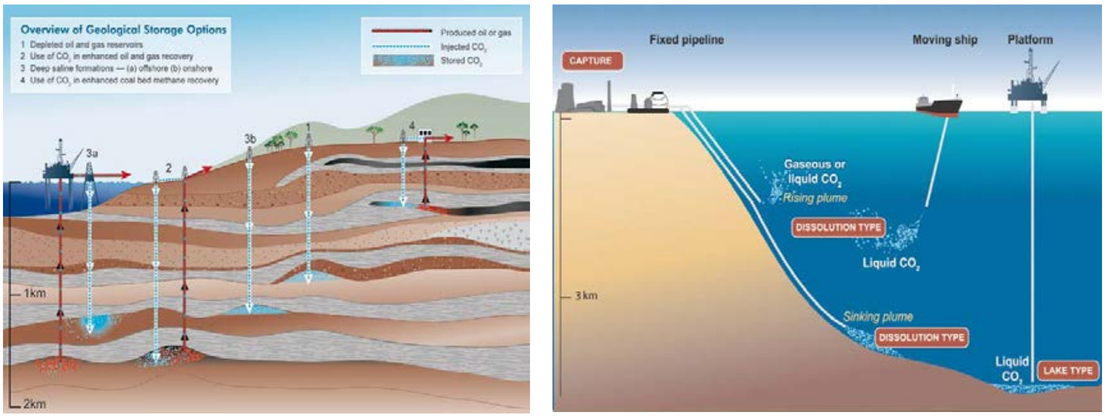


Figure 2.2.1 Overview of geological and ocean CO_2 storage concepts [18].

One way or another, the CCS methods will sooner or later let the CO_2 trickle out in the atmosphere. However, there is still another method called mineral carbonation that could store the CO_2 for a longer time than the above alternatives. Calcium and magnesium carbonates ($CaCO_3$ and $MgCO_3$) are formed in nature by a process called "weathering" of rocks, where calcium and magnesium ions are leached out of silicate rocks with water and react with CO_2. The two carbonates are common in nature and if disposed there are low environmental risks and very low risks of ecological disasters [19]. This thesis will focus on mineral carbonation of industrial by-products, giving $CaCO_3$ because the product has a market value that could make the mineral carbonation processes more attractive for investors.

2.3 Calcium Carbonate

Calcium carbonate ($CaCO_3$) is present only on our planet and possibly on Mars. On earth it is one of the most common minerals and usually associated with existence of water [8] [20]. In nature, calcium carbonate is present in three different polymorphs or crystal forms, calcite, aragonite and vaterite, of which calcite is the most common one. The different crystal forms may occur in different crystal structures. For instance, calcite may occur in hexagonal, prismatic, rhombohedral and scalenohedral structures, when aragonite only occurs in different hexagonal and prismatic structures [8] [21] (see Figure 2.3.1).

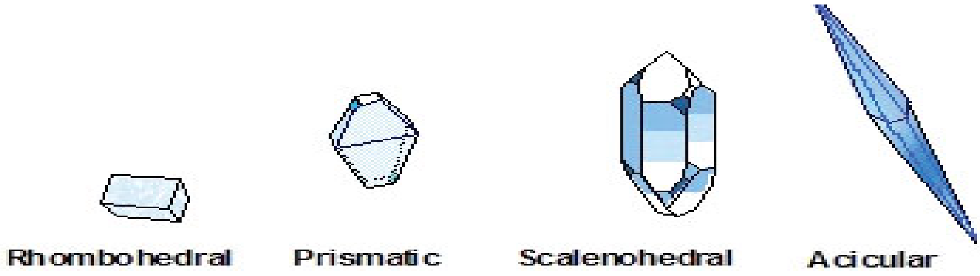


Figure 3.2.1 Examples of different crystal structures for calcium carbonate [21].

The largest industrial calcium carbonate source is limestone which can be found all over the world. Limestone consists mostly of calcite, but the other polymorphs are also found. Limestone is mainly used in the construction and cement industry but also used as fillers and pigments in for example paper and plastic. The calcium carbonate found in nature and used in industry is called GCC (ground calcium carbonate) [8] [22]. In papermaking, $CaCO_3$ is mainly used for improving the whiteness, brightness, opacity, color, printing capability and the smoothness of the paper [8] [21]. Printing paper can have a mineral content (such as calcium carbonate) up to 40 % [8]. Cellulose is often more expensive than the minerals, and it is therefore more profitable to use as much as possible of the filler minerals to lower the paper production costs [21].

Precipitated calcium carbonate or commonly called PCC has the same chemical formula as GCC ($CaCO_3$) but instead of crushing limestone the PCC is created by precipitation, this makes PCC cleaner and purer than GCC. When precipitating calcium carbonate the crystal forms, structures and size can be adjusted, unlike GCC where the structure is generally calcite with a large size distribution of the rhombohedral particles [20] [23]. The difference between PCC and GCC can be seen in Figure 2.3.2, where the PCC is to the left and the crushed GCC is to the right. Figure 2.3.2 clearly shows the size distribution differences between the particles in the PCC and the GCC.

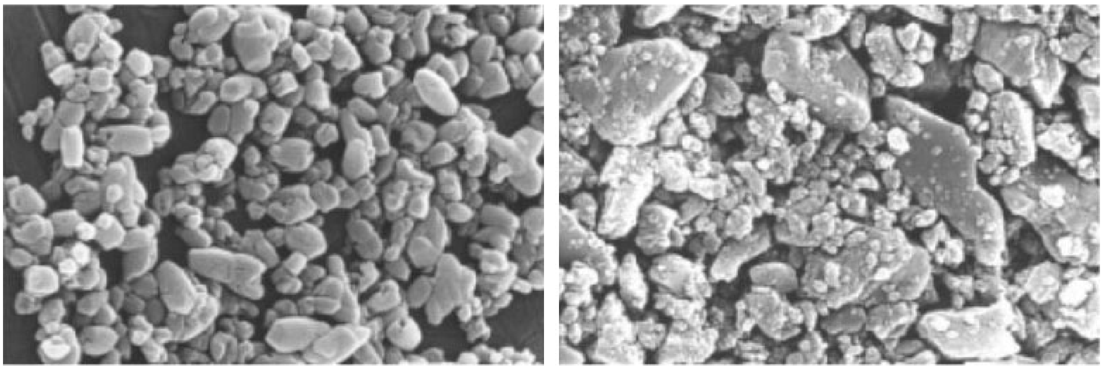


Figure 2.3.2 Size distribution differences between PCC (left) and GCC (right), with the same median particle size (0.7 µm) [23].

PCC can be tailored for the end user, having a better quality and being more valuable than the GCC. PCC is used in several industries such as in the paper, plastic, rubber and paint industry, see Figure 2.3.3.

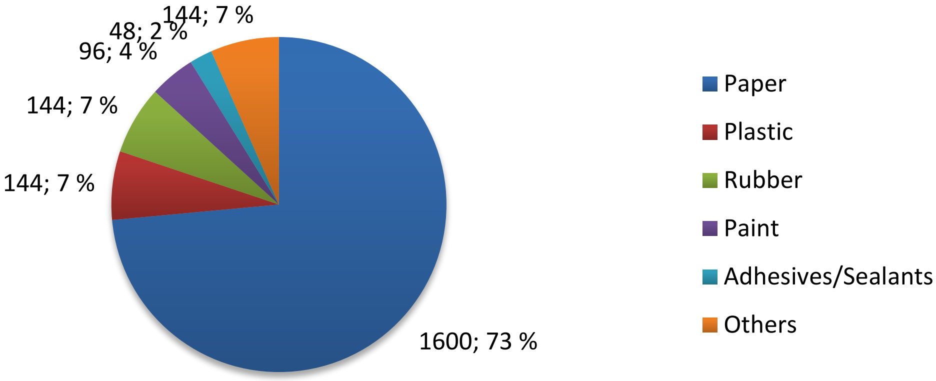


Figure 2.3.3 PCC consumption in North America, in kilotons year 2011 [11].

Different industries require different kinds of PCC and some are stricter with respect to purity than others. Specialty Minerals is the largest PCC producer in the world (2012) producing over 4 million ton of different PCC qualities each year, while in Finland the paper industry is the largest consumer [23] [24]. Calcite is the most common crystal form for commercial PCC, the rhombohedral and prismatic crystal structures of calcite are preferred in paper coating but also as fillers. For paper filling the scalenohedral structure is preferred, due to the unique shape that makes the light scatter in a way improving the opacity of the paper [20] [21].

Aragonite PCC is often shaped as orthorhombic needle-like crystals, called acicular. Aragonite is not as stable as calcite and in aqueous solutions it will within some months transform into calcite, at room temperature [25]. Nonetheless aragonite clusters have similar properties as scalenohedral calcite and it is especially good for thin layer paper coating because it does not affect the gloss of the paper [20] [26]. Vaterite is often hollow and spherically shaped, because calcium carbonate forms around a CO_2 bubble. When the CO_2 is removed the calcium carbonate structure remains as a round hollow shell [27]. Vaterite is more unstable than aragonite and if it is exposed to water it takes only a few hours for it to transform to calcite [25]. Due to the instability of the vaterite it is in general not used commercially [20] [21].
Figure 2.3.4 shows SEM pictures of different PCC crystal structures.

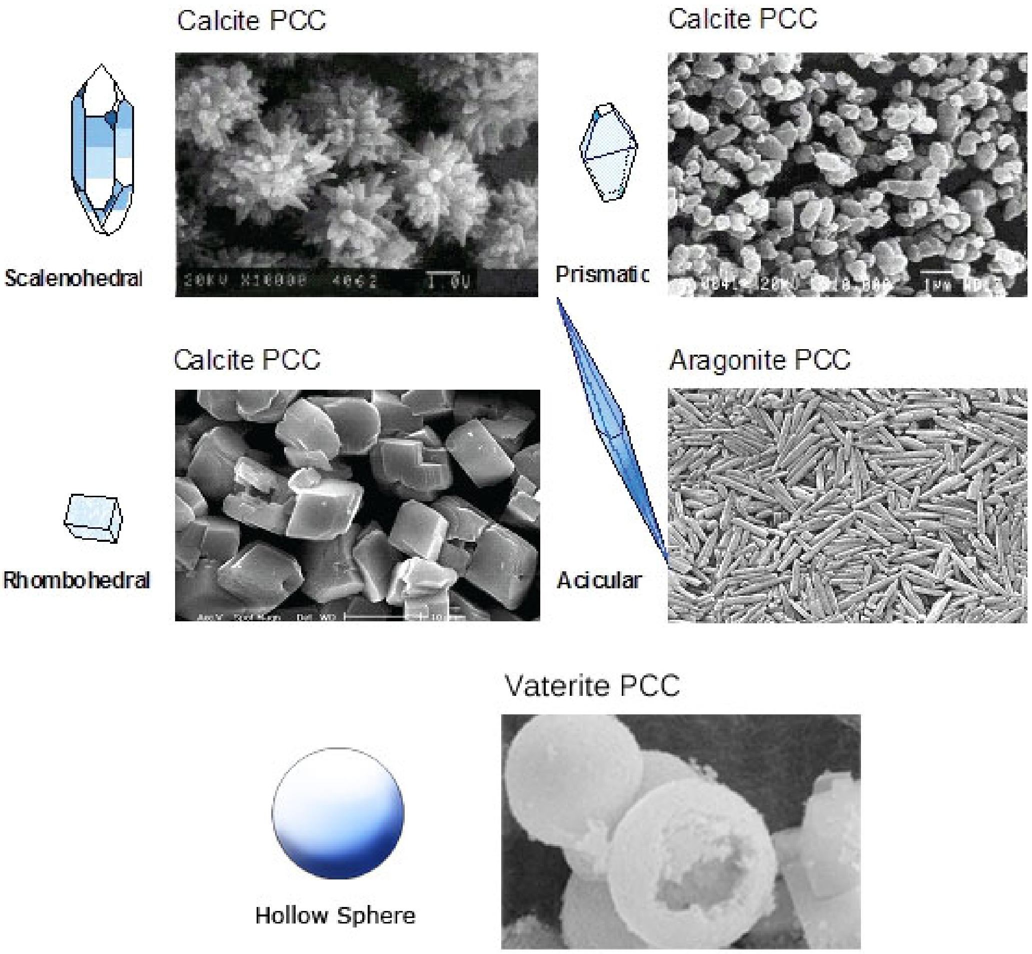


Figure 2.3.4 Five different crystal structures of PCC [21] [27]

2.4 PCC manufacturing processes used in the industry today

There are several ways of producing PCC, some more cost effective than others. The most common methods are precipitation with gaseous carbon dioxide, the lime soda process and the Solvay process where the PCC is a by-product from ammonia production [8]. In this thesis the focus will be on precipitation using carbon dioxide. A description of a PCC production process can be seen in Figure 2.4.1, where limestone is the main input to the process.

After the limestone breaker (see Figure 2.4.1) the limestone is burnt at around 1000 °C and the endothermic reaction R2.4.1 takes place ($\Delta H = 163 \frac{\mathrm{kJ}}{\mathrm{mol}}$ at 1000 °C) [11]. In this reaction CaO and CO_2 are formed [2] [11] [28].

Burning of limestone: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ R2.4.1

The CaO will continue to the so-called lime slaker, where water is added to form $Ca(OH)_2$. This reaction (R2.4.2) is exothermic with reaction enthalpy $\Delta H = -65 \frac{\mathrm{kJ}}{\mathrm{mol}}$ at 20 °C [11].

Slaking of quicklime: $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$ R2.4.2

After the lime slaking the $Ca(OH)_2$ slurry, also called milk of lime, is filtered to take away large particles, often larger than 40 μm. The viscosity of milk of lime is regulated by adding water, if the slurry has too high viscosity for pumping. The amount of water is about 90 wt-%. at this stage [24]. The milk of lime is then pumped into the carbonator (see Figure 2.4.1) where CO_2 (possibly from R2.4.1) is added. In the carbonator an exothermic reaction (R2.4.3) takes place, with a reaction enthalpy $\Delta H = -113 \frac{\mathrm{kJ}}{\mathrm{mol}}$ at 20 °C [11] and $CaCO_3$ (PCC) is precipitated. The dry solids content, of the PCC is at this stage between 14 wt-%. and 18 wt-%. [24].

Precipitation $Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$ R2.4.3

The slurry from the precipitator, containing PCC with 82-86 wt-% water is then filtered. The filtrate will be re-circulated to the lime slaking and the PCC slurry will continue to a dryer if the customer expects a dry PCC powder. The filter cake of PCC has, depending on the particle size 40-60 wt-% solid matter, after filtration. The dryness (dry solids content) of the product depends on the customer requirements but it can fluctuate between 20 % to about 100 % solid matter, by weight [24].

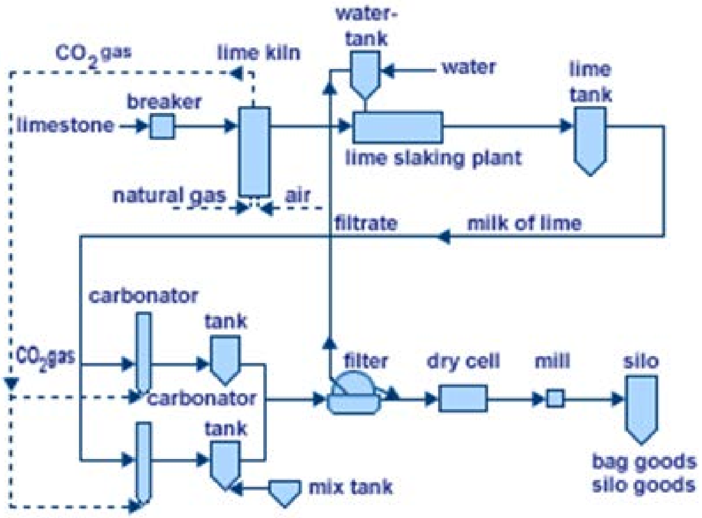


Figure 2.4.1 Process description for a typical PCC plant [28].

The PCC production by precipitation with gaseous carbon dioxide can also be used for reducing CO_2 emissions of for example a paper mill near the PCC production site. In that case the paper mill provides the PCC manufacturing process with CO_2 and CaO is used for the process instead of limestone. This method then excludes the burning of limestone (R2.4.1), thus the CO_2 emissions are actually produced elsewhere. The paper mill reduces its CO_2 emissions and can sell extra CO_2 emission rights to the market. The PCC from the process is led directly into the paper mill, reducing the costs of transportation significantly. This way of producing PCC needs cleaning of the CO_2 before it can be used in the process because emissions from different facilities typically contain other compounds besides the CO_2. Especially the sulfur amount in the flue gas must be reduced with a scrubber before the gas can be sent to the PCC production process [24].

2.5 PCC Product quality

The product quality of PCC depends on the requirements set by the end user. As earlier stated the largest user of PCC is the paper industry; therefore in this thesis the focus will be on the PCC product quality preferred by the paper industry. The crystal form and structure are important factors for the end use of the PCC, as well as the particle size and the size distribution [11]. Based on the size, crystal form and structure, other properties of the PCC can be presumed, for example, stability, density, refractive index and brightness. For paper filling the size and size distribution of the PCC particles are often preferred to be 90 % < 2 µm [11]. Besides the size and the type of PCC particles, the purity of the product is essential. An impure PCC mixture can infect the PCC with unwanted colors, affecting the properties of the PCC or the paper and in worst case, even make the product hazardous (paper should be clean enough so children can eat it). The usual problem is sulfur from sulfur dioxide in flue gases which makes the PCC acidic and may cause serious damage to the end product. The sulfur content in the PCC has an upper limit of 5 ppm in commercial PCC [29].

The main question concerning the purity of the PCC for this thesis was the NH_4Cl solvent salt content. NH_4Cl is not a hazardous chemical, in fact it is used in sweets called salmiak or salty liquorice and is frequently eaten by humans. NH_4Cl does not affect the color of the PCC because it is white. However, NH_4Cl makes the PCC particles stick to each other like a glue and at the same time it makes the solution slightly acidic. Because no PCC manufacturer produces PCC using NH_4Cl and CO_2, a limit for NH_4Cl amount in the PCC is difficult to find. For this thesis the aim is to lower the NH_4Cl content to the extent that the acidity and the stickiness are reduced while the NH_4Cl salt is recovered.

Another important factor is how the PCC should be distributed, in the sense of dryness. It is unnecessary to spend energy on drying the PCC to a dry powder if the end user needs it as wet slurry. As earlier stated, the PCC manufacturing plant is often located next to a process where PCC is needed, for example, a paper mill. In this case there is no need for dry PCC, as the PCC is pumped, through pipes, into the wet paper manufacturing process. According to Karlsson [24] most PCC is delivered to paper mills via pipes at 20 wt-% dry content.

If the PCC is not produced next to the customer and there is a need for transportation by truck, the dry solid content has to be as high as possible, because the customer does not want to pay for the transportation of water. The dryness of the PCC must not exceed the point where the PCC slurry cannot be pumped anymore. To be able to pump the PCC slurry the dry content needs to be around 70 wt-% [24]. A >70 wt-% dry rhombohedric calcite with the particle size >10 µm (see Chapter 3.2.3 – 3.2.4) is obtainable by filtering the slurry, without any energy use for heating to evaporate the water. Because most of the PCC produced is sold to the paper industry, the demand of dry PCC powder is less than the wet PCC slurry. For instance all PCC produced by Speciality Minerals in Finland is sold as slurry [24]. There is however a need for dry PCC as well, but the high production costs due to the energy demanding drying process makes the product more expensive.

2.6 PCC manufacturing process with steel converter slag

Slag from the iron and steel industry is, as earlier stated, a by-product/waste material. To use the slag for PCC production would increase the value of the slag and generate an economic profit instead of paying for disposal. Steel converter slag contains a large amount of calcium (see Chapter 2.1.2) and therefore offers the opportunity to use that calcium for PCC production. In previous research [6] [9] [30] it has been shown that ammonium salts selectively extract free lime (calcium oxide) CaO and the calcium from dicalcium silicate ($2CaO * SiO_2$) from the steel slag. PCC can thus be produced with the help of ammonium chloride and clean CO_2. The process is producing PCC at atmospheric pressure and temperatures below 100°C. Teir et al. sketched a simplified $CaCO_3$ manufacturing process for a steel mill (Figure 2.6.1).

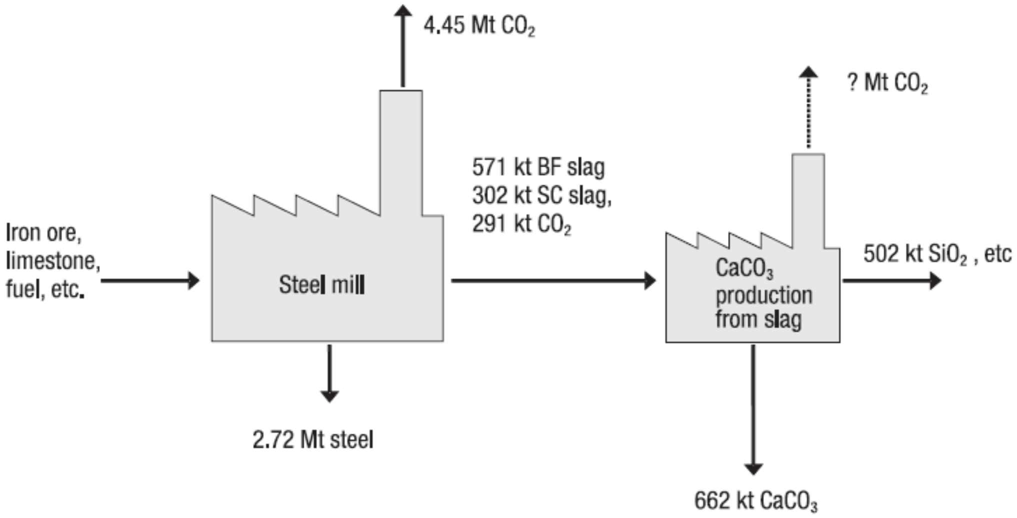


Figure 2.6.1 A simplified precipitated calcium carbonate manufacturing plant next to a steel mill [31].

2.6.1 Chemical theory for PCC production with steel converter slag

The chemical reaction for the extraction of calcium can be seen in R2.6.1. The reaction occurs in an aqueous solution where calcium oxide present in slag is mixed with an ammonium salt NH_4X. “X” represents chloride, nitrate or acetate ions. The products of the reaction are a calcium salt and ammonium hydroxide dissolved in water [6] [9] [30].

$$CaO(s) + 2NH_4X(aq) + H_2O(l) \rightarrow CaX_2(aq) + 2NH_4OH(aq) \qquad \text{R2.6.1}$$

The ammonium hydroxide created in the first reaction (R2.6.1) is mixed with CO_2 and produces water and ammonium carbonate (R2.6.2).

$$2NH_4OH(aq) + CO_2(g) \leftrightarrow (NH_4)_2CO_3(aq) + H_2O(l) \qquad \text{R2.6.2}$$

The ammonium carbonate from the second reaction (R2.6.2) reacts with CaX_2 and precipitates $CaCO_3$ (PCC). In the water, while the solid PCC is formed, the ammonium salt remains in solution and can be reused (see reaction R2.6.3).

$$(NH_4)_2CO_3(aq) + CaX_2(aq) \leftrightarrow CaCO_3(s) + 2NH_4X(aq) \qquad \text{R2.6.3}$$

Previous research [9] suggests that ammonium chloride or NH_4Cl may be the best ammonium salt to use for PCC production. Ammonium chloride was not only the cheapest alternative, but also the safest ammonium salt that was tested during that research, unlike ammonium nitrate that might have problems with legislation. Ammonium acetate was also tested during the research, but the results were not equally good as with chloride and nitrate (for example, acetic acid evaporation).

Using ammonium chloride for the PCC production process with steel converter slag, the reactions will summarize as below (R2.6.4-R2.6.6) [2] [10], where the CaO is the free CaO found in the slag plus the CaO bound in di-calcium silicate.

$$CaO(s) + 2NH_4Cl(aq) + H_2O(l) \rightarrow CaCl_2(aq) + 2NH_4OH(aq) \qquad \text{R2.6.4}$$

$$2NH_4OH(aq) + CO_2(g) \leftrightarrow (NH_4)_2CO_3(aq) + H_2O(l) \qquad \text{R2.6.5}$$

$$(NH_4)_2CO_3(aq) + CaCl_2(aq) \leftrightarrow CaCO_3(s) + 2NH_4Cl(aq) \qquad \text{R2.6.6}$$

2.6.2 The process for PCC production with steel converter slag and ammonium chloride

Previous research [2] has shown that a continuous PCC production set-up with steel converter slag, ammonium chloride and carbon dioxide works on laboratory scale. The process is operated as continuous, to be able to monitor and adjust the process according to different qualities of incoming steel slag. A continuous process set-up should also produce a constant quality of the finished PCC product. The basic principle of the PCC production process can be seen in Figure 2.6.2. The steel slag is added to the aqueous solution in the extraction reactor and it reacts with the circulating ammonium chloride (see R2.6.4), after which the residue from the slag is removed from the process product solution. The calcium chloride and the ammonium hydroxide continue to the carbonation reactor where carbon dioxide is added. During carbonation a two-staged reaction takes place, see R2.6.5 and R2.6.6. PCC is precipitated after which it is removed from the process while the ammonium chloride solution is recirculated to the first step [2] [10] [11].

