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Concept design for demonstration plant for production of precipitated calcium carbonate from steelmaking slag and carbon dioxide

Master's thesis for the degree of Masters of Science in Technology submitted for inspection.

Espoo 28.11.2016
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Tiivistelmä

Teräs on laajalti käytetty rakennusmateriaali, se on osana muodossa tai toisessa lähes kaikessa koneenrakennuksessa. Vuonna 2015 raakaterästä valmistettiin 1621 miljoonaa tonnia ja terästeollisuus aiheutti lähes 7 % ihmisen hiilidioksidipäästöistä. Teräksen valmistus on yksi suurimmista teollisuuden hiilidioksidipäästöjen aiheuttajista. Slag2PCC-projektin päämääränä on kehittää taloudellisesti kilpailukykyinen prosessi vähentämään terästeollisuuden hiilidioksidipäästöjä. Tämä tehdään sitomalla hiilidioksidi stabiiliin mineraalimuotoon. Slag2PCC-prosessissa teräksen valmistuksessa syntyvä hiilidioksidi sidotaan teräskuonasta erotettuun kalsiumiin ja näin tuotettuun kalsiumkarbonaattiin. Slag2PCC-projekti on edennyt menestyksekkäästi laboratorio- ja pilottivaiheen läpi ja seuraava askel on suuremman demonstraatiolaitoksen toteutus.

Demonstraatiolaitoksen pohjana käytetään olemassa olevaa pilottilaitosta. Tässä työssä esitellään nykyinen pilottilaitos ja tarvittavat parannustoimenpiteet mitä, laitokselle on tehtävä. Tässä työssä esitellään teknologiaselvitys ja konseptisuunnitelma demolaitoksen toteuttamista varten. Kirjallisuudesta, laboratoriotesteistä ja asiantuntiahaastatteluiden pohjalta on koostettu mitoitusohjeistuksia, konseptipiirroksia sekä materiaali- ja teknologiavalintoja helpottamaan tulevia demolaitoksen suunnittelu- ja toteutusvaiheita.

Työssä esitellään mobiilin, laivakontteihin asennetun tuotantolaitoksen konseptisuunnitelma kalsiumkarbonaatin valmistamiseksi teräskuonasta ja hiilidioksidista. Laitoksen osafunktioille on tehty teknologia- ja laitteistoselvitys. Työssä on selvitetty ja esitetty laitoksen rakennusmateriaalien vaatimukset ja annettu sopivat materiaaliehdotukset. Työssä on lisäksi esitelty alustavia mitoituslaskelmia demonstraatiolaitoksen laitteiston jatkosuunnittelua varten.

Avainsanat teräskuona, kalsiumkarbonaatti, konseptisuunnitelma, hiilidioksidi

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Abstract of master's thesis

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Abstract

Steel is widely used construction material. It is part of every modern production line in a form or another. Steelmaking is one of the biggest causes of industrial carbon dioxide emissions. In 2015, 1621 million tons of raw steel was manufactured and steel industry caused almost 7 % of mankind's CO_2 emissions. Slag to PCC project aims to develop economically competitive method to reduce steel industries CO_2 emissions. This is achieved by binding CO2 in to stable mineral form. In slag2PCC process CO2 is bound to calcium that is extracted from steelmaking slag. This process produces precipitated calcium carbonate. Slag2PCC project has been successful in bot laboratory and pilot scale and now next step is to upscaling of the process to demonstration scale.

Demonstration plant is based on existing pilot plant. This thesis introduces the pilot plant and required improvements that this plant needs. This thesis goes through the technology research and concept design for demonstration plant. Thesis compiles guidelines for design parameters and material choices, design sketches and technology ratings based on literature, laboratory tests and interviews with consultants to ease the following design and manufacturing phases.

This work introduces concept design work for mobile demonstration plant for calcium carbonate production from steelmaking slag and carbon dioxide that is assembled in shipping containers. Work introduces sub function technology choices and initial dimensioning calculations for further development.

Keywords PCC, steelmaking, slag, concept, design, CO_2

Foreword

This thesis is part of slag to PCC research project and was carried out at department of and energy technology of Aalto University. I would like to thank Mika Järvinen, Arshe Said and Petri Kuosmanen for giving me this chance work in project and for guidance with work itself. I would also like to thank Carla, Owais and whole staff of energy department for being the awesome coworker that they are.

Espoo 28.11.2016

Niko Lagus

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Symbols

A	(m^2)	Face area of a filter
D	(m)	Diameter
D_i	(m)	Inner diameter
C	(m)	Off bottom clearance
E	(-)	Fractional efficiency of motor and pump
F	(-)	Ratio, fittings and installation cost to pipe purchase cost
F_L	(-)	Durand Factor
H_y	(h)	Operational hours per year
J	(-)	Fractional frictional loss trough fittings
K	($/kWh)	Cost of electricity
K_f	(-)	Ratio, annual fixed charge to initial pipe installed cost
N	(rps)	rotation speed
N_{js}	(rps)	Impeller rotation speed for just suspended state
Np	(-)	impeller power number
P	(W)	Power
Q	(m^3/s)	Volumetric flow rate
R	(-)	Medium resistance
S	(-)	Zwietering Constant
V	(m^3)	filtrate volume collected
X	(-)	mass ration between solids and liquid in suspension times 100
X_p	($/m)	Price for new 0.0254m inner diameter pipe
c	($kg\ m^{-3}$)	solid concentrating in the feed
d_p	(m)	particle diameter
g	(9.81 m/s)	acceleration due to gravity
Δp	(Pa)	static pressure drop
t	(s)	time
v	(m/s)	velocity
v_c	(m/s)	transitional flow speed from stationary bed to asymmetric flow
α	($m\ kg^{-1}$)	specific cake resistance
μ	($N\ s\ m^{-2}$)	Viscosity
ν	(m^2/s)	kinematic viscosity
μ_c	(Pa·s)	Fluid viscosity
ρ	(kg/m^3)	fluid density
ρ_l	(kg/m^3)	density of liquids
ρ_s	(kg/m^3)	density of solids

Abbreviations

AISI	American iron and steel institute
BOF	Basic oxygen furnaces
CO_2	Carbon dioxide
DC	Dry cargo
DSS	Duplex stainless steel
EAF	Electric arc furnaces
GCC	Ground calcium carbonite
HC	High cargo
ISO	International organization for standardization
PBT	Pitched blade turbine
PCC	Precipitated calcium carbonite
PREN	Pitting resistance equivalence number
RF	Refrigerated
rps	rotations per second
SD	Systematic design
SDS	Safety data sheet
SS	Stainless steel
UNS	Unified numbering system
X2PCC	Process to produce calcium carbonate from steel making slag

1 Introduction

World is struggling to move towards sustainable future. In one hand governments and industry are pushing greener values, more environment friendly legislation and regulations. In the other hand global population growth combined with ever growing standards of living and goals for economic growth are putting increasing pressure to environment.

Steel is widely used construction material in today's society. In 2015 world crude steel production was 1621 million tons. Steel production is also very energy and carbon intensive process. For every ton of steel produced, 1.8 tons of carbon dioxide (CO_2) is emitted. Steel making contributed approximately 6.7% of worlds CO_2 emissions.(World steel association, 2015)

One possible way to reduce CO_2 emissions in steel making, is to store CO_2 in a stable mineral form. Slag2PCC projects aims to do this by combining solid waste from steel making process, steelmaking slag, and steel plants flue gases to valuable end product. This is done by extracting calcium from steelmaking slag and binding CO_2 from steel plants flue gases to extracted calcium. This process forms precipitated calcium carbonite (PCC) that can be used in paper industry as filler material.

1.1 Background

Slag2PCC project has gone through laboratory and pilot scale test phases. In these phases research have focused on calcium extraction from steel making slag and carbonation process of calcium rich solution. Construction of pilot plant also required research and design work on process equipment for small scale production quantities. Now projects has moved to demo scale test phase. In this thesis research will concentrate on upscaling the Slag2PCC pilot plant and streamlining the process work flow.

1.2 Research task

This thesis work aims to answer following research questions.

- What are the essential problems in demo-plant upscaling process?
- What is the function structure of demo-plant?
- What working principles and technologies can be used to fulfill sub function demands?
- What is the combined working principle for demo plant?
- What are the evaluation criteria for principle solutions?

1.3 Goals

The goal of this research is to provide concept design for shipping container mounted demonstration plant and reasoning behind the concept design. This thesis should provide

basis for further design phase of upscaling process. This thesis should be coherent documentation of the design process for Slag2PCC pilot plant upscaling to demonstration scale.

1.4 Scope of research

This thesis focuses on the technical perspective of Slag2PCC demo plant upscaling from the mechanical engineering stand point. Objective is to review and chose working principles for the required equipment in demo plant and provide layout sketch for equipment. Work focuses on conceptual design phase of design process.

1.5 Methods

Research will begin with existing equipment review combined with literature research. This gives start point for further discussions with equipment manufacturers and experts. Design work flow will follow recommendations and guidelines of Systematic Design (SD) methodology on engineering design.

2 State of the art

This chapter goes through current state of X2PCC project. Chapter will explain how X2PCC process works, what kind of materials are processed. Chapter will also introduce pilot plant, pilot plants layout and what challenges research team has had with the pilot plant.

2.1 X2PCC process

Figure 1 is a simplified process diagram which consist of two process stages. These stages are extraction stage and carbonation stage. In extraction stage calcium is extracted from the steelmaking slag by dissolving it with ammonium chloride solvent. Spent slag is separated from solvent and discarded. Calcium rich ammonium chloride solvent is used in carbonation phase. In carbonation phase, calcium is carbonated with carbon dioxide. This reaction forms precipitated calcium carbonite (PCC) and removes calcium from solvent. After all calcium has reacted, PCC and ammonium chloride solvent are separated. PCC is collected and solvent is recycled to extraction reaction.

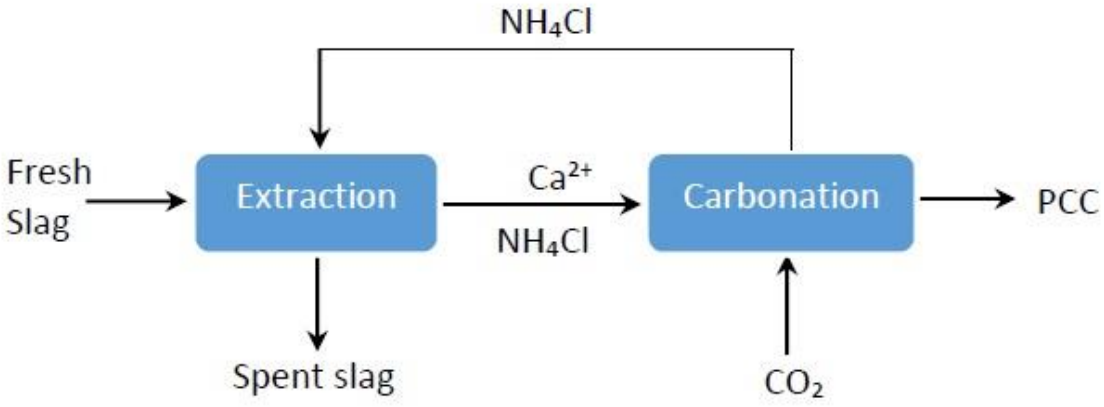


Figure 1. X to PCC rough process flow(Mattila et al., 2012)

2.2 Processed Materials

This subsection gives general information about the materials that are processed in slag to PCC process. This subsection will also give basic comparison between conventional PCC manufacturing and slag to PCC process.

2.2.1 Steelmaking slag

Steel manufacturing process produces several types of solid waste material called slag. Figure 2 represents simple schematic of steelmaking process and rough values for raw materials and byproduct streams.

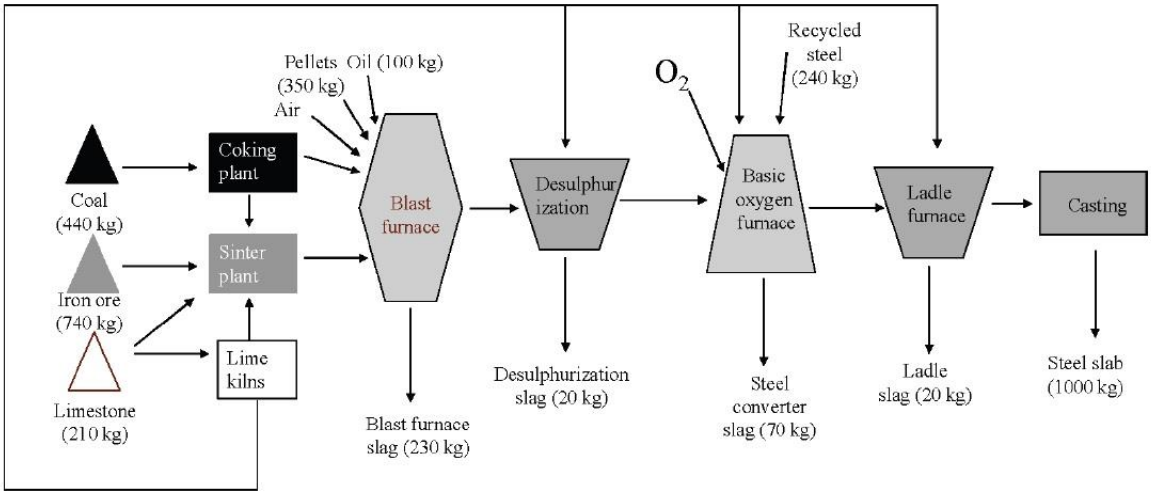


Figure 2. Simple schematic of typical integrated steel manufacturing process with some rough values for raw material and byproduct streams(Eloneva et al., 2008)

Blast furnace slag is widely used raw material in cement manufacturing and has well established markets. However steel making slag is much less utilized. Steel making slag is common name for slags produced in electric arc furnaces (EAF) and basic oxygen furnaces (BOF). Slag to PCC project aims to produce PCC from steelmaking slag. Table 1 gives the compositions of different slag types produced in steel manufacturing. (Zappa, 2014)

Table 1. Examples of iron and steel slag compositions percentages (adapted from(Anon, 2016a))

	Blast furnace slag	Converter slag	Electric arc furnace slag	
			Oxidizing slag	Reducing slag
CaO	41.7	45.8	22.8	55.1
SiO_2	33.8	11.0	12.1	18.8
T-Fe	0.4	17.4	29.5	0.3
MgO	7.4	6.5	4.8	7.3
Al_2O_3	13.4	1.9	6.8	16.5
S	0.8	0.06	0.2	0.4
P_2O_5	<0.1	1.7	0.3	0.1
MnO	0.3	5.3	7.9	1.0

Before steelmaking slag can be used in slag to PCC process it needs to be grinded to fine powder and slag powder has to be dry. Figure 3 shows the particle size distribution of grinded steelmaking slag used in slag to PCC pilot plant.

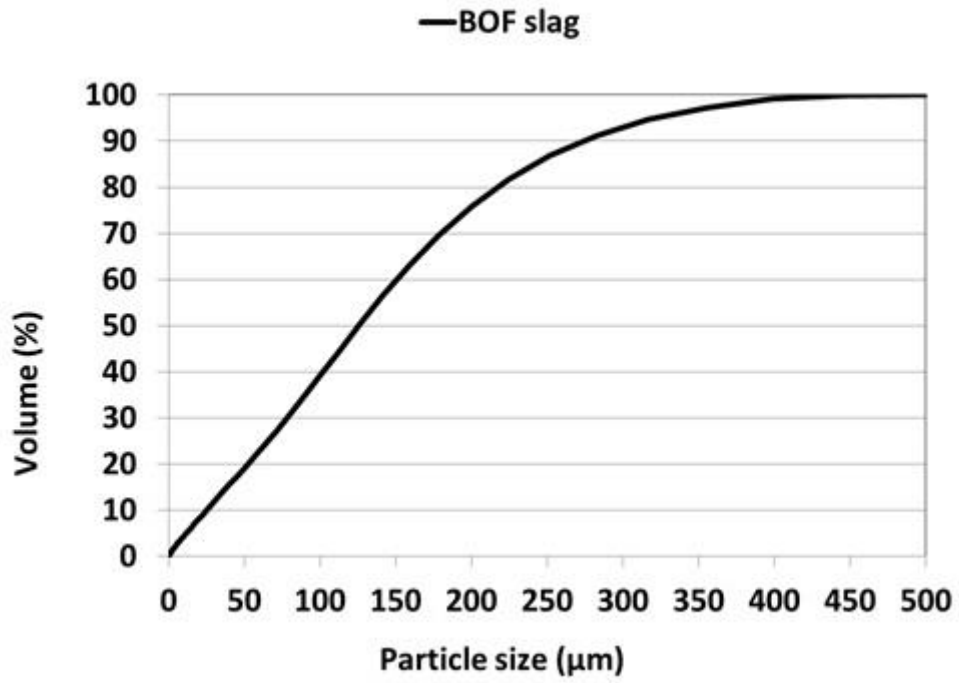


Figure 3.Steelmaking slag particle size distribution.(Said, 2016)

2.2.2 Ammonium chloride solvent

Calcium has to be extracted from steelmaking slag, so that it can be used to produce PCC. This extraction is done by dissolving calcium with 1 molar ammonium chloride (NH_4Cl) water solvent.

Ammonium chloride solvent is corrosive and acidic liquid. It corrodes many metals such as steels and copper(Craig and Anderson, 1994). It can also cause skin irritation and serious eye irritation. 2 molar ammonium chloride solvent has hazardous material identification system (HMIS) ratings 2 for health, 0 for fire and reactivity and personal protection class C.(Anon, 2016b)

When calcium dissolves from steel slag, extraction reaction forms ammonium hydroxide ($NH_4(OH)$). Ammonium hydroxide isn't that corrosive, but it is more aggressive towards rubbers and elastomers than ammonium chloride(Craig and Anderson, 1994) (Anon, 2016c). .Ammonium hydroxide solution with 3% volumetric concentration has following HMIS ratings and forms basic solvent with water(Anon, 2016d).

- Health 2
- Fire 0
- Reactivity 0
- Personal protection class H

2.2.3 Precipitated calcium carbonate

Calcium carbonite ($CaCO_3$) is common mineral that exist in three anhydrous polymorphs witch are calcite, aragonite and vaterite. Calcite is most staple of these phases in atmospheric pressure and room temperature. Slag to PCC process aims to produce second of these phases, aragonite. (Zappa, 2014)

Calcium carbonite is a versatile mineral and is used widely in different industrial fields such as paper making. Calcium carbonate can be produced by mining and refining limestone. This so called natural calcium carbonate can also be called ground calcium carbonite (GCC). Figure 4 shows generic flow sheet for ground calcium carbonate refining process. (Zappa, 2014)

Calcium carbonite can also be produced synthetically in industrial precipitate process. This product is of higher quality than GCC and is called precipitated calcium carbonate. There are many different ways to produce PCC, but the three most used ones in industrial scale are carbonation process, lime-soda process and solvay process(Mattila and Zevenhoven, 2013). Figure 5 shows simplified schematic of these three PCC manufacturing processes.(Zappa, 2014)

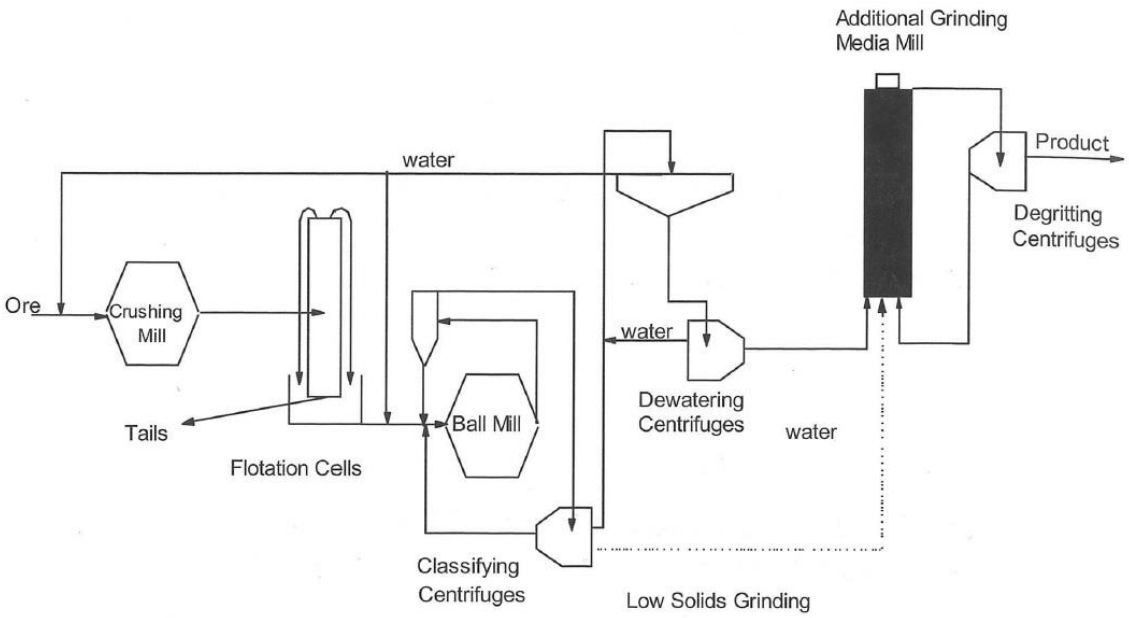


Figure 4. Generic flow sheet for ground calcium carbonite processing. (Wakeman and Tarleton, 2005)

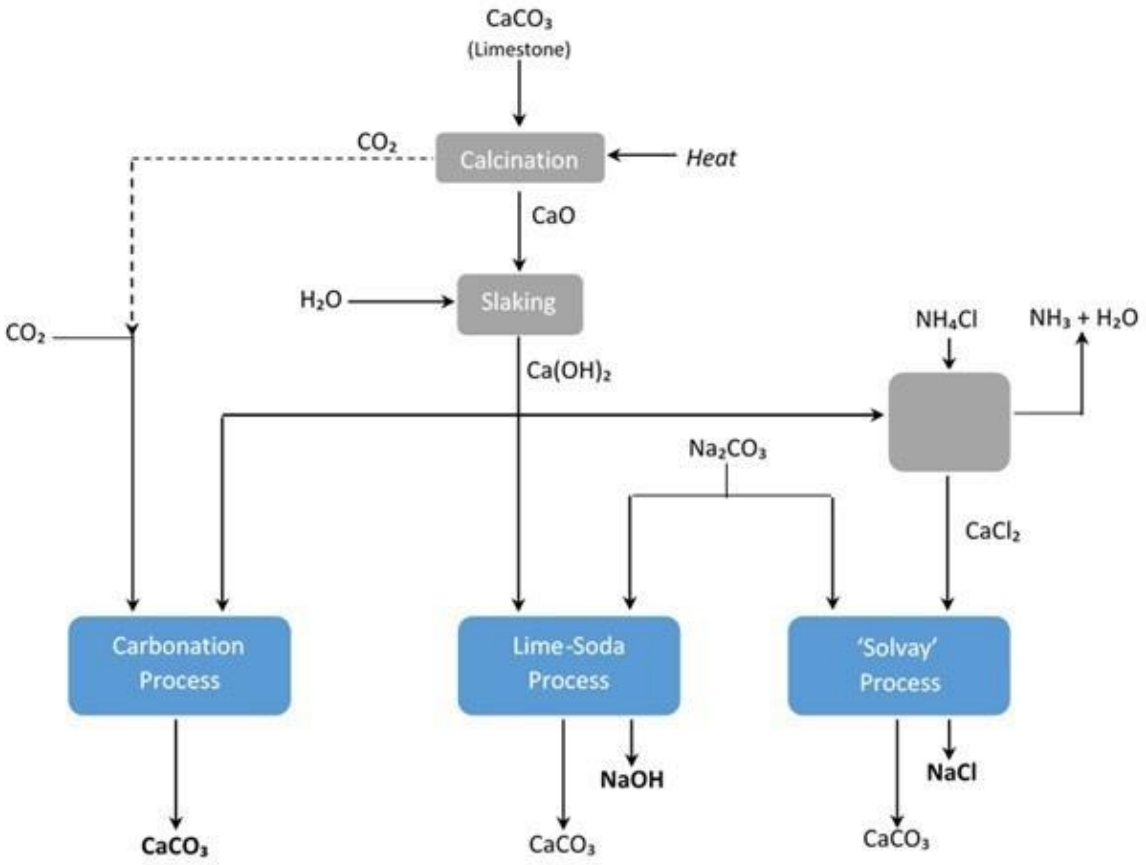


Figure 5. Three main production methods of PCC. (Zappa, 2014)

Big difference between these commercial PCC and GCC manufacturing methods and slag to PCC process is that slag to PCC method uses recyclable solvent and instead of pure water in process. This means that slag to PCC process requires sophisticated solid/liquid separation methods in process for solvent collection and PCC purification.

2.3 Pilot plant

This sub section introduces the exiting pilot plant. Section will go through structure and operation of pilot plant and also list problems and challenges that research team has faced while conducting experiments with the pilot.

2.3.1 Pilot plant description

Figure 6 shows schematic for slag to PCC pilot plant situated in Otaniemi, Aalto University. Plant has three (3) reactors, but only two of these reactors were used in experiments. In typical experiment setting solvent is pumped to extraction reactor. When required amount of solvent is inside the reactor steel slag is manually loaded to the reactor. Slag and solvent are mixed roughly 40 minutes and then mixture is filtered after it reaches target pH reading. Extraction filtration is 3 stage process. First, slag slurry is pumped to sedimentation vessel that isn't represented in figure below. Sedimentation is required to speed up filtration

process. After sedimentation, diluted slurry is pumped through quantitative bag filter and finally trough polishing cartridge filter.

Filtered calcium rich solvent is stored temporally in a holding tank. Calcium solvent is then pumped through heat exchanger to the carbonation reactor. In carbonation reactor solvent is mixed and bubbled with CO_2, this process carbonates calcium in solvent, form PCC and regenerates solvent for further use in extraction reaction. Carbonation is stopped by cutting of CO2 flow when mixture reaches target pH. Carbonation takes roughly 40 minutes. After carbonation PCC and solvent are separated with identical quantitative and qualitative filters that were used in slag-solvent separation. After filtration PCC is collected from quantitative filters and stored. Solvent is collected to recycled solvent tank where it can be taken to upcoming calcium extraction.

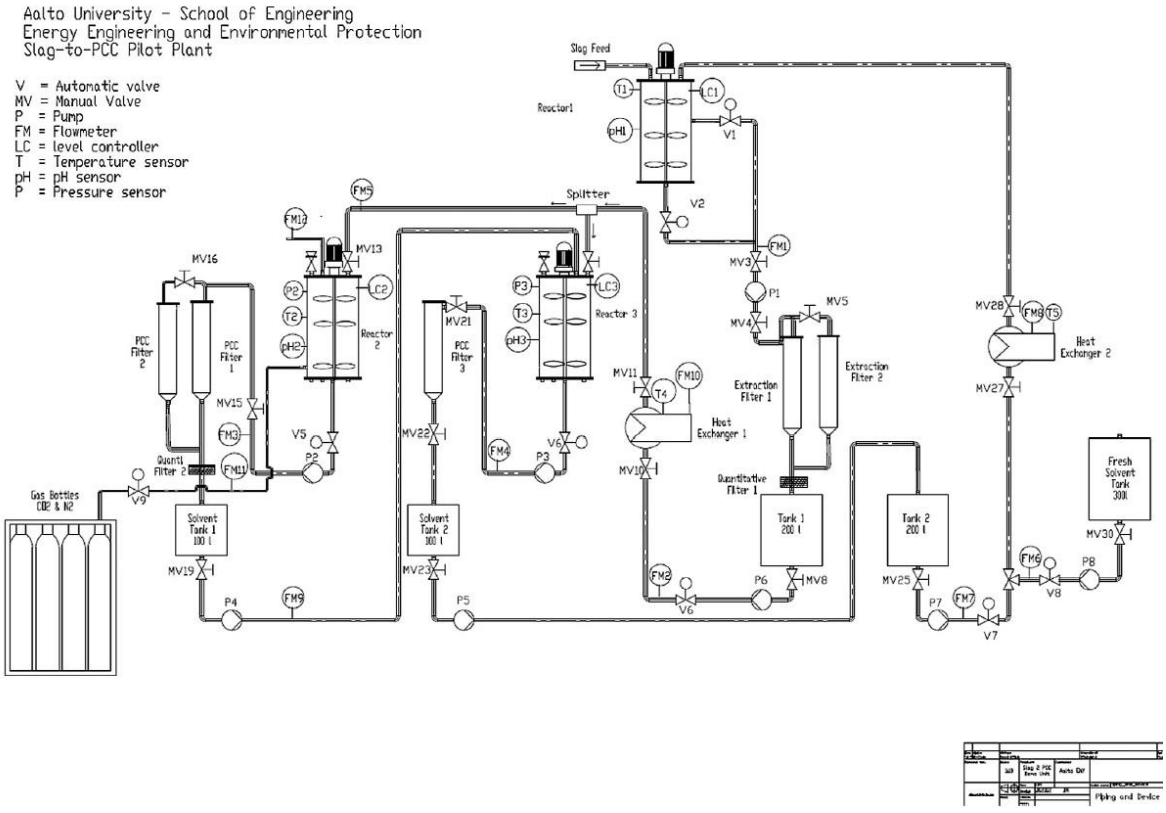


Figure 6.Slag to PCC pilot plant.(Said et al., 2016)

Table 2 lists the main components in X2PCC pilot plant. Table also gives brief description of type and specifics of the components such as construction materials, dimensions or performance characteristics.

Table 2. The key components of the pilot plant. (Said et al., 2016)

Name	Number of units	Type	Description
Reactors	3	Stainless steel, AISI 304	V = 200l, h= 1m d = 0.5m
Reserve tanks	5	Plastic tanks	2 x 200l, 1x 300l, 2x100l
Quantitative filters	5	Amazon bag filters	Bag filter housing: 1 µm
Qualitative filters	3	HOH filter housing	2 x 1 µm and 1 x 0.45 µm
Slag feeder	1	Rotary valve	RV-RVR 02, 10 rpm
Pumps	8	Pumps SELF, Mag 22T8	0.35 kW, 20 l/min
Heat exchangers	2	Fixed plate	FP 40-59-1-NH
Agitators	3	Pitched blade impeller	CML and HLS, 0.37 kW, 202 and 170 rpm
Pipes		Stainless steel AIS 316	¾ in.
Hoses		VEPA, 19 x 27 mm	EPDM 110C, 15 bar, ¾ in.
pH sensors	3	Jumo, 0030u151	0-12 pH
Temperature sensors	5	Pt-100	
Liquid flow meters	10	210, DN10	Max 32 l/min
Gas flow meters	2	Rotameter and Aalborg, GFM57	

2.3.2 Main problems and challenges

One purpose of pilot scale testing is to verify test results that have been acquired in laboratory scale tests and further test production process. Slag to PCC team has acquired promising results with the pilot plant that have confirmed laboratory scale findings. However research team faced some challenges and found out points to improve in upscaling process with pilot plant.

First area that needs improvement is reactors. It was challenging to acquire proper solid suspension in these reactors. Reactor designs need to be improved and for better solid suspension. Most likely causes for poor performance in pilot plants reactors are (Zappa, 2014):

- Large ration between liquid height and reactor diameter
- Flat bottom
- Lack of bafflers
- Sub optimal impeller choice
- Material corrosion resistance

Filtration system also needs to be improved. Current bag filter system produces too wet cake isn't able to wash cake free of ammonium chloride solvent, does not collect finest particles from slurry and is too time consuming. Filtration system needs to produce much drier, washed cake and clear filtrate.

Equipment materials and types need to be also chosen more carefully. There has been axel seal failures in liquid pumps that pump calcium rich solvent. Axel seals hardened and started to leak solvent trough them causing axel bearing failure(Desyatnyk, 2016). Failure was most likely caused by incompatible materials, as axel sealing material, Viton, isn't recommended to be used in contact with ammonium hydroxide(Anon, 2016c).

Pilot plant also has some corrosion problems. Reactors were manufactured from AISI 304 grade stainless steel. This resulted in severe corrosion inside the carbonation reactor. Corrosion was much milder in extraction reactor, but both of these reactors were painted with corrosive resistant coating. Also brass parts and fittings needed to be replaced, as solvent corroded then severely.

There was also one valve failure due to corrosion and scaling. Figure 7 and Figure 8 show corrosion damage and scaling in failed valve 9. Valve was sealed shut. This valve shuts off CO_2 flow to the carbonation reactor. Valve material is AISI 316 grade stainless steel. From the figures below we can see that scaling and corrosion was much more sever in reactor side of the valve. This is most likely caused by solvent that was trapped in to the valve as valve 9 was probably never flushed with water. Gas bottle side of valve shows much less scaling and some crevice corrosion and pitting. The valve leading to carbonation reactor (MV13) was also once completely clogged with PCC scaling.

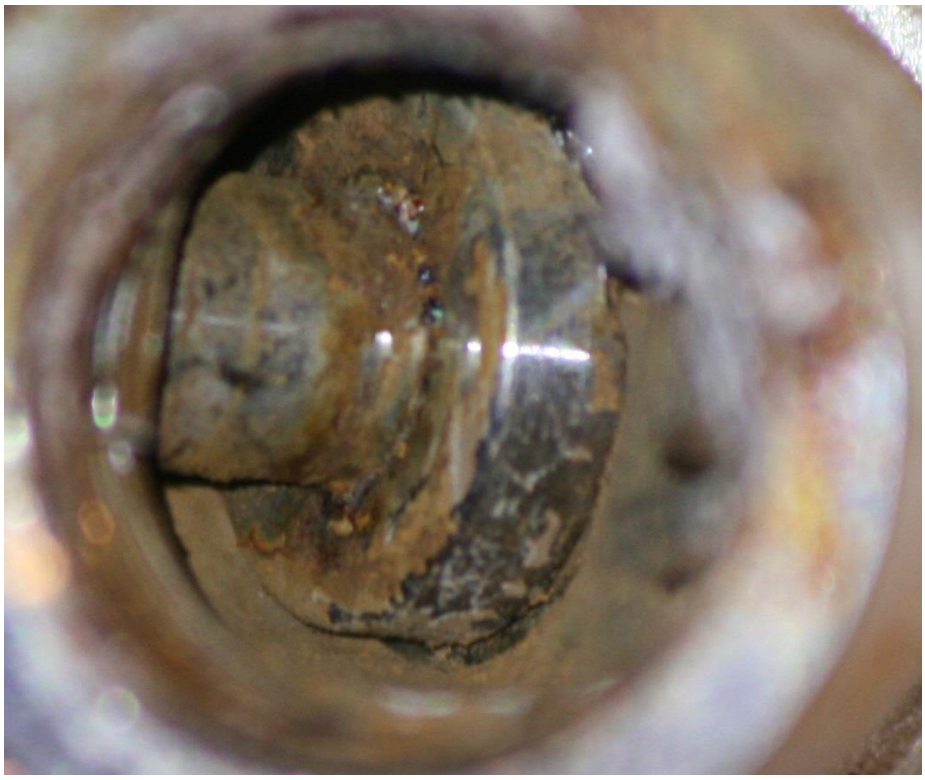


Figure 7. Corrosion and scaling in valve 9 CO_2 side.