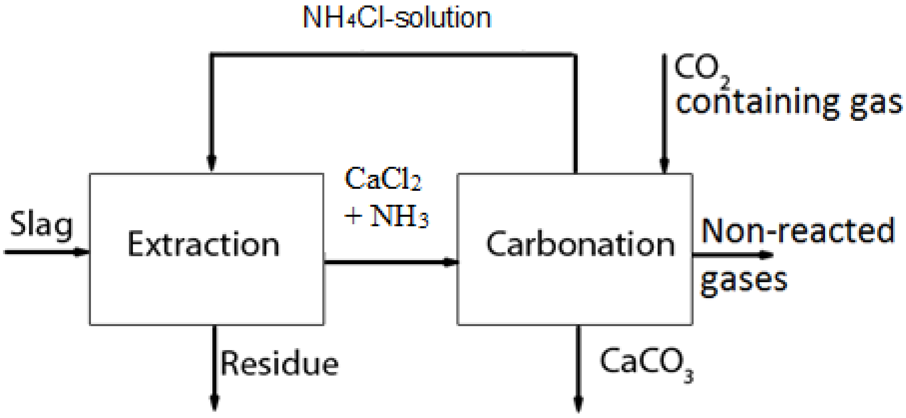


Figure 2.6.2 The process concept for continuous PCC production [10].

The process lay-out for the continuous PCC production process can be seen in Figure 2.6.3. The extraction stage is in the bottom left of Figure 2.6.3 where steel slag is added and slag residue taken out through sedimentation in the canister above. The reactor in the bottom right corner is where the carbonation takes place; there CO_2 is added and PCC taken out through sedimentation and filtration in the sedimentation canister above. As seen in the figure, the process is a closed loop where the only compounds that should enter the process are steel slag and CO_2 and the compounds coming out are PCC and slag residue. Figure 2.6.4 shows a picture of the laboratory scale setup used for H-P Mattilas doctoral research (2010-2014), note that the left reactor on in the in Figure 2.6.4 is on the right side in Figure 2.6.3.

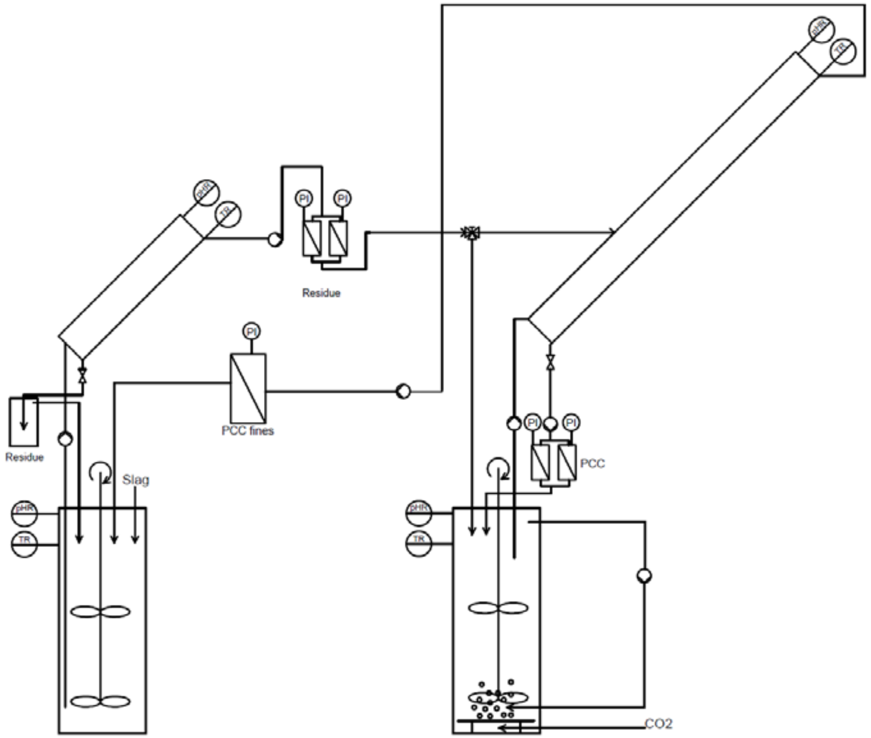


Figure 2.6.3 process description for continuous PCC production (2).

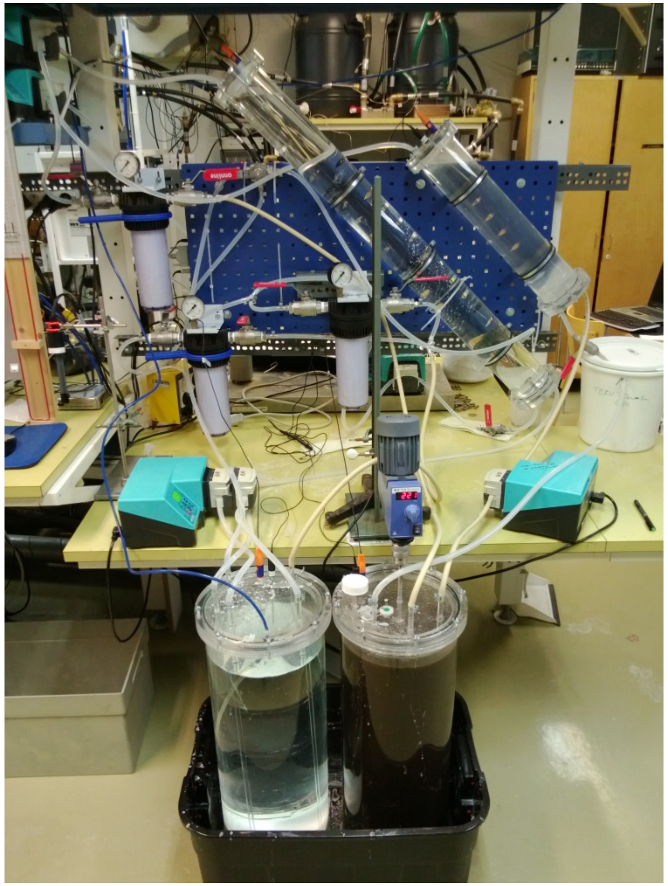


Figure 2.6.4 Picture of the process for a continuous PCC production process with steel converter slag and ammonium chloride (Picture by Mattila).

3 Removal of NH_4Cl from PCC manufactured from steel converter slag

When using ammonium chloride to produce PCC from steel converter slag there will be some salt left in the PCC product. A typical experiment gave results of 3-5 %-wt Cl in the dry PCC, later lower contents of NH_4Cl were found. The ammonium chloride should be removed from the product and reused in the PCC production process to improve the quality of the product and to give a better economic viability. To start, a method for estimating the amount of ammonium chloride in the PCC using pH was tested. Secondly, a method for removing the NH_4Cl with water from PCC-NH_4Cl mixtures with cross-current and counter-current batch filtration was tested both theoretically and experimentally.

3.1 Theoretical and experimental study of measuring ammonium chloride content in calcium carbonate solutions by measuring pH

Ammonium chloride is a salt that affects the pH of a mixture when dissolved in water. The questions are:

- Would the ammonium chloride affect the pH significantly, so the purity of the PCC could be measured with a pH-meter.
- Would the presence of PCC have so much impact on the mixture that there would be problems with the measurement of the pH.

For measuring the pH of ammonium chloride and calcium carbonate solutions it is essential to know how much the different substances affect the pH, and, how much of the different substances will be dissolved in a specific amount of water. Knowing the solubility of the different substances and the pH when mixed with water reveals the amount of ammonium chloride present in the PCC-NH_4Cl mixture. The solubility of calcium carbonate is dependent on the amount of carbon dioxide dissolved. Therefore the carbon dioxide content in the water solution has to be taken into consideration.

The next sections will demonstrate the theory and experimental studies of measuring the NH_4Cl content in PCC-NH_4Cl mixture based on pH-values. It shows that pH measuring works as a measuring method that also can reveal the PCC crystal form.

3.1.1 Solubility of ammonium chloride in water

The solubility of ammonium chloride in water depends on the temperature [32] but nevertheless it does dissolve in water quite well (Table 3.1.1). Ammonium chloride dissolves according to the reaction R3.1.1.

$$NH_4Cl \leftrightarrow NH_4^+ + Cl^- \qquad \text{R3.1.1}$$

A problem arises when the NH_4Cl salt precipitates on or in the PCC particles and more water is needed for removing the salt. The PCC particle size also has an impact on the water amount needed for washing. The solubility of NH_4Cl changes almost linearly with temperature, making it possible to interpolate or extrapolate the solubility for a specific temperature, $T(°C)$. In the experimental studies the temperatures are between 20 ℃ and 25 ℃. Also the Equations E3.1.1 or E3.1.2 can be used, taken from the trend line in Microsoft Excel, with the regression coefficient R^2= 0,999845.

Table 3.1.1 solubility of NH_4Cl in water [32].

Unit	**10 ℃**	**15 ℃**	**20 ℃**	**25 ℃**
mol NH_4Cl/kg water	6.199	6.566	6.943	7.331
g NH_4Cl/g water	0.332	0.351	0.371	0.392

$$Molality\left(\frac{\mathrm{mol\ NH_4Cl}}{\mathrm{kg\ H_2O}}\right) = 0.07546 \cdot \left(\frac{\mathrm{T}}{\mathrm{°C}}\right) + 5.4392 \qquad \text{E3.1.1}$$

$$Concentration\left(\frac{\mathrm{kg\ NH_4Cl}}{\mathrm{kg\ H_2O}}\right) = 0.004037 \cdot \left(\frac{\mathrm{T}}{\mathrm{°C}}\right) + 0.290954 \qquad \text{E3.1.2}$$

Theoretically, the amount of water needed for dissolving all ammonium chloride to water can be calculated from equation E3.1.3, with the temperature $\left(\frac{\mathrm{T}}{\mathrm{°C}}\right)$.

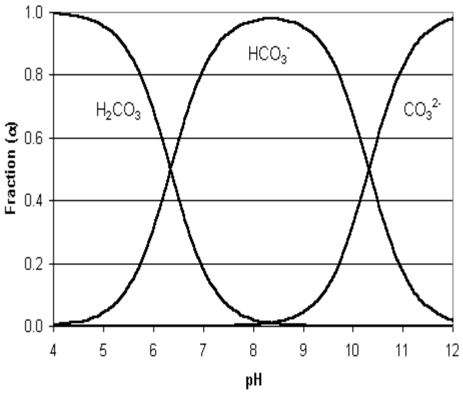
$$m_{water} = \frac{m_{NH_4Cl}}{\left(0.004037 \cdot \left(\frac{\mathrm{T}}{°\mathrm{C}}\right) + 0.290954\right)} \qquad \text{E3.1.3}$$

For example, 1 g NH_4Cl needs 2.55 g water to be dissolved at 25 °C.The amount of water needed for removing NH_4Cl from the PCC is larger than this theoretical value (see Chapter 3.2). However, it gives a lower limit for the amount of water needed. The amount of water needed is not only depending on the percentage (if the percentage is relatively low) of NH_4Cl but also on the efficiency of the method of separating the solution from the PCC (e.g. a filter).

3.1.2 Solubility of carbon dioxide in water

According to Tegethoff et al. [8] the solubility of calcium carbonate in water is about 0,013 $\frac{\mathrm{mg\ CaCO_3}}{\mathrm{g\ H_2O}}$. However, if dissolved CO_2 is present as well, the amount of calcium carbonate dissolved could multiply by 100 times. Thus, it is important to know the content of dissolved carbon dioxide in the water. When carbon dioxide dissolves in pure water $H_2CO_3(aq)$ is formed (see R3.1.3). $H_2CO_3(aq)$ is a weak acid and decreases the pH of the water solution.

Water often contains alkaline ions, for example dissolved calcium carbonate, known as hard water [8]. The pH of the aqueous solution affects the reactions taking place when carbon dioxide is dissolving (see Figure 3.1.1). When the pH increases at low pH (< 5) water-carbon dioxide solution, the percentage of H_2CO_3 decreases while HCO_3^- increases (see R3.1.4). When the pH increases to a value above 9, HCO_3^- starts to decrease and the amount of CO_3^{2-} ions increases in the solution (see R3.1.5).



$$CO_2(g) \leftrightarrow CO_2(aq) \qquad \text{R3.1.2}$$

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3(aq) \qquad \text{R3.1.3}$$

$$H_2CO_3(aq) \leftrightarrow \; H^+ + HCO_3^- \qquad \text{R3.1.4}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \qquad \text{R3.1.5}$$

Figure 3.1.1 The total carbonates (mole) versus pH and reactions, for dissolved carbon dioxide in water[33-35].

The solubility of carbon dioxide in water is dependent on temperature and CO_2 pressure. The higher the temperature, the less carbon dioxide can be dissolved (see Figure 3.1.2). The higher the CO_2 pressure, the more carbon dioxide can be dissolved and vice versa. In this thesis the solutions will be operated at atmospheric pressure (assumed constant at 101,325 kPa).

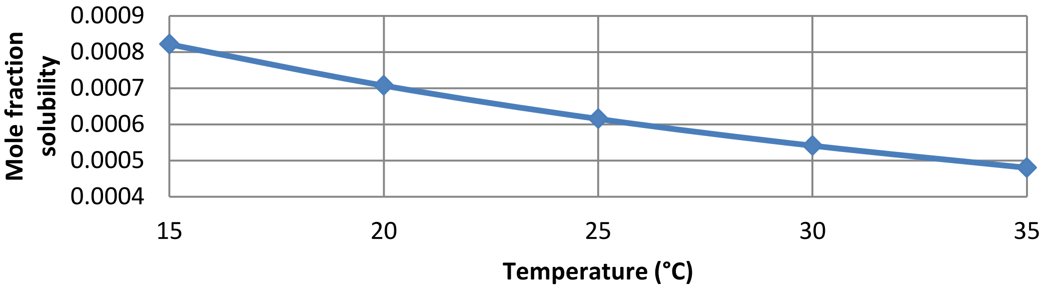


Figure 3.1.2 Solubility of carbon dioxide in water at atmospheric pressure 101,325 kPa CO_2 [32].

3.1.3 Solubility of calcium carbonate in water

As stated above, the solubility of calcium carbonate is dependent on the pH of the solution affected e.g. by the dissolved carbon dioxide content in the water. The carbon dioxide reacts with the calcium carbonate and forms $Ca(HCO_3)_2$ (see reaction R3.1.6) [8].

$$CaCO_3(s) + H_2CO_3(aq) \leftrightarrow Ca^{2+}(aq) + 2HCO_3^-(aq) \qquad \text{R3.1.6}$$

Therefore it is important to have a carbon dioxide free solution when measuring the solubility of calcium carbonate in water. The main reactions that appear when calcium carbonate dissolves in pure water are given in R3.1.7 and R3.1.8. Reaction R3.1.9 is the sum of the other reactions.

$$CaCO_3(s) \leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq) \qquad \text{R3.1.7}$$

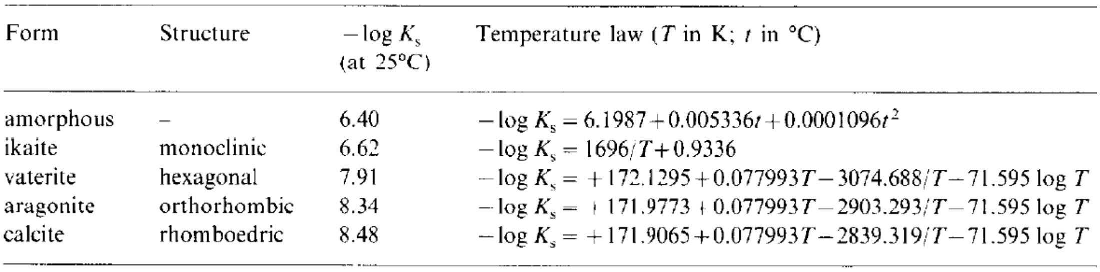
$$CO_3^{2-}(aq) + H_2O(l) \leftrightarrow OH^-(aq) + HCO_3^-(aq) \qquad \text{R3.1.8}$$

$$CaCO_3(s) + H_2O(l) \leftrightarrow HCO_3^-(aq) + OH^-(aq) + Ca^{2+}(aq) \qquad \text{R3.1.9}$$

The calcium ion Ca^{2+} will increase the pH and affect the pH the most due to its high pK_b while the carbonate ion CO_3^{2-} will decrease the pH to some extent (see Chapter 3.2.2). Later calculations will use the reaction R3.1.9 for pH measurement (see Chapter 3.2).

As mentioned in Chapter 2.3, precipitated calcium carbonate can have several different crystal forms. The different forms of PCC have different solubilities that are dependent on pressure and temperature. This thesis will deal with atmospheric pressure only and the focus will be on temperature changes. Table 3.1.2 shows the equations for the solubility constants for each form of calcium carbonate dependent of the temperature. The information from Table 3.1.2 is also expressed in Figure 3.1.3 where the solubility constant is plotted against temperatures between 15°C and 35 °C. Note that in all cases except aragonite the solubility will decrease with increasing temperature. As seen in Figure 3.1.3, the most stable form of calcium carbonate having the lowest solubility is calcite. Calcite is also the most stable calcium carbonate under different pressures [36].

Table 3.1.2 Solubility products for the various forms of calcium carbonate [37].



Form	Structure	$-\log K_s$ (at 25°C)	Temperature law (T in K; t in °C)
amorphous	–	6.40	$-\log K_s = 6.1987 + 0.005336t + 0.0001096t^2$
ikaite	monoclinic	6.62	$-\log K_s = 1696/T + 0.9336$
vaterite	hexagonal	7.91	$-\log K_s = +172.1295 + 0.077993T - 3074.688/T - 71.595 \log T$
aragonite	orthorhombic	8.34	$-\log K_s = +171.9773 + 0.077993T - 2903.293/T - 71.595 \log T$
calcite	rhomboedric	8.48	$-\log K_s = +171.9065 + 0.077993T - 2839.319/T - 71.595 \log T$

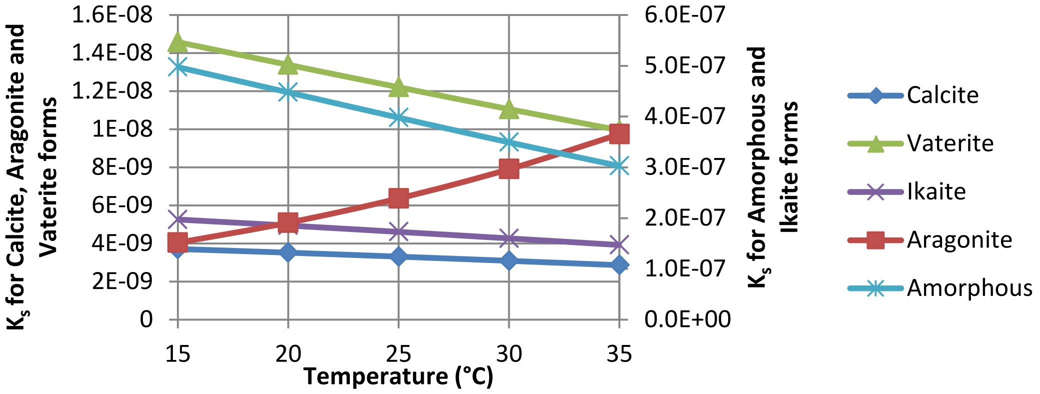


Figure 3.1.3 K_s for different forms of calcium carbonate plotted against the temperature at atmospheric pressure. The left y-axis includes the K_s for Calcite, Aragonite and Vaterite. The right y-axis represents the K_s for Amorphous $CaCO_3$ and Ikaite.

In general, the solubility of calcium carbonate in water is low. Some forms of calcium carbonate dissolve better than others. The differences in solubility of two calcium carbonate forms can be seen in Figure 3.1.4.

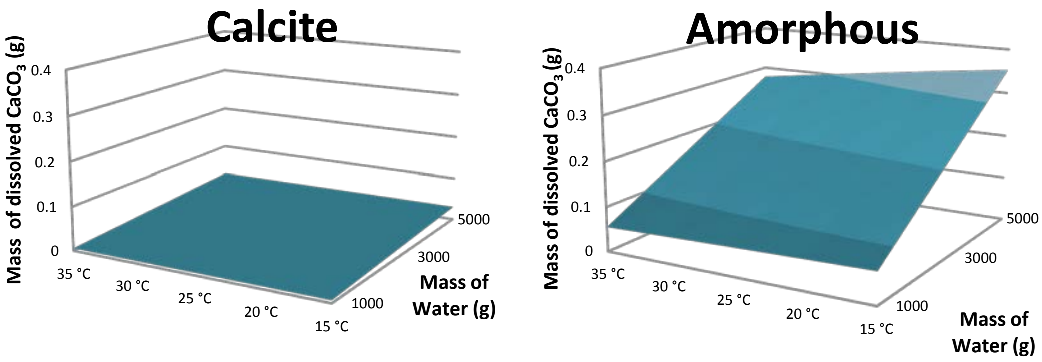


Figure 3.1.4 Solubility of $CaCO_3$ (g) (calcite and amorphous $CaCO_3$) in different water amounts (g) for different temperatures (°C) [37].

The 3D graphs in Figure 3.1.4 are plotted in 2D in Figure 3.1.4 to be able to produce an equation of the slope coefficients for all the different forms of PCC.

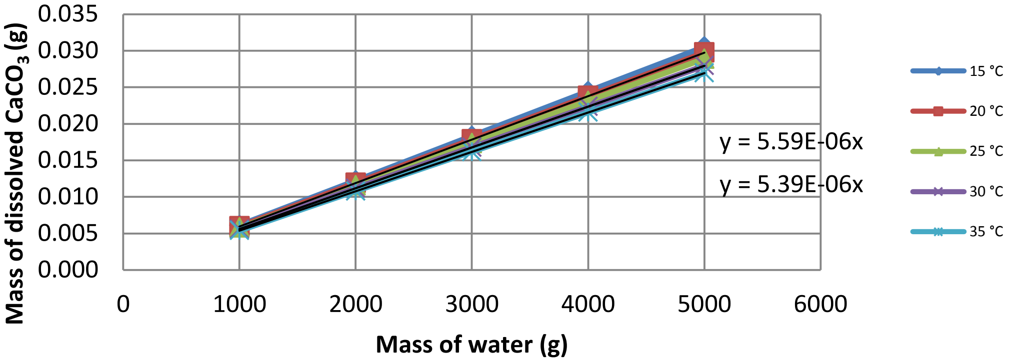


Figure 3.1.4 Mass of dissolved calcite (g) plotted against mass of water (g) in various temperatures. Equations for the temperatures 25 ℃, 30 ℃ and 35 ℃ are shown.

An equation for the slope coefficient makes it possible to measure the amount of $CaCO_3$ dissolved in water for different temperatures. The slope coefficient is then multiplied by the mass of water in the solution, giving how much more $CaCO_3$ is dissolved by the temperature change for various temperatures, see Chapter 3.2.4 for the equations. The equations for the slope coefficients for the different forms of $CaCO_3$ are given in Equations E3.1.4 to E3.1.8.

Calcite
$$s\left(\frac{T}{°C}\right) = -2.86 \cdot 10^{-10}\left(\frac{T}{°C}\right)^2 - 2.17 \cdot 10^{-8}\left(\frac{T}{°C}\right) + 6.50 \cdot 10^{-6} \qquad \text{E3.1.4}$$

Aragonite
$$s\left(\frac{T}{°C}\right) = -2.86 \cdot 10^{-10}\left(\frac{T}{°C}\right)^2 - 3.37 \cdot 10^{-8}\left(\frac{T}{°C}\right) + 7.84 \cdot 10^{-6} \qquad \text{E3.1.5}$$

Vaterite
$$s\left(\frac{T}{°C}\right) = -2.00 \cdot 10^{-10}\left(\frac{T}{°C}\right)^2 - 9.30 \cdot 10^{-8}\left(\frac{T}{°C}\right) + 1.35 \cdot 10^{-5} \qquad \text{E3.1.6}$$

Ikaite
$$s\left(\frac{T}{°C}\right) = +8.71 \cdot 10^{-9}\left(\frac{T}{°C}\right)^2 + 6.56 \cdot 10^{-7}\left(\frac{T}{°C}\right) + 2.72 \cdot 10^{-5} \qquad \text{E3.1.7}$$

Amorphous
$$s\left(\frac{T}{°C}\right) = -2.91 \cdot 10^{-9}\left(\frac{T}{°C}\right)^2 - 6.18 \cdot 10^{-7}\left(\frac{T}{°C}\right) + 8.06 \cdot 10^{-5} \qquad \text{E3.1.8}$$

3.1.4 Theoretical background for measuring pH for ammonium chloride solutions

For measuring the pH the substance needs to be mixed with water, and ammonium chloride easily dissolves. Therefore an assumption can be taken; all NH_4Cl from a PCC-NH_4Cl mixture will dissolve if there is water added in such an amount that it is possible to measure the pH of the PCC-NH_4Cl aqueous solution. A small amount of PCC will dissolve in water and affect the pH measurement, by giving a higher value. Nevertheless, when ammonium chloride (NH_4Cl) is dissolved in water the pH can be determined theoretically. Figure 3.1.5 shows the pH decreasing rapidly when the amount of ammonium chloride increases. The pH can be calculated from the amount of H^+ according to R3.1.11.

$$NH_4Cl \leftrightarrow NH_4^+ + Cl^- \tag{R3.1.10}$$

$$NH_4^+ \leftrightarrow NH_3 + H^+ \tag{R3.1.11}$$

$$H_2O \leftrightarrow H^+ + OH^- \tag{R3.1.12}$$

From the reaction R3.1.11 the constant K_b for NH_3 can be obtained while from reaction R3.1.12 the constant K_w can be obtained. The equation E3.1.10 gives the constant K_a for NH_4^+.

$$K_a\left(\frac{T}{°C}\right) = \frac{K_w\left(\frac{T}{°C}\right)}{K_b\left(\frac{T}{°C}\right)} \tag{E3.1.8}$$

With the constant K_a and the molarity of the ammonium chloride, equal to $[NH_4^+]$ (see R3.1.10) the pH can be calculated with the equations E3.1.9 to E3.1.11 [38], where c_{NH_4Cl} is the concentration of NH_4Cl in the water solution.

$$K_a\left(\frac{T}{°C}\right) = \frac{[H^+][NH_3]}{[NH_4^+]}, \qquad [H^+] = [NH_3], [NH_4^+] = c_{NH_4Cl} - [H^+] \tag{E3.1.9}$$

$$[H^+] = \frac{-K_a\left(\frac{T}{°C}\right) \pm \sqrt{K_a\left(\frac{T}{°C}\right)^2 + 4 \cdot K_a\left(\frac{T}{°C}\right)}}{2} \qquad \text{E3.1.10}$$

$$pH = -\log([H^+]) \qquad \text{E3.1.11}$$

The pH of different percentages of NH_4Cl is shown in Figure 3.1.5 at 25°C. The color of the line used in the chart depends on the amount of water. Equations for different amounts of water are shown next to the chart.