Figure 8. Corrosion and scaling in valve 9 reactor side.

3 Materials and methods

This section of the thesis goes through the requirements for X2PCC demo plant. This section will also give rating methods for technical solutions and theoretical background knowledge about sub functions of the demonstration plant and working principles of technologies.

3.1 Process workflow

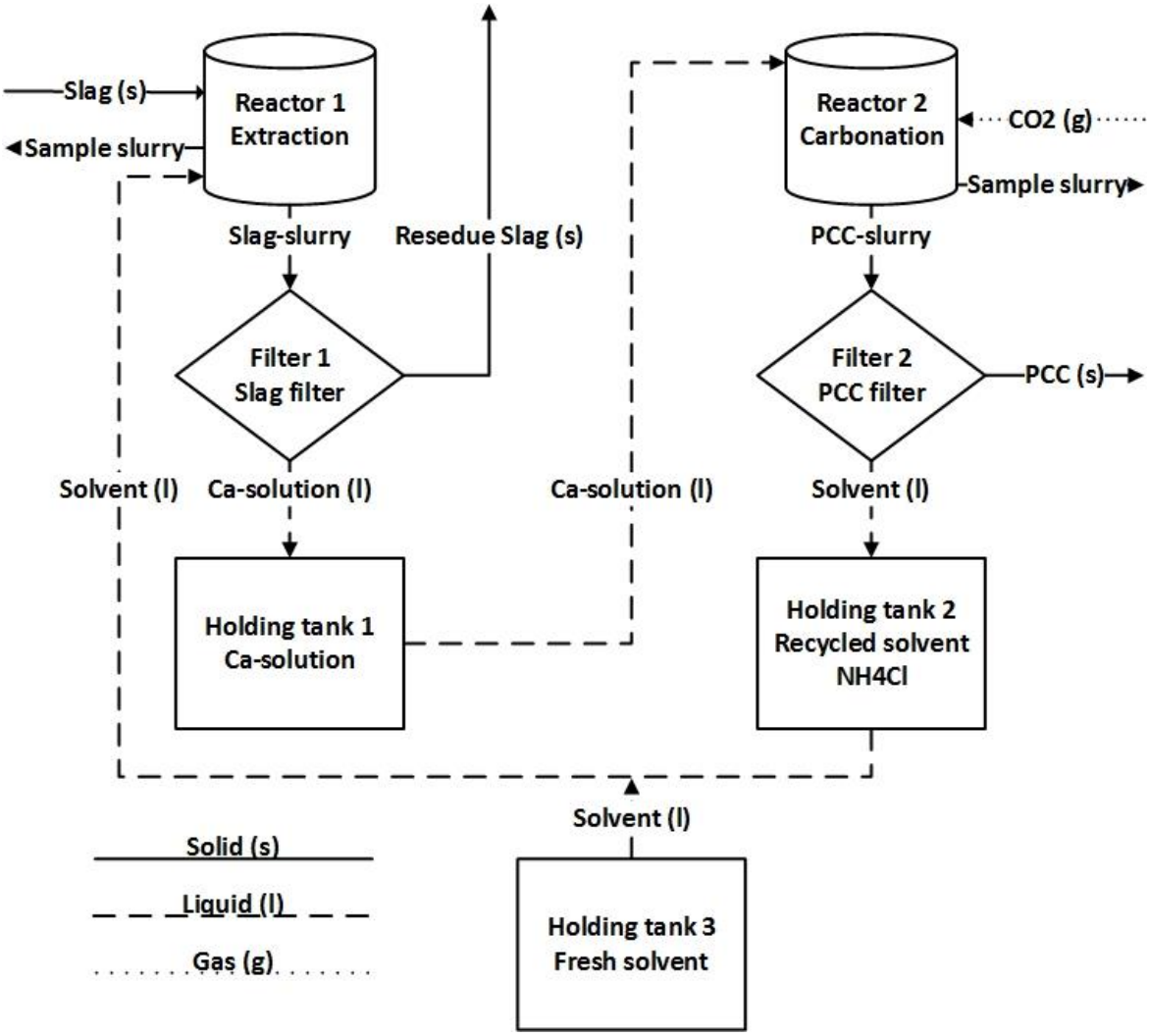


Figure 9. X2PCC process material block flow diagram.

Figure 9 shows the process flow in X2PCC demo-plant and demonstrates the connections of the sub-functions in the system. Sub-functions of X2PCC demo-plant are:

- extraction reaction
- slag and solvent separation
- Carbonation reaction
- PCC and solvent separation
- material transportation
- solvent storing

Extraction reaction has two material inputs and one main output. Material inputs are solid slag and liquid solvent. Result of this reactor is the residue slag slurry. Process temperature, pH and tank level are measured and it is possible to take slurry samples in different phases of the extraction reaction. This function holds steelmaking slag and ammonium chloride solvent and keeps them in well mixed slurry composition for efficient calcium dissolving reaction.

Slag and solvent separation takes the end product of the extraction reaction and separates residue slag from calcium rich solvent. It then guides residue slag out of the system and calcium solution to solvent storage.

Carbonation reaction receives calcium rich solvent batch and continuous CO_2 gas flow. Reactor keeps liquid solvent and CO_2 gas well mixed for efficient precipitation reaction of precipitated calcium carbonite. Process temperature pH and CO_2 flow rate are measured. Reactors material output is PCC slurry.

PCC is separated from the solvent in the PCC filter. Filter receives mixture of PCC and ammonium chloride solvent from the carbonation reactor. PCC is removed from the system and solvent is guided to holding tanks for reuse in extraction reaction.

Holding tank 1 and 2 are buffer tanks for extraction and carbonation reactors. Circulating solvent is stored in these tanks before it is pumped to reactors. Holding tank 3 is storage for fresh ammonium chloride water solution. This solution is used to compensate solvent losses in slag and PCC filtration phases of the process.

Material transportation takes care of transporting process materials. It needs to pump ammonium chloride solvent, slag and PCC slurries, and removing residue slag and PCC from the demo-plant.

3.1.1 Material recycling

Solvent is recycled in the process. Extraction reaction removes calcium from steelmaking slag. Calcium dissolves to solvent and solvent is primed for carbonation reaction. In carbonation reaction calcium is removed from solvent when it reacts with carbon dioxide and form PCC. This reaction regenerates solvent for reuse in extraction reaction. However, complete solvent recycling isn't possible as there will be some losses in slag and PCC filtration.

X2PCC demo-plant will also use water for system flushing and cake washing in PCC and slag filters. Recycling and reusing of waste water could be possible. As an example cake wash water could be used multiple times before water is directed to waste system. However there isn't test data about feasibility of these methods and they need to be tested.

3.1.2 End product quality

X2PCC demo plant has two different end products, residue slag and PCC. Poth of these products need to be clean of ammonium chloride solvent. This means that filters 1 and 2 need to first remove solvent from slag and PCC slurries, and then wash the residue slag and PCC cakes.

3.2 Environmental constraints

Demo plant will be installed outside in Raahe and process equipment is assembled in to shipping containers. Plant should be fully functional while equipment is still in shipping containers. Demo plant will have 25 by 25 meter area for the equipment, waste and raw material storage. It is common that temperatures go under freezing point in 8 months in year and only from June to September air temperature stays over 0 ^{o}C over the whole day and night. This means that casing of the technical equipment requires heating as does water and solvent pipes that run outside of the heated equipment containers.

All the water that is produced by X2PCC demo plant needs to be collected for further processing. Mainly this will mean that waste waters of the process are collected to a tank for further processing. . Waste water will be highly diluted solution with NH_4CL and $NH_4(OH)$ also small amounts of slag and PCC particles are present. Waste water is produced in cake and equipment washing.

3.3 Reactor designs

In chemical processes, reactors and their design have the up most importance (Coker, 2001). Reactor choice, optimization and design is a science of its own. However this work focuses on upscaling of X2PCC pilot plant and will only present designs that will improve on existing reactor choices.

There are two reactors in demonstration plant, the extraction reactor and carbonation reactor. Similarities between these reactors are:

- Reactors need to keep the process materials well mixed
- Reactor have liquid and fine solid particles in them
- Reactors output is slurry
- Reactors process corrosive materials
- Reactors have similar volume requirement
- Both reactors have similar installation area
- Both reactors will have atmospheric pressure
- Neither of reactors require temperature control

Both precipitation and extraction reactions require high mass transfer rates. This means that demo plant reactor should have even solid concentration through the whole reactor volume.

Due to these similarities reactors dimensions and designs will have lot in common, for instance reactor dimensions will be identical. However there are few key differences between these reactors. Extraction reaction is two phase reaction, there will be only solids, steelmaking slag, and liquid, ammonium chloride solvent, in the reactor. All the reactants are also loaded to the reactor at the start of reaction. Carbonation reaction is three phase reaction. It has gas, liquid and solid components. This means that carbonation rector needs both solid suspension and gas dispersion. Also, unlike in extraction reaction, CO_2 is fed in to the reactor continuously through whole reaction time.

3.3.1 Reactor types

Extraction reactor is single batch reactor, meaning that all materials needed in reaction are loaded into the reactor in the start of the reaction. In extraction reactor calcium is extracted from steelmaking slag with solvent. Reaction is dissolution reaction that aims to removes only calcium from steelmaking slag. Slag powder and liquid solvent are measured into the reactor while slurry mixture inside the reactor is mixed. Solid suspension is required through the whole reaction.

Carbonation reactor is semi-batch reactor. Liquid solvent is pumped in to the reactor as a batch, but CO_2 is added to the reactor through whole reaction time with constant flow. Reaction starts when CO_2 flow is switched on and ends when CO_2 flow is cut off. Solid suspension and gas dispersion are both required through the whole reaction time.

3.3.2 Dimensioning and geometry

Figure 10 shows a standard layout for agitated vessel with single impeller and sparger ring. Single impeller is usually sufficient for solid suspension when the fraction of tank diameter T and liquid depth H is below 1.3 ($H/T < 1.3$). Small aspect rations can cause higher mixer power consumption, as impeller diameter rises. So called standard fraction between liquid height and tank diameter is one (1).(Paul et al., 2004)

Vessel has four (4) bafflers on the sides to improve flow pattern and mixing results. Baffler width is between one tenth and twelfth of tank diameter and there is small cap between the vessel wall and bafflers. This cap should be one to two percent of tank diameter to prevent solid build up near the bafflers. Baffler length is dictated by liquid level and impeller clearance. Baffler's upper edge should be on the liquid level and lower edge on the same height as impellers blades bottom edge.(Paul et al., 2004)

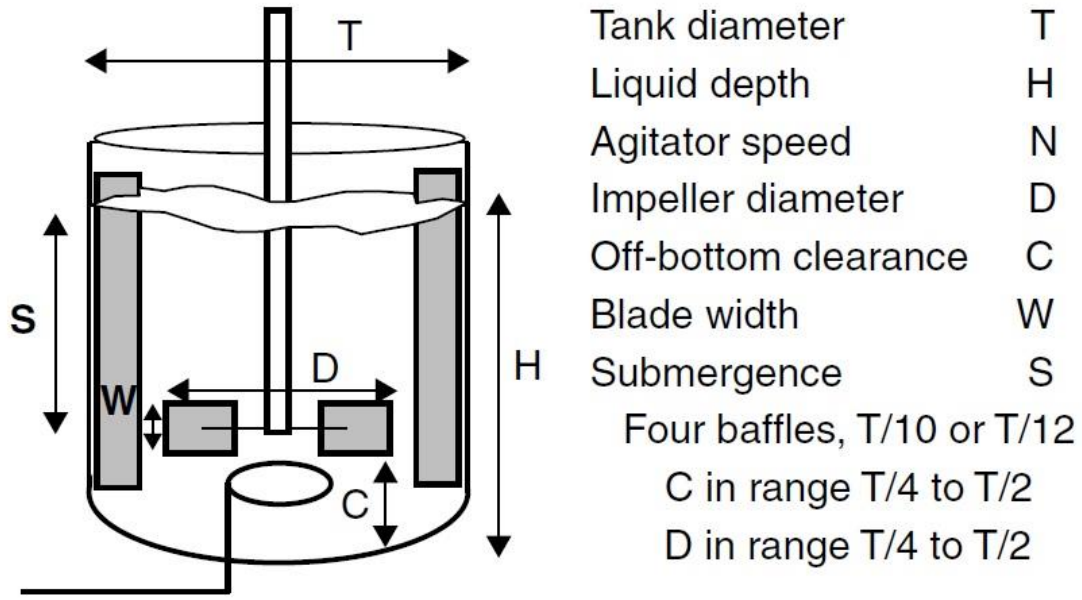
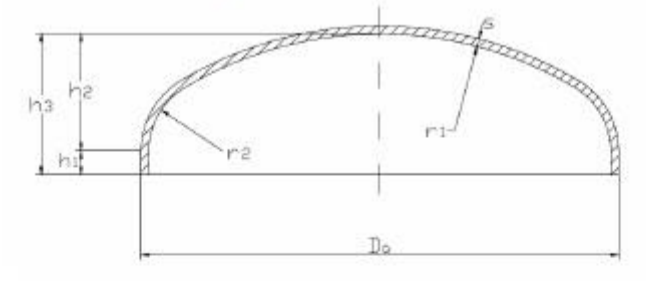


Figure 10. Standard layout for agitated vessel with single impeller and H~T. (Paul et al., 2004)

Dished bottom should be used in vessels that are designed for solid suspension. Dished bottom will decrease the required impeller speed for just suspended state from 10 to 20 %, when compared to flat headed vessels. Preferred head geometries are ASME dished, elliptical or torispherical heads. Different head geometries will have different flow patterns, but these three standard shapes are all suitable for solid suspension.(Paul et al., 2004)

Figure 11 shows examples of standard dished head geometries and how these heads are dimensioned.

Semi ellipsoidal head DIN 28013

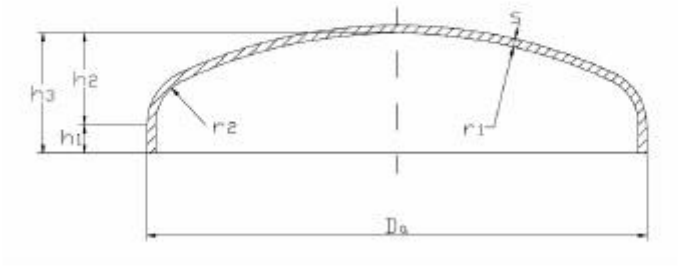


$r_1 = 0{,}8 \times D_a$ $\quad h_1 \geq 3 \times s$

$r_2 = 0{,}154 \times D_a$ $\quad h_2 = 0{,}255 \times D_a - 0{,}635 \times s$

$h_3 = h_1 + h_2$

Torispherical head DIN 28011



$r_1 = D_a$ $\quad h_1 = 3{,}5 \times s$

$r_2 = 0{,}1 \times D_a$ $\quad h_2 = 0{,}1935 \times D_a - 0{,}455 \times s$

$h_3 = h_1 + h_2$

Figure 11. Example of standard dished tank head forms from a tank head manufacturers website (Anon, 2016e)

3.3.3 Reactor agitators and accessories

Both reactors in demo plant will have a mixer. Mixing of liquids is usually done with mechanical agitator in stirred vessels, but there are other methods such as mixing with jet-mixers. Mechanical mixer is typically a device that consist motor, gearbox. Mixer power consumption for mechanical agitator can be estimated with equation below. (Paul et al., 2004)

$$P = N_p \rho N^3 D^5 \quad (1)$$

Where:

P = power (W)
N_p = impeller power number (-)
ρ = fluid density (kg/m^3)
N = rotation speed (rotations/second)
D = impeller diameter

Table 3. Power numbers of various impellers under turbulent conditions with four standard baffles.(Paul et al., 2004)

Impeller type	N_p
Concave- or hollow-blade turbine	4.1
Ekato MIG-3 impellers, D/T = 0.7	0.55
Ekato Intermig-2 impellers, D/T = 0.7	0.61
High-share disk at Re = 10 000	0.2 (lower for lower Re)
Lightning A310	0.3
Chemineer HE3	0.3
The following are all for D = T/3, C=T/3 and balde width W = D/5:	
45°BPT; 4 blades	1.27
45°PBT; 6 blades	1.64
Marine propeller (1.0 pitch)	0.34
Marin propeller (1.5 pitch)	0.62
Smith or concave- or hollow-blade with 6 blades	4.4

Table 3 gives power numbers for several impeller types in vessel with bafflers under turbulent conditions. Equation below gives correlation with impeller clearance C for PBT power number. When standard baffles are used, and impeller diameter is in typical range of one third to half of the tank diameter, changing impeller diameter has very little effect on power number.(Paul et al., 2004)

$$N_p \propto \left(\frac{C}{D}\right)^{-0.25} \quad (2)$$

Where:
N_p = impeller power number (-)
C = impeller clearance from tank bottom (m)
D = impeller diameter (m)

Required rotation speed for of bottom suspension, or complete suspension, in stirred tanks can be estimated with Zwieterings method. Following equation is dimensional form of this equation.(Paul et al., 2004)

$$N_{js} = Sv^{0.1}\left[\frac{g_c(\rho_s - \rho_l)}{\rho_l}\right]^{0.45} X^{0.13} d_p^{0.2} D^{-0.85} \quad (3)$$