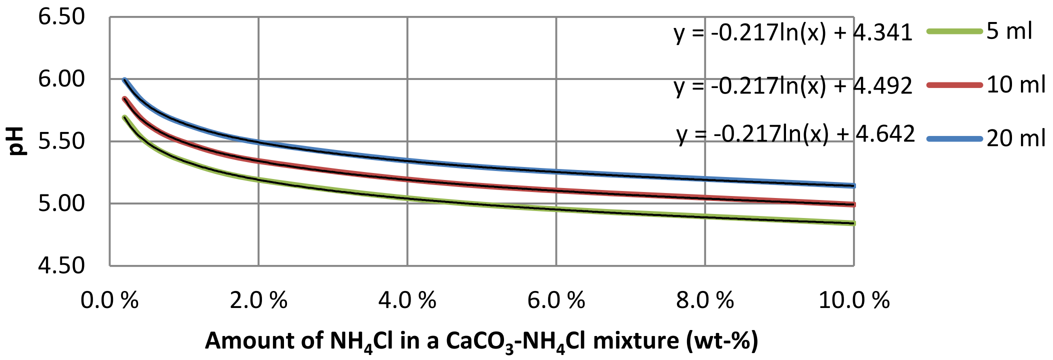


Figure 3.1.5 Theoretically calculated amount of NH_4Cl *in* $CaCO_3$ *with pH as measurement factor without any* $CaCO_3$ *dissolved in different amount of water, at 25*°C.

The constants K_b for NH_3 and K_w change rapidly with temperature. Figure 3.1.6 shows how the constants pK_w and pK_b vary with the temperature, pK_w values are shown on the left y-axis and the pK_b values are seen on the right y-axis.

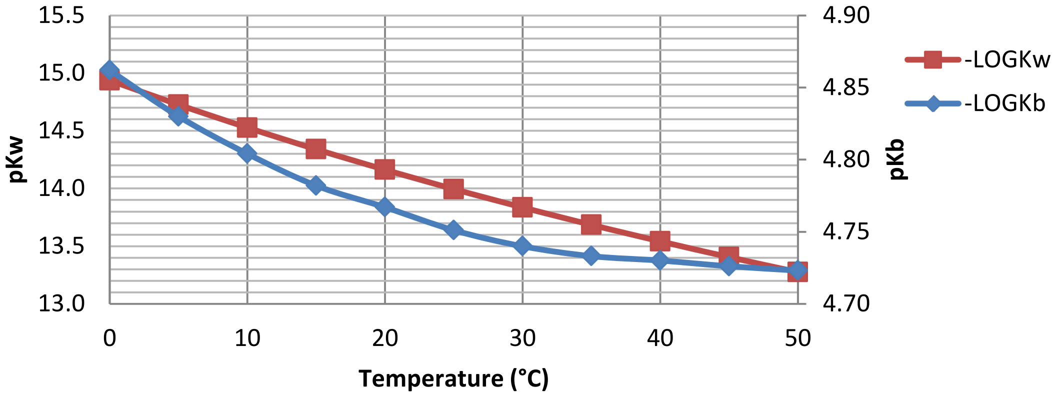


Figure 3.1.6 Constants pK_w (left) and pK_b for NH_3 (right) for different temperatures at atmospheric pressure [32] [39].

Different aqueous volumes shown in Figure 3.1.5 will give a higher or lower pH depending on the temperature, as shown in Figure 3.1.7.

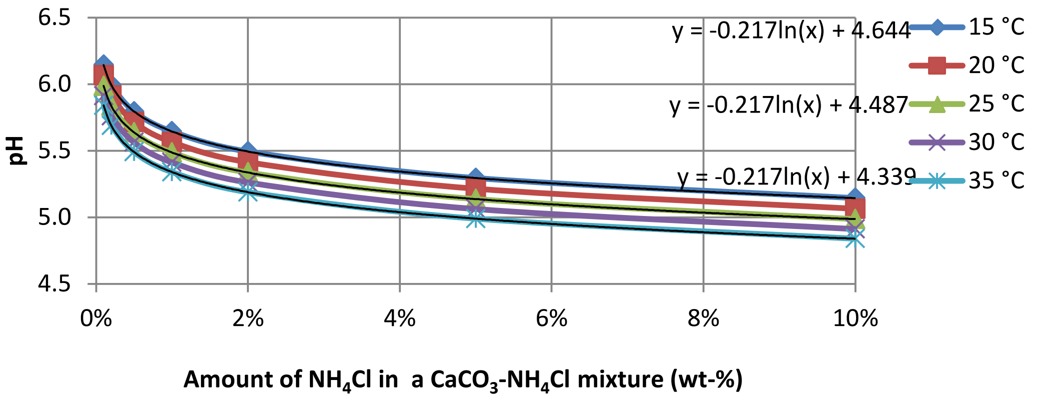


Figure 3.1.7 Theoretically calculated amount of NH_4Cl in dry $CaCO_3$ with pH as measurement factor without any $CaCO_3$ dissolved, in 10 ml water, for temperatures between 35°C to 15°C.

When the temperature and the volume of the water vary the slope coefficient stays the same, -0,217 in all the equations of Figure 3.1.5 and Figure 3.1.7. The change is seen in the constant that affects the intercept of the line (Figure 3.1.7). There is therefore a need for an equation that gives the correct intercept for the lines. The equation is similar to Equations E3.1.3 to E3.1.7, with a function of the temperature for different volumes of water. Equation E3.1.12 shows the intercept of the line as a function of the temperature for a water mass ten times the PCC-NH_4Cl mass and Equation E3.1.13 for twenty times larger (other masses of water can be used but using 10 and 20 times more water simplifies the experimental measurements).

$$y_{10}\left(\frac{T}{°\mathrm{C}}\right) = -1.52 \cdot 10^{-2}\left(\frac{T}{°\mathrm{C}}\right) + 4.87 \qquad \text{E3.1.12}$$

$$y_{20}\left(\frac{T}{°\mathrm{C}}\right) = -1.52 \cdot 10^{-2}\left(\frac{T}{°\mathrm{C}}\right) + 5.02 \qquad \text{E3.1.13}$$

These equations will be used later on in the thesis where there is only a need for two volumes of water (10 ml and 20 ml) to calculate the content of NH_4Cl in the PCC-NH_4Cl solution.

3.1.5 Theoretical background for measuring pH for calcium carbonate

As mentioned, calcium carbonate dissolves differently in water at various temperatures. This will change the pH, due to varying amounts of dissolved Ca^{2+} and HCO_3^-, and temperature will change the value of the dissociation constant K_b (see Figure 3.1.8).

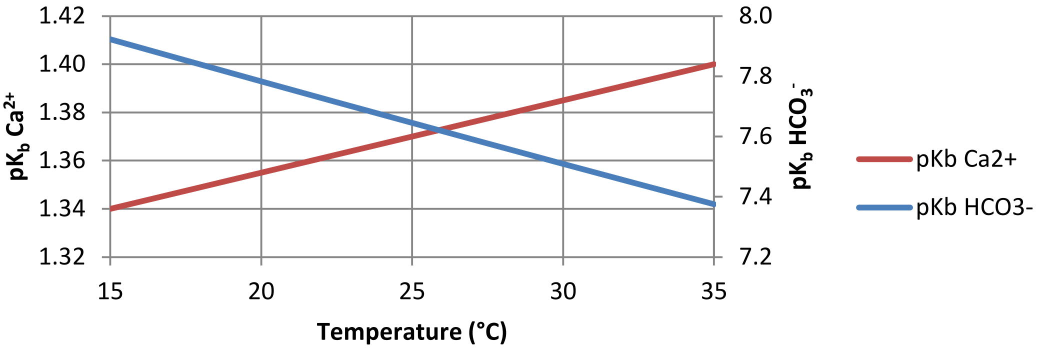


Figure 3.1.8 pK_b for Ca^{2+} and HCO_3^- plotted against the temperature (°C) [40].

For calculating the pH of dissolved calcium carbonate in pure water, the reaction R3.1.9 is used for the Equations E3.1.14 to E3.1.17 [38], where $c\left(\frac{T}{°\mathrm{C}}, \frac{m_w}{g}\right)$ is the concentration of the dissolved $CaCO_3$ in the aqueous solution. m_w indicates the mass of water used.

$$K_{Ca^{2+}}\left(\frac{T}{°C}\right)\cdot K_{HCO_3^-}\left(\frac{T}{°C}\right)=\frac{[HCO_3^-]\cdot[OH^-]\cdot[Ca^{2+}]}{[CaCO_3]} \qquad \text{E3.1.14}$$

$$[HCO_3^-]=[Ca^{2+}]=[OH^-],[CaCO_3]=c\left(\frac{T}{°C},\frac{m_w}{g}\right)-[OH^-] \qquad \text{E3.1.15}$$

$$[OH^-]\approx\sqrt[3]{c\left(\frac{T}{°C},\frac{m_w}{g}\right)\cdot K_{Ca^{2+}}\left(\frac{T}{°C}\right)\cdot K_{HCO_3^-}\left(\frac{T}{°C}\right)} \qquad \text{E3.1.16}$$

$$pH=-Log\left(\frac{K_w\left(\frac{T}{°C}\right)}{[OH^-]}\right) \qquad \text{E3.1.17}$$

Different forms of calcium carbonate have different solubilities, thus the concentration $c\left(\frac{T}{°C},\frac{m_w}{g}\right)$ will be different and therefore also the pH. Measuring pH can then also be used to distinguish between the different types of calcium carbonate. The pH for calcium carbonate in pure water can fluctuate between 9 and 11 depending on temperature and crystal form of the calcium carbonate particle.

There are some reactions that occur when $CaCO_3$ dissolves in water that can be neglected according to Brečevič et al. [36]. They affect the pH but not in the extent that a correction for it is needed (see reaction R3.1.13 to R3.1.16) [34] [36] [25].

$$Ca^{2+}+OH^-\leftrightarrow CaOH^+ \qquad \text{R3.1.13}$$

$$Ca^{2+}+2OH^-\leftrightarrow Ca(OH)_2 \qquad \text{R3.1.14}$$

$$Ca^{2+}+HCO_3^-\leftrightarrow CaHCO_3^+ \qquad \text{R3.1.15}$$

$$Ca^{2+}+2HCO_3^-\leftrightarrow Ca(HCO_3)_2 \qquad \text{R3.1.16}$$

If the solution is saturated by carbon dioxide, the Reaction R3.1.15 should not be excluded, because it will affect the pH with a value of 0.003 to 0.011 [34]. This thesis will not add any CO_2 into the solution when measuring the amount of NH_4Cl in the PCC, therefore R3.1.15 will be excluded.

3.1.6 Experimental verification of measuring the amount of NH_4Cl in a NH_4Cl and $CaCO_3$ mixture via pH

Equipment

Weight:	Radwag AS220/X (10 mg – 220 g, accuracy 0.1 mg)
pH meter:	ELIT P14 114-75 Epoxy Body Combination pH electrode ELIT 9808 (pH accuracy 0.01) ELIT software
Thermometer:	ELIT 8701 (Accuracy ± 0.2 ℃)
Magnetic stirrer:	IKA Yellow line MAG HS 7(max 10 l water, speed range 100 – 1500 min^{-1})

When calculating a case with dissolved PCC, the Ca^{2+} ion with a large basic dissociation constant will increase the pH rapidly. However the lines plotted in Figure 3.1.5 and Figure 3.1.7 will only move vertically, keeping the same slope coefficient. Therefore, the assumption was that the dissolved PCC will only increase the intercept in the plotted lines keeping the same slope coefficient, thus increasing the pH.

The first experiment was carried out to prove and recognize that the theoretical assessment from above was correct. Clean calcium carbonate (rhombohedric calcite, Sigma-Aldrich) with a purity of 99.5 % -100.5 % dry basis (SEM picture, Appendix 1) was weighed in seven different batches (Figure 3.1.9) and NH_4Cl with a purity of ≥ 99 % (VWR) was added. The total mass of the dry NH_4Cl and the dry $CaCO_3$ was around 1.00 g. The solution was mixed with a magnetic mixer for more than 3-4 minutes (see Figure 3.1.9). The pH was then measured in all the batches. The experiments were carried out in atmospheric pressure and temperatures between 21.1 ℃ and 21.7 ℃.

Figure 3.1.9 Scale, calcium carbonate, batches, pH- and temperature- meter and magnetic stirrer used for the experiment.

Figure 3.1.10 shows the experimental results from the first experiment compared with the theoretical values without calcium carbonate is dissolved in water. The pH for 0 % NH_4Cl was a bit low in this experiment due to human errors, but this was later tested and should be around pH 9,65 (Table A1 in Appendix 2). The results from the experiment show that the experimental data is similar to the theory presented above. The slope coefficient stays the same even though calcium carbonate is added. The calcium carbonate increases the pH and moves the line vertically upwards (Figure 3.1.10). The result shows that pH measurements can be used to see how much NH_4Cl is present in the PCC. However, an equation is needed to make the information received from measuring the pH easier to use.

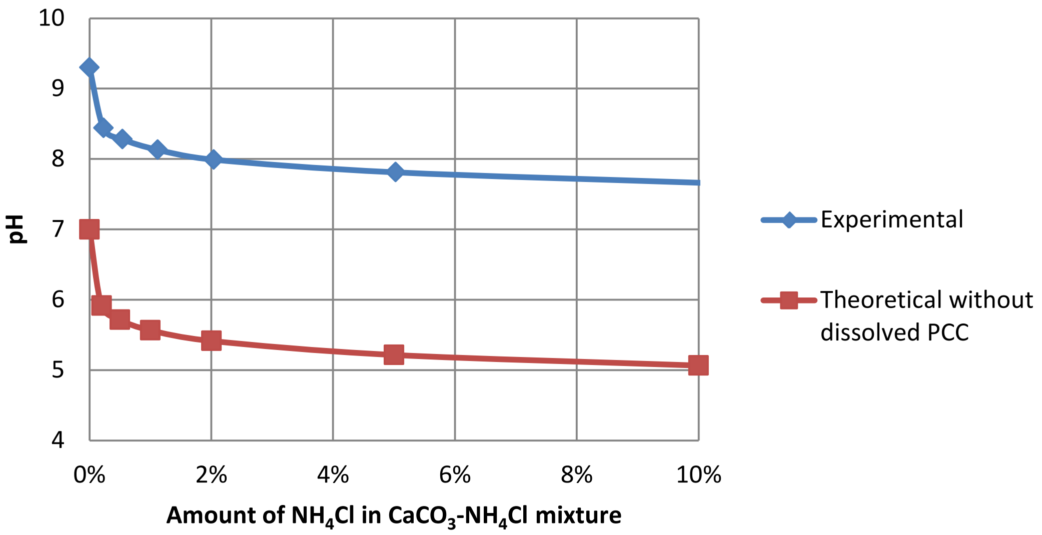


Figure 3.1.10 Experimental results compared with calculated results without any dissolved calcium carbonate in 10 ml water.

3.1.7 Theoretical conclusions taken in to experimental practice

The experiments and the theory from earlier will be used as a measuring tool to calculate the NH_4Cl content in dry PCC by measuring pH from two volumes of water. The idea is to have a specific amount of PCC containing NH_4Cl and mix it with water, ten times the weight of the PCC-NH_4Cl mixture, here to 10 ml water. Then measure the pH of the water-PCC-NH_4Cl solution. With that amount of water, all the NH_4Cl will dissolve and a specific amount of $CaCO_3$ will dissolve as well. When adding the same amount of water again (the water content is now twenty times the PCC-NH_4Cl content), here to 20 ml, slightly more PCC will dissolve. All the NH_4Cl is already dissolved, the molarity being less than the previous measurement (with ten times the water), thus a difference in the pH is obtained. The difference will then tell the content of the NH_4Cl in the PCC-NH_4Cl solution through a model equation, assuming that the PCC crystal form in known. See Figure 3.1.11 for a visual example of the pH measurements, where 1 g PCC-NH_4Cl mixture is mixed with 10 g water and 20 g water.

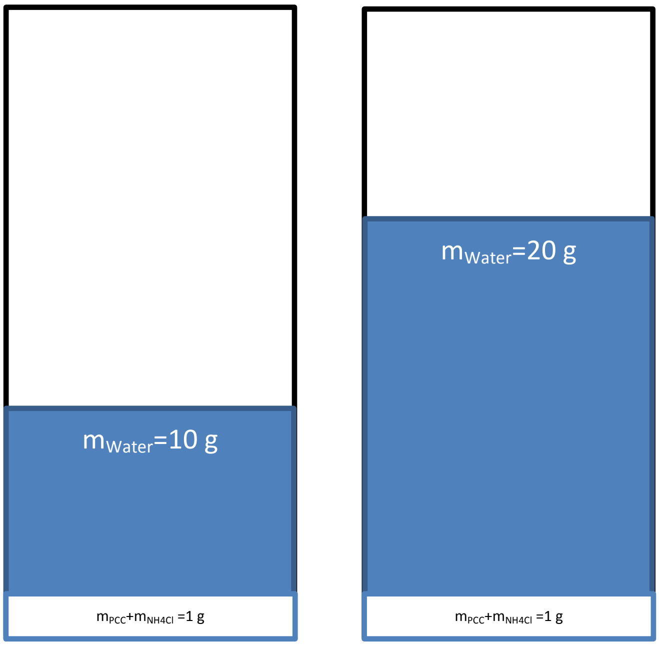


Figure 3.1.11 Example of measuring the pH of PCC-NH_4Cl-water solution with the mass 1 g for the PCC-NH_4Cl solution.

The equation uses the slope coefficient $-0{,}217ln(x)$ as obtained from calculations discussed in Chapter 3.1.5 and verified in the experiment above. However, two pH parameters must be added: one pH parameter “y” for the molarity of NH_4Cl in the solution and another parameter “z” for the amount of PCC dissolved. As Chapter 3.1.5 explained; the pH is dependent on the volume of the water and the temperature and therefore “y” and “z” are too. Equations E3.1.17 and E3.1.18 give the equations used.

$x = percentage\ of\ NH_4Cl\ in\ a\ mixture\ of\ dry\ NH_4Cl\ and\ dry\ PCC$

$y\left(\frac{T}{°C},\frac{m_w}{g}\right) = pH\ parameter\ for\ the\ molarity\ of\ NH_4Cl$

$z\left(\frac{T}{°C},\frac{m_w}{g}\right) = pH\ parameter\ for\ dissolved\ CaCO_3$

$$pH = -0{,}217ln(x) + y\left(\frac{T}{°C},\frac{m_w}{g}\right) + z\left(\frac{T}{°C},\frac{m_w}{g}\right) \qquad \text{E3.1.17}$$

$$x = e^{\left(\frac{y\left(\frac{T}{°C},\frac{m_w}{g}\right)+z\left(\frac{T}{°C},\frac{m_w}{g}\right)-pH}{0.217}\right)} \qquad \text{E3.1.18}$$

The y-parameter (Figure 3.1.12) is the theoretical value of the pH for NH_4Cl with no dissolved PCC. “y” is dependent on the temperature and the volume of the water, and as explained earlier, there is a need for two different masses of water, here ten and twenty times the mass of the PCC-NH_4Cl mixture mass (E3.1.12-E3.1.13). The z-parameter is the difference between the theoretical pH without dissolved calcium carbonate and the pH with no NH_4Cl dissolved, including the temperature (see E3.1.19 and E3.1.20).

$$z\left(\frac{T}{°C},\frac{m_w}{g}\right) = s\left(\frac{T}{°C}\right)\cdot m_w + z_{0\%} \qquad \text{E3.1.19}$$

$$z_{0\%} = -Log([H^+]_{0\%}) - 7 \qquad \text{E3.1.20}$$

$z_{0\%}$ (Figure3.1.12) stands for the difference between the theoretical pH without dissolved calcium carbonate and the pH with no calcium carbonate dissolved. $s\left(\frac{T}{°C}\right)$ stands for the pH change due to a temperature change and is dependent on the crystal form of the PCC, see E3.1.3 to E3.1.7.

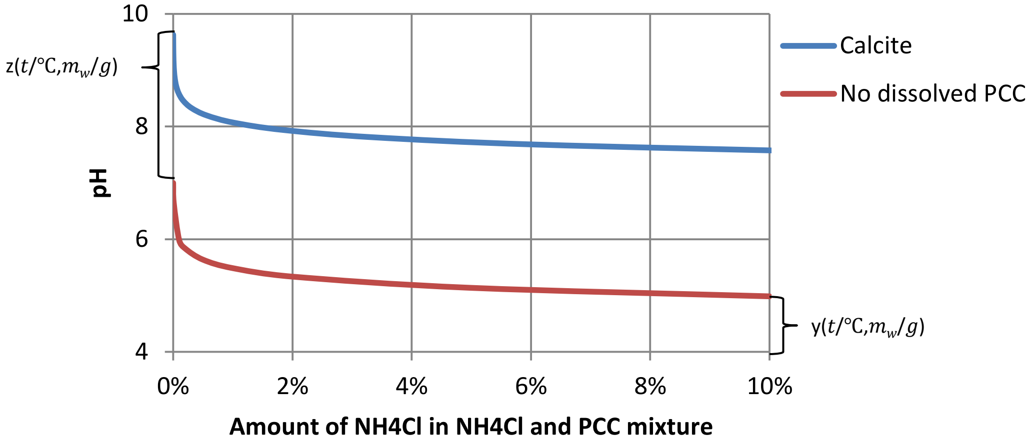


Figure 3.1.12 z-parameter and y-parameter plotted with 1 g calcite-NH_4Cl mixtures in 25 °C and 10 g water.

Thus, the methode allows for determining the amount of NH_4Cl in a PCC-NH_4Cl mixture and the crystal form of the PCC with two measurements of pH in two different water volumes, at a certain temperature.

To illustrate the method for determining the NH_4Cl content in PCC and the PCC crystal form, a graph is plotted in a logaritmic scale for a certain temperature (Figure 3.1.13). The method was tested with rhombohedral crystal form calcite samples from two different suppliers, Sigma-Aldrich (purity 99.95-100.05 %) and Merck Millipore (purity 99.99 %). The sample from Sigma-Aldrich had larger PCC particles than the sample from Merck Millipore, determined from SEM pictures (Appendix 1). The NH_4Cl was obtained from VWR (purity ≥ 99 %). The test was carried out the same way as discussed in previous chapter, but with three batches. The NH_4Cl concentrations in the PCC were 1, 2 and 3 wt-%. The temperature in the lab fluctuated during the test between 21,4 ℃ and 22,3 ℃. Thus, the pH measurements do not fit the graph exactly due to a fixed temperature (22 ℃)in the graph (Figure 3.1.13). Nevertheless, the test shows that the measuring method works good enough to determine the amount of NH_4Cl in a PCC-NH_4Cl mixture and the crystal form of the PCC. However, with NH_4Cl contents above 5 wt-% in the PCC-NH_4Cl mixture is, the method becomes gradually more inaccurate, because a small difference in pH causes large changes in the NH_4Cl content. The focus of this work is on NH_4Cl fractions below 5 wt-% in the PCC-NH_4Cl mixture.

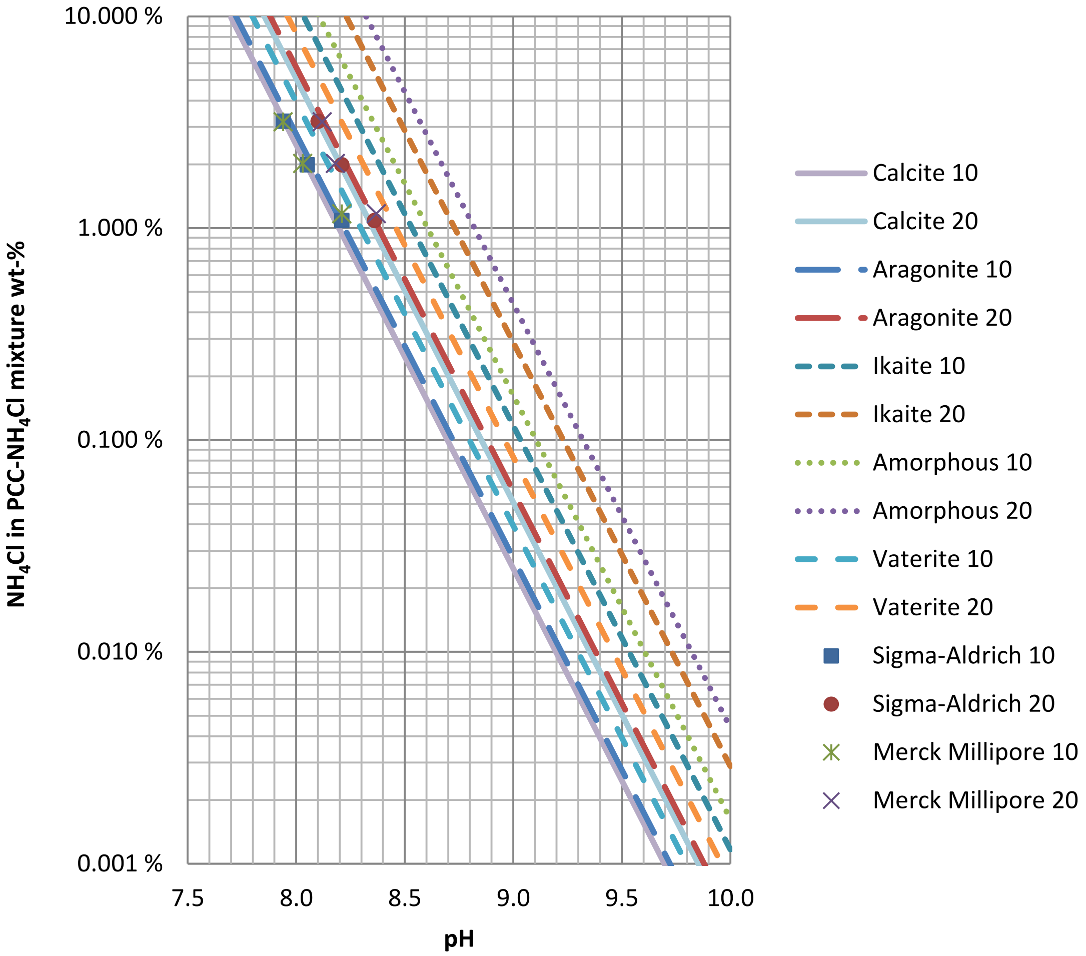


Figure 3.1.13 Different crystal forms of PCC plotted in a logarithmic graph of NH_4Cl in an PCC-NH_4Cl mixture (wt-%) as a function of solution pH at 22 °C.

The measuring method with a graph for a certain temperature limits the measurements to that specific temperature. However if the temperature is stable, the graph works well as a measuring tool. The graph is read via the two pH measurements (in this case $pH_{10\,g}$ and $pH_{20\,g}$) at the same temperature. From the two pH measurements: follow the pH-gridlines vertically until they cross a line for a specific crystal form. When these two crossings form a horizontal line at a certain percentage, the amount of NH_4Cl in the PCC-NH_4Cl mixture and the crystal form of the PCC are determined.

The above method for measuring the NH_4Cl content in PCC-NH_4Cl mixture was tested with PCC produced from steel converter slag. However, the method above gave the result 0.9 wt-% while the theoretically estimated mass fraction was 2.3 wt-% [41]. The large difference may be caused by poor calibration of the pH equipment (Xplorer GLX Pasco, accuracy 0.01 pH units) or other impurities in PCC produced from steel converter slag which affects the pH value. Also the theoretical calculation may not be based on valid assumptions.

3.2 Washing PCC-NH_4Cl mixtures and NH_4Cl recovery

This chapter covers the washing of PCC-NH_4Cl mixtures with a batch setup. Theoretical simulations and experimental studies of two different washing methods, crosscurrent and countercurrent, were done to study the efficiency of washing of PCC-NH_4Cl mixtures.

3.2.1 Theoretical background for washing PCC-NH_4Cl mixtures

A continuous countercurrent washing process is one of the possibilities for washing the PCC-NH_4Cl mixture to recover the NH_4Cl solvent. Using gravity for settling, as frequently used in continuous processes, the PCC in a countercurrent system could however give problems due to the small size of the PCC particles. Stokes' law (see E3.2.1) [42] gives the relative velocity, with respect to the surrounding medium of the particles during settling.

$$\omega_p = \frac{g \cdot d_p^2 \cdot (\rho_p - \rho_F)}{18 \cdot \eta_F} \qquad \text{E3.2.1}$$

In this equation, g represents the gravity, d_p is the particle diameter, ρ_p is the particle density, ρ_F is the water density and η_F is the water viscosity. From Equation E3.2.1 (Appendix 3) the required settling velocity for the PCC particles would be too low (about $0.000208\ \frac{m}{s}$) for countercurrent washing with settling by vertical flows. The approach would require small flows and long residence times, which makes it an unpractical alternative.

A batch filtration setup seems to be a better option to be used with PCC. The filter type should not matter (see Chapters 3.2.3–3.2.4) for determining the separation factor of NH_4Cl from PCC-NH_4Cl mixture with water, and the amount of washing water needed. Two batch filtration setups were tested; a countercurrent and a crosscurrent setup. Figure 3.2.1 a) illustrates a crosscurrent batch setup while b) shows a countercurrent batch setup. The setups consist of separate washing stages with a specific amount of water. A chosen amount of PCC-NH_4Cl mixture is added to the water in the first batch, dissolving all NH_4Cl from the solid mixture. The PCC-NH_4Cl mixture is then filtered and (now containing less NH_4Cl) put into next water filled stage. The same procedure is repeated for all stages.

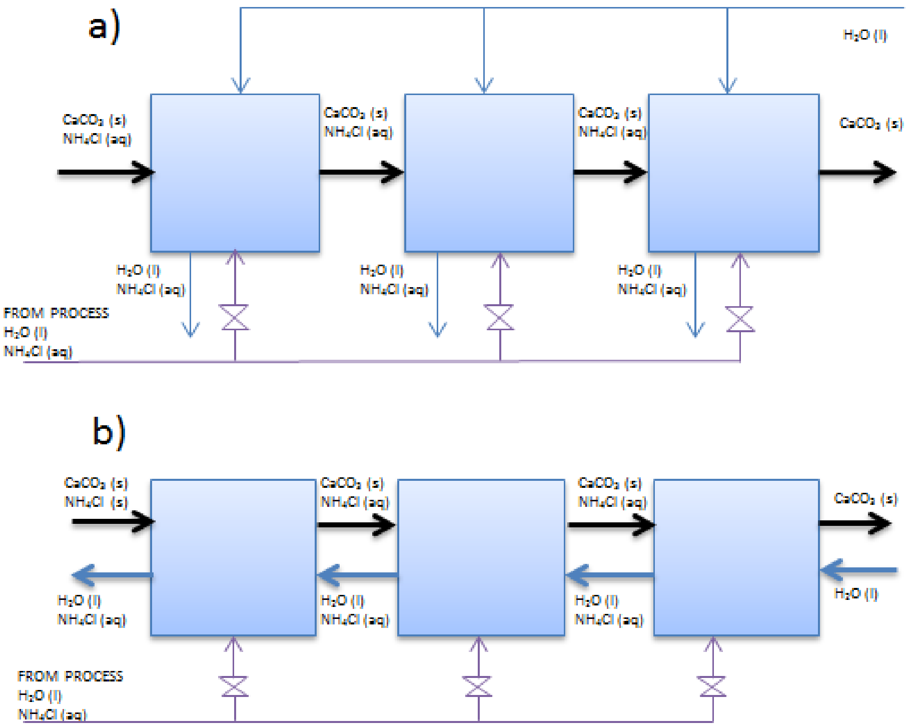


Figure 3.2.1 Illustrative overview of a) crosscurrent and b) countercurrent batch filtration setups.

The differences between the setups are that the water from one stage is reused in another stage in the countercurrent setup while the water would be reused in the same stage in the crosscurrent. However, the first calculations are done assuming no water inflow or outflow. Thus, the stages stay full with water and the PCC-NH_4Cl mixture is filtered and moved to the next stage.

This means that the first calculation step is the same for both setups. The separation process is presented in Figure 3.2.2, showing the PCC in a), containing an amount of unwanted NH_4Cl (the small dots). In b) water is added to dissolve the NH_4Cl and after mixing in c) all (or at least most) NH_4Cl is dissolved in the water, leaving the PCC almost free from NH_4Cl in d). A challenge follows when the PCC is to be removed from the water containing dissolved NH_4Cl, but this is similar to separating PCC from the water in the first place.

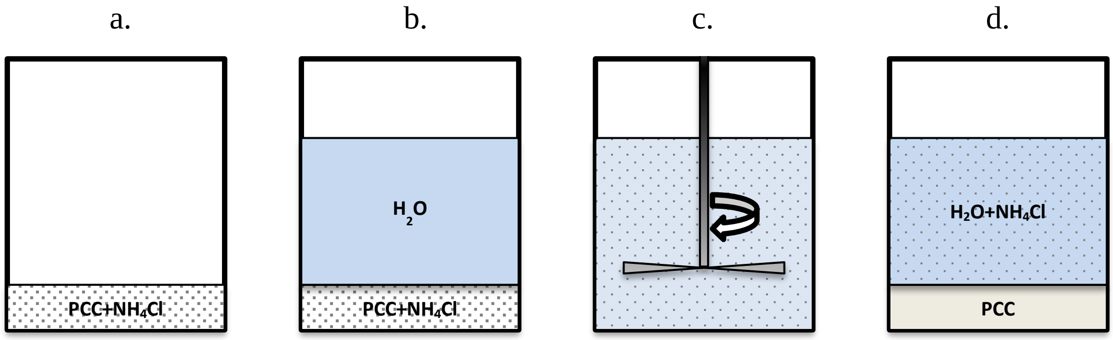


Figure 3.2.2 The separation process of separating NH_4Cl from PCC-NH_4Cl mixture with water.

When filtering the mixture in d) the dry content of the filter cake can be from 60 wt-% to 80 wt-% depending on the particle size of the PCC and the filtration method. Left in the filter cake is thus typically 40 wt-% to 20 wt-% water containing dissolved NH_4Cl. The separation can be described by the separation factor S which gives the value of NH_4Cl transferred divided by the NH_4Cl not transferred [43]. The transfer from the first stage into the next can be seen in Equation E3.2.2

$$S = \frac{x_i}{x_{i+1}} \cdot \frac{m_{w\,stage}}{m_{\,PCC}} = K \cdot \frac{m_{w\,stage}}{m_{PCC}} \qquad \text{E3.2.2}$$

m_{PCC} is the mass of the PCC (g), $m_{w\,stage}$ is the mass of the water in one stage (g), x_i is the NH_4Cl mass fraction in the water solution, where i is specifying which stage is referred to. x_{i+1} is the NH_4Cl fraction in water associated with the PCC. K is the equilibrium constant that can be determined by x_i and x_{i+1}. x_0 (i = 0) is the first batch and can be calculated with Equation E3.2.3.

$$x_0 = \frac{y_0 \cdot m_{PCC-NH_4Cl}}{y_0 \cdot m_{PCC-NH_4Cl} + m_{w\ in\ stage}} \qquad \text{E3.2.3}$$

y_i is the NH_4Cl content in the solid PCC-NH_4Cl mixture and y_0, the input to the first stage, is known (It was input information for the experiments done). To calculate x_1, the dry solids content (kg/kg) d of the filter cake needs to be known. The mass of the water part of the H_2O-NH_4Cl solution in the wet PCC can then be determined with Equation E3.2.4.

$$m_{w\ in\ PCC} = \frac{1-d}{d} \cdot m_{PCC} \qquad \text{E3.2.4}$$

The mass of the NH_4Cl transferred from one stage to the next through the wet PCC can be calculated with the combination of Equations E3.2.3 and E3.2.4. When the mass of the transferred NH_4Cl is known x_{i+1} can be calculated, see Equation E3.2.5.

$$x_{i+1} = \frac{m_{i\ NH_4Cl\ (aq)}}{m_{w\ in\ batch} + m_{i\ NH_4Cl\ (aq)}} = \frac{x_i \cdot m_{w\ in\ PCC}}{m_{w\ in\ batch} + x_i \cdot m_{w\ in\ PCC}} \qquad \text{E3.2.5}$$

All stages have the same volume, thus when the small amount of water from the wet PCC is added to the next stage, the total water volume will be the same as in the first stage. When x_i and x_{i+1} are known, the separation factor S can be used for the rest of the calculations (but only for stages where fresh water is used). With S the values of x_{i+1} can be calculated with Equation E3.2.6 instead of E3.2.5.

$$x_{i+1} = \frac{x_i}{S} \qquad \text{E3.2.6}$$

The difference in the two filtering methods, the crosscurrent and the countercurrent, starts when the water inflow is calculated. S will remain unchanged for all stages in the calculations above, until the NH_4Cl content (y) in PCC is below about 0.018 wt-%, then the equilibrium constant (K) will rapidly decrease from K ≈ 32 to less than 1.5 (Chapter 3.2.5) due to adsorption, see Chapter 3.2.2.

Calculations for crosscurrent batch filtration

For calculating the water flow for the crosscurrent batch filtration process seen in Figure 3.2.1, the same water is used in all stages without in- or outflows. This will indicate how much water is needed. If the PCC (filter cake) from the last stage has an acceptable (small) content of NH_4Cl it can be determined that the water in all stages can be reused at least once. Thus, the water in a stage does not need to be changed to fresh water for the next PCC-NH_4Cl mixture. Therefore the total water flow is less than the water volume, fed to the crosscurrent stages per PCC-NH_4Cl mixture, see Equation E3.2.7 to E3.2.8.

$$f_{w\ cross}\left(\frac{g\ H_2O}{g\ PCC}\right) = \frac{m_{H_2O\ in\ batch}\ (g)}{m_{PCCmixture}\ (g) \cdot r} \cdot n \qquad \text{E3.2.7}$$

$$\dot{m}_{water\ in}\left(\frac{g}{s}\right) = \dot{m}_{PCCmixture}\left(\frac{g}{s}\right) \cdot\ f_w \qquad \text{E3.2.8}$$

f_w is the fraction of water needed for a specific mass flow of PCC into the filtration process. r is how many times the water in a stage can be reused and n is the number of stages.

The reuse of the water will increase the content of NH_4Cl in both the water and the PCC. To calculate the content of NH_4Cl in the water when reusing, it is necessary to add the content from the last use to the next use. NH_4Cl taken away in the earlier stage must be removed, too. See Equations E3.2.9 and E3.2.10 for calculating the content of NH_4Cl in water, for reuse of the first stage output in second stage. $m_{i,r}$ is the value for stage i and PCC batch r.

$$m_{i,r\ NH_4Cl\ (aq)} = y_i \cdot m_{i\ PCC-NH_4Cl} + m_{i,r\ NH_4Cl\ (aq)} - m_{i+1,r\ NH_4Cl\ (aq)} + \sum_{0\leq r} m_{i,r}\ , \qquad i = 0 \qquad \text{E3.2.9}$$

$$x_{i,r+1} = \frac{m_{i,r+1\ NH_4Cl\ (aq)}}{m_{\ w\ in\ batch} + m_{i,r+1\ NH_4Cl\ (aq)}}, \qquad i = 0 \qquad \text{E3.2.10}$$

When the first stage from the reuse is calculated the rest of the stages in that reuse can be calculated as well. The separation factor S can be implemented into the equation for calculating the rest of the NH_4Cl content in the stages, see Equation E3.2.11.

$$m_{i,r\,NH_4Cl\,(aq)} = \frac{m_{i-1,r\,NH_4Cl\,(aq)}}{S} + m_{i,r-1} - \frac{m_{i,r-1\,NH_4Cl\,(aq)}}{S} \quad ,r \wedge i > 0 \qquad \text{E3.2.11}$$

The calculations above are illustrated in Figure 3.2.3. The NH_4Cl content from the previous reuse is to be added to the current stage, in this case $m_{i,r-1}$. For example, the NH_4Cl in the filtrate from $m_{0,0}$, should be added to $m_{0,1}$. The NH_4Cl that was removed with the PCC between the stages should be subtracted, as in Equation E3.2.9.

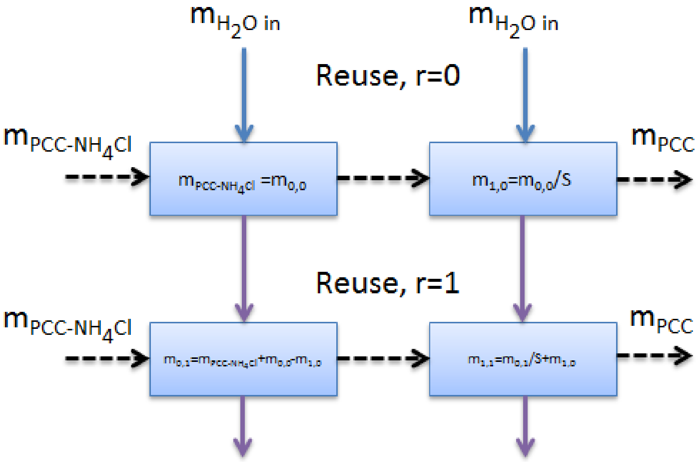


Figure 3.2.3 Illustration on the crosscurrent mass flows of NH_4Cl and on how i and r are used in the calculations above. The blue arrows are incoming fresh water, the black arrows indicate the PCC flows and the purple arrows are the filtrate flows.

However, it was found that the value for the equilibrium constant, K, determined from experiments, will not be the same as when clean water is used (in Equation E3.2.6), see Chapter 3.2.3. It is also to be noted that the PCC will (slightly) dissolve as well, Table 3.1.2 in Chapter 3.1.3 gives the amount of PCC dissolved in each stage. The dissolved PCC must be taken into consideration when calculating the amount of PCC removed during the filtration stages.

Calculations for countercurrent batch filtration

The mass balance calculations for the water inflow for a counter current filtration setup start as mentioned with no water inflow. Water is reused the same way as in the crosscurrent batch filtration, except that incoming PCC-NH_4Cl mixture is not placed in the first stage but in the second and from the second in the third. Figure 3.2.4 illustrates the countercurrent filtration setup, where the red arrows show where the filtrate is moved.

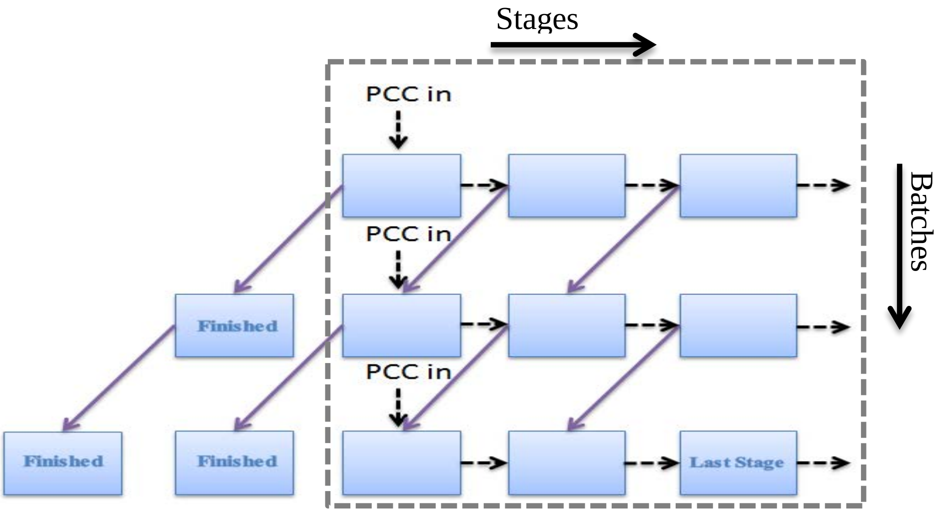


Figure 3.2.4 The principle of countercurrent batch filtration, where the black arrows indicate the PCC flows and the purple arrows are the filtrate flows.

The method above forms a matrix (here called stage matrix); the amount of stages times the amount of PCC batches ($Stages \times Batches$), excluding the stages to the left marked “Finished” (Figure 3.2.3). The stages to the right contain clean water before the PCC-NH_4Cl mixture is added. When the water from the last stage from the first batch is used in the first stage for the last batch, it must be determined if the PCC in the stage marked “Last stage” contains an acceptably small amount of NH_4Cl. In that case, it can be determined that the amount of water into the system can be less than the volume of one batch per volume of PCC-mixture in, and, thus, the water flow in can be slower. To determine the smallest amount of water needed for the countercurrent batch setup to obtain a certain NH_4Cl content in PCC, less water is used in the stages. Equation E3.2.12 (similar to E3.2.7) was used.

$$f_{w\ counter}\left(\frac{g\ H_2O}{g\ PCC}\right) = \frac{m_{H_2O\ in\ batch}\ (g)}{m_{PCCmixture}\ (g)\cdot u} \qquad \text{E3.2.12}$$

u represents how many times the water volume in the stages should be divided. Thus, u is maximized to the point that the NH_4Cl content in the PCC from the last stage is acceptable. When f_w is determined Equation E3.2.8 gives the necessary mass flow of water into the system.

The calculations for the NH_4Cl content in the PCC-NH_4Cl mixture in the different stages are done similarly in the crosscurrent as in the countercurrent batch setup but with a slight difference. See Figure 3.2.5 to illustrate the calculations below.

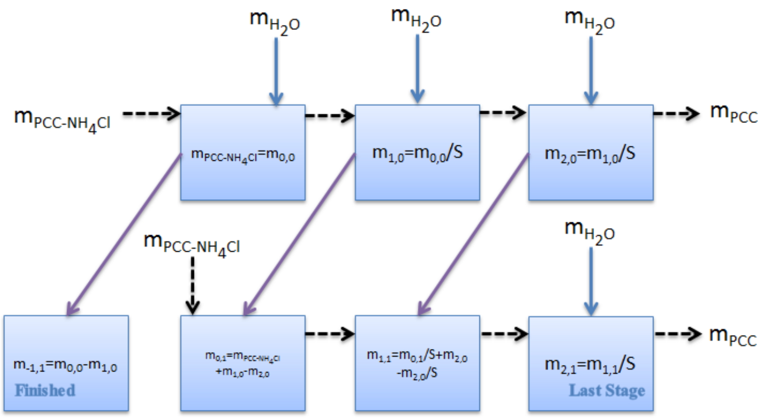


Figure 3.2.5 Illustration on the mass flows of PCC and NH_4Cl for $m_{a,i}$ in countercurrent batch filtration. The blue arrows are incoming fresh water, the black arrows indicate the PCC flows and the purple arrows are the filtrate flows.

The first row in the stage matrix is already defined earlier. The first column is calculated with mass balance Equation E3.2.13.

$$m_{i,a+1} = m_{PCC-NH_4Cl} + m_{i+1,a} - m_{i+2,a}\,, \qquad i = 0 \qquad \text{E3.2.13}$$

i indicates the countercurrent washing stage while a indicates which PCC batch is treated. m_{PCC-NH_4Cl} is the NH_4Cl content in the PCC-NH_4Cl mixture fed to the system. For the rest of the NH_4Cl masses in the stage matrix Equation E3.2.14 is used.

$$m_{i+1,a+1} = \frac{m_{i,a+1}}{S} + m_{i+2,a} - \frac{m_{i+2,a}}{S}, \qquad i \wedge a > 0 \qquad \text{E3.2.14}$$

These two equations can be used until the last column. However, in the last column there is no NH_4Cl content, because fresh water is added whenever the PCC is filtered away. Therefore Equation E3.2.15 is then to be used instead.

$$m_{i+1,a+1} = \frac{m_{i,a+1}}{S} \qquad \text{E3.2.15}$$

To determine the S value for Equations E3.2.15 and E3.2.16 Equation E3.2.2 is used. The equilibrium constant (K) in the counter current batch setup was as for the crosscurrent batch setup experimentally tested and it changes according to the fraction of NH_4Cl in the PCC, due to adsorption (Chapter 3.2.3)

Using process water for the PCC washing

Process water from the continuous PCC production process using steel converter slag can be used for the washing of the PCC. Reusing process water would decrease the use of fresh water into the system. The process water contains the same percentage of NH_4Cl as the PCC coming into the washing system. Nonetheless, there is a possibility to use the process water if the stages in the filtering systems have a higher NH_4Cl content than the process water. In that case, some of the purple process water flow shown in Figure 3.2.1 can be used for the washing. When a stage has a higher percentage of NH_4Cl than the process water from continuous PCC production process, the valve opens to the stage so process water can enter (Chapter 4.1). For the best effect, the process water will replace the water present in a stage with higher concentration of NH_4Cl than the process water (mass of water in a stage equals the process water in). The necessary mass flow of process water can be calculated with Equation E3.2.16 to E3.2.17.

$$f_{process}\left(\frac{g\ process}{g\ PCC}\right) = \frac{m_{process}\ (g) \cdot b}{m_{PCCmixture}\ (g)} \qquad \text{E3.2.16}$$

$$\dot{m}_{process\ in}\left(\frac{g}{s}\right) = \dot{m}_{PCCmixture}\left(\frac{g}{s}\right) \cdot f_{process} \qquad \text{E3.2.17}$$

Here, *b* indicates how many stages will be replaced by using process water from the continuous PCC production process.

When using the process water from the continuous PCC production process it is necessary to use the cleanest possible process water, which is the return flow of NH_4Cl to the extractor. From the lab scale process, the best place to take the process water would be after both the settling stage of the PCC and the PCC filter (Figure 3.2.6). All PCC should be removed in the final filter and there is no steel slag that would affect the quality of the PCC during the washing.