Where:
N_{js} = Impeller rotation speed for just suspended state (rps)
S = dimensionless number that is function of impeller type, liquid hight and tank diameter ratio and impeller position
ν = kinematic viscosity of the liquid (m^2/s)
g_c = gravitational constant (9.81 m/s^2)
ρ_s = dencity of solid particles (kg/m^3)
ρ_l = dencity of the liquid (kg/m^3)
X = mass ration between solids and liquid in suspension times 100 (kg solids/ kg liquid)
d_p= particle diameter (m)
D = impeller diameter (m)

It needs to be stated that this method gives reliable results only with low viscosity fluids, vessel geometries that have defined value S. There are also differing opinions about how well parameter X fits experimental data as it is defined above. Some authors state that $X^{0.13}$ fits experimental data when slurry volumetric concentration stays between 2 to 40 %.(Paul et al., 2004)

Some state that $X^{0.13}$ gives accurate results with solid concentrations between 2 and 15 wt%. For conservative designs, the exponent of 0.32 for X can be used. With this modification, Zwietering correlation can provide predictions within 20% up to 35wt%.(Ayranci and Kresta, 2014)

In solid suspension systems in stirred vessels, where uniform suspension is desired, impeller speed should be higher than just suspended rotation speed. Table below provides correlation of power and impeller speed dependency on mixing criteria and settling velocity of solid particles in mixture.(Oldshue, 1983)

Table 4. Impact of Desired Result on Mixing Design. (Oldshue, 1983)

		Power Ratio at Settling Velocity (ft/min)		
Suspension Criteria	Speed ratio	16-60 Difficult	4-8 Moderate	0.1-0.6 Easy
On-bottom motion	1	1	1	1
Complete off-bottom suspension	1.7	5	3	2
Total uniformity	2.9	25	9	4

For solid suspension downward pumping, axial flow impeller is recommended. These kind of impellers can achieve just suspended state with lower power consumption than a pitched

blade or disk turbines do. In gas dispersion, radial flow patterns are preferred. Carbonation reactor requires both solid suspension and gas dispersion. In this situation, 45° pitched blade impeller outperforms Rushton and disk turbines in solid suspension. It is usually the case, that solid suspension requires higher rotation speeds than gas dispersion in three phase reaction. Increasing gas flow rates also seem to increase required impeller rotation speed for just suspended state.(Paul et al., 2004)

Jet mixers are typically used in large storage tanks to homogenize tank content. Jet mixing system is compact solution for this purpose. Also if system has pump installed for filling or emptying storage tank, this pump can be utilized for driving jet mixer. Jet mixers can be used also for solid suspension and following equation estimates the required jet speed for just suspended state.(Paul et al., 2004)

$$V_{js} = 2\left(\frac{\rho_s - \rho_l}{\rho_l}\right)^{2.08} \frac{v^{0.16} g^{0.42} T^{1.16} d_p^{0.1} C_w^{0.24}}{D_j} \quad (4)$$

Where:

V_{js} = minimum jet velocity for off-bottom suspension (m/s)
ρ_s = density of solid particles (kg/m^3)
ρ_l = density of the liquid (kg/m^3)
ν = kinematic viscosity of the liquid (m^2/s)
g = gravitational constant (9.81 m/s^2)
T = vessel diameter
d_p= particle diameter
C_w = percentage weight fraction of solids
D_j = jet diameter

For carbonation reactor gas sparger system is required. Ring sparger with smaller diameter than impeller can be used. Commonly these spargers have evenly distributed gas holes and diameter of 0.8 times the impeller diameter(Paul et al., 2004).

Both reactors require temperature, slurry level and pH sensors. Tank level can be measured without contact to the slurry, but sensor should still be corrosive resistant. pH and temperature sensors should have quick release connectors to the reactor such as triclamp. Quick release is needed for easier scale removal from the sensors surfaces.

3.4 Piping system

This subchapter goes through requirements for the piping system for the X2PCC demonstration plant. Chapter will also list the evaluation methods and criteria that are used to find solution candidates and how to rank and dimension them. In slurry piping section chapter lists methods to dimension pipe diameter and flow velocities for slurry conveying. Liquid piping section goes through requirements and conditions for liquid piping. Pumps and instrumentation sections list the specifications for pumps, valves and metering devices in the demo plants pipe system.

3.4.1 Slurry piping

There are many methods to convey solid materials. In X2PCC case reactors need to be emptied from slurry and slurry needs to be separated in to solid and liquid components. So in demo plant, slurry piping is needed to connect reactors and filtration equipment.

This subsection will go through some basics of slurry transportation. Section will give methods for pipe dimensioning, means to evaluation required upper and lower flow speed limits in slurry systems and material choice guidelines.

Heterogeneous slurry flow can be categorized in four different flow regimes which are(Abulnaga, 2002):

- Flow with stationary bed
- Flow with moving bed
- Heterogeneous mixture with all solids in suspension
- Pseudo homogenous or homogeneous mixture with all solids in suspension.

The level of suspension in slurry piping is effected by the solid particle size, solid concentration in slurry and flow velocity. Abulnaga summarizes these effects in the Figure 12 and Figure 13.

In Figure 12 we can see the principle of how the nature of flow regime changes with solid material particle size and mean velocity of the sludge. As flow velocity increases the slurry will have increasingly homogenous state. Increasing particle size will have an opposite effect.

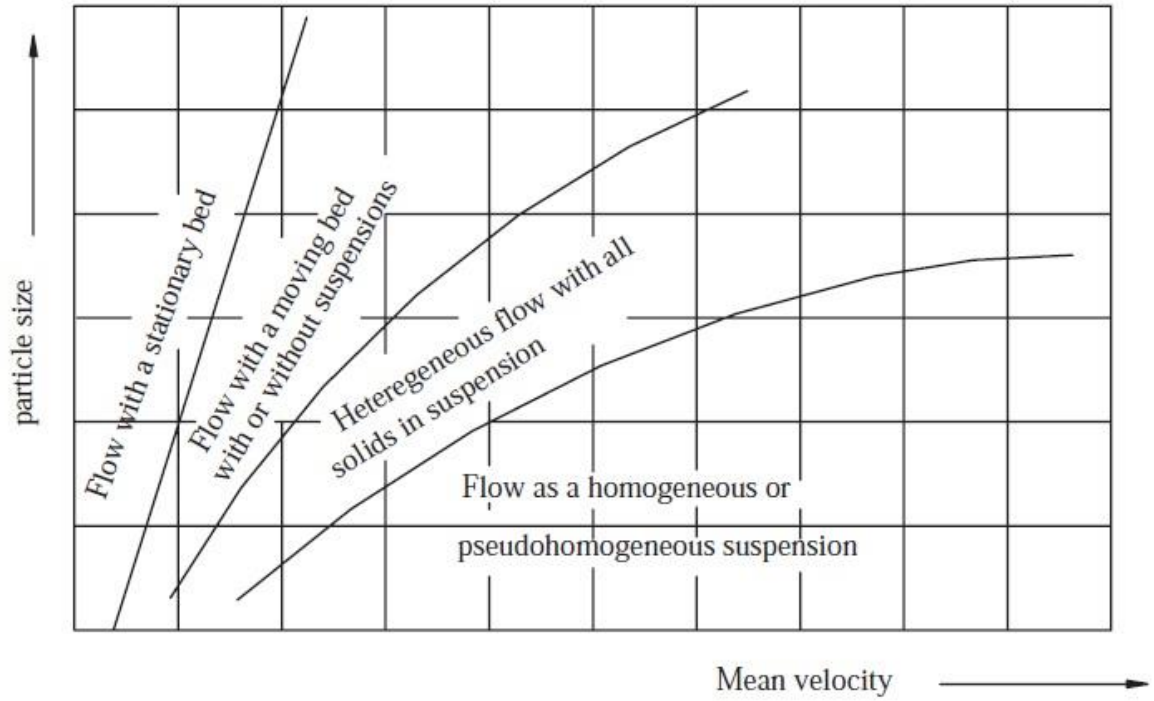


Figure 12. Effect of particle size and flow velocity to slurry flow regimes in pipes. (Abulnaga, 2002)

Figure 13 shows the effect of solid concentration and flow velocity. Increasing solid concentration has similar effect on flow as increasing particle size.

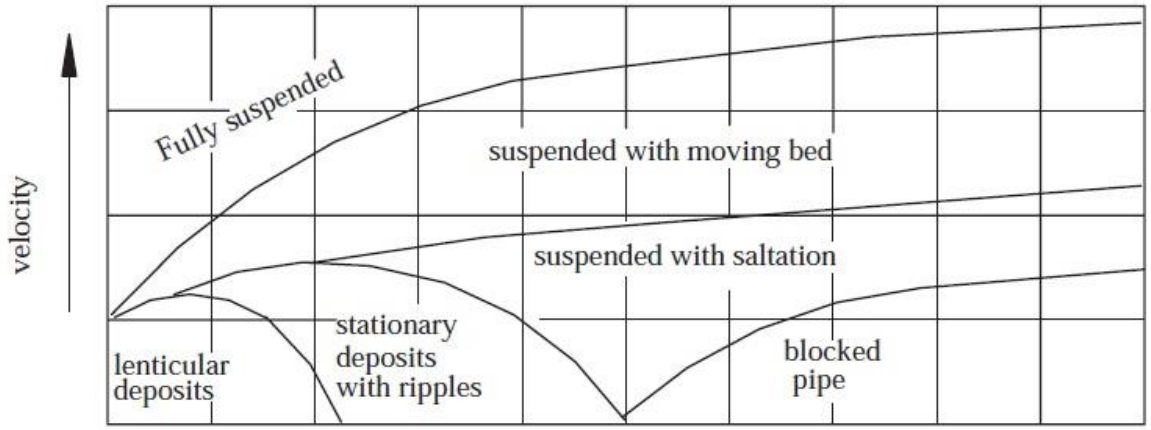


Figure 13. Effect of changing flow velocity and solid concentration in slurry flow. (Abulnaga, 2002)

Corresponding to four flow regimes in Figure 12 we can define four different transition velocities for a slurry flowing in a specific pipe. These transition velocities are(Abulnaga, 2002):

- v_1, velocity at which lower half of the pipe has stationary bed
- v_2, velocity at which coarse particles in slurry form moving bed and finer particles are carried by liquid flow
- v_3, velocity at which all particles move as an asymmetric suspension
- v_4, velocity at which solid particles and carrying liquid form a symmetric suspension

Abulnaga (2002) provides visualization of these boundary velocities and connections they have to flow regimes and pressure losses in pipe in Figure 14. Figure 14 also shows comparison of pressure losses between water and a slurry.

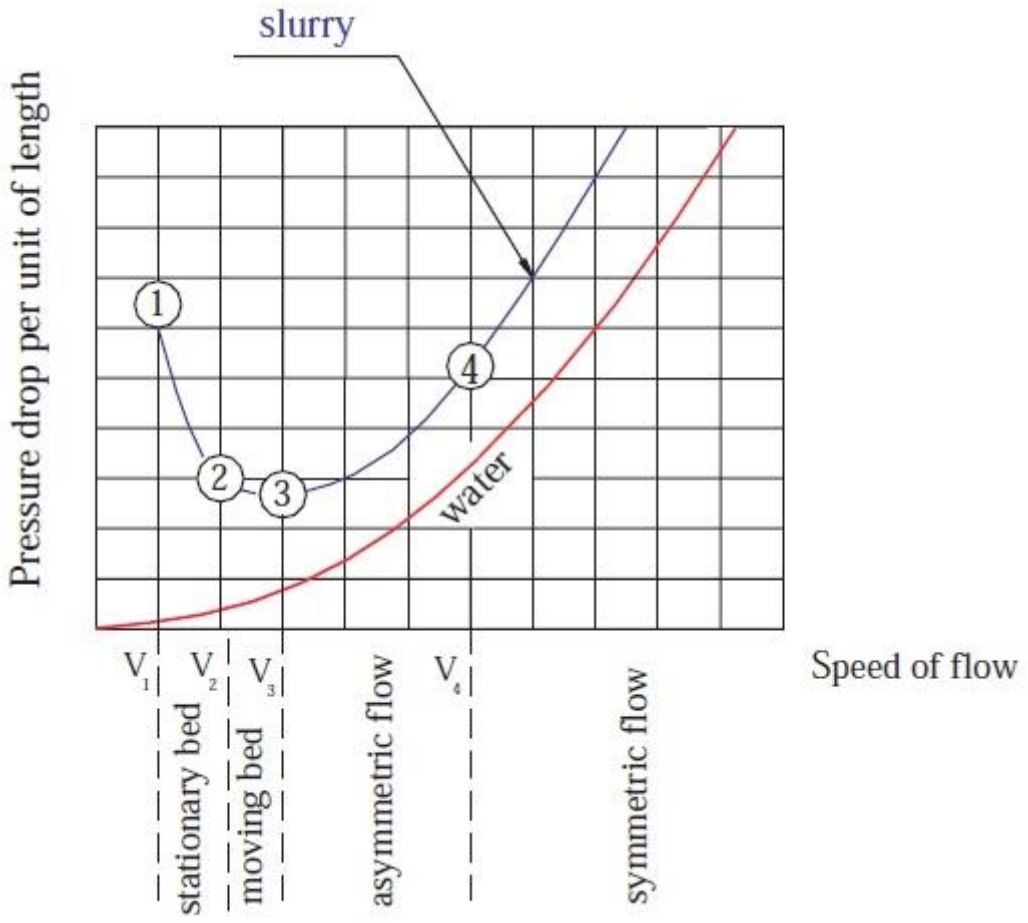


Figure 14. Transition velocities and flow regions in slurry pipes. Pressure drop in pipe per unit length as a function of flow speed. (Abulnaga, 2002)

In slurry transportation we are most interested in third transition velocity v_3 and slightly higher flow speeds. With this flow speed slurry transportation system will have smallest pressure losses as can be seen in Figure 14. Also flow velocities higher than third translation velocity, or critical velocity, prevent bed formation in the bottom of the pipe work. In the other hand higher carrying velocities will also introduce increased power consumption and wear in slurry line(Metso, 2015). For these reasons slurry transportation system should

operate with flow velocities slightly higher than v_c. Abulnaga provides following equation to calculate this critical transition speed from (Durand and Condolios, 1952):

$$v_3 = v_c = F_L\{2gD_i[(\rho_s - \rho_l)/\rho_l]\}^{\frac{1}{2}} \quad (5)$$

Where,
v_3 = transitional flow speed from stationary bed to asymmetric flow (m/s)
F_L= is the Durand factor based on grain size and volume concentration (-)
D_i= pipe inner diameter (m)
g = acceleration due to gravity
ρ_s= density of solids in the slurry (kg/m^3)
ρ_l= density of the liquid carrier (kg/m^3)

According to Abulnaga, Durand velocity factor F_L is typically represented in a graph for narrow particle size distribution. Figure below is an example that he gave.

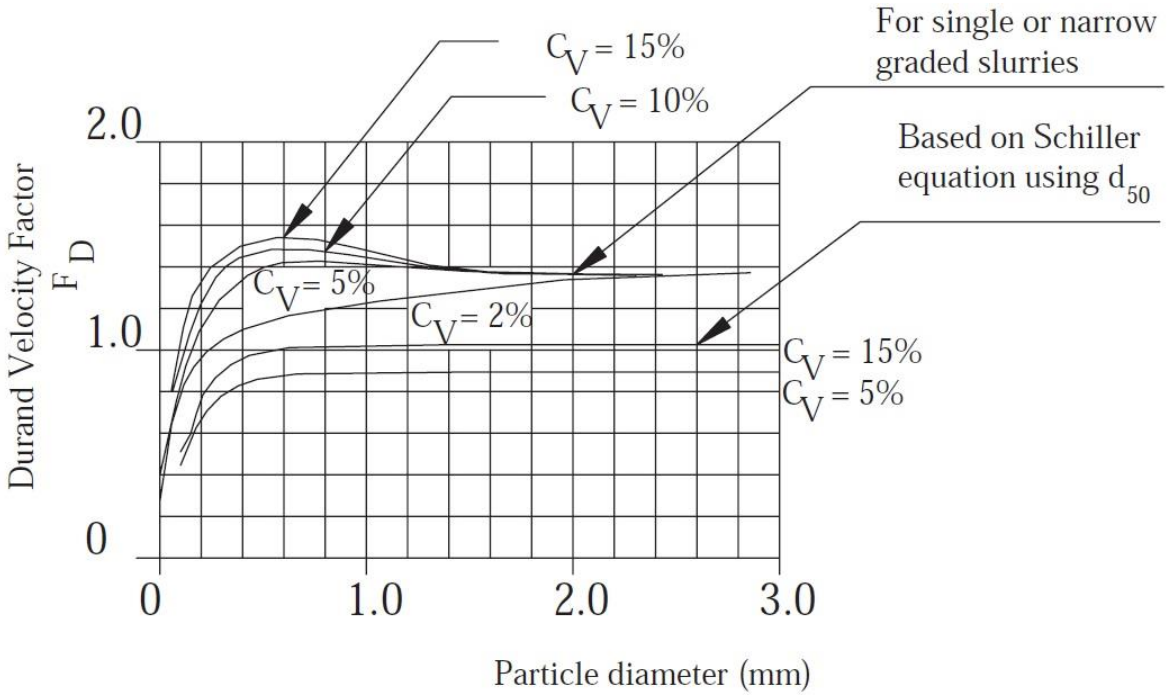


Figure 15. Graph to determine Durand velocity factor for slurry with certain consentration and particle size. (Durand, 1953)