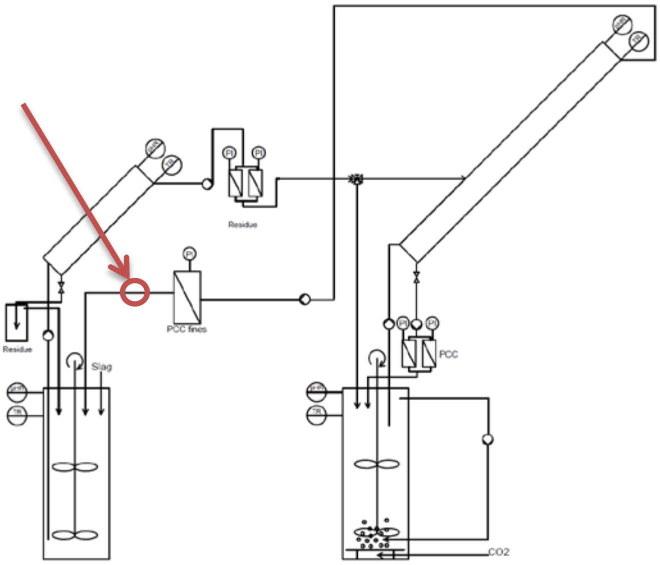


Figure 3.2.6 Process description for continuous PCC production from steel converter slag and a suggestion for where to take process water for washing [2].

Implementation of theories to mathematical simulations in Matlab

Several Matlab programs were created for this study, implementing the theory and calculations above to compare them with the experimental results and to calculate system parameters (Appendix 4). The Matlab programs attempted to simulate the experiments as accurately as possible. In experiments the NH_4Cl content in a stage is measured as in a) in Figure 3.2.7.

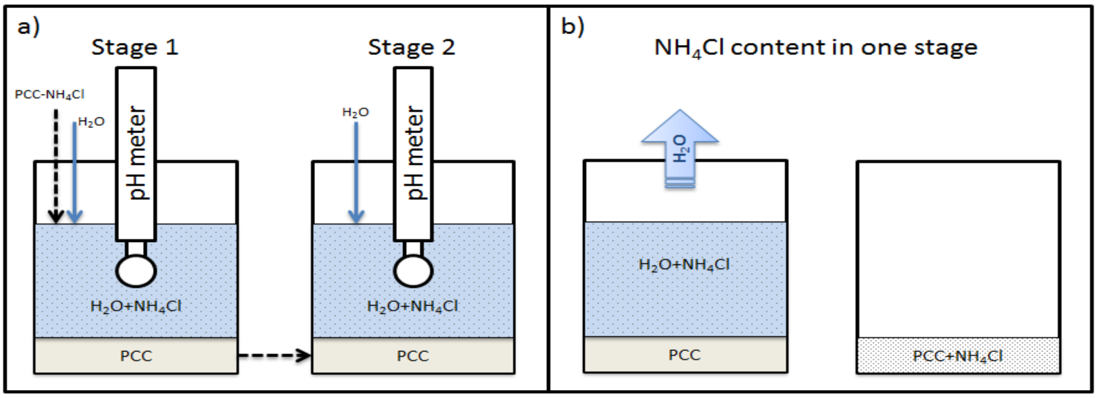


Figure 3.2.7 Illustration of measuring the NH_4Cl content both in experiments and in the mathematical simulations.

When the NH_4Cl content is measured in a specific stage, it means that the PCC would have the same amount of NH_4Cl in it, if the water would evaporate, see b) in Figure 3.2.7. This also means that, what is measured in stage two (Figure 3.2.7) is actually the NH_4Cl content in the PCC moved from filtering step one, as in Figure 3.2.8.

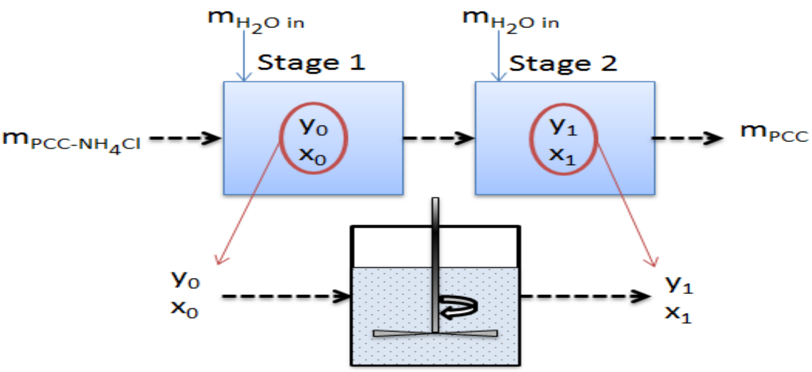


Figure 3.2.8 Illustration on how the stages are represented in the steps of a batch filtration setup.

The amount of filtering steps in the batch filtration process is then one less the number of stages in the same process. In this way the mathematical simulation in Matlab correlates with the experimental data. Thus, the experimental and theoretical data should be read as the example in Figure 3.2.9.

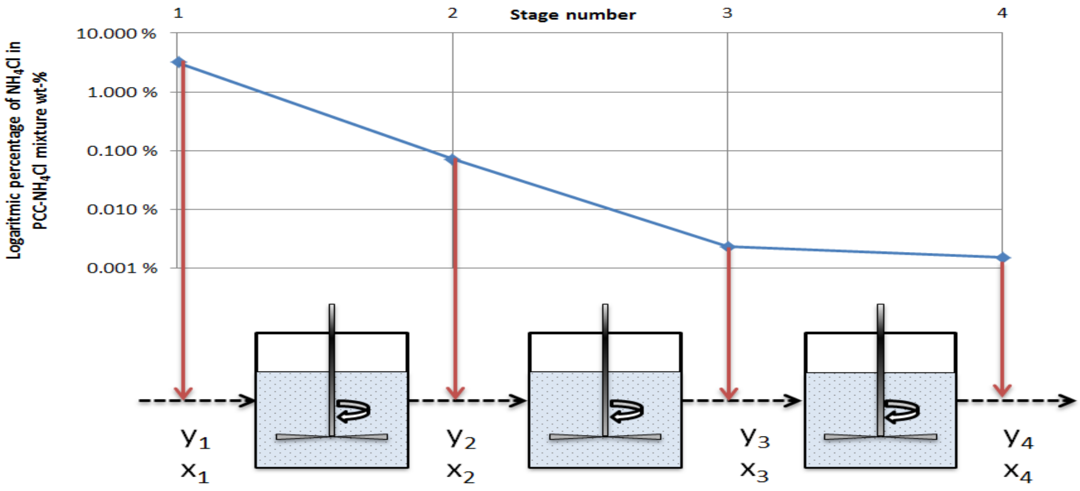


Figure 3.2.9 Illustration on how the theoretical and experimental data are represented in the steps of a batch filtration setup.

3.2.2 Adsorption of water to PCC with NH_4Cl content

When water is present with calcium carbonate a force called adsorption draws the water to the $CaCO_3$. According to Al-Hosney et al. [44] it is enough with 5 % relative humidity (RH) to form a thin layer of water on commercially available $CaCO_3$ particles (OMYA Company). The calcium ion (Ca^{2+}) draws the OH^- ions to the surface of $CaCO_3$ (particle), according to Reaction R3.2.1 [45].

$$Ca^{2+} + CO_3^{2-} + H_2O \rightarrow \overset{\overset{H}{O^-}}{Ca^{2+}} + HCO_3^- \qquad \text{R3.2.1}$$

Neagle et al. [45] measured the amount of water adsorbed on $CaCO_3$ (calcite) by heating $CaCO_3$ from 273 K to 1073 K. The measurements showed a weight loss of 5,2 wt-% after heating the $CaCO_3$ to 873 K. Above this temperature the weight loss is connected to calcination, i.e. loss of CO_2. Thus, 5,2 wt-% of a dry PCC at room temperature was adsorbed water. Neagle et al. also showed that drying a sample of $CaCO_3$ at 573 K for 24 hours caused a weight loss of 4,6 wt-%.

The validity of these measurements was tested with commercial PCC (Table A2

Appendix 2). Even though the obtained result is not exactly the same as Neagle et al. measured, it shows that PCC adsorbs water to such an extent, that it becomes important when removing NH_4Cl from the PCC.

The adsorbed water makes it difficult to remove low concentration NH_4Cl from the PCC because a small amount of NH_4Cl remains dissolved into the thin layer of water bound to the PCC surface. Thus, there will always be some amount m_∞ of NH_4Cl left in the PCC. Figure 3.2.10 illustrates the effect of adsorbed water on the washing of the PCC. The water is adsorbed to the PCC's porous structure at its surface. The orange dots illustrate NH_4Cl and in a) the NH_4Cl is stuck to a dry PCC particle. When the PCC particle is put in water b) the NH_4Cl dissolves and a thin layer of water (the dark blue) is formed around the PCC particle. In this layer of adsorbed water a few NH_4Cl particles are dissolved. When the aqueous solution from b) is filtered away in c) the PCC stays wet and in that water a certain amount of NH_4Cl is dissolved. When the wet PCC from c) is put in water d) the concentration of NH_4Cl in the water is relatively small compared to b). When the aqueous solution in d) is filtered off in e) the only NH_4Cl left is the NH_4Cl dissolved in the adsorbed water. When the water in e) is evaporated in room temperature the thin layer of dissolved water will remain f). In g), when the PCC is dried at high enough temperatures the adsorbed water is removed, but left on/in the PCC particle is a small amount of NH_4Cl.

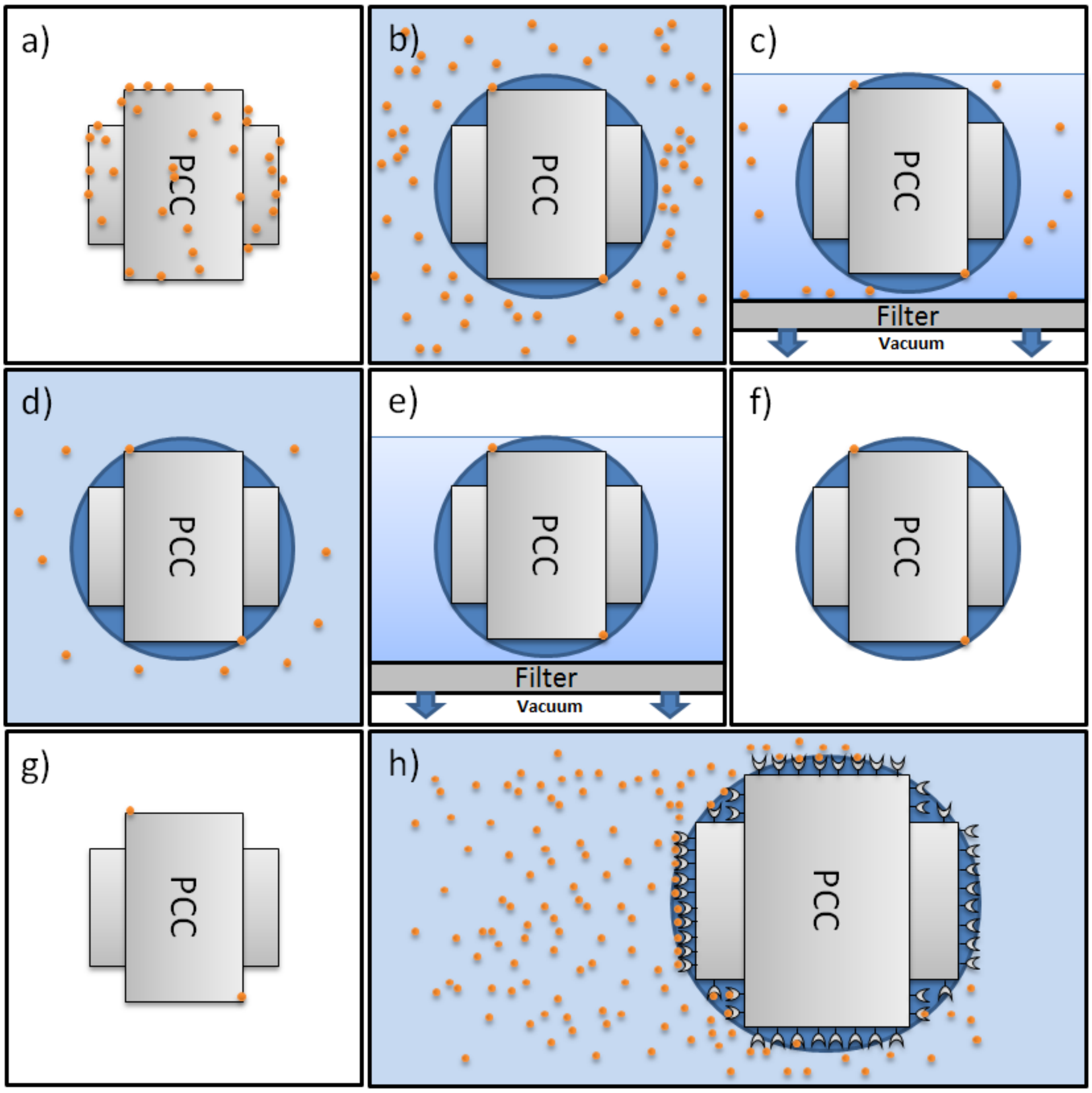


Figure 3.2.10 A step by step illustration of washing and filtering rhombohedral calcite with adsorbed water. The orange dots illustrate NH_4Cl and the dark blue layer around the PCC particle illustrates the adsorbed water.

h) in Figure 3.2.10 shows a simplified illustration on how NH_4Cl stays with the PCC particle, the same way as the water adsorbs the PCC. The illustration is based on the Langmuir expression and his four assumptions listed below (de Haan and Bosch [46]).

- The adsorbed molecule or atom is held at definite, local sites
- Each site can accommodate only one molecule or atom
- The energy of adsorption is constant over all sites, and
- There is no interaction between neighboring adsorbents

In other words, the PCC has a certain amount of sites the NH_4Cl can be attached to and when those sites are occupied there cannot be any more NH_4Cl adsorbed, this is also valid for the adsorbed water.

3.2.3 Experimental studies of washing PCC-NH_4Cl mixtures with a vacuum filter

Crosscurrent batch filtration

The crosscurrent batch filtration method was tested with four measurement stages with 50 ml of water. A chosen amount of PCC-NH_4Cl mixture was added to the water, 3 and 5 wt-% of NH_4Cl (with a purity of ≥ 99 % from VWR) in 97 and 95 wt-% of PCC (Merck Millipore, Appendix 1). After 3-4 min (when all NH_4Cl had dissolved into the water) the PCC-NH_4Cl mixture was filtered with a vacuum filter (Figure 3.2.17), using a filter paper with 2 µm pore size (Whatman 589/3). The filter cake (PCC with less NH_4Cl) was moved to the next stage and the same procedure was repeated 3 times. The filter cake dry solid content was measured to 72-74 %, by weighing a PCC batch both as wet and after about 24 hours in an oven at 108 °C. After last stage the PCC-NH_4Cl mixture was almost NH_4Cl free. The reuse of the (filtrate) water was done in the same way as the first wash, but reusing the (filtrate) water from the earlier stages. The pH was measured in all process stages to determine the NH_4Cl content in the solids. Figure 3.2.11 shows the results from two of the experiments. The fourth stage is not following the downward trend of the earlier three, i.e., it has a different S factor than the other washing steps.

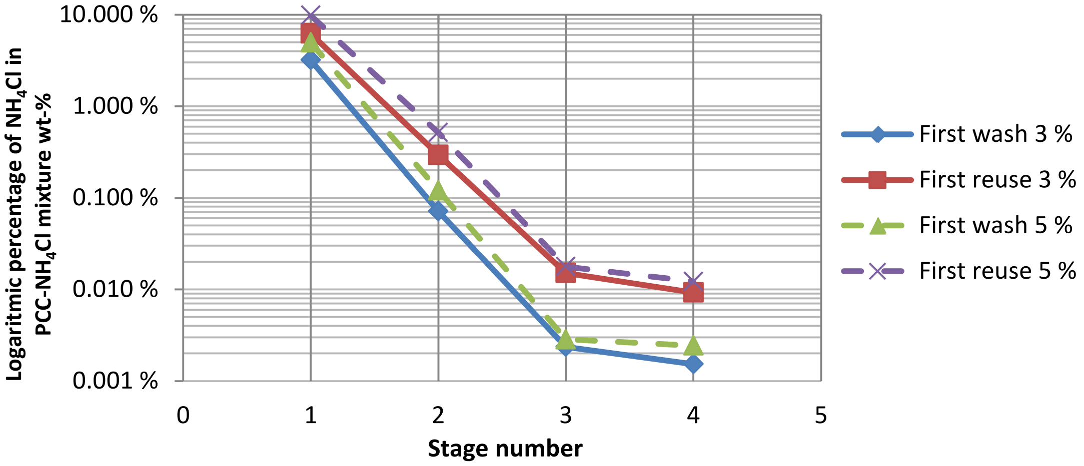


Figure 3.2.11 Experimental results from two trials of removing NH_4Cl from a PCC-NH_4Cl mixture (3 % and 5 % NH_4Cl) with crosscurrent batch filtration.

The equilibrium constant (K), changing with the NH_4Cl content, was tested through comparison of all equilibrium constants from all the experimental results, for crosscurrent and countercurrent batch filtration. The experimental data can be seen in Figure 3.2.12, where a trend line is added with the correlation coefficient (R^2) 0.982 to create an equation for the equilibrium constant as a function of the NH_4Cl content (Equation 3.2.18 and 3.2.19).

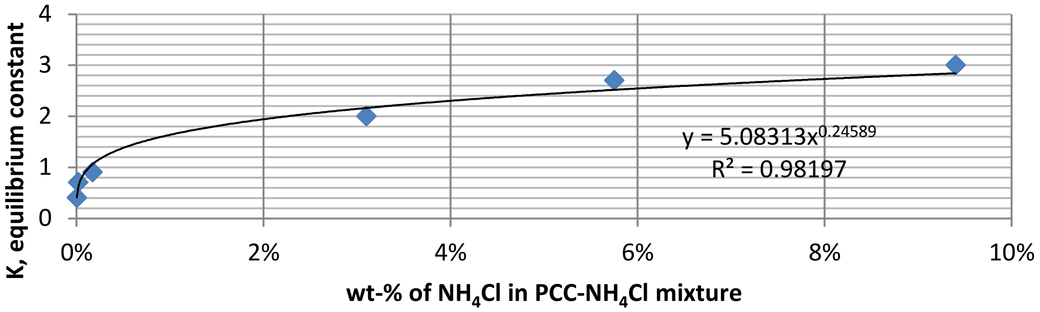


Figure 3.2.12 Experimentally tested equilibrium constants from both crosscurrent and countercurrent batch filtration.

In the crosscurrent setup, the K value for each stage is determined by the value of $y_{0,r+1}$ in every reuse, with the Equation E3.2.18

$$K_{crosscurrent} = 5.083 \cdot y_{i,r+1}^{0.246}, \qquad i = 0 \qquad \text{E3.2.18}$$

The K value changes because of adsorption (Chapter 3.2.2): some NH_4Cl dissolves in water present in the PCC porous structure or as its surface. Thus, some amount m_∞ of NH_4Cl cannot be washed out. Knowing the NH_4Cl content in the stages will also give the NH_4Cl concentration for the PCC. For the countercurrent setup where clean water is added to the last stage only, the S value changes every time the water is reused from another stage. Equation E3.2.19 is used in the countercurrent batch setup for evaluation of the equilibrium constant K (see also E3.2.18).

$$K_{countercurrent} = 5.083 \cdot y_{i,a}^{0.246} \qquad \text{E3.2.19}$$

These equations were implemented to the theoretical calculations, after which the theoretical calculations were compared with the experimental results. Figure 3.2.13 shows the comparison of the theoretical (blue) and the experimental values (red). The error bars indicate a 5 % error due to, for example, human error or bad calibration of the equipment. Because the error bars from the theoretical calculation overlap with the error bars from the experiments it can be concluded that the theory is in good correlation with the experiments. The theoretical calculation can therefore be determined as accurate, for the crosscurrent batch filtration setup.

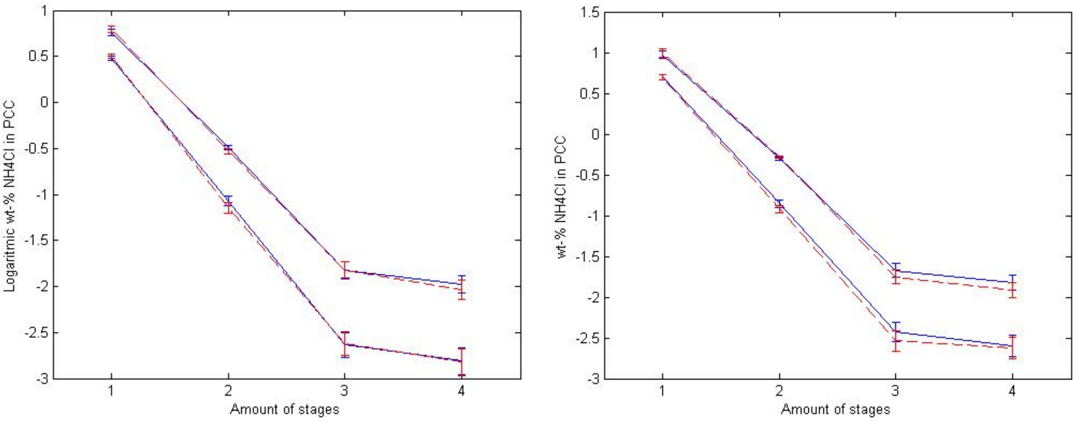


Figure 3.2.13 Theoretical results (blue) compared with experimental results (red) in a crosscurrent batch setup. The left figure has the starting y value set to 3 % (NH_4Cl content in PCC) and the right x starting value was set to 5 %.

Countercurrent batch filtration

The countercurrent batch filtration setup was tested experimentally the same way as the crosscurrent setup except with different reuse of the filtrate from each stage. The reuse of the filtrate was carried out as in Figure 3.2.4, but with four stages in the first and second rows of the stage matrix. The pH and temperature were measured in every step to determine the NH_4Cl content. The experiments were again carried out with two different y-values (NH_4Cl fraction in PCC), 3 % and 5 %. The results can be seen in Figure 3.2.14.

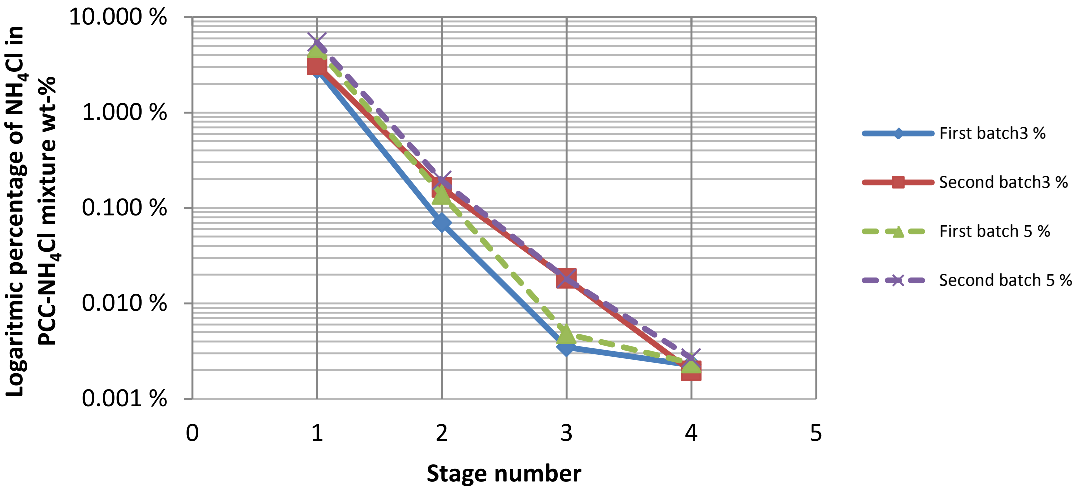


Figure 3.2.14 Experimental results from two experiments of removing NH_4Cl from a PCC- NH_4Cl mixture (3 % and 5 % NH_4Cl) with countercurrent batch filtration.

When comparing the experimental results with the theoretical results in Figure 3.2.15, a clear correlation can be seen. Thus, the equation for the equilibrium constant (E3.2.12 and E3.2.17) combined with theory given in previous chapters can be used for calculating the efficiency of the countercurrent batch filtration method.

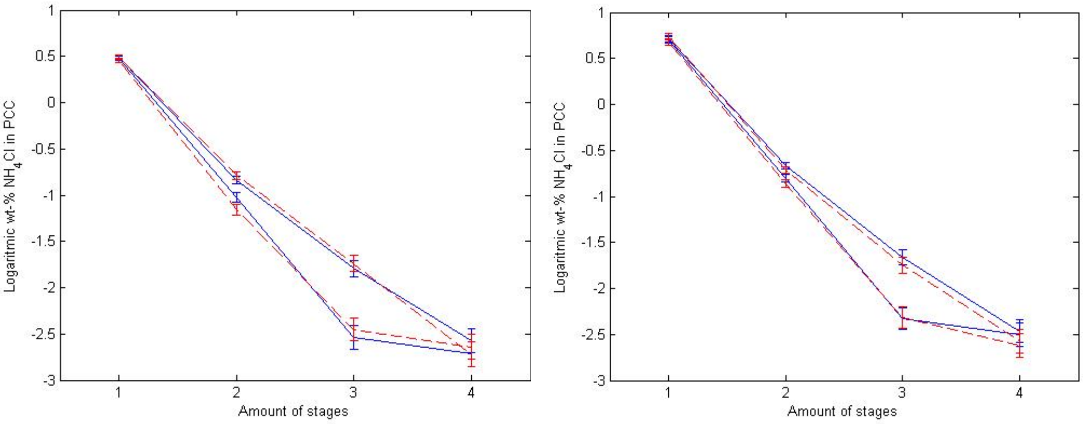


Figure 3.2.15 Theoretical results (blue) compared with experimental results (red) in a countercurrent batch setup. The left figure has the starting y value set to 3 % (NH_4Cl content in PCC) and the right x starting value was set to 5 %.