Following equation is numerical method for calculating Durand velocity factor(Schiller and Herbich, 1991). Unlike Figure 15. Graph to determine Durand velocity factor for slurry with certain consentration and particle size. (Durand, 1953) equation below gives Durand velocity factor for slurry with wide grain size:

$$F_L = \{(1.3 * C_v^{0.125})[1 - exp(-6.9 d_{50})]\} \quad (6)$$

Where:
F_L= is the Durand factor based on grain size and volume concentration (-)
C_v = Volumetric solid concentration in the slurry (-)
d_{50} = Particle diameter so that 50% of particles in slurry are smaller (mm)

Many researchers and authors have worked on defining Durand factor and critical flow speed for slurry and there are many different methods to determine required flow velocities in slurry pipes, such as two layer model. There isn't clear consensus on the field what method is best suited for slurry line engineering however Durand method has gathered large user experience base probably because of its simplicity. Durand method tends to give conservative evaluation for required flow velocity to achieve full suspension in slurry pipe. (Roitto, 2014)

Additional factors that can cause problems or even pipe blockage in slurry transportation system are vertical and incline flow. In vertical flow, flow speed is recommended to be 4 to five times as high as the hindered steeling velocity of the solids in the slurry. Typically critical flow speed in slurry pipe are much greater than hindered settling velocity of slurry's solid particles. In other words, if slurry piping has vertical sections and pipe dimensioning is done correctly, incline sections shouldn't cause problems. Incline flow is more problematic case and should be taken in consideration.(Roitto, 2014)

In incline pipe sections flow speed is required to increase to keep the satisfactory level of solid suspension in pipe line. This flow speed can be 50% greater than the critical flow speed in horizontal pipes. Required increase is at its highest at the incline of 30% and starts to decrease at the higher incline angles. Incline factor Δ_D can be determined from Figure 16. (Wilson and Tse, 1984)

Required increase in flow velocity in incline pipe line can be calculated with equation below:

$$v_{incl.} = \Delta_D (2g(S_s - 1)D_i)^{1/2} \quad (7)$$

Where:
$v_{incl.}$ = The velocity increase that is required in incline pipe flow (m/s)
g = Acceleration of the gravity (9.81 m/s^2)
S_s = Specific gravity of solid particles
D_i = Pipe internal diameter (m)
Δ_D = Incline angle factor

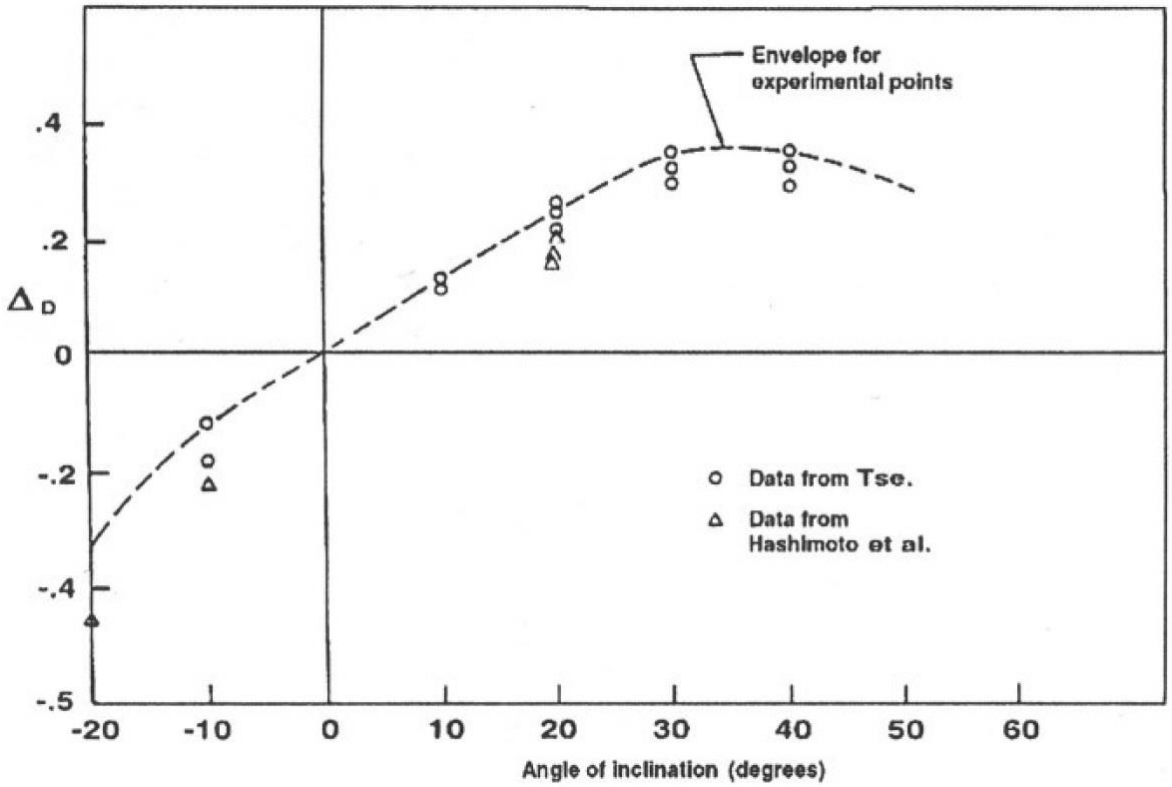


Figure 16. Effect of incline angle on deposition velocity (Wilson et al., 2008)

As stated earlier in this chapter higher flow velocities introduce higher pressure losses and wear rates in slurry transportation pipes. Following guidelines for maximum flow speed should be followed to ensure minimum wear in slurry pipeline(Roitto, 2014):

Particle diameter (mm)	Maximum flow velocity (m/s)
< 0.08	4
0.08 – 0.9	5
0.9 – 4.8	6
> 4.8 (< 400 mm pipe diameter)	6
> 4.8 (> 400 mm Pipe diameter)	8

Table 5. Maximum recommended velocities in slurry pipes by particle size and pipe diameter. (Roitto, 2014)

Regarding the material choices in slurry transportation systems, Roitto (2014) stated in his work that authors seemed to prefer elastomer pipelines in slurry systems over hard metal liners. He reported that elastomers outperform hard metals in applications where particle diameters remain under 250 μm.

In addition to flow speed recommendations and material selections in slurry conveying systems Roitto (2014) listed following general guidelines for slurry piping design:

- Pipe length should be kept at minimum to reduce pressure losses.
- To reduce further pressure losses and wear, pipes should be as straight as possible.
- Pipe bends should be wide, as wide bends reduce pressure losses and wear. Bend radius should be long as or longer than three times the pipe diameter.
- Sloped pipes help emptying the system.
- Pipes should be equipped with drain lines and flushing inlets.
- Pockets and blind spots should be avoided in slurry piping system.
- Number of pipe fittings should be kept at minimum.
- Low flow velocity areas should be eliminated from slurry transporting system
- Piping should be easy to dismantle for maintenance purposes.

3.4.2 Liquid piping

Maximum flow speeds in liquid pipelines are limited in practice by the occurrence of erosion and economic factors. Rising flow speeds result in rising friction losses in piping system that requires increasing power output form pump system. Typically there isn't serious erosion problems in liquid piping systems with flow speeds from 3 to 5 m/s. However more conservative flow speed upper limit of 2 to 3 m/s should be used if there isn't specific knowledge about fluid transportation system.(Couper, 2010)

Couper (2010) states that piping can take 25 to 40% of the total investment costs in a chemical plant. However this is the case with full size facilities. In the X2PCC demo plant case, piping costs will, most likely, be much lower. He provides following equations for economic optimum pipe diameter calculation. Doth equations are for pipe diameters higher than 0.0254 m.

$$D = Q^{0.448}\rho^{0.123}\mu_c^{0.025}\frac{\left[1.63\times10^{-6}K(1+J)H_y\right]^{0.158}}{\left[(1+F)X\times E\times K_f\right]^{0.158}} \quad (8)$$

Equation above is for turbulent flow conditions and equation below is for laminar flow conditions (N_{Re} for pipe is lower than 2100).

$$D = Q^{0.364}\mu_c^{0.2}\frac{\left[4.39\times10^{-4}K(1+J)H_y\right]^{0.182}}{\left[(1+F)X\times E\times K_f\right]^{0.182}} \quad (9)$$

Where:
D = The economically optimum pipe diameter (m)
Q = Volumetric flow rate in pipe (m^3/s)
ρ = fluid density (kg/m^3)
μ_c= fluid viscosity (Pa·s)
K = Electricity cost ($/kWh), typically 0.05 $/kWh
J = Fractional frictional loss trough fittings, typically 0.35 (-)
H_y = Operational hours per year, 8,760 for full year.
E = Fractional efficiency of motor and pump, typically 0.5
F = Ratio, fittings and installation cost to pipe purchase cost, typically 1.4
K_f= Ratio, annual fixed charge to initial pipe installed cost, typically 0.2
X = $/m for new 0.0254m inner diameter pipe, typically 2.43$/m for carbon steel

3.4.3 Valves and Instrumentation

Most of the valves in the system are used as isolation valves. They will close pipe ways to the filters, liquid containers, pumps and reactors for process requirements and maintenance. This means that most of the valves will be 2 port on/off valves. Reactors will require bottom mounted flush valves and some three port valves are required for wash and waste water management. Main requirements for all of these valves are that that they need to be corrosive resistant and automated. Manual valves can be used to isolate system components for maintenance. CO_2 feed valve to extraction reactor needs to be able to restrict gas flow.

3.4.4 Pumps

Demonstration plant will have slurry and liquid piping systems in it. This means, that slurry and liquid pumps are both needed. In pilot plant design only one pump type was used for slurry and liquid pumping, however this might not be economically feasible in demo plant scale.

Common factor for both of the pump types, liquid and slurry pumps in this case, is that both have to pump corrosive ammonium chloride solution. Also pumps should be easy to maintain without special tools or facilities.

Liquid pumps will work as batch transfer pumps. They will transport liquid solvent from solvent containers to the reactors of the system. This means that their flow capacity is decided by the reactor size and reactors filling time. Pumps don't need to transfer fluid into pressurized system. However required pump head will change while solvent is transferred from containers to reactor as source tanks liquid height degreases. This will cause variable static head for liquid pumps that should be considered. In this case, pumps should be designed for the average static head (Mackay, 2004).

Slurry pumps will empty reactors and feed slurry to the filtration system. Pumps need to process corrosive slurry, but they might have additional requirements depending on filtration system. For instance, different filtration technologies require different slurry feed characteristics. Decanter centrifuges function best with specific and even slurry flow. This

might require on sight testing, so pump would need a variable speed drive. On the other hand, some pressure filters require higher slurry feed pressure, but feed flow can wary.

3.5 Solid liquid separation

This subsection introduces the requirements and conditions for solid/liquid separation in X2PCC demonstration plant. It will also go through the basic principles few separation technologies. Individual equipment characteristics and performance is discussed in more detail in sub section 4.4 Filtration systems.

3.5.1 Goals and parameters of the separation

There are two different slurries in demo plant system. Both of these slurries need to go through solid-liquid separation process. First slurry is formed in the extraction reactor. This slurry has residue slag as solid component and calcium rich solvent as liquid component. Solvent, liquid part of the first slurry, is required in the carbonation reaction. Residue slag should also be collected and stored as it goes through further recycling processes. Second slurry is formed in carbonation reaction. This slurry has PCC as its solid component and ammonium chloride solvent as its liquid component. PCC is the end product of the X2PCC process and solvent is reactant in the extraction process. As both slurries have valuable solid and liquid component, both separation processes have same goals that are:

- Produce particle free solvent
- Produce solvent free solids
- Have little process material losses

.

Table 6. Sludge properties

Particle size (µm)	Solids mass%	Liquid component	Solid component	Solid loading (kg/h)
<250	27	Solvent (ca-rich)	Residue slag	800
<60	16	Solvent	PCC	400

Table 6. Sludge properties, summarizes physical properties of the slurries. Both slurries have fine particles in them that need to be removed and collected from solvents. Separation technology needs to be able to collect particles that have diameter smaller than 1 micron. Both slurries also have valuable liquid component so separation technology has to collect filtrate and store it. This means that system needs to produce dry cake as dryer cake means greater filtrate recovery rate.

In the other hand system is required to produce clean cake as solid components of the slurries are valuable end products. This means that all the exes solvent that mechanical filtration cannot remove from the cake needs to be washed off. Slurries also have quite high solid content so separation system needs to be able to process thick slurries.

There are few other process parameters that effect the choice of separation system that need to be considered. First, filtrates of both separation processes are corrosive. This means that separation equipment needs to be acid resistant. Second, both filtrates release ammonium fumes, so separation equipment needs to form closed system. Third, all waste water needs to be collected and treated. This means that washing efficiency needs to be considered. Finally the size of separation equipment needs to be considered as demo plant should be mobile unit. To summarize, separation equipment needs to be able to perform following tasks:

- Handle slurry with high solid loading
- Parts contacting the process materials need to be corrosion resistant
- Equipment needs to form a closed system
- Filtrate fine particles
- Produce dry cake
- Efficient cake washing
- Produce high quality filtrate
- System is fully automated

3.5.2 Vacuum filtration

This chapter goes through the basics of vacuum filtration and lists typical equipment that is required to run vacuum filter. Chapter also goes through a few filter types that could be used in X2PCC demo plant.

In vacuum filters, filtrate is separated from cake with pressure difference that is created with vacuum. Vacuum is created behind the filter medium so that atmospheric pressure pushes filtrate through the filter medium. This limits theoretical pressure difference in vacuum filters to 100kPa, but in practice filtration pressure is limited typically from 70 to 80kPa or less.

Even thou vacuum filters have limited pressure range, they are still widely used. Relatively cheap and simple filters can yield comparable dry cake to pressure filters with slurries that have small amount of fine particles. Vacuum filter technology can also provide continues filtration in large industrial scale that can dry, wash and provide wide range of other process requirements.

There are multiple different types of vacuum filtration machines, but they all work on same principle and these systems require some key components to function. (Wakeman and Tarleton, 2005) introduced the following list:

- filter medium
- support for filter medium
- a vacuum system
- filtrate receiver to disengage air system from filtrate
- drain lines for air and filtrate from filtrate receiver
- a solid discharge system
- filtrate discharge system

Figure 17 shows an example layout for vacuum filters filtrate receiver system. Cake can usually be removed from filter medium with mechanical scraper

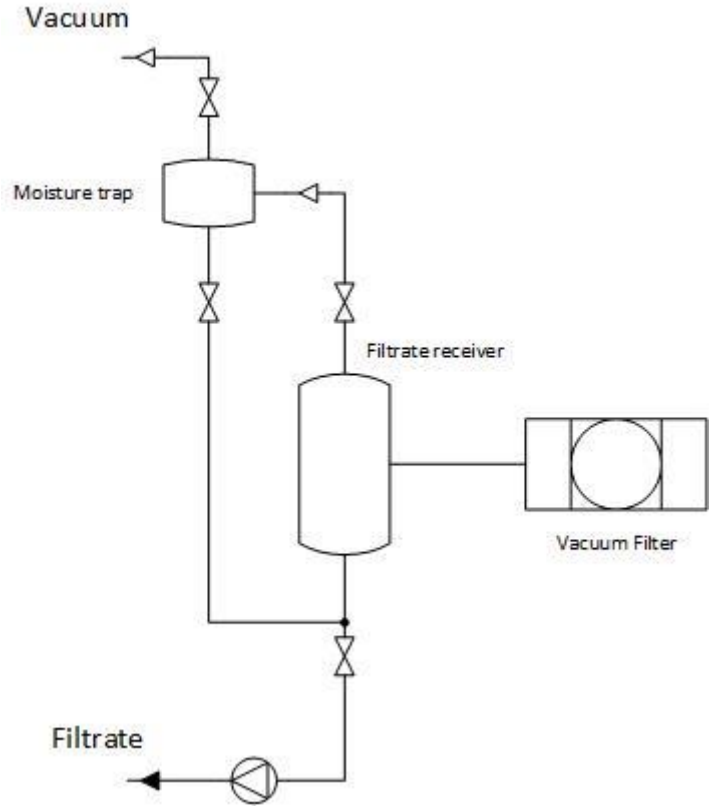


Figure 17. Vacuum filter filtrate receiver system(Wakeman and Tarleton, 2005)

In vacuum filters, filtrate is "drawn" by vacuum pump trough the filtering medium. Filtrate needs to be removed from the vacuum pumps air flow and this task is carried out by filtrate reciever. Filtrate reciever collects filtrate from the pressure system and lets dry air trough it. Filtrate is then discharged from reciever via pump or gravity. Moisture trap is optional component in this sytem, that is usually installed only to systems that have aggressive filtrate.

Vacuum filter capacity can be evaluated according to equation for constant pressure operation.

$$\frac{t}{V} = \frac{\alpha \mu c}{2A^2 \Delta p} + \frac{\mu R}{A \Delta p} \quad (10)$$

Where,
t = time (s)
V = filtrate volume collected (m^3)
α = specific cake resistance ($m\ kg^{-1}$)
μ = Liquid viscosity ($N\ s\ m^{-2}$)
c = solid concentrating in the feed ($kg\ m^{-3}$)
A = Face are of a filter (m^2)
Δp = static pressure drop (Pa)
R = Medium resistance

Second term represents losses in the filter medium and typically these losses are much smaller than losses in filter cake. This method gives a rough estimation for the filter performance.

3.5.3 Pressure filters

Pressure filters remove liquid from cake with pressure above atmospheric levels. Filtrate gets pushed through filter medium. This overpressure is created either by slurry pump, mechanical compression of the cake or pressurized filter chamber. Filtration pressure can be as high as 100bars. Because of this higher filtration pressure, pressure filters can produce dryer cake than vacuum filter and process slurries that have high amounts of fine particles. Equation x shows simple calculation for batch pressure filters dry cake production capacity Y ($kg\ m^{-2}\ s^{-1}$). This equation neglects the filter medium resistance.(Svarovsky, 2000)

$$Y = \left[\frac{2\Delta p f c}{\alpha \mu t_c}\right]^{\frac{1}{2}} \quad (11)$$

Where,
Δp = pressure drop (Pa)
f = ration of filtration to cycle time (-)
c = solid concentrating in the feed ($kg\ m^{-3}$)
α = specific cake resistance ($m\ kg^{-1}$)
μ = Liquid viscosity ($N\ s\ m^{-2}$)
t_c = cycle time

We can see that filters dry solid production increases when filtration pressure or feed slurry's solid concentration increases. However this only applies if term α, specific cake resistance, stays constant. Cake resistant may increase with higher filtration pressure as cake is compressed, so in some cases higher filtration pressure may produce lover dry solid yield. Also, if increase in α with Δp is small, higher pressure increases solid production. Pressure

filters can process diluted slurries and also feeds that have high solid concentration. Figure 18 demonstrates basic workflow of filtration cycle in diaphragm filter press.

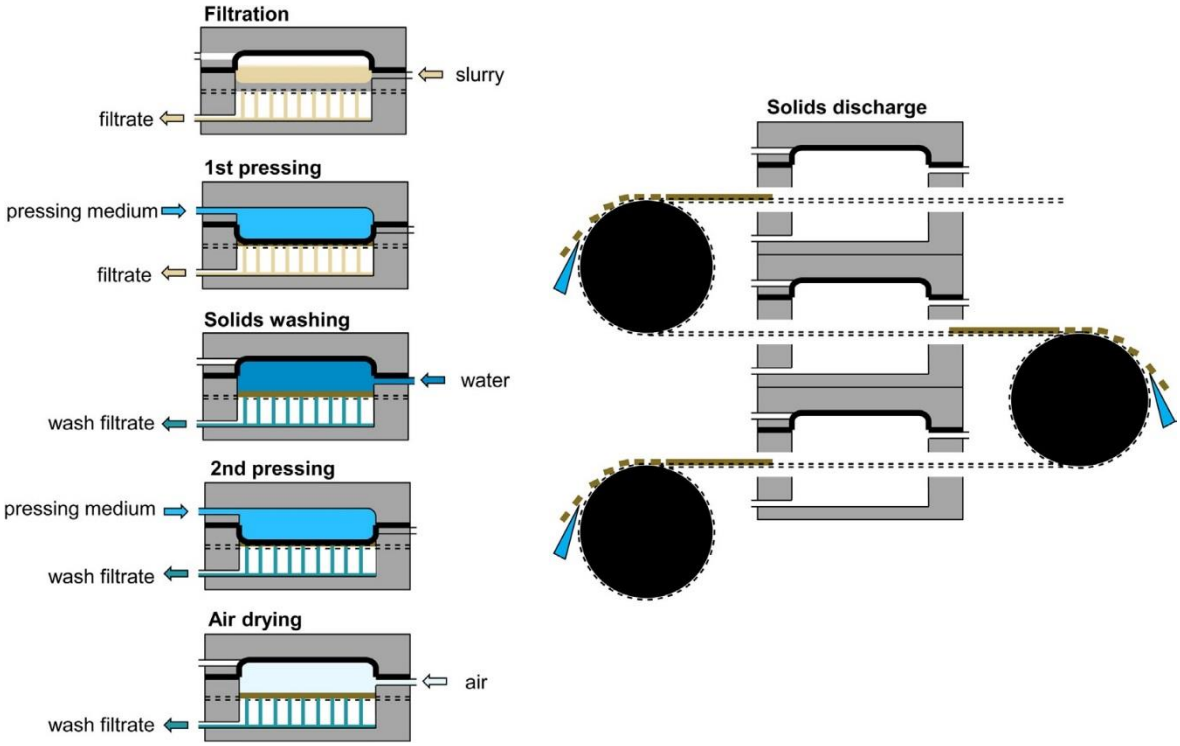


Figure 18. Diaphragm filter work cycle.(Teir et al., 2016)

3.6 Solvent storages

Demonstration plant requires three (3) closed chemical containers for the ammonium chloride solvent. Two of these containers will function as buffer containers after solid/liquid separation and third one is a reserve tank for fresh solvent. Buffer tanks need to be large enough to withhold filtrate from single batch. Solvent reserve should be large enough that it can compensate solvent loss for multiple batches.

All the solvent containers will have drain port in the bottom of the tank. Fill port can be situated in the top surface of the container. Tank material should be chemically inert. Solvent tanks will operate in atmospheric pressure. Maximum temperature inside solvent tanks is 60 °C and ambient temperature will be 22 °C.

3.7 Construction materials

Ammonium chloride water solution is corrosive liquid. Even at the relatively low concentration and temperatures, that are used in X2PCC process, ammonium chloride will severely attack carbon steels and can cause pitting corrosion in stainless steels (Craig and Anderson, 1994). This means that material chooses need to take in account corrosion effect on vetted parts.

Pitting resistance equivalence number (PREN) is a rating system for alloy steels pitting corrosion resistance. Greater PREN value states better corrosion resistance. It has been observed, that only chromium (Cr), molybdenum (Mo) and nitrogen (N) provide effective protection from localized corrosion attack in stainless steels. Following equation explains how PREN rating is calculated for stainless steel type (Li and Bell, 2004)

$$PREN = \%Cr + 3.3(\%Mo) + 16(\%N) \quad (12)$$

Where:
PREN = Pitting resistance equivalence number
%Cr = chromium percentage in stainless steel
%Mo = molybdenum percentage in stainless steel
%N = nitrogen percentage in stainless steel

Table 7 shows how common stainless steel types compare to each other regarding to their PREN ratings. Ammonium chloride doesn't cause general nor pitting corrosion in materials with PREN rating over 40(Toba et al., 2012) (Toba et al., 2014). According to Toba et al (2012), only super duplex and high performance nickel alloy 625 steel could be completely pitting resistance free from the material list of table below. However these test results were attained with ammonium chloride solvent that has higher molarity and temperature than solvent used in demonstration plant. Carbon steel and 304 alloy should be protected from ammonium chloride contact. These materials have shown sever corrosion damage in pilot plant(Zappa, 2014).

Table 7. Nominal chemistries and PREN ratings for common duplex and austenitic stainless steel grades. (Schulz et al., 2014)

Type	Alloy	UNS	Cr	Ni	Mo	N	Cu	Mn	PREN
Austenitic SS	304L	S30403	18	9	-	-	-	1	18
Austenitic SS	316L	S31603	17	10-14	2.5	-	-	1	24
Austenitic SS	317L	S31703	18	11.6	3.1	0.05	-	1.5	29
Lean DSS	2001	S32001	20	1.7	0.3	0.15	0.3	5	23
Lean DSS	2304	S32304	23	4	-	0.10	-	1	24
Lean DSS	2101	S32101	21.5	1.5	0.3	0.2	0.3	5	26
Lean DSS	2202	S32202	22.7	2	0.3	0.21	0.2	1.3	27
Lean DSS	2003	S32003	20	3.5	1.7	0.15	-	2	28
Standard DSS	2205	S32250	22.1	5.6	3.1	0.16	-	-	35
Super DSS	F255	S32550	25.5	5.7	3.1	0.17	1.8	0.8	38
Super DSS	2507	S32750	25	7.0	4.0	0.3	-	0.1	41
Super DSS	Z100	S32760	25	7.0	3.5	0.22	0.7	0.5	41
Nickel Alloy	625	N06625	22	64	9.0	-	-	0.2	52

Many elastomers and polymers, such as ethylene propylene, are ammonium chloride and ammonium hydroxide resistant(Anon, 2008). However this should be confirmed case by case for each material. Many common rubbers are resistant to ammonium chloride, but fewer are not attacked by ammonium hydroxide(Anon, 2016c).

As an example, Viton rubber is ammonium chloride resistant, but shouldn't be used in contact with ammonium hydroxide(Anon, 2016c). This has been confirmed in practice in X2PCC pilot plant. Viton axel seals in few liquid pumps hardened and leaked solvent trough to the pumps axel bearing, causing pump failure(Desyatnyk, 2016).

3.8 System layout

Demonstration plant is assembled in to shipping containers. ISO standard shipping containers should be used and 20' container types are recommended. Equipment can be divided to four (4) different containers. Layout inside the shipping containers should be designed so, that process equipment is easy to install and field repairs can be done unhindered. Possible equipment lay out could be filtration container, reactor container, chemical container and operator container.

Table 8 lists inside dimensions of some shipping containers. Table gives dimensions for 20' and 40' dry cargo (DC) containers, high cargo (HC) containers and refrigerated containers (RF). RF containers are also available in as a higher variant. These RF HC containers have 250mm higher inside sealing than normal RF container. RF containers are designed to maintain their inside temperature. Table 9 summarizes the outside dimensions of the shipping container types introduces in Table 8. More specific information can be found in ISO 668 and ISO 1496 standards("ISO 668:2013," 2013) ("ISO 1496-1:2013," 2013).

Table 8. Interior dimensions of some shipping container variants. (Anon, 2016f)

Container type	Length (mm)	Width (mm)	Height (mm)
20' DC	5898	2340	2370
20' HC	5898	2340	2690
20' RF	5025	2225	2169
20' RF HC	5025	2225	2419
40' DC	12030	2340	2370
40' HC	12030	2340	2690
40' RF	11580	2250	2290
40' RF HC	11580	2250	2419

Table 9. Exterior dimensions of some chipping container types. (Anon, 2016f)

Container type	Length (mm)	Width (mm)	Height (mm)
20' DC	6050	2440	2590
20' HC	6050	2440	2896
20' RF	6050	2440	2590
20' RF HC	6050	2440	2896
40' DC	12192	2440	2590
40' HC	12192	2440	2896
40' RF	12192	2440	2590
40' RF HC	12192	2440	2896

4 Results

This chapter introduces the design choices and results of discussions with equipment manufacturers. Chapter will also go through initial dimensioning calculations liquid and slurry hoses, required mixer speed and power takes and estimate required installed motor powers required for the pumps in demonstration plant. Chapter will also go through the filtration system rating as filtration was identified to be most expensive and complicated subsystem in X2PCC demonstration plant.

4.1 Material choices

In demonstration plant case, probably most important factor in material choice is that how aggressively solvent attacks building material. Solvent has two aggressive components in it witch are ammonium chloride and ammonium hydroxide. A rule of thumb is that ammonium chloride attacks metals, ammonium hydroxide attacks rubbers and chemically inert plastics are not effected by either.

Ammonium chloride solvent causes corrosion in steels and non-ferrous metals. For wetted metal parts, only alloyed steels are recommended and SS should have minimum PREN rating of 24. Alloyed steels are not generally effected by ammonium hydroxide.(Craig and Anderson, 1994)

Rubbers are more likely to be attacked by ammonium hydroxide, but are often not effected by ammonium chloride(Anon, 2016c). Ammonium hydroxide was most likely the cause of seal failures in pilot plants liquid pumps. It should be checked that sealing materials, elastomer hoses and rubber liners are ammonium hydroxide resistant. Synthetic rubbers, such as EPDM, seem to have sufficient resistance.

4.2 Reactor designs

Figure 19 shows the 3d model of reactor concepts in demonstration plant. Both reactors will have capacity of 2.5 m^3 and they will have standard ration of one to one (1) between reactor diameter and liquid height. Reactor inner diameter is 1500 mm. Reactor bottom has torispherical tank head profile according to DIN 28011 standard. This head shape was chosen due to its lower height profile. Reactor top head will be flat for because of height restrictions. AS leak protection reactor could have double layer shell with leak detection.

Both reactors will have a top mounted mechanical mixer. Extraction reactor should have high efficiency axial flow impeller (such as lightning A-310) for solid suspension. Carbonation reactors mixer could have 45 pitched blade turbine (PBT). This impeller geometry should perform well with low gas rate systems solid suspension duties.

Connectors for material inlets and reactor liquid level are situated in top cover of the reactor. Inlets for temperature and pH sensor go through reactor wall. There will also be maintenance hatch in the reactor wall.

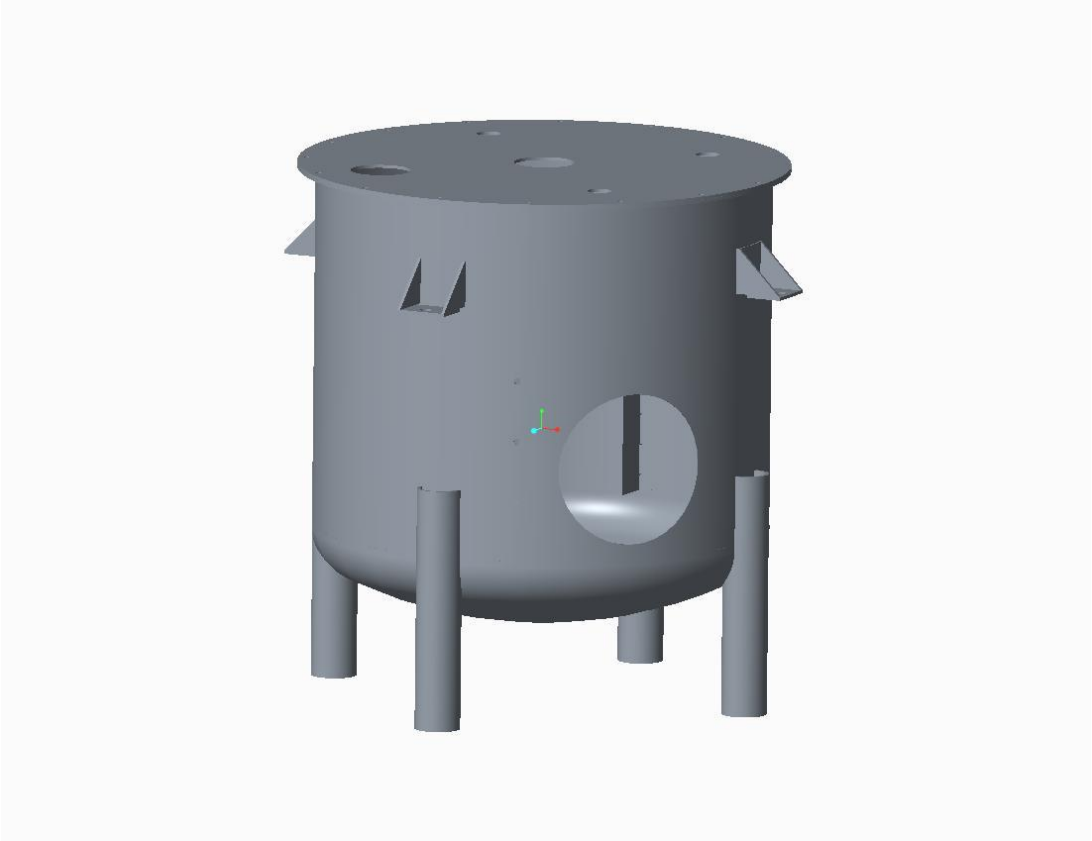


Figure 19. Reactor concept.

Maintenance hatches are typically installed in the top side of reactor above the liquid level(Ramm-Schmidt and Snellman, 2016). This offers a few advantages over maintenance hatch that is situated under liquid level. In non-pressurized reactor this means that maintenance hatch can be opened even when reactor is full. As sealing isn't emerged in liquid, it does not need to take hydrostatic pressure of liquids inside reactor and mostly needs to hold splatters instead of being completely wetted.

In X2PCC demonstration plant, reactors will be installed inside a shipping container. This means that there isn't enough room above the reactor to perform maintenance operations, while reactor is installed to its place. Wall mounted maintenance hatch offers the possibility to perform repairs and other operation inside reactor while it is on its place inside shipping container.

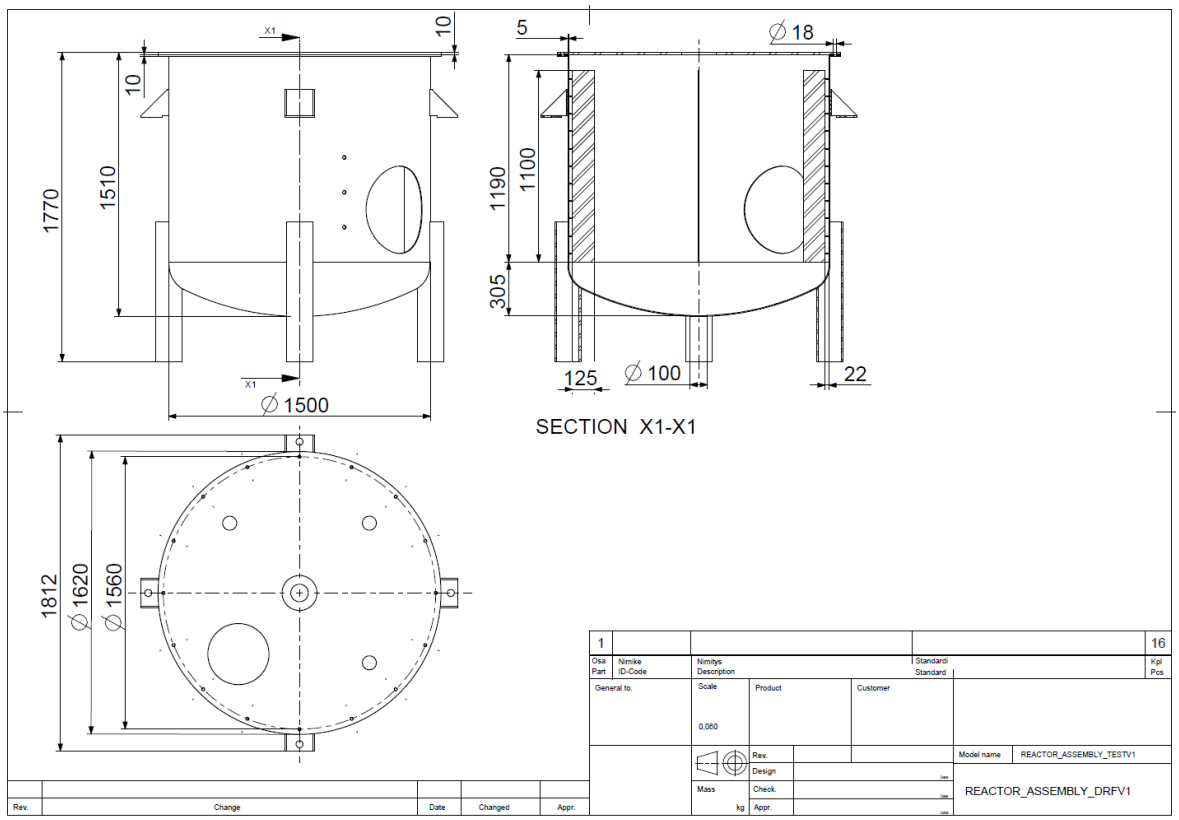


Figure 20. Extraction reactor dimension sketch.