3.2.4 Experimental studies of washing PCC-NH_4Cl mixtures with a pressure filter

To determine the difference between using vacuum filters and pressure filters for washing, a test was done with a pressure filter Labox 25, with the filter cloth Tamfelt 71-2209K3. The experiment was done with the same fraction of NH_4Cl in the PCC as with the vacuum filter, in this case 3 wt-%. The filter setup was set to countercurrent filtration because it needs lesser water than the crosscurrent filtration. The pressure was set to 16 bar for 3 minutes to provide a PCC product with about the same dry solid content as in vacuum filtration. The pressure filter needed a 4 times larger mass of PCC and water than the vacuum filter, due to the size of the Labox 25. Because everything was in proportion, the mass differences in the different experiments should not matter. Figure 3.2.16 shows the theoretical values in blue, the experimental data with the vacuum filter in red and the experimental data with the pressure filter in green.

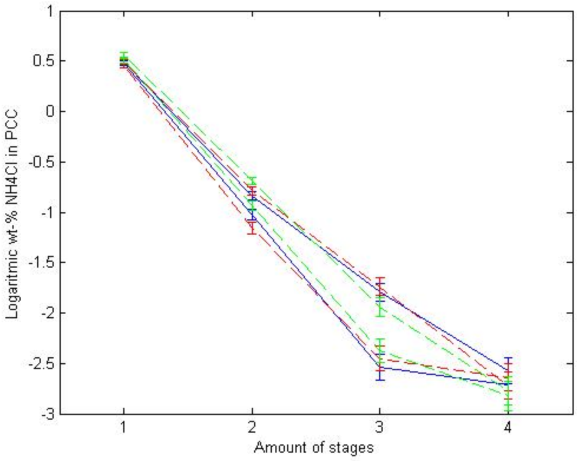


Figure 3.2.16 Comparison of experimental tests of pressure filter (green), vacuum filter (red) and theoretical values (blue).

As seen in the figure, the 5 % error bars show that the measurements do not significantly differ from each other. Thus, the pressure filter at 16 bar gives the same result as the vacuum filter under 0.02 bar. The possible difference is so small that the choice of filter type, vacuum or pressure is not important. Figure 3.2.17 shows the two different filters, vacuum filter to the left and the Labox 25 pressure filter to the right.

Figure 3.2.17 The vacuum filter (left) and the pressure filter (right) used for the experimental tests.

3.2.5 Theoretical and experimental conclusions and comments for washing PCC-NH_4Cl mixture

The theoretical calculations from previous chapters show very good correlation with the experimental tests, thus the presented theory can be used for calculating the washing efficiency for a crosscurrent and a countercurrent batch filtration. However, there are two comments that should be made for a complete overview of the filtering methods.

- The adsorption of the NH_4Cl in the PCC explains why it is slightly easier to remove the NH_4Cl from the PCC in clean water than the mass balances show in E3.2.2 to E3.2.6 (when the concentration (y) is > 0.018 wt-%) Thus, the dry solid content of the PCC mixture appears higher than it is in practice (1-2 wt-% dryer) when calculating with for example Equation E3.2.4. It seems as if the NH_4Cl not adsorbed to the PCC is flushed into the water and makes it easier to be removed through filtration. This “flushing” is included in the varying equilibrium constant (K) in Equation E3.2.18 and E3.2.19.

- As seen in Figure 3.2.13 and Figure 3.2.15, the equilibrium constant (K) changes rapidly at the third stage from a value of about 32 to a value of 1.5. This is the point where the adsorption has a great impact on the washing. This rapid change in the washing was only seen when NH_4Cl-free water was added to all the stages in the washing systems. Thus, it was seen in the crosscurrent setup and in the first row at the countercurrent setup. The rapid K change is to be taken into the calculations when clean water is used for a more accurate answer. However, when taking the countercurrent batch filtration setup into practice there will not be any clean water added to the different stages. Therefore the rapid change in the equilibrium constant, when clean water is used, will not affect the washing in practice (see Figure 3.2.9).

4 Water and energy usage for the washing of PCC-NH_4Cl mixture

To use the smallest amount of water for washing the (wet) PCC-NH_4Cl product mixtures, the countercurrent batch filtration would be the better alternative. When using water ten times the mass of PCC-NH_4Cl mixture with 1.00 wt-% NH_4Cl, the countercurrent filtration gave 0.0019 wt-% NH_4Cl in the finished PCC product while the crosscurrent gave 0.0296 wt-%. To reduce the use of external water even more, process water from the PCC production process could be used for the washing.

4.1 Usage of water from the PCC production process with steel converter slag

As earlier stated, there is an opportunity to use process water from the PCC production. However, the process water has the same fraction of NH_4Cl, as the PCC that is in need of washing. Therefore the use of process water is limited. Typically this is possible only in the first column of the stage matrix. But if there are many of stages with small water flows, other stages can use the process water as well.

Figure 4.1.1 shows an example of the differences the PCC production process water makes for the washing process. On the left a washing system with process water is shown and on the right a washing system without process water. In both cases the PCC to be washed contains 1 wt-% NH_4Cl in a 4 × 4 stage countercurrent filtration with a water flux of 2.0 $\frac{\mathrm{g\,H_2O}}{\mathrm{g\,PCC}}$.

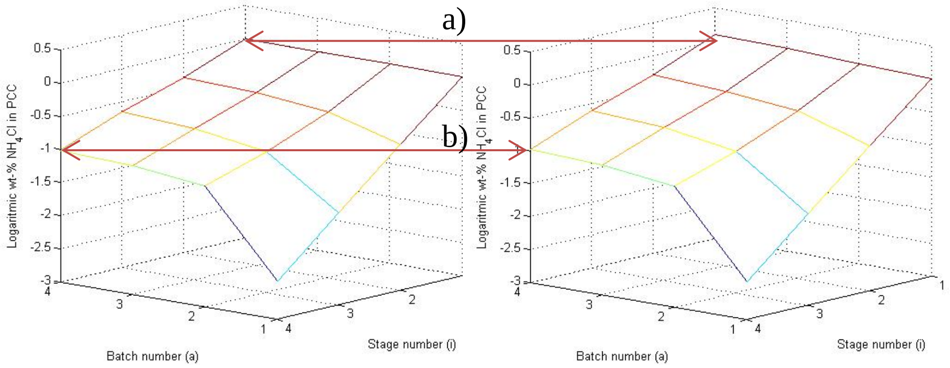


Figure 4.1.1 Comparison between countercurrent batch filtration, with process water from PCC production (left) and without process water (right).

Arrow a) (Figure 4.1.1) shows the difference of NH_4Cl fraction in the first stage in the two washing systems. The system with the process water intake has a lower NH_4Cl fraction than the washing system without process water. This also affects the NH_4Cl fraction in the product from the last stage, arrow b). The Equation E4.1.1 is used for determining the mass of water needed per mass of PCC.

$$k_{process\ water} = \frac{\dot{m}_{process\ water\ for\ washing\ PCC}}{\dot{m}_{PCC}} \qquad \text{E4.1.1}$$

in this case, $k_{process\ water} = 1.2\ \frac{\mathrm{g\ process\ H_2O}}{\mathrm{g\ PCC}}$, gave 0.0973 wt-% NH_4Cl in the PCC product when using process water and 0.1052 wt-% without using any process water. There is a clear difference between these alternatives.

4.2 Amount of water needed for washing PCC-NH_4Cl mixtures

To minimize the cost of the washing process the water consumption is an important feature. The water needed for removing NH_4Cl from PCC is dependent on mainly four things:

- How much NH_4Cl is in the PCC product before washing
- How much NH_4Cl can be left in the end product
- The efficiency of the filtering method
- Number of filtration stages

With the Matlab simulation programs based on the theories above, an estimation of the needed washing water amount can be calculated. Figure 4.2.1 shows an overview of the water amount needed for washing two different samples, with 3 wt-% and 1 wt-% of NH_4Cl in PCC. Clearly, the amount of water needed is smaller with a smaller amount of NH_4Cl in the PCC. The samples are washed in 3-5 washing stages, more stages equaling to less washing water needed. The logarithmic x-axis shows the PCC end product's NH_4Cl concentration. From the different concentrations an assumption can be done on how many stages the filtering process needs. For example, if the PCC end product is allowed to have the concentration 0.100 wt-% of NH_4Cl, the process needs around five times the weight of the incoming PCC as washing water independent of the amount of stages. However, if the amount of NH_4Cl in the PCC end product needs to be around 0.001 wt-%, the amount of stages in the washing process has a large impact on the water consumption.

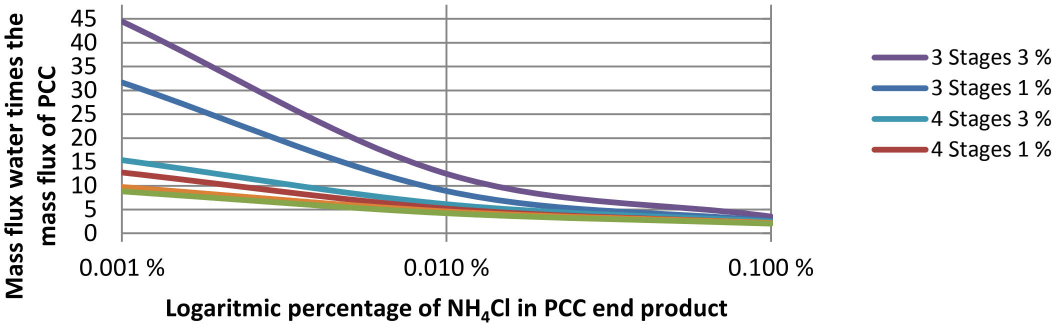


Figure 4.2.1 The required water amount for washing PCC with two different concentrations of NH_4Cl *(3 wt-% and 1 wt-%), as a function of the concentration of* NH_4Cl *allowed in the end product.*

The x-axis in Figure 4.2.1 represents the k-value; it determines how much water is needed per mass of PCC, seen in Equation E4.2.1 (similar to Equation E4.1.1)

$$k_{water\ for\ washing\ PCC} = \frac{\dot{m}_{water\ for\ washing\ PCC}}{\dot{m}_{PCC}} \qquad \text{E4.2.1}$$

4.3 Energy consumption for washing PCC-NH_4Cl mixtures

Energy consumption for washing PCC-NH_4Cl mixtures correlates directly with washing water needs. The water used for the washing can be reused, however; before it is reused the NH_4Cl has to be removed from the aqueous solution. One option for separating water and the NH_4Cl is the evaporation of the water from the solution. After that, the NH_4Cl can be reused in the PCC production process while the water can be reused in the washing process. Evaporating water is an energy intensive process as seen in Figure 4.3.1

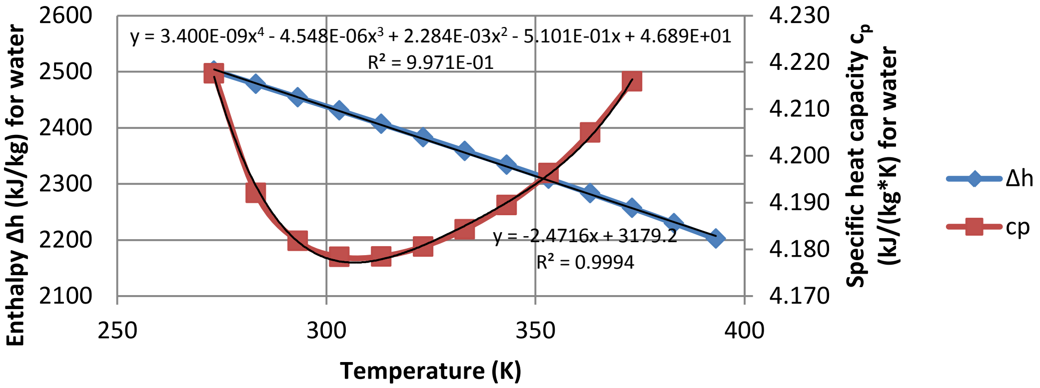


Figure 4.3.1 The left y-axis gives the enthalpy for evaporating water in different temperatures [47] *and the right y-axis gives the specific heat capacity for water in different temperatures* [32].

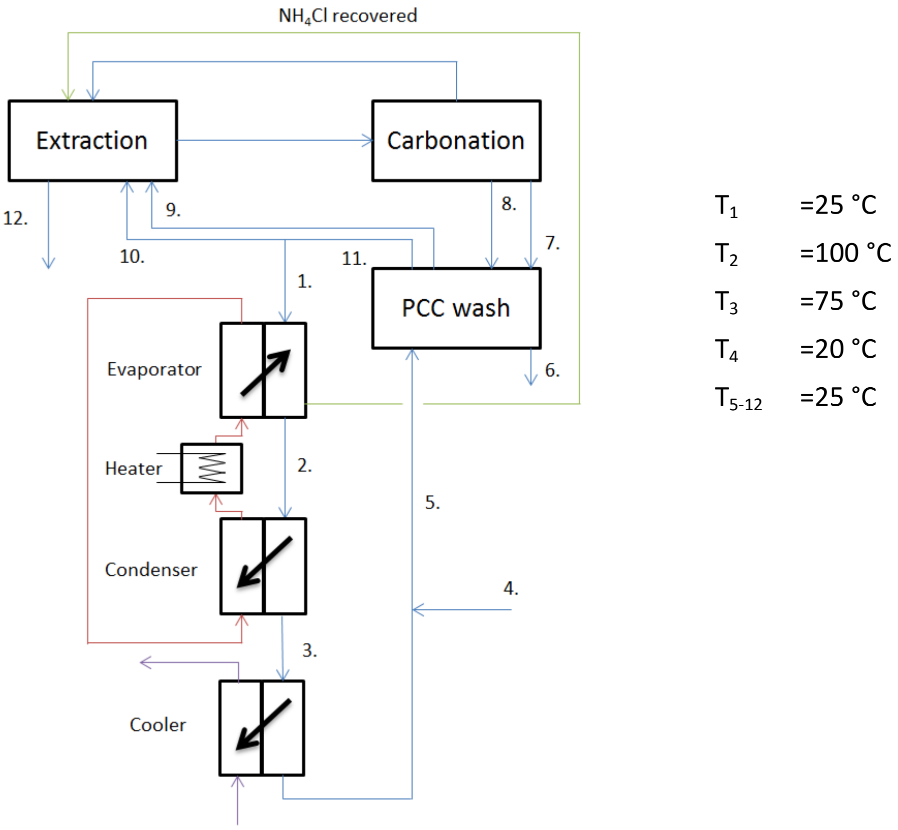
The data from Figure 4.3.1 creates two equations E4.3.1 and E4.3.2 with the correlation coefficients (R^2) 0.9994 and 0.9971. The equations are later used for calculating the energy need for the washing process.

$$\Delta h\left(\frac{T}{K}\right) = -2{,}472 \cdot \left(\frac{T}{K}\right) + 3179 \qquad \text{E4.3.1}$$

$$c_p\left(\frac{T}{K}\right) = 3.400 \cdot 10^{-9} \cdot \left(\frac{T}{K}\right)^4 - 4.548 \cdot 10^{-6} \cdot \left(\frac{T}{K}\right)^3 + 2.284 \cdot 10^{-3} \cdot \left(\frac{T}{K}\right)^2 - 0.510 \cdot \left(\frac{T}{K}\right) + 46.885 \qquad \text{E4.3.2}$$

Δh is the enthalpy for evaporating water in different temperatures and c_p is the specific heat capacity of water in different temperatures. Because the water evaporation process requires a lot of energy (heat > 100 °C) it is essential to minimize the water to be evaporated. The aqueous solution in PCC production process is in a closed loop, however, when slag residue and PCC are removed from the process some water is removed as well. The amount of water depends on the dry solids content of the slag residue and the PCC leaving the process. The water loss from the PCC production process can directly be substituted by water from the washing process. This lowers the amount of water in need of evaporation. To decrease the external energy needed for the evaporation, the heating medium can be preheated with a condenser.

Figure 4.3.2 shows the water flows in blue for the PCC production process and the washing system including a suggestion for the separation of NH_4Cl and water. The red flows show the heating medium and the green flow is the recycled NH_4Cl. The extraction stage and the carbonation stage are parts of the PCC production process also seen in Figure 2.6.2 in Chapter 2.6.2. The temperatures shown (Figure 4.3.2) are typical examples of what the temperatures for a certain heat flow could be.



T_1 =25 °C
T_2 =100 °C
T_3 =75 °C
T_4 =20 °C
T_{5-12} =25 °C

Figure 4.3.2 A concept of the PCC production process and the washing system for the PCC product including a suggestion for the separation of NH_4Cl and water. The blue arrows are water flows, the red arrows are the heating medium flows, the purple arrows are cooling medium and the green arrow is the recycled NH_4Cl flow. The numbers specify a specific flow, which the heat- and mass flows are determined below.

The water flows out from the PCC production process are: the water inside the slag residue (12.) and the water inside the outgoing PCC (8.). However, from the carbonation stage a certain amount of water can be used for the PCC washing process (7.).

To calculate the external energy (heat) needed for the evaporation, the water flows out and into the system need to be determined. That is done via water mass balances and energy balances.

The mass flows of water in (1.-3.) are equal to each other. These mass flows are therefore calculated with E4.3.3.

$$\dot{m}_1 = \dot{m}_2 = \dot{m}_3 = \dot{m}_{PCC} \cdot k_{water\,for\,washing\;\,PCC} - m_{10} \qquad \text{E4.3.3}$$

The k-value is the water needed for washing the PCC, which is determined with Equation E4.2.1. The water flow in (4.) is the fresh water into the system. This flow equals to the water flows out from the system via the slag residue and the PCC. Thus also (10.) equals to (4.) (Equation E4.3.4).

$$\dot{m}_4 = \dot{m}_{10} = \dot{m}_6 + \left(1 - d_{slag\,residue}\right) \cdot \dot{m}_{slag\,residue} \qquad \text{E4.3.4}$$

$$\dot{m}_{slag\,residue} = 3.2 \cdot \dot{m}_{PCC} \qquad \text{E4.3.5}$$

As Equation E4.3.6 shows, the amount of slag residue is 3.2 times the mass of PCC product produced, thus when producing for example 100 g of PCC there will be 320 g of slag residue [41]. This value changes depends on the used steel converter slag.

The outgoing water flow (6.) equals to the water inside the washed PCC, being dependent on the dry solids content d_{PCC}. Because the PCC particle keeps its crystal form and size during washing, the dry content will stay the same. Therefore Equation E3.4.6 can be determined.

$$\dot{m}_6 = \dot{m}_8 = (1 - d_{PCC}) \cdot \dot{m}_{PCC} \qquad \text{E3.4.6}$$

The water mass flow at (5.) is the sum of the fresh water intake (4.) and the mass flow (3.), which gives Equation E4.3.7.

$$\dot{m}_5 = \dot{m}_3 + \dot{m}_4 \qquad \text{E4.3.7}$$

The water mass flow from (7.) is used for washing the PCC. The washing water is later flowing back to the PCC production process. This means that the water flow in (9.) equals to (7.), (Equation E4.3.8).

$$\dot{m}_7 = \dot{m}_9 = \dot{m}_{PCC} \cdot k_{process\,water} \qquad \text{E4.3.8}$$

The k-value gives the amount of water taken for the PCC washing from the PCC production process, determined by Equation E4.1.1. The water mass flow coming out from the PCC wash, (11.), is the sum of the flows (1.) and (10.) (Equation E4.3.9).

$$\dot{m}_{11} = \dot{m}_1 + \dot{m}_{10} \qquad \text{E4.3.9}$$

To complete the calculations for the amount of external heating required, energy balances are needed. Since the heat medium is preheated with a condenser the amount of external energy needed is the energy flow from the evaporator subtracted by the energy flow from the condenser. This gives the Equation E4.3.10.

$$\dot{Q}_{Heater} = \dot{Q}_{Evaporator} - \dot{Q}_{Condenser} + \dot{Q}_{Cooler} \qquad \text{E4.3.10}$$

Energy is required in the evaporator to evaporate all water from the water-NH_4Cl mixture. This is directly calculated with the water mass flow and temperature of incoming water to the evaporator (1.) Equation E4.3.11. However, the required energy for evaporating the water from a water-NH_4Cl solution is a little more than for evaporating water. But since the NH_4Cl content is relatively small (0.0025 $\frac{g\,NH_4Cl}{g\,washing\,water}$ for a PCC product at 1 wt-% washed to 0.01 wt-% NH_4Cl) it will be neglected in this study.

$$\dot{Q}_{Evaporator} = \dot{m}_1 \cdot \Delta h\left(\frac{T_1}{K}\right) \qquad \text{E4.3.11}$$

The energy flow from the condenser is determined through subtracting the energy flow from (2.) with the energy flow from (3.), also seen in Equation E4.3.12.

$$\dot{Q}_{Condenser} = \dot{Q}_2 - \dot{Q}_3 \qquad \text{E4.3.12}$$

The energy flow from (2.) is known via the energy flow from the evaporator and the energy inflow to the evaporator (1.), also seen in Equation E4.3.13.

$$\dot{Q}_2 = \dot{Q}_{Evaporator} + \dot{Q}_1 \qquad \text{E4.3.13}$$

The energy flow from (1.) is calculated same way as for “n” in Equation E4.3.14. Because the mass flows and temperatures are known for each n both the specific heat capacity and the energy flow can be calculated (E4.3.14).

$$\dot{Q}_n = \dot{m}_n \cdot T_n \cdot c_p\left(\frac{T_n}{K}\right), \qquad n = 1, 3, 4, 6, 7, 8, 9, 11 \qquad \text{E4.3.14}$$

Since all other energy flows are determined, an energy balance for the PCC wash gives the energy flow in (5.), see Figure 4.3.3 and Equation E4.3.15.

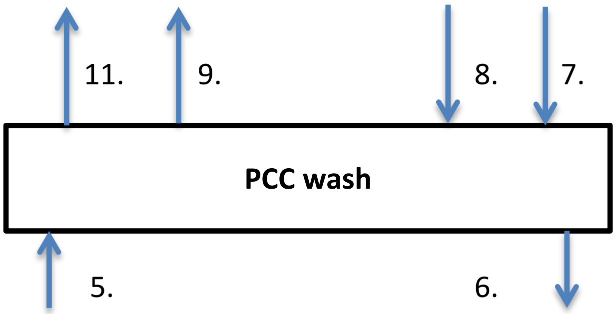


Figure 4.3.3 Illustration of the water flows in and out from the PCC washing process.

$$\dot{Q}_5 = \dot{Q}_6 + \dot{Q}_9 + \dot{Q}_{11} - \dot{Q}_7 - \dot{Q}_8 \qquad \text{E4.3.15}$$

The last energy flow needed for the determination of the required external heating is the energy flow out ($\dot{Q}_{cooler}$). This can be obtained with Equation E4.3.16.

$$\dot{Q}_{cooler} = \dot{Q}_3 + \dot{Q}_4 - \dot{Q}_5 \qquad \text{E4.3.16}$$

5 Washing steel slag residue and NH_4Cl recovery

Washing the slag residue from the PCC production process is done to recover and reuse the NH_4Cl from the slag solids, and to facilitate the further processing of the residue. The same batch filtration setup as for the PCC wash and the same recovery method, evaporation of the washing water can be used also for this purpose.

5.1 Theoretical and experimental studies of washing steel slag-NH_4Cl mixtures

The steel slag residue washing was analyzed the same way as for the PCC both theoretically and experimentally, with a countercurrent batch filtration setup. The mass balances for NH_4Cl in Chapter 3.2.1 will therefore be used the same way for washing the steel slag as for washing PCC. The difference between washing PCC and steel slag is the different equilibrium constant K, which was experimentally determined.

5.1.1 Experimental studies of washing steel slag-NH_4Cl mixtures

The wash was done with a countercurrent batch filtration setup at atmospheric pressure and temperatures between 20.7 ℃ and 22.3 ℃. The experiments were done with four stages with steel slag residue (received originally from Ruukki Metals). The amount of NH_4Cl in the slag residue was unknown but the sample was from an extraction experiment with the molarity. 0.65 M, of NH_4Cl, in water during 60 min at ≈ 20 ℃.

The sample mass was 5 g, and it was washed with 50 ml of water in every stage for 3-5 min. The Cl^- content was measured in each filtrate with an ELIT 2182 ion selective electrode (ISE) with the reference electrode ELIT 003N. The accuracy of the ISE was on the electrode slope at 25 °C: 54 ± 5 mv/decade, however the values fluctuated quite a lot when the measuring was done. The experimental data will therefore only be used as an indication on how the washing proceeds from one stage to another. The dry solids content in the filter cake was measured (using the same method as in Chapter 3.2.3) to be about 76 wt-%. Figure 5.1.1 shows the experimental data of the filtrate composition.