Figure 20 shows a sketch drawing of extraction reactor. It possible and main dimensions of extraction reactor.

Table 10 summarizes values of used parameters for just suspended rotation speed for impellers for both reactors. Both impellers are downward pumping. Value for parameter S for carbonation reactor is from Appendix 1 and for extraction reactor from table provided by (Hawkins, 2013). N_{js} is calculated with equation (3) from sub section 3.3.3. Required power is calculated with equation (1) and parameters and results are summarized in Table 11. Impeller power numbers are from Table 3 and power number for carbonation reactor is adjusted with equation (2).

Table 10. Parameters and results for impeller speed calculations for just suspended state in extraction and carbonation rectors.

Reactor (impeller type)	S (-)	v (m^2/s)	g (m/s^2)	ρ_s (kg/m^3)	ρ_l (kg/m^3)	X (-)	d_p (µm)	D (m)	N_{js} (rpm)
Extraction (A-310)	6.9	10^(-6)	9.81	3.5	1.05	50	250	0.5	243
Carbonation (PBT 45°)	4.5	5*10^(-6)	9.81	2.7	1.05	23	60	0.5	85

Table 11. Power requirements for mixers with just suspended rotation speed.

Reactor (Impeller type)	N_p (-)	ρ (kg/m^3)	N (rps)	P (W)
Extraction (A-310)	0.3	1050	4.05	653
Carbonation (PBT 45°)	1.36	1050	1.41	126

4.3 Filtration technology

Initial dewatering technology elimination was done by consulting relative performance characteristics of different separation equipment. Following criteria were used to narrow down the technology list:

- Solid product needs to be solid cake after separation
- Washing is needed
- Liquid recovery is needed
- Feed particle size are 1-200 µm
- Solid feed concentration is 14 to 24 % by mass

Some equipment types were also discarded because of their physical size, as an example vertically installed vacuum filters. Following table summarizes filtration technologies that passed initial elimination. These devices were further evaluated and discussed with equipment filtration manufacturers and providers.

Table 12. Adapted relative performance characteristics of solid/liquid separation equipment. (Wakeman and Tarleton, 2005) (Tarleton, 2007)

Equipment type	Solid product state	Washing	Liquid product quality	Crystal breakage	Particle size (µm)	Solid mass% in feed
Scroll decanter	4 C	3	4	3	1-5000	4-40
Basket (peeler)	9 C	6	5	5	2-1000	4-30
Nutsche (pressure)	6 C	8	8	8	1-200	1-20+
Rotary drum (vacuum)	6 C	7	7	8	1-200	1-20+
Filter press	6 C	8	8	8	1-100	<1-30+
Diaphragm filter press	8 C	8	8	8	1-200	<0.3-30+
Tube press	8 C	4	7	7	1-200	0.3-30+

In solid product state column, C means that filter produces solid cake. Performance is rated with numbers from 1 to 9. Higher number value means better performance. Solid product state states how dry cake certain filtration technology can achieve, 9 being the driest cake and 1 having highest liquid content in cake. Washing column rates the cake washing capabilities of the filtration system. Liquid product quality rates the filtrate cleanliness after filtration process. Crystal breakage column rates the amount of damage filtration technology causes to solid particles. High value means less damage to solid component.

In the table above, solid product state, liquid product quality and washing are important evaluation factors. Filtrate quality and cake state effect the recyclability of ammonium chloride solvent. All the solvent that can't be removed from the cake without washing will, most likely, be lost and is replaced with fresh solvent. Poor filtrate quality will effect PCC quality and solvent recycling. Washing capabilities effect the residue slag and PCC product quality.

Nutsche filters and basket centrifuges had to be discarded due to equipment size(Ramm-Schmidt and Snellman, 2016). It appeared, that it would be challenging to mount these devices with required capacity in shipping containers.

Decanter centrifuges appeared to be strong choice for dewatering duty. This technology requires relatively small floor space, doesn't require pneumatic or hydraulic support systems and is used in traditional PCC manufacturing. However, decanters would require separate washing system after solvent removal(Söderlund, 2016). These machines also have strong cut of point around 10 µm range, particles smaller than this can pass through the centrifuge. Decanter centrifuges are also more suited for continues process, as they have reduced filtration performance at the start of machine(Ramm-Schmidt and Snellman, 2016).

Pressure and vacuum filtration systems were found to be adequate for X2PCC process PCC filtration and washing in lab scale filtration tests(Teir et al., 2016). These tests were performed with diaphragm pressure filter and vertical vacuum filter. Both systems provided clear filtrate, good cake washing and high filtrate removal rate.

Further evaluation of rotary drum vacuum filters and discussions with filter manufacturers ended in conclusion, that this technology wouldn't perform optimally in X2PCC process. Amount of small particles and over all distribution of fine particles in slurries are problematic for rotary vacuum filtration.(Colpaert, 2016)

This would seem to contradict with good results in laboratory vacuum filtration tests, but difference in performance can be explained with different cake forming mechanism between top and bottom fed vacuum filters. Bottom fed vacuum filter will suck finer particles to filter medium first and this leads to undesirable particle size distribution in cake. In top fed vacuum filters, gravity will, to some extent, automatically pre-coat filter medium with coarser particles due to heavier particles settling faster. This effect does improve filtration performance. Svarosky (2000) demonstrates these two different cake forming mechanisms in Figure 21 and Figure 22.

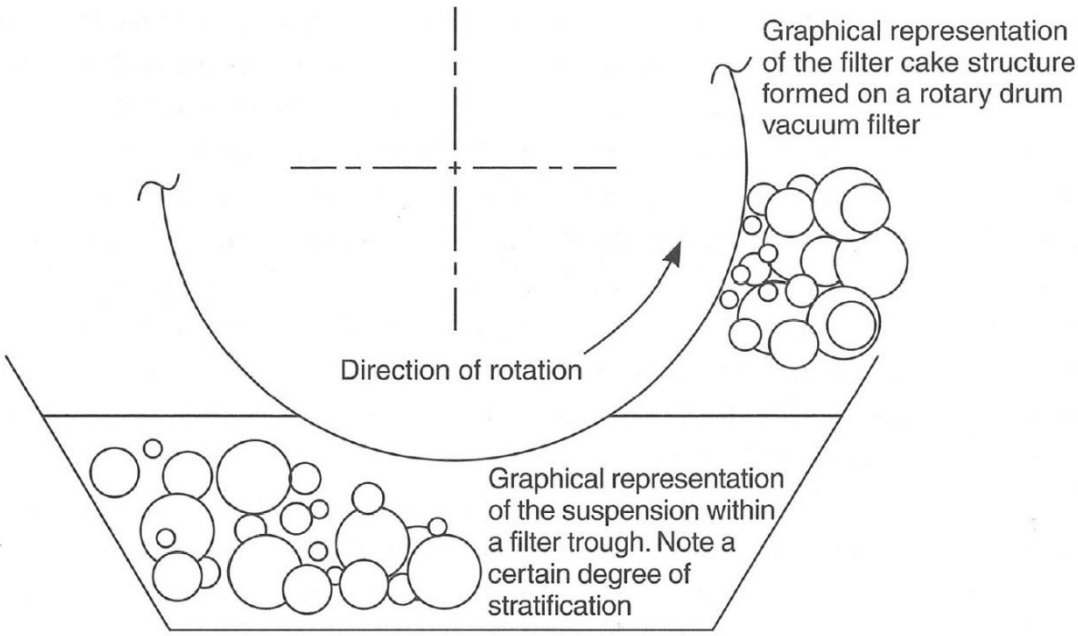


Figure 21. Graphical representation of cake formation mechanism in rotary vacuum filter. (Svarovsky, 2000)

Favorable classification, which is presented in Figure 22, can be artificially enchanted with pre classifying system. System feeds coarser particles from the slurry first to the filter medium and finer particles on top of pre-coated medium. One way of achieving this, is to use hydrocyclone with relatively coarse cut size.

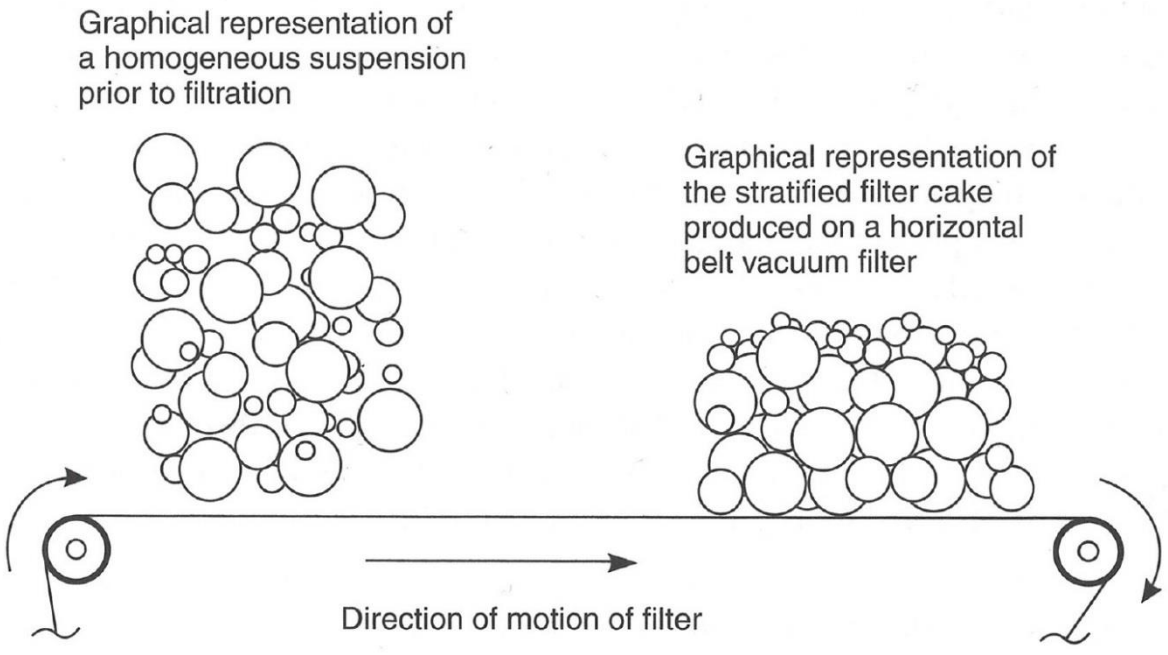


Figure 22. Schematic of automatic pre classification due gravity in a horizontal belt vacuum filter. (Svarovsky, 2000)

Figure 23 shows schematic of how coarse fraction of the slurry is fed to filter medium as precoating for slurry consisting finer particles. It needs to be stated, that these systems need

to be correctly calibrated case by case or precoating will only hinder the performance of filtering system.

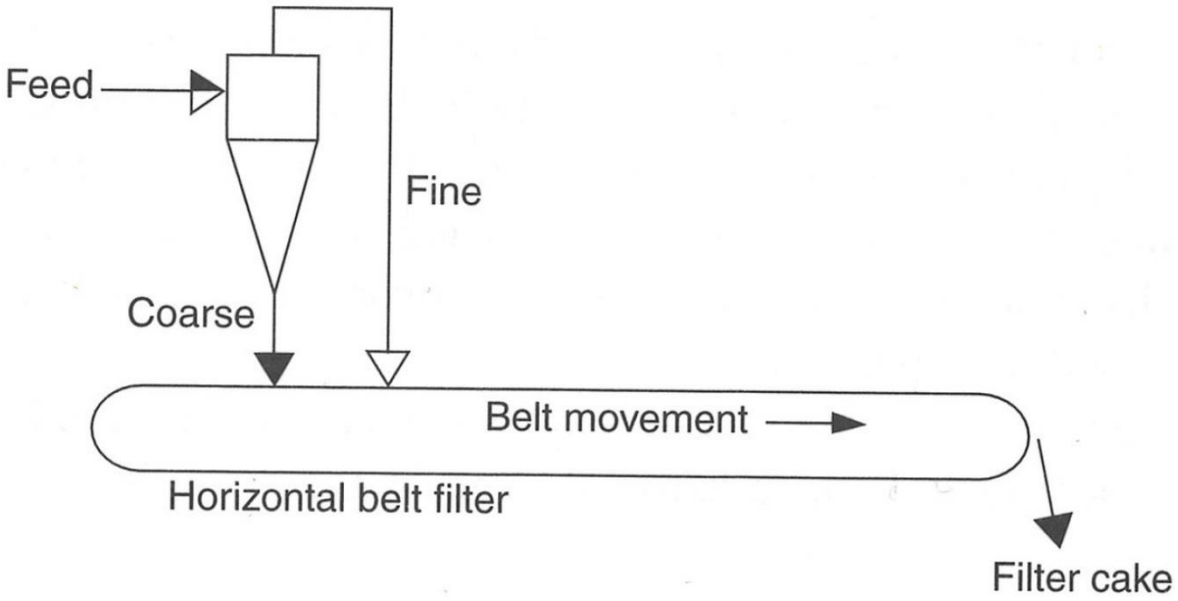


Figure 23. The use of hydrocyclone as precoating system for a vacuum belt filter. (Svarovsky, 2000)

Vacuum filtration systems were ruled out, as X2PCC process would require horizontally installed system that would require to large floor space(Svarovsky, 2000). However these systems might be competitive solution for full scale plant that operates in continuous mode. After filter technology evaluation by literature research, manufacturer interviews and laboratory tests conclusion was that pressure filtration system would be most suited for demonstration plants solid/liquid separation duties.

Vertical plate press or tube press machines were chosen as best solution candidates for X2PCC demonstration plant. These systems were also filtration solution recommendations that filter manufacturers offered in interviews(Söderlund, 2016) (Colpaert, 2016) (Ramm-Schmidt and Snellman, 2016). It is possible to install these machines in shipping containers, they produce excellent filtrate quality and dry cake. It was also evaluated, that membrane pressure filtration could perform required solid/liquid separation and washing duties in single stage without polishing filtration (Teir et al., 2016). The deciding factors between tube and plate presses systems are the equipment size and cake washing capabilities.

Tube presses were developed for demanding dewatering duties of slurries with large amount of small particles. They are membrane pressure filters that can offer filtration pressures up to 160 bar. They are easy to install and are well suited to be used as mobile or temporary filtration unit and there are examples of them being installed in to shipping container for field use, some systems can be mounted in shipping container(Anon, 2016g). They offer cake washing by displacement method, but it is uncertain if washing quality can meet X2PCC process requirements for cake purity(Colpaert, 2016). It is recommended that filtration and wash tests are performed with tube press equipment.(Wakeman and Tarleton, 2005)

Plate press systems are much larger systems, but machines with adequate filtration capacity can be installed in 40' shipping container(Söderlund, 2016). In other words plate press filtration system can take up to four (4) times more floor space than tube press system would in X2PCC demonstration plant. Nevertheless plate press filtration system was chosen due to more complete information of systems performance characteristics.

Plate press machines were chosen for filtration equipment as there was more complete data available about their performance in X2PCC process. Literature review, interviews with machine manufacturers and laboratory test date all supported the choice of filter press systems. Tube press filters could most likely produce even drier cake than plate press in more compact system, but tube presses cake washing capabilities requires testing.

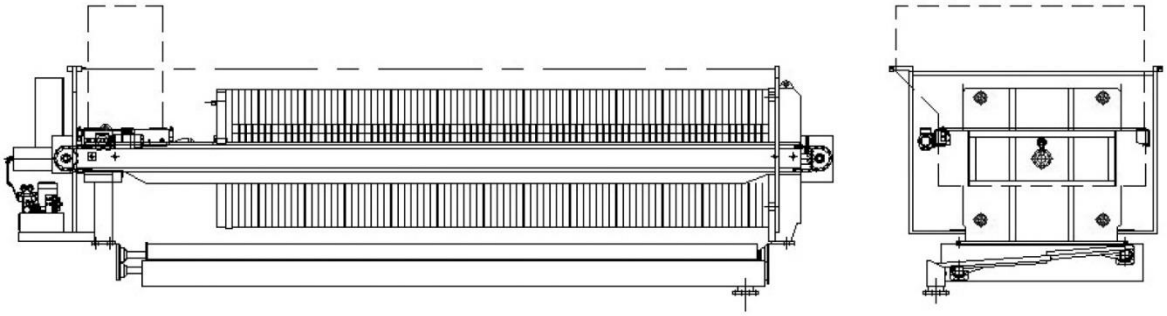


Figure 24. Vertical plate press filter. (Anon, 2015)

Figure 24 shows basic structure of plate press filter. Slurry is pumped to filter plate pack from one end of the machine. After filter is filled with slurry, cake is mechanically compressed. After mechanical compression, cake wash water can is introduced trough slurry feed port. Cake is dewatered from the wash water and filter plates are separated from each other. Filter bottom plate opens and cake falls out of the machine.