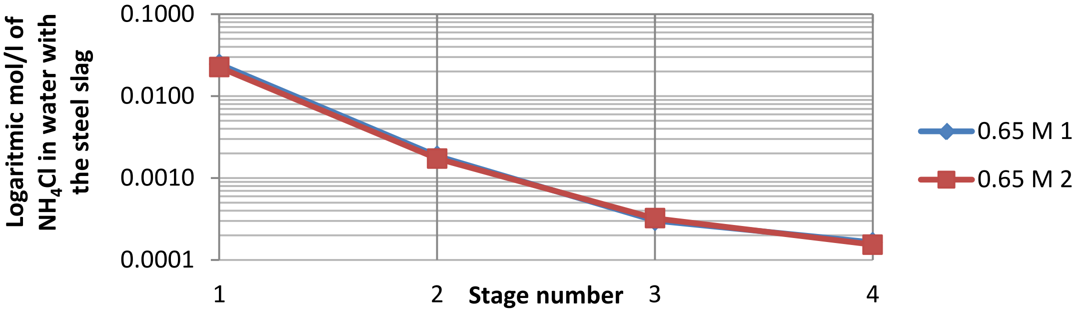


Figure 5.1.1 Experimental data for countercurrent batch filtration with a steel slag-NH_4Cl mixture. The y-axis is the logarithmic concentration (mol/l) of NH_4Cl in slag filtrate and the x-axis indicates in which specific stage.

The NH_4Cl is not as easy removable from the steel slag as from the PCC. This may be because the slag residue has such a high moisture content that NH_4Cl adsorbs easily to the slag particle.

Nevertheless, the equilibrium constant K for the NH_4Cl separation from steel slag was determined from the experimental data obtained. As earlier for PCC the equilibrium constant is not linear due to adsorption when washing NH_4Cl from slag residue. The data can be seen in Figure 5.1.2.

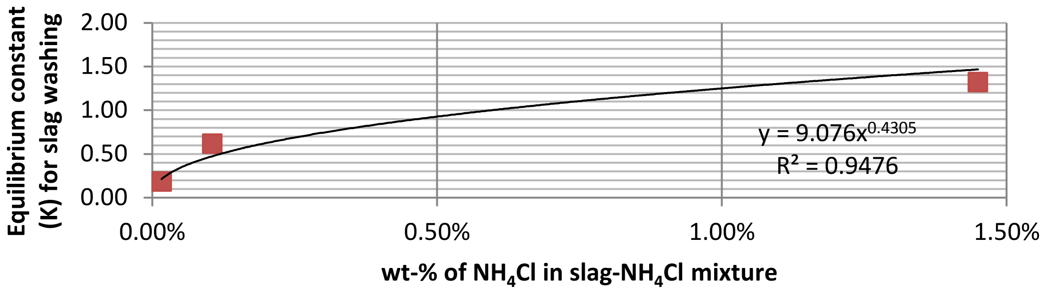


Figure 5.1.2 *Experimentally tested equilibrium constants from countercurrent batch filtration of slag residue.*

From Figure 5.1.2 the equilibrium constant (K) is determined with the correlation coefficient (R^2) 0.95, seen in Equation E5.1.1.

$$K_{countercurrent\ slag} = 9.076 \cdot y_{i,a}^{0.4305} \qquad \text{E5.1.1}$$

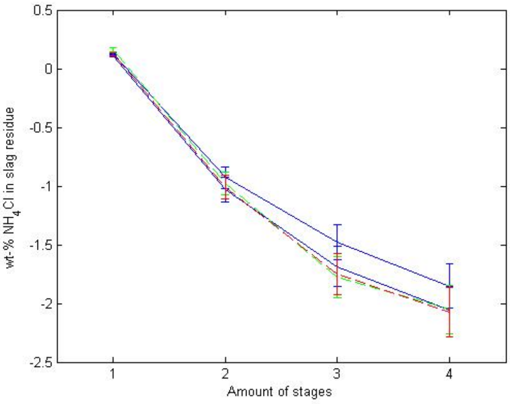


Figure 5.1.3 Experimental data (green and red), compared with theoretical simulation data (blue).

Figure 5.1.3 shows the experimental data from Figure 5.1.1. The blue lines show the theoretical data formed with Equation E5.1.1. The experimental data in red is not correlating well with the theoretical data. This was because the two slag residue samples unfortunately had different starting values of NH_4Cl in the slag residue in the first stage (green, 1.45 wt-% and red, 1.33 wt-%, respectively). The red values should be a bit larger than the green values, see Equation E3.2.13. However, the experimental data is still very close to the theoretical data and therefore the equilibrium constant equation (E5.1.1) is used in this study.

5.2 Amount of water needed for washing Slag-NH_4Cl mixtures

Analysis of washing steel slag-NH_4Cl mixtures to recover the NH_4Cl was done with the same theory as washing PCC see Chapter 4.2. The difference is that washing slag residue requires a lot more water than washing PCC, not only because of the slag residue is 3.2 times larger in mass than the PCC but also due to the quite different equilibrium constant (K).

Process water from the PCC production process would be available for washing the slag residue. However, due to the large amount of water needed from the PCC production process and the small difference in the result the process water makes it is unfeasible to use it. The mathematical simulation program created in Matlab (Appendix 4) is used to illustrate the water usage. Figure 5.2.1 shows the difference in the water consumption with and without process water, for washing 1.00 wt-% of NH_4Cl in the slag residue to 0.10 wt-% and 0.01 wt-% NH_4Cl. The data marked with "p" involves using process water. The arrows show that the water consumption is lower if process water is used; however, the amount of process water needed becomes extremely high, which means almost twice the fresh water use. This will affect the energy usage significantly (see next chapter) and therefore it is recommended that no process water is used for the slag washing.

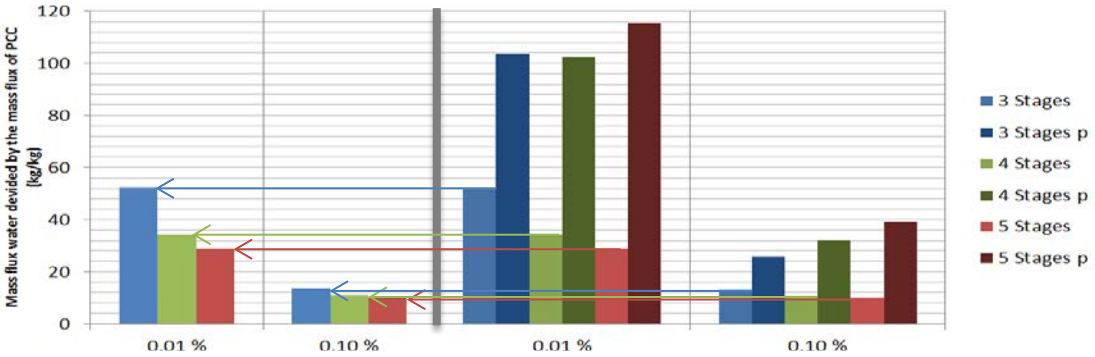


Figure 5.2.1 The graph illustrates the water consumption for three, four and five stages in a countercurrent batch filtration setup for two different NH_4Cl weight percentages in the washed slag residue (0.01 wt-% and 0.1 wt-%). Left of the gray bar no process water is used and right of the gray bar process water is used. The stages marked with a "p" indicate how much process water is added.

The y-axis in Figure 5.2.1 shows the mass flux of water divided by the mass flux of the slag residue, also seen in Equation E5.2.1.

$$k_{water\ for\ washing\ slag} = \frac{\dot{m}_{water\ for\ washing\ slag}}{\dot{m}_{slag}}, \qquad where\ \dot{m}_{slag} = 3.2 \cdot \dot{m}_{PCC} \qquad \text{E5.2.1}$$

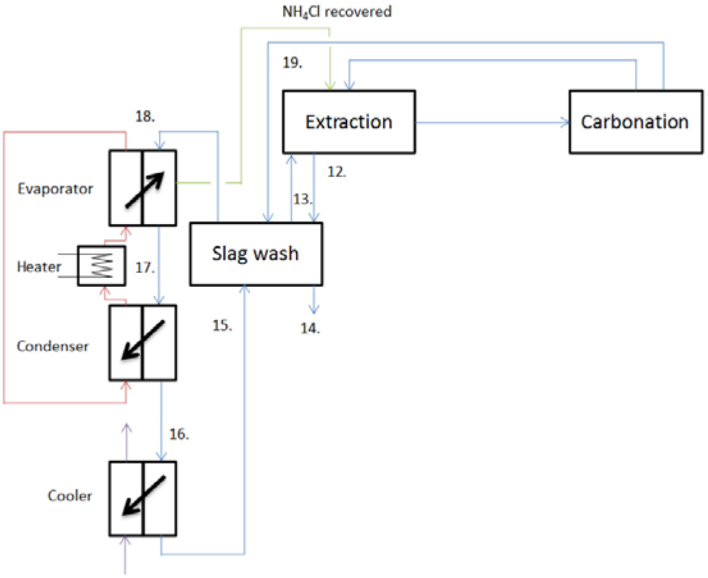
Since there is a possibility to use process water for washing the slag residue Equation E5.2.2 could be used.

$$k_{process\ water\ for\ washing\ slag} = \frac{\dot{m}_{process\ water\ for\ washing\ slag}}{\dot{m}_{slag}} \qquad \text{E5.2.2}$$

However, as earlier stated, process water should not be used because of large energy usage.

5.3 Energy consumption for washing Slag-NH_4Cl mixtures

The energy consumption for washing the slag residue correlates with the water use for slag washing, as for the PCC washing. The recovery of the NH_4Cl from the washing water can be done through evaporation of the water. A suggestion of the NH_4Cl recovery setup can be seen in Figure 5.3.1. The temperatures shown are typical examples of what the temperatures for a certain heat flow could be.



$T_{12\text{-}15}$ =25 °C

T_{16} =75 °C

T_{17} =100 °C

T_{18} =25 °C

T_{19} =25 °C

Figure 5.3.1 A concept of the PCC production process and the washing system for the slag residue, including a suggestion for the separation of NH_4Cl and water. The blue arrows are water flows, the red arrows are the heating medium flows and the green arrow is the recycled NH_4Cl flow. The numbers specify a specific flow, for which the heat- and mass flows are determined below.

Mass and energy balances determine the end use of energy for the slag residue wash and NH_4Cl recovery. The water mass flow (12.) is the water fed to the washing system with the wet slag residue from the extraction in the PCC production process. The slag residue fed to the washing is assumed to have the same dry solids as the slag residue coming out of the wash (14.). Therefore the water flows (12.) and (14.) are equal to each other (Equation E5.3.1).

$$\dot{m}_{12} = \dot{m}_{14} = \dot{m}_{slag} \cdot \left(1 - d_{slag}\right) \qquad \text{E5.3.1}$$

where d_{slag} slag is the dry solids content of the slag residue (kg/kg) The water mass flows (15.-18.) are within the NH_4Cl separation process, which is a closed loop where no water is exiting or added. Therefore are the mass flows inside the NH_4Cl separation process equal to each other (Equation E5.3.2).

$$\dot{m}_{15} = \dot{m}_{16} = \dot{m}_{17} = \dot{m}_{18} = \dot{m}_{slag} \cdot k_{water\ for\ washing\ slag} \qquad \text{E5.3.2}$$

where $k_{water\ for\ washing\ slag}$ is a constant indicating how much water (kg/kg) is needed for a certain mass of slag residue, determined with Equation E5.2.1. The mass flow (19.) is the PCC production process water used for washing the slag residue. The mass flow (13.) is the flow of process water used in the washing. Therefore (19.) and (13.) are equal to each other (Equation E5.3.3).

$$\dot{m}_{19} = \dot{m}_{13} = \dot{m}_{slag} \cdot k_{process\ water\ for\ washing\ slag} \qquad \text{E5.3.3}$$

where $k_{process\ water\ for\ washing\ slag}$ is a constant indicating the amount of process water (kg/kg) used for a certain mass of slag residue, determined with Equation E5.2.2. To determine the energy content in the mass flows the Equation E4.3.14 is used for $n = 12, 13, 14, 16, 18,$ n specifying which flow is calculated. Flow (17.) from the evaporator is determined by adding the energy from the evaporator to flow (18.) (Equation E5.3.4).

$$\dot{Q}_{17} = \dot{Q}_{Evaporator\ slag} + \dot{Q}_{18} \qquad \text{E5.3.4}$$

where $\dot{Q}_{17}$ and $\dot{Q}_{18}$ are enthalpy streams. The energy flow to the evaporator is determined by the energy usage to evaporate the water flow from (18.), (Equation E5.3.5).

$$\dot{Q}_{Evaporator} = \dot{m}_{18} \cdot \Delta h \left(\frac{T_{18}}{K}\right) \tag{E5.3.5}$$

Since all energy flows in and out of the slag wash are determined except for flow (15.) an energy balance can determine it, see Figure 5.3.2 and Equation E5.4.6.

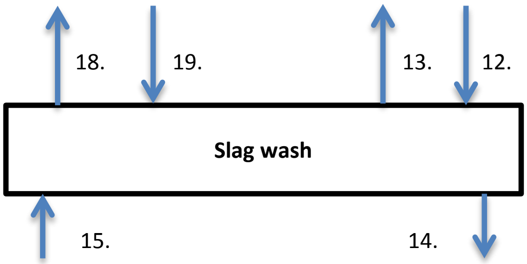


Figure 5.3.2 Illustration of the water flows in and out from the slag residue washing process.

$$\dot{Q}_{15} = \dot{Q}_{13} + \dot{Q}_{14} + \dot{Q}_{18} - \dot{Q}_{12} - \dot{Q}_{19} \tag{E5.4.6}$$

When the flows (15.) and (17.) are determined energy flow to the heating medium in condenser can be calculated with Equation E5.4.7.

$$\dot{Q}_{Condenser\ slag} = \dot{Q}_{17} - \dot{Q}_{16} \tag{E5.4.7}$$

To determine the energy flow in the cooler the Equation E5.4.8 is used.

$$\dot{Q}_{Cooler} = \dot{Q}_{16} - \dot{Q}_{15} \tag{E5.4.8}$$

The external energy needed, for the slag washing process, from the heater is then determined via Equation E5.4.9.

$$\dot{Q}_{Heater} = \dot{Q}_{Evaporator} - \dot{Q}_{Condenser} + \dot{Q}_{Cooler} \tag{E5.4.9}$$

The condenser is preheating the heating medium with the energy the washing water received from the evaporator. The temperatures of the heating medium are dependent on its mass flow and the area and specific heat transfer coefficient of the heat exchangers at the evaporation and the condensation. However, the temperature of the heating medium should be 120-150 °C otherwise not all the water will evaporate in the evaporator.

6 Water and energy usage for the PCC and steel slag washing

To summarize the water and energy need for the washing system and NH_4Cl recovery from both the PCC and slag residue the theory from Chapter 4.3 and Chapter 5.3 are merged and a suggestion on how the system could look is seen in Figure 6.1.1. The temperatures shown are typical examples of what the temperatures for a certain heat flow could be.

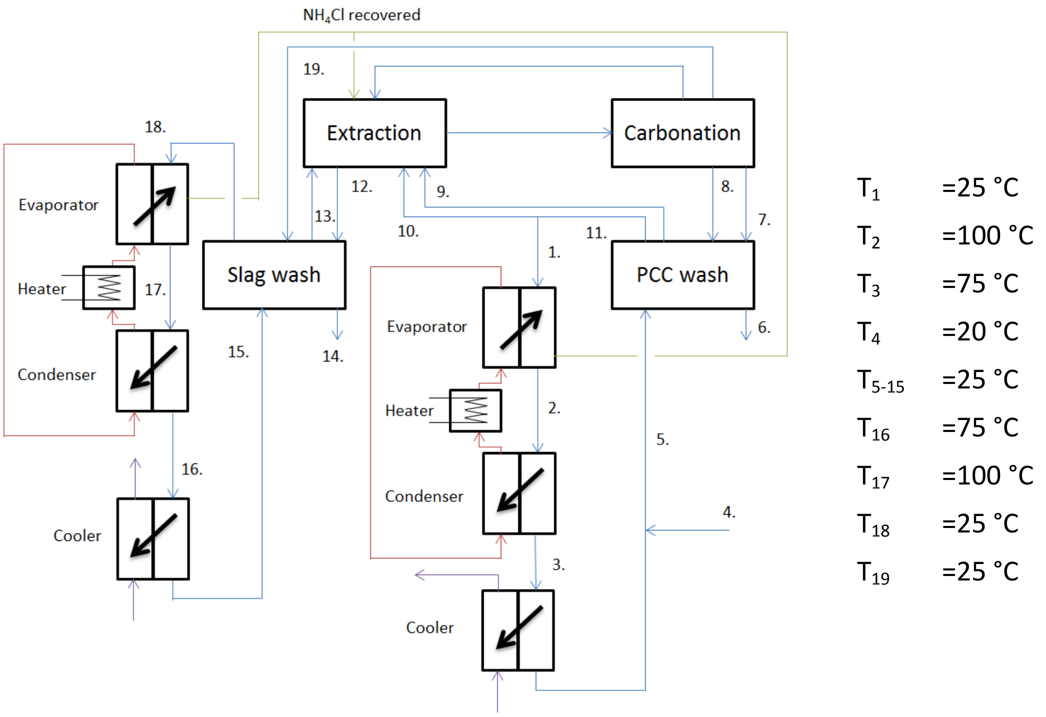


Figure 6.1.1 *A concept of the PCC production process including the washing system for PCC and slag residue, including a suggestion for the separation of* NH_4Cl *and water. The blue arrows are water flows, the red arrows are the heating medium flows and the green arrow is the recycled* NH_4Cl *flow.*

The total mass flow of fresh water into the washing system is limited to flow (4.) in Figure 6.1.1, which equals the sum of the flows (6.) and (14.), (Equation E6.1.2)

$$\dot{m}_{fresh\,water} = \dot{m}_4 = \dot{m}_6 + \dot{m}_{14} = \dot{m}_{slag} \cdot (1 - d_{slag}) + (1 - d_{PCC}) \cdot \dot{m}_{PCC} \qquad \text{E6.1.2}$$

As seen in Equation E6.1.2 the mass of fresh water ($\dot{m}_{fresh\,water}$) is fed to the system at the same rate as the water coming out with the wet PCC and the wet slag residue. The fresh water use is minimized, at the same time preventing any washing water leaving the system to possibly pollute the environment. The regulation on how much NH_4Cl is allowed to be released into the environment is unknown and not considered here (future work). No washing water leaves the washing process, except for the water coming out with the wet solids.

The total energy usage for the combined systems is the sum of the two heaters in the NH_4Cl separation processes (determined in the Equations E4.3.10 and E5.4.8), which can be seen in Equation E6.1.1.

$$\dot{Q}_{External\,tot} = \dot{Q}_{Heater\,PCC} + \dot{Q}_{Heater\,slag} \qquad \text{E6.1.1}$$

The energy calculations are done with the assumption that there are no heat losses, thus, the washing process is assumed to be well isolated. The energy need for heating the dissolved PCC and NH_4Cl in the washing water is also neglected due to the small amounts present. The energy (electric power) need for the vacuum/pressure filtration, pumps and solid feeders are also neglected due to the unknown sizes and positioning of the facilities.

The energy use is not optimized, for example the flows (3.) and (16.) could preheat the flows (1.), (4.) and (18.), the out coming solids could preheat for example flow (4.) and so on. Therefore, the energy calculations should only be used as an indication on how much energy input (as heat) is needed.

The effect of temperatures on the washing processes

The temperatures for (3.) and (16.) are dependent on the efficiency of the heat exchangers and the type of the heating medium used. The area of the heat transfer surface and the heat transfer coefficient of the heat exchangers are important as well.

The temperature difference between the carbonation stage and the washing stages are critical when the energy consumption is to be minimized. If the washing stages have a high temperature and the carbonation stage has a low temperature the external heaters would need a large amount of external energy, especially if the mass flows from the carbonation stage are large. As earlier stated, when using water from the PCC production process for washing, the mass flow of process water is cooling down the washing water and more external energy is needed. Figure 6.1.2 shows the external energy needed for the NH_4Cl recovery from the PCC washing filtrate, for three different temperature differences between the PCC washing and the PCC production process. The carbonation temperature was set to 25°C, the PCC product before the wash has a content of 1.00 wt-% NH_4Cl and after the washing a content of 0.01 wt-% (99 wt-% of the NH_4Cl in the PCC recovered).

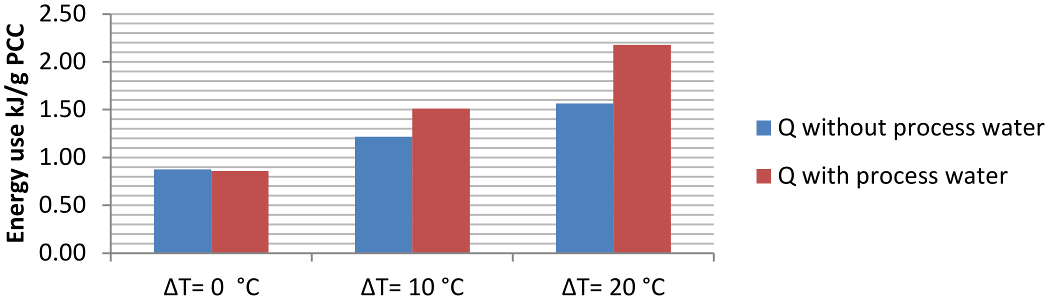


Figure 6.1.2 The energy (heat) consumption for three different temperature differences between the PCC washing filtrate and the PCC production process.

The energy consumption for using process water is a lot larger than if the process water is not used. However, when the temperature difference is zero the energy consumption is smaller with the process water than without. This is because the process water cools the washing water and there is no need for any energy from the cooler. However, the external energy in this case is transferred to the PCC production process, where the heat is unwanted. The same happens for the other temperature differences; all extra energy needed for the NH_4Cl separation process moves directly to the PCC production process.

The external energy needed for recovering the NH_4Cl from the slag residue filtrate is very high due the large amount of water needed for the washing. Figure 6.1.3 shows the energy need for recovering the NH_4Cl from the slag residue filtrate under the same conditions as for the PCC filtrate in Figure 6.1.2 (note that the y-axis is different from Figure 6.1.2). However, since the amount of water needed for the washing process of the slag residue is so large, the content of NH_4Cl was set to decrease from 1.00 wt-% to 0.1 wt-% (90 wt-% of the NH_4Cl in the slag residue recovered).

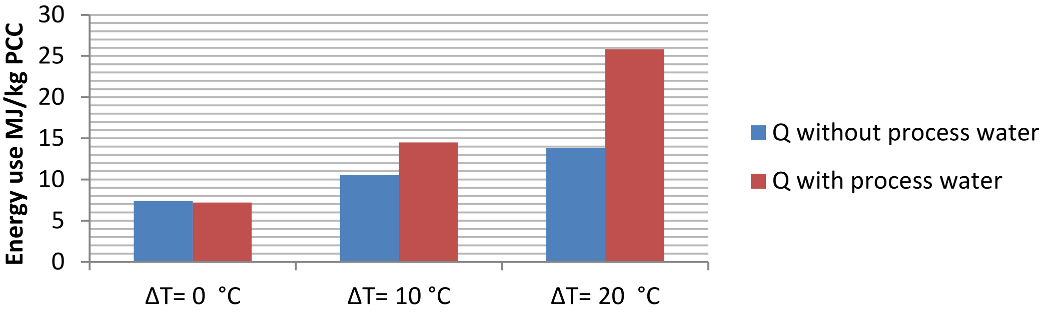


Figure 6.1.3 *The energy (heat) consumption for three different temperature differences between the slag residue washing (from 1.00 wt-% NH_4Cl in slag residue to 0.1 wt-%) filtrate and the PCC production process.*

The amount of external energy needed is excessively large when using process water for the washing processes (PCC and slag residue), especially if the heat is directly moved to the PCC production process where it is unwanted. Instead of using process water for the washing, more washing water could be added for the same energy usage and at the same time make the products more NH_4Cl free. However, the amount of water and energy needed for washing slag residue is so large (even if no process water is used) that it would be probably more reasonable not to wash/recover the NH_4Cl from the slag residue at all assuming that this does not affect possible further processing of the material.

Economic evaluation of recovering NH_4Cl

The estimation of the energy and water demand as actual costs for production of one kg PCC under the same circumstances as above at 25 °C with $\Delta T = 0$ °C, is shown in Figure 7.1.1. The prices of the consumed substances were assumed to: water 0.001 $\frac{€}{\mathrm{kg}}$ [48], district heating heat excluding taxes 0.04473 $\frac{€}{\mathrm{kWh}}$ [49] and NH_4Cl 0.14 $\frac{€}{\mathrm{kg}}$ [50]. The NH_4Cl recovered is treated as saved money and the external water and energy (heat) needs are seen as costs.

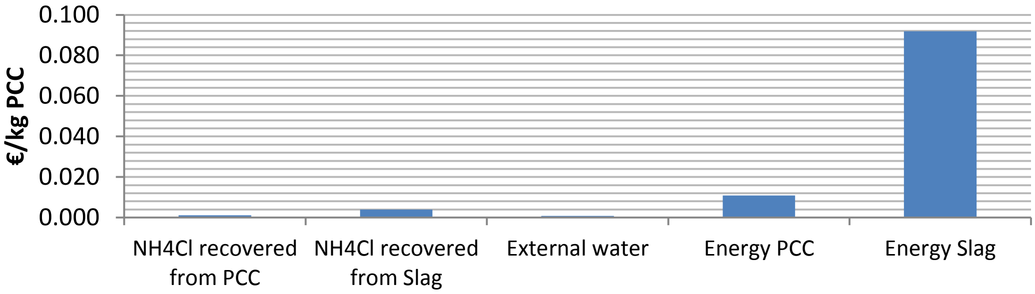


Figure 7.1.1 A typical cost scenario of washing 1 kg of PCC and slag residue while recovering the NH_4Cl.

Figure 7.1.1 shows the large price for recovering NH_4Cl from slag residue. The high price depends on the large amount of water needed. Therefore, the best alternative in this case would be to leave the NH_4Cl in the slag residue and avoid large energy costs, as in Figure 7.1.2. This means a loss of 0.032 $\frac{kg\ NH_4Cl}{kg\ PCC}$ if the slag residue has 1.00 wt-% NH_4Cl in the slag residue leaving the process.

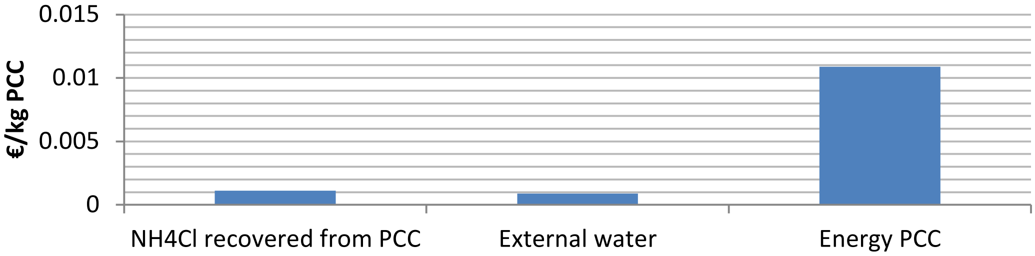


Figure 7.1.2 A typical cost scenario of washing 1 kg PCC while recovering the NH_4Cl.

Figure 7.1.2 shows the energy and water costs of washing the PCC-NH_4Cl mixture and recovering the solvent salt. Also seen in Figure 7.1.2, is the NH_4Cl recovered, which is how much money is saved on the NH_4Cl recovery. The money saved from the NH_4Cl recovery does not cover the energy costs of evaporating the water from the washing filtrate.

As earlier stated, the setup of the NH_4Cl recovery process is not fully optimized and therefore optimizing for a certain integration with other processes it could lower the energy cost somewhat. The water is set to a closed loop, so no water will exit or enter the system, except the water exiting with the solids. This could also be optimized: if NH_4Cl-water solutions are allowed to enter the environment, an economic balance for water, energy and NH_4Cl cost could be set up.

7 Conclusions and future work

Conclusions

In this study a method for estimating the NH_4Cl concentration in commercial PCC by using pH and temperature measurements was successfully developed. In principle, the method also reveals the structural form of the PCC; however, the only structural form tested in practice was rhombohedral calcite.

The washing and recovering of the PCC production solvent salt, NH_4Cl, was tested with cross- and countercurrent (batch) filtration. Since the latter was more efficient it was determined that it should be used for the washing processes. Experimental results show that during separation of NH_4Cl and PCC (rhombohedral calcite) the solids adsorb water containing dissolved NH_4Cl. This makes it difficult to remove NH_4Cl at low concentrations. Thus, the equilibrium constant (K) changes depending on the concentration of NH_4Cl in water attached to PCC. An equation was created based on experimental data to determine the equilibrium constant for different NH_4Cl concentrations in water attached to PCC.

Mathematical simulations were successfully made using Matlab. The simulations provide data on how much water is needed for recovering a certain amount of NH_4Cl from the wet PCC. For example, if the PCC product contains 1.00 wt-% NH_4Cl and is washed with a four stages countercurrent batch filtration (equals 3 washing reactors) to a concentration of 0.01 wt-% (99 wt-% of the NH_4Cl in the PCC recovered), the mass of water needed is 5.2 times larger than the mass of the PCC.

Experiments and theoretical simulations were made for washing slag residue and retrieving the NH_4Cl from that as well. It was discovered that the adsorption of NH_4Cl to slag residue was higher than the adsorption between NH_4Cl and PCC (rhombohedral calcite). An equation was then created from experimental data, to simulate the equilibrium constant (K) for removing NH_4Cl from water attached to slag residue. Due to the small K values it means that the amount of water needed for the recovery of the NH_4Cl is very large. For example, slag residue with 1.00 wt-% NH_4Cl washed with a four staged countercurrent batch filtration (equals 3 washing reactors) to a concentration as high as 0.1 wt-% (90 wt-% of the NH_4Cl in the slag residue recovered) gives the mass flow of water 3.4 times the mass of the slag residue (equals about 11.0 times the mass of the PCC product).

Process water from the PCC production process could be used for washing both PCC and slag residue. However, the amount of process water needed to make a difference in the amount of NH_4Cl left in the finished product would be very large. For example, to reduce the NH_4Cl content of 1.00 wt-% to 0.1 wt-% in slag residue (90 wt-% of the NH_4Cl in the slag residue recovered), the amount of fresh water needed reduces from 11.0 times the mass of the PCC product to 10.7. However, the amounts of water from the PCC production process become 32.1 times the mass of slag residue. This is not a sustainable option; mostly because the energy (heat) needed for separating the NH_4Cl from the washing water becomes very large. The usage of PCC production process water should therefore be excluded from the washing systems.

Heat was used to separate the NH_4Cl from the washing water, through evaporating the water. The energy needs are therefore quite high. A suggestion on how the separation process could look like was produced and a mathematical simulation model was created. A typical example: the PCC product before the wash has a content of 1.00 wt-% NH_4Cl and after the washing a content of 0.01 wt-% (99 wt-% of the NH_4Cl in the PCC recovered), the temperature difference between the PCC production process (25 °C) and the washing process is 0 °C. This gave the energy input need to be $0.88\,\frac{\mathrm{kJ}}{\mathrm{g\ PCC}}$, as a temperature between 120 °C and 150 °C which is depending on the efficiency of the heat exchangers.

The energy usage when removing NH_4Cl from slag residue filtrate becomes a lot larger due to the large amount of water needed. For a typical example: when reducing the fraction of 1.00 wt-% NH_4Cl in slag residue to as high as 0.1 wt-%, the temperature difference between the PCC production process (25 °C) and the washing process is 0 °C, gave the energy input need of $2.31\,\frac{\mathrm{kJ}}{\mathrm{g\ slag\ residue}}$ (equals to $7.40\,\frac{\mathrm{kJ}}{\mathrm{g\ PCC}}$) (90 wt-% of the NH_4Cl in the slag residue recovered), as a temperature between 120 °C and 150 °C which is depending on the efficiency of the heat exchangers.

The cost of heating and evaporating water to recover NH_4Cl from washing filtrates becomes a lot larger than the profit gained from the solvent salt recovered. However, depending on environmental regulations on how much NH_4Cl is allowed to enter the environment with waste water, an optimization on energy, water and NH_4Cl costs could be done. The amount of NH_4Cl allowed in the finished products (both in the PCC and the slag residue) becomes then a question for the customer.

Future work

Due to the large amount of energy needed for the separation of NH_4Cl from water through evaporation, other ways to separate solvent salts from water with less energy use should be studied. One option could be membranes, which would use osmosis or reverse osmosis to separate the solvent salt from water. Suitable membranes for NH_4Cl separation are difficult to find [51]. However, membrane technologies are constantly improving, especially when membranes are used for producing environmentally friendly electricity with fresh- and sea water (containing NaCl). For that the pressure-retarded osmosis (PRO) is used and the membrane technologies, such as thin film composites (TFC) and asymmetric cellulose acetate are used [52].

The method for measuring the amount of NH_4Cl in PCC which also reveals which crystal form the PCC particle obtains was only tested with rhombohedral calcite. This should be tested with different crystal forms to prove the accuracy of the method. Also the reason(s) for the inaccurate results with the PCC from the actual slag2PCC process should be studied.

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Appendix

Appendix 1

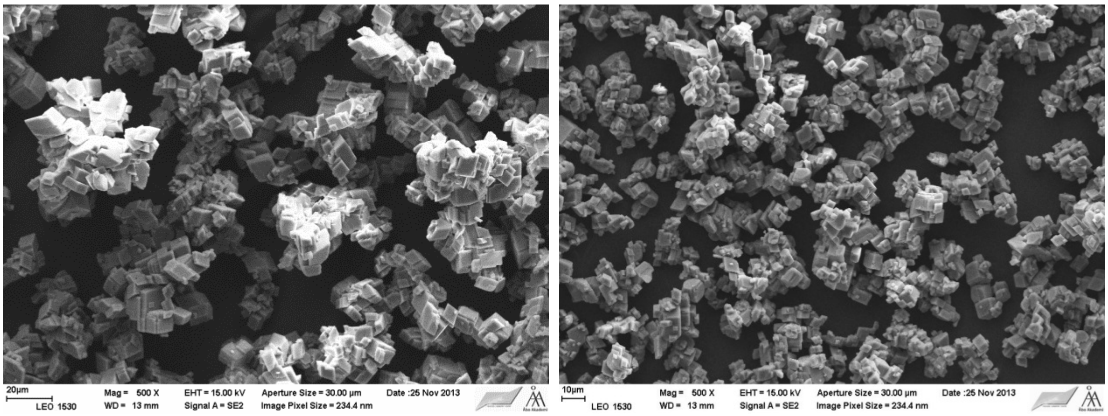

Figure A1 A SEM picture of rhombohedric calcite produced by Sigma-Aldrich 398101-500G (left) and Merck Millipore 1.02066.0250 (right).

Appendix 2

Table A1 pH measurements for commercial PCC (Sigma-Aldrich and Merck Millipore).

	9.10.2013	11.11.2013	Average
pH	9.63	9.67	9.65

Table A2 Mass loss for commercial PCC (Merck Millipore) samples, to study the amount of adsorbed water.

Sample	Wet PCC (g)	Dry PCC (g)	Water in wet PCC (g)	Water in PCC %	PCC %
300 °C 24 h	4.7194	3.8008	0.9186	19.46 %	80.54 %
300 °C 7 h	3.0143	2.4351	0.5792	19.22 %	80.78 %
100 °C 24 h	2.9257	2.3689	0.5568	19.03 %	80.97 %

Appendix 3

Calculation for the velocity of settling of 15 µm PCC particles in water.

$$\omega_p = \frac{g \cdot d_p^2 \cdot (\rho_p - \rho_F)}{18 \cdot \eta_F} = \frac{9.81\ \frac{m}{s^2} \cdot (1.5 \cdot 10^{-5}\ m)^2 \cdot \left(2700\ \frac{kg}{m^3} - 1000\ \frac{kg}{m^3}\right)}{18 \cdot 0.001\ \frac{kg}{m \cdot s}} = 0.000208\ \frac{m}{s}$$

Appendix 4

Matlab code for specifying the amount of water and energy (heat) needed for washing different contents of NH_4Cl in PCC and slag residue.

```
clear all
clc
clf

mw=10;               %mass of water (times the mass of PCC)
Dry=0.76;            %wt-% dry solids in PCC
AminPCC=0.01;        %wt-% NH4Cl in PCC
Stages=4;            %How many times one PCC sample is treated
Usage=1.9785;        %How meny times the process is reused

praminslag=0.01;        %wt-% NH4Cl in slag
mwslag=32;              %REMEMBER 3.2 TIMES LARGER MASS OF SLAGG THAN PCC
Stagesslag=4;           %How many times one PCC sample is treated
Usageslag=2.992;        %REMEMBER K IS LOWER THAN THE PCC AND THERE IS NEED
FOR A LOT OF WATER
slagtimesPCC=3.2;       %How many times more slag there is compared with the
PCC

%¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤ENERGY_CALCULATION_DATA¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤

dslagg=0.8;             %wt-% dry solids of slagg
Twashout=25;            %temp. PCCwash out (C)
Tfresh=20;              %temp. fresh water in  (C)
Tcarbonator=25;         %temp. carboator (C)
Textractorout=25;       %temp. extractor (C)
Twashoutslag=45;        %temp. Slag residue wash out (C)

Temp_con_out=2*Twashout;             %temp. PCC condensator (C)
Temp_con_out_slag=2*Twashoutslag;    %temp. Slag condensator (C)
dpricenetto=6.36;                    %district heating price cent/kwh

%¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤PCC_CALCULATIONS¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤

msample=1;
Times=Stages;
n=Stages;
t=Times;
S1=1.5;
Pr_system=AminPCC;
T=Twashoutslag;

Rv = zeros(n,t);
aqv = zeros(n,t);
prv = zeros(n,t);
expdat3 =zeros(3,3);
useofsystem =zeros(n,n);

mw=mw/Usage;
Ks=10^(-171.9065-
0.077993*(273.15+T)+2839.319/(273.15+T)+71.595*log10(273.15+T));%Ks for
CaCO3, rhomboedric calcite
dew=-0.00000474*T^2-0.00001626*T+1.00041486;         %density of water
xks=(Ks)^(0.5)*(100.09)/1000;                        %(gCaCO3)/cm^3(H20)
mPCCaq=xks/dew*mw;                                   %dissolved CaCO3 in
water
PCCin=msample-AminPCC;
aqv(1,1)=AminPCC;                     %mass of NH4Cl dissolved in water
prv(1,1)=aqv(1,1)/(mw+aqv(1,1));      %NH4Cl procent/100 i vatten
Rv(1,1)=aqv(1,1)/(aqv(1,1)+PCCin);
```

```
H2Oin=((1-Dry)/Dry)*PCCin;

i=1;
a=1;
u=0;

while a<2
    while i<n
            PCCin=msample-AminPCC-(i-1)*mPCCaq;    %dry PCC in
            aq=prv(i,a)*H2Oin;
            prv(i+1,a)=aq/(mw+aq);
                Rv(i+1,a)=(aq)/(aq+PCCin); % procent av NH4Cl i PCC om
vattnet torkars bort från en "reaktor", detta gjort för att bara kunna lätt
byta om till pH med mitt program
                aqv(i+1,a)=aq;
                S=(aqv(1,1))/aqv(2,1);
                if Rv(i,a)>=0.00018
                    Rv(i+1,a)=(aq)/(aq+PCCin);  %procent av NH4Cl i PCC om
vattnet torkars bort från en "reaktor", detta gjort för att bara kunna lätt
byta om till pH med mitt program
                    aqv(i+1,a)=aq;
                    S=(aqv(1,1)-aqv(2,1))/aqv(2,1);
                else
                       S= 50.83127*Rv(i,a)^0.24589;
                       S=S/Usage;
                   if u<=0
                      aq=aqv(i,a)/S1;
                      aqv(i+1,a)=aq;
                      Rv(i+1,a)=aq/(aq+PCCin);
                      u=u+1;
                   else
                          aq=aqv(i,a)/S;
                          aqv(i+1,a)=aq;
                          Rv(i+1,a)=aq/(aq+PCCin);
                   end
                end
            i=i+1;
    end
    a=a+1;
end

a=1;
while a<=n-1
    i=1;
    while i<=n-1
        Rv(1,a+1)=AminPCC/msample+Rv(2,a)-Rv(2,a)/S;

           if i<n-1
                  S= 50.83127*Rv(i,a+1)^0.24589;
                  S=S/Usage;
                  Rv(i+1,a+1)=Rv(i,a+1)/S+Rv(i+2,a)-Rv(i+2,a)/S;
           else
                  S= 50.83127*Rv(i,a+1)^0.24589;
                  S=S/Usage;
                  Rv(i+1,a+1)=Rv(i,a+1)/S;
          end
        i=i+1;
    end
a=a+1;
end

totsystemuse=sum(useofsystem(:)/Usage);
Rv=Rv.*100;
prv=prv.*100;

%¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤PLOTTING_PCC¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤
```

```
figure(1)
clf
plot(log10(Rv),'.-b')
xlabel('Amount of stages')
ylabel('Logaritmic wt-% NH4Cl in PCC')
title('wt-% NH4Cl in PCC vs. Amount of stages')
set(gca, 'XTick',1:1:n)

fprintf('Water flux konstant : %f g_w/g_PCCmix \n',mw);
fprintf('Water from system konstant in: %f g_w/g_PCCmix \n',totsystemuse);
fprintf('%f wt-procent NH4Cl in dry PCC after all washing \n',Rv(n,t));

%¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤SLAGG_CALCULATIONS¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤

msampleslag=msample*slagtimesPCC;
AminSlag=msampleslag*praminslag; %Ammoniumchloride is there in one gram of
PCC  (g)
Times=Stagesslag;
n=Stagesslag;
t=Times;
Rvslag = zeros(n,t);
useofsystemslag =zeros(n,n);
mwslag=mwslag/Usageslag;
Slagin=msampleslag-AminSlag;

Rvslag(1,1)=AminSlag/msampleslag;

i=1;
a=1;
u=0;

while a<2
    while i<n
            Kslag=9.07604* Rvslag(i,a)^0.43046;
            Sslag=Kslag*mwslag/msampleslag;
            Rvslag(i+1,a)=Rvslag(i,a)/Sslag;  %procent av NH4Cl i PCC om
vattnet torkars bort från en "reaktor", detta gjort för att bara kunna lätt
byta om till pH med mitt program
            i=i+1;
    end
    a=a+1;
end

a=1;
while a<=n-1
    i=1;
    while i<=n-1
        Kslag=9.07604* Rvslag(1,a)^0.43046;
        Sslag=Kslag*mwslag/msampleslag;
        Rvslag(1,a+1)=AminSlag/msampleslag+Rvslag(2,a)-Rvslag(2,a)/Sslag;
           if i<n-1
                  Kslag=9.07604* Rvslag(i,a)^0.43046;
                  Sslag=Kslag*mwslag/msampleslag;
                  Rvslag(i+1,a+1)=Rvslag(i,a+1)/Sslag+Rvslag(i+2,a)-
Rvslag(i+2,a)/Sslag;
           else
                  Kslag=9.07604* Rvslag(i,a)^0.43046;
                  Sslag=Kslag*mwslag/msampleslag;
                  Rvslag(i+1,a+1)=Rvslag(i,a+1)/Sslag;
          end
        i=i+1;
    end
a=a+1;
end

totsystemuseslag=sum(useofsystemslag(:));
Rvslag=Rvslag.*100;
```

```
figure(2)
clf
plot(log10(Rvslag),'.-b')
xlabel('Amount of stages')
ylabel('Logaritmic wt-% NH4Cl in slag')
title('wt-% NH4Cl in slag vs. Amount of stages')
set(gca, 'XTick',1:1:n)

fprintf('\nWater flux konstant for slag: %f g_w/g_PCCmix \n',mwslag);
fprintf('Water from system konstant in: %f g_w/g_PCCmix
\n',totsystemuseslag);
fprintf('%f wt-procent NH4Cl in dry slag after all washing \n',Rvslag(n,t));

%¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤ENERGY_CLACULATIONS_PCC¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤

mPCC=msample/1000;             %kg
dPCC=Dry;                      %dry solids of PCC
Washingwaterconstant=mw;       %washingwater constant for the amount of
water needed to fulfill the requirements
Washingwaterconstantp=totsystemuse;       %mass washingwater from process
per mass PCC
Temp_con_out=Temp_con_out+273.15;

%¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤

taxd=0.29;                                          %district heating price
tax
dpricebrutto=((dpricenetto*(1-taxd))/100)/3600;    %district heating price
€/kJ
mslaggre=mPCC*slagtimesPCC;
Tcarbonator=Tcarbonator+273.15;
Twashout=Twashout+273.15;
Tfresh=Tfresh+273.15;

m10=mPCC*(1-dPCC)+mslaggre*(1-dslagg);
m9=mPCC*Washingwaterconstantp;
m8=mPCC*(1-dPCC);
m7=m9;
m6=m8;
m4=m10;
m3=mPCC*Washingwaterconstant-m10;
m2=m3;
m1=m3;
m5=m4+m3;
m11=m1+m10;

NH4ClinPCC=AminPCC;
NH4ClinPCCclean=Rv(Stages,Stages)*mPCC;
NH4ClinPCCtoheater=(1-m10/m1)*(NH4ClinPCC-NH4ClinPCCclean);

Qinevp=m1*(-2.4716*Twashout+3179.2);
Q1=m1*Twashout*(0.00000000340035*Twashout^4-
0.00000454756469*Twashout^3+0.00228394483192*Twashout^2-
0.51006982283635*Twashout+46.88548111985730);
Q2=Qinevp+Q1;
Q3=m3*Temp_con_out*(0.00000000340035*Temp_con_out^4-
0.00000454756469*Temp_con_out^3+0.00228394483192*Temp_con_out^2-
0.51006982283635*Temp_con_out+46.88548111985730);
Q4=Tfresh*m4*(0.00000000340035*Tfresh^4-
0.00000454756469*Tfresh^3+0.00228394483192*Tfresh^2-
0.51006982283635*Tfresh+46.88548111985730);
Q6=Twashout*m6*(0.00000000340035*Twashout^4-
0.00000454756469*Twashout^3+0.00228394483192*Twashout^2-
0.51006982283635*Twashout+46.88548111985730);
```

```
Q7=Tcarbonator*m7*(0.00000000340035*Tcarbonator^4-
0.00000454756469*Tcarbonator^3+0.00228394483192*Tcarbonator^2-
0.51006982283635*Tcarbonator+46.88548111985730);
Q8=Tcarbonator*m8*(0.00000000340035*Tcarbonator^4-
0.00000454756469*Tcarbonator^3+0.00228394483192*Tcarbonator^2-
0.51006982283635*Tcarbonator+46.88548111985730);
Q9=Twashout*m9*(0.00000000340035*Twashout^4-
0.00000454756469*Twashout^3+0.00228394483192*Twashout^2-
0.51006982283635*Twashout+46.88548111985730);
Q10=Twashout*m10*(0.00000000340035*Twashout^4-
0.00000454756469*Twashout^3+0.00228394483192*Twashout^2-
0.51006982283635*Twashout+46.88548111985730);
Q11=Twashout*m11*(0.00000000340035*Twashout^4-
0.00000454756469*Twashout^3+0.00228394483192*Twashout^2-
0.51006982283635*Twashout+46.88548111985730);
Q5=Q6+Q9+Q11-Q7-Q8;
Qcooling=Q3+Q4-Q5;

if Qcooling<0
     Qcooling=Qcooling*-1;
end

Qoutcond=Q2-Q3;
Qneeded=Qinevp-Qoutcond+Qcooling;
Costofenergy=Qneeded*dpricebrutto;

fprintf('\nExternal heating needed for washing PCC %f kJ/g_PCCmix
\n',Qneeded);
fprintf('Price of heating PCC(if it would have gone to district heating) %f
€/g_PCCmix \n',Costofenergy);
fprintf('Recovered NH4Cl from PCC from heater %f g/g_PCCmix
\n',NH4ClinPCCtoheater);
fprintf('External water needed for PCC %f g/g_PCCmix \n',m4*1000);

%¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤ENERGY_CLACULATIONs_SLAGG¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤¤

Temp_con_out_slag=Temp_con_out_slag+273.15;
Textractorout=Textractorout+273.15;
Twashoutslag=Twashoutslag+273.15;

m19=mslaggre*totsystemuseslag;
m12=mslaggre*(1-dslagg);
m13=m19;
m14=m12;
m15=mslaggre*mwslag;
m16=m15;
m17=m16;
m18=m17;

NH4Clinslag=praminslag*msampleslag;
NH4Clinslagclean=Rvslag(n,n)/100*msampleslag;
NH4Clinslagtoheater=(NH4Clinslag-NH4Clinslagclean);

Q12=m12*Textractorout*(0.00000000340035*Textractorout^4-
0.00000454756469*Textractorout^3+0.00228394483192*Textractorout^2-
0.51006982283635*Textractorout+46.88548111985730);
Q19=m19*Tcarbonator*(0.00000000340035*Tcarbonator^4-
0.00000454756469*Tcarbonator^3+0.00228394483192*Tcarbonator^2-
0.51006982283635*Tcarbonator+46.88548111985730);
Q13=m13*Twashoutslag*(0.00000000340035*Twashoutslag^4-
0.00000454756469*Twashoutslag^3+0.00228394483192*Twashoutslag^2-
0.51006982283635*Twashoutslag+46.88548111985730);
Q14=m14*Twashoutslag*(0.00000000340035*Twashoutslag^4-
0.00000454756469*Twashoutslag^3+0.00228394483192*Twashoutslag^2-
0.51006982283635*Twashoutslag+46.88548111985730);
```

```
Q16=m16*Temp_con_out_slag*(0.00000000340035*Temp_con_out_slag^4-
0.00000454756469*Temp_con_out_slag^3+0.00228394483192*Temp_con_out_slag^2-
0.51006982283635*Temp_con_out_slag+46.88548111985730);
Q18=m18*Twashoutslag*(0.00000000340035*Twashoutslag^4-
0.00000454756469*Twashoutslag^3+0.00228394483192*Twashoutslag^2-
0.51006982283635*Twashoutslag+46.88548111985730);

Qinevpslag=m18*(-2.4716*Twashoutslag+3179.2);
Q17=Qinevpslag+Q18;
Q15=Q13+Q14+Q18-Q19-Q12;
Qoutcondslag=Q17-Q16;
Qcoolingslag=Q16-Q15;

if Qcoolingslag<0
    Qcoolingslag=Qcoolingslag*-1;
end

Qneededslag=Qinevpslag-Qoutcondslag+Qcoolingslag;
Costofenergyslag=Qneededslag*dpricebrutto;

fprintf('\nExternal heating needed for washing slag %f kJ/g_PCCmix
\n',Qneededslag);
fprintf('Price of heating PCC(if it would have gone to district heating) %f
€/g_PCCmix \n',Costofenergyslag);
fprintf('Recovered NH4Cl from slag from heater %f g/g_PCCmix
\n',NH4Clinslagtoheater);
fprintf('External water needed for slag 0 g/g_PCCmix \n');
```