4.4 Piping system

This sub section goes through recommendations for piping system in X2PCC demonstration plant. Chapter will first introduce recommended materials for pipes and hoses and give initial results of initial dimensioning calculations. Later on subsection gives recommendations for valve and pump types.

4.4.1 Pipes and valves

Elastomer hoses were chosen as build material for the piping system as they meet all the design demands. They are easy to assemble and dismantle and don't require special tools or education to handle such as welding equipment. There are also many elastomer that are not effected by ammonium chloride or ammonium hydroxide. Steel pipes offer better temperature resistance and structural intercity, but neither of these are required in demonstration plant. Liquid and ambient temperatures will stay low and inside shipping containers hoses can be attached to container walls for additional support. Between containers flexible hoses will also give leeway for plant assembly. It is desirable to have one

hose type used in all lines in demonstration plant. This would mean, that only one type of hose is needed for spare parts.

Pinch valves could be competitive choice in demonstration plant for two port valves because of following reasons. They would be suitable in both liquid and slurry lines as they are full bore valves, this would reduce the number of valve types required. They are also self-cleaning, just opening and closing valve removes possible scaling. They are also corrosion resistant, as only wetted part is elastomer hose inside the valve.

All three port valves in demonstration plant are in contact with solvent. This means that they need to be corrosion resistant. AISI 316 grade steel has been sufficient valve material in pilot plant disregarding one valve failure. If steel valves are chosen, valve material should have same or greater corrosion resistance than 316 AISI grade stainless steel and these valves should be flushed regularly to prevent crevice corrosion. Stainless steel grades corrosion resistance can be evaluated by comparing their PREN ratings. Another option is to choose polymer lined or polymer valves.

Table 13 summarizes the assumed initial parameters for critical flow velocity in slurry pipe. Table 14 and Table 15 summarize the results of critical flow velocity calculations for steel making slag slurry and PCC slurry. Parameter v_{30} is the critical flow velocity in pipe, with 30° incline angle and Q_{30} is the volumetric flow with critical flow speed in pipe with incline. We can see from these tables that slag slurry requires much higher critical velocity than PCC slurry.

Table 13. Assumed parameters for critical flow velocity calculations.

	ρ_s (kg/l)	ρ_l (kg/l)	d_{50} (mm)	C_v (-)
Slag slurry	3.2	1.15	0.15	0.125
PCC slurry	2.7	1.05	0.03	0.076

Table 14. Results of critical flow velocity calculations for slag slurry.

D_i (m)	F_l	V_c (m/s)	v_{30}	Q_{30} (m^3/h)
0.025	0.646	0.575	0.904	1.6
0.038	0.646	0.709	1.115	4.6
0.050	0.646	0.814	1.279	9.0
0.063	0.646	0.910	1.430	15.8

Table 15. Results of critical velocity calculations for PCC slurry.

D_i (m)	F_l	V_c (m/s)	v_{30}	Q_{30} (m^3/h)
0,025	0,176	0,157	0.467	0,8
0,038	0,176	0,193	0.576	2,3
0,050	0,176	0,222	0.660	4,7
0,063	0,176	0,248	0.738	8,2

Slurry pipe lines will feed slurry from reactors to filter presses with maximum design flow speed of 13m^3/h. Reactors are emptied form the bottom of the reactor. This means that slurry hoses will most likely have at least small incline. For the slag slurry, hose with 63mm inner

diameter could be best option for slurry transportation. This hose diameter would give design flow volume of 13m^3 with flow speed a bit over critical flow velocity.

However slurry is fed to the filter press. This means that flow velocity will decrease while reactor is emptied. Using hose with inner diameter of 50mm would ensure, that slurry flow speed would stay over critical flow velocity longer through filtration process. Flow speed would also stay well under 3 m/s, which is the recommended maximum conservative liquid flow speed in pipelines. It seems that 50mm inner diameter is suitable choice for demonstration plant slurry and liquid piping.

4.4.2 Pumps

Demonstration plant will have two types of pumps. There will be slurry pumps for filter press feed pumps and liquid pumps for reactor feed pumps. These two pumps will have quite different tasks and demands. Table 16 lists requirements for reactor and filter press feed pumps.

Table 16. Pump requirements in demonstration plant.

Requirement category	Filter press feed pump	Reactor feed pump
Pumped material	Slurry, corrosive	Liquid, corrosive
Chemical types	NH_4CL, $NH_4(OH)$	NH_4CL, $NH_4(OH)$
Dry running	Occasional	Occasional
Flow rate type	Changing	Constant
Maximum flow (m^3)	13m^3	13m^3
Head	Changing, low to high	Slightly changing, low

Figure 25 shows a typical graph for head loss and trough put in filter press feed pump. At the start of the filtration, pump produces high flow with low head loss. When filter chambers fill with slurry and cake formation progresses. Cake resistance increases, causing increasing pressure in the feed pump. This is quite demanding scenario for pump, so it isn't surprising that 90% of operational problems in filter presses are caused by feed pump failure(Prasad and Subramanian, 2014). This will also mean that slurry lines in X2PCC demonstration plant will have suboptimal slurry flow speed in the end of chamber filling cycle.

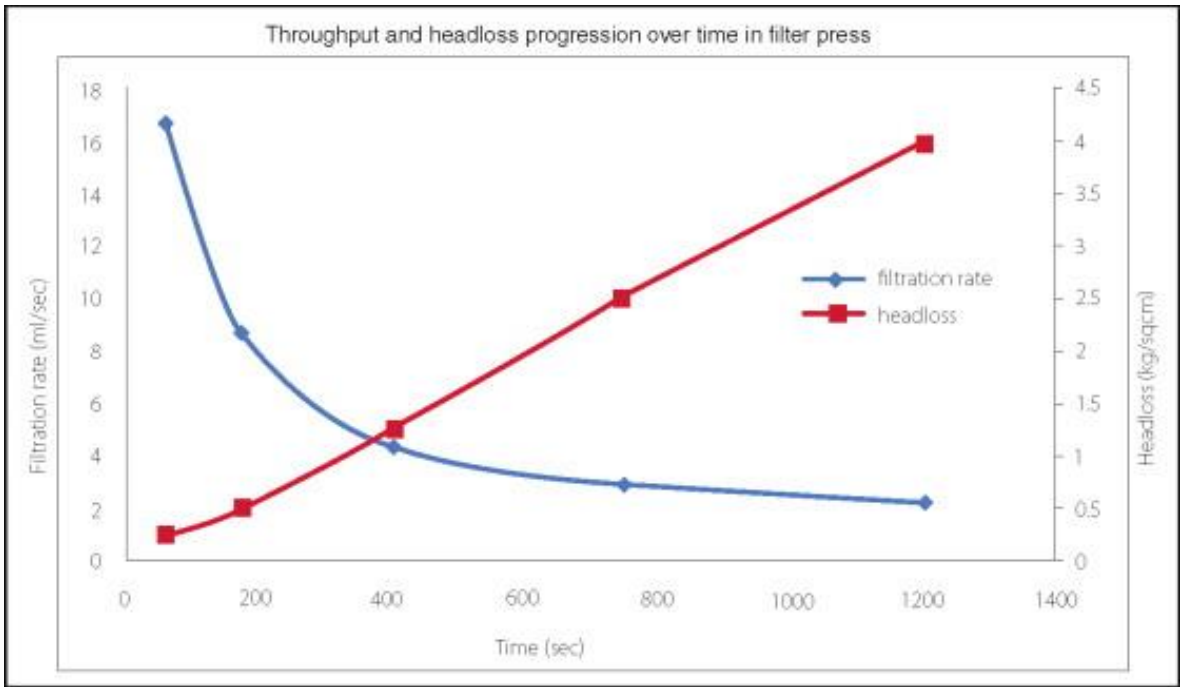


Figure 25. Filter press pump through putt and head loss. (Prasad and Subramanian, 2014)

Positive displacement pumps are recommended as filter press feed pumps(Prasad and Subramanian, 2014). Two different positive displacement pump types were considered, these types are air operated diaphragm pump and peristaltic pump. Neither of these pumps have axel sealing. Both of these pump types are well suited to pump corrosive liquids and slurries. In hose pump only elastomer hose is in contact with pumped fluid and diaphragm pumps are available in materials, such as polymers, that are not effected by ammonium chloride or ammonium hydroxide(Tapflo, 2016). Some dry running is acceptable for both of these pump types(Rayner, 1995).

Diaphragm pumps are more compact and have lower initial investment cost when compared to peristaltic pumps. The size and cost difference is caused by electrical motor and drive that drives peristaltic pump. In the other hand diaphragm pumps have higher operational costs. These pumps have low operating efficiency due to compressed air operation, this causes higher operating costs. In filter press feed pump use, both of these pump types should be design so, that they operate around halve of the maximum flow capacity at the high flow part of the filtration. (Manninen, 2016)

Figure 26 and Figure 27 show performance characteristics of similar capacity peristaltic and diaphragm pumps. In X2PCC demonstration plant case, maximum flow rate of 13 m^3/h is required from filter press feed pumps. This means that hose pump would require 3 to 4 kW installed pump motor power. Air operate pump would require maximum air flow that is higher than 2 Nm^3/min. This would require approximate compressor with installed motor power of 5 to 10 kW(Anon, 2016h).

According to these estimations peristaltic pump could be competent choice for filter press feed pump. Air operated pump should only be considered if it can be operated with pressurized air system that is installed for filters operations.

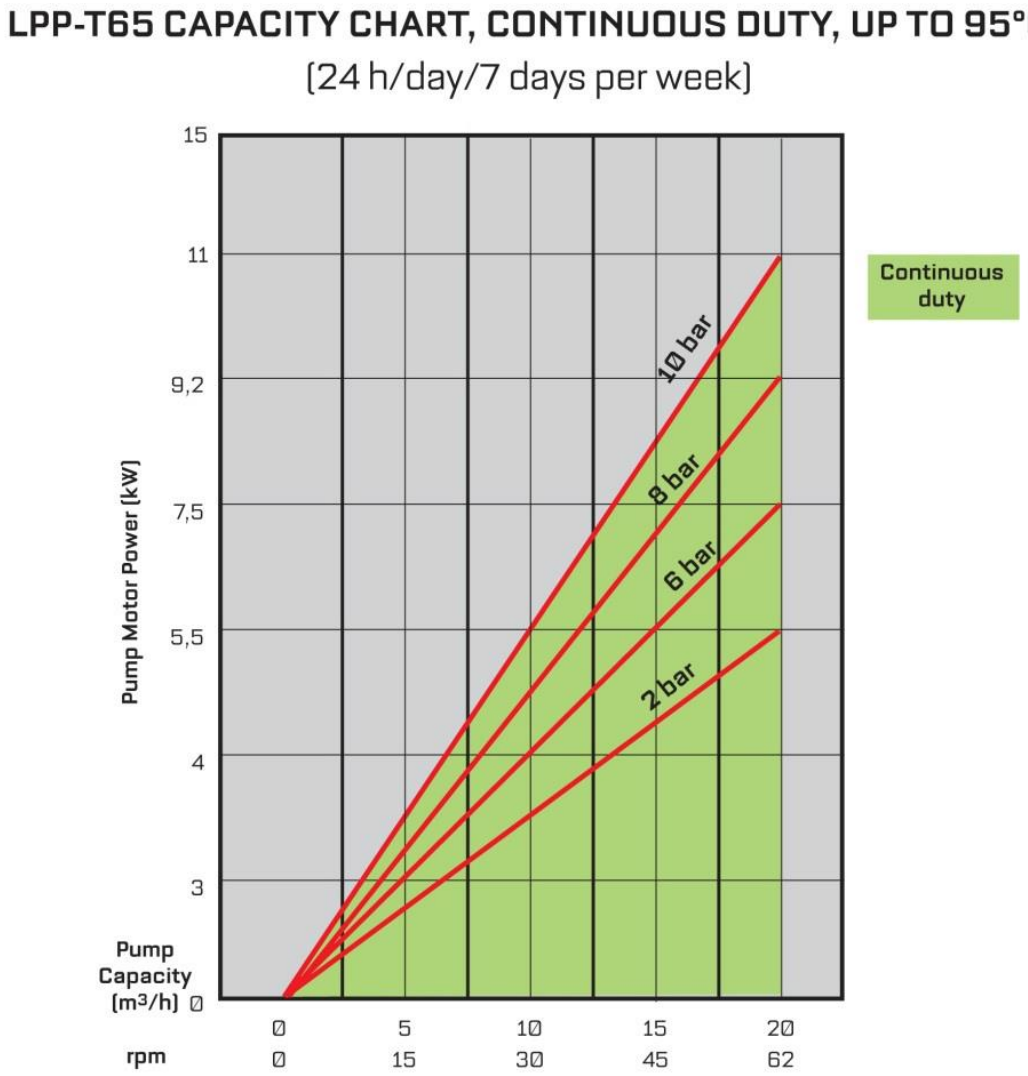


Figure 26. Peristaltic pump characteristic curve. (Anon, 2013)

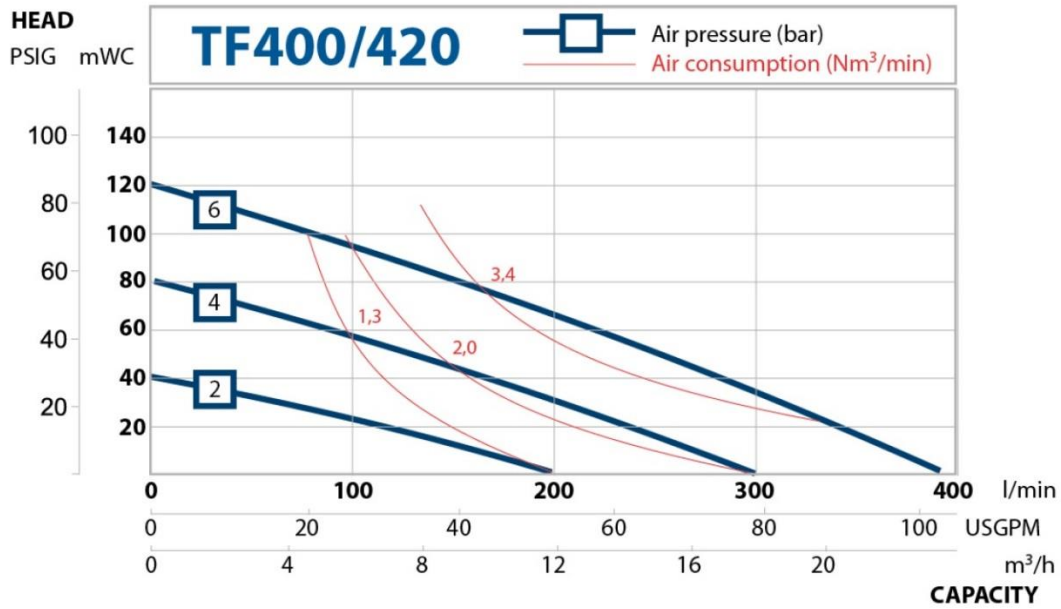


Figure 27. Air operated diaphragm pump performance. (Tapflo, 2016)

There are two different philosophies how to choose liquid pumps for demonstration plant. First one is to choose same pumps type and model that is used as feed pump for filter presses. Second one is to choose different pump type that is better optimized for liquid transfer.

The advantage with first method is that this can limit the number of pump types in plant to one. This would mean that number of pump spare parts is halved and one spare pump could replace every single one of the malfunctioning pumps. Downsides would be that reactor feed pumps would be suboptimal for their duties. Reactor feed pumps will have much smaller head than filter press feed pumps. The head variance is also much smaller and flow rate will stay constant. In addition reactor feed pumps will only process liquids with minimal amount of solid particles.

Choosing same pump for reactor feeding and press feeding would result in oversized liquid pump. In practice, this would mean less efficient, larger and more expensive liquid pumps. Centrifuge pump that is dimensioned for reactor feeding in demonstration plant would be much smaller, cheaper and efficient than hose pump that is dimensioned for filter press feeding. Self-priming centrifuge chemical pump that can take occasional dry running is recommended for reactor feed pump.(Viskari, 2016)

4.5 Demo-plant layout

Figure 28 shows the physical layout of the demonstration plant and hose connections between the equipment containers. Plants process equipment is assembled in two 40’ high cargo (HC) shipping container and one on 20’ HC shipping container. Beneath the 40’ containers are storage space for PCC and residue slag that falls out from bottom of the filters. Large grey box inside blue container represents the allocated space for filter press.

40’ slag and PCC processing containers will withhold the filtration systems and reactors. 40’ containers need to be elevated from the ground level, because filter press is emptied from the bottom of the device. Filtrate can be drained with gravity from the filter press to the chemical tanks in chemical container.

Chemical container will withhold three chemical tanks. Two of them are buffer tanks in the process and one of them is for fresh ammonium chloride solvent reserves. Chemical tank will also have two liquid pumps, these pumps will feed solvent from buffer tanks to reactors one and two.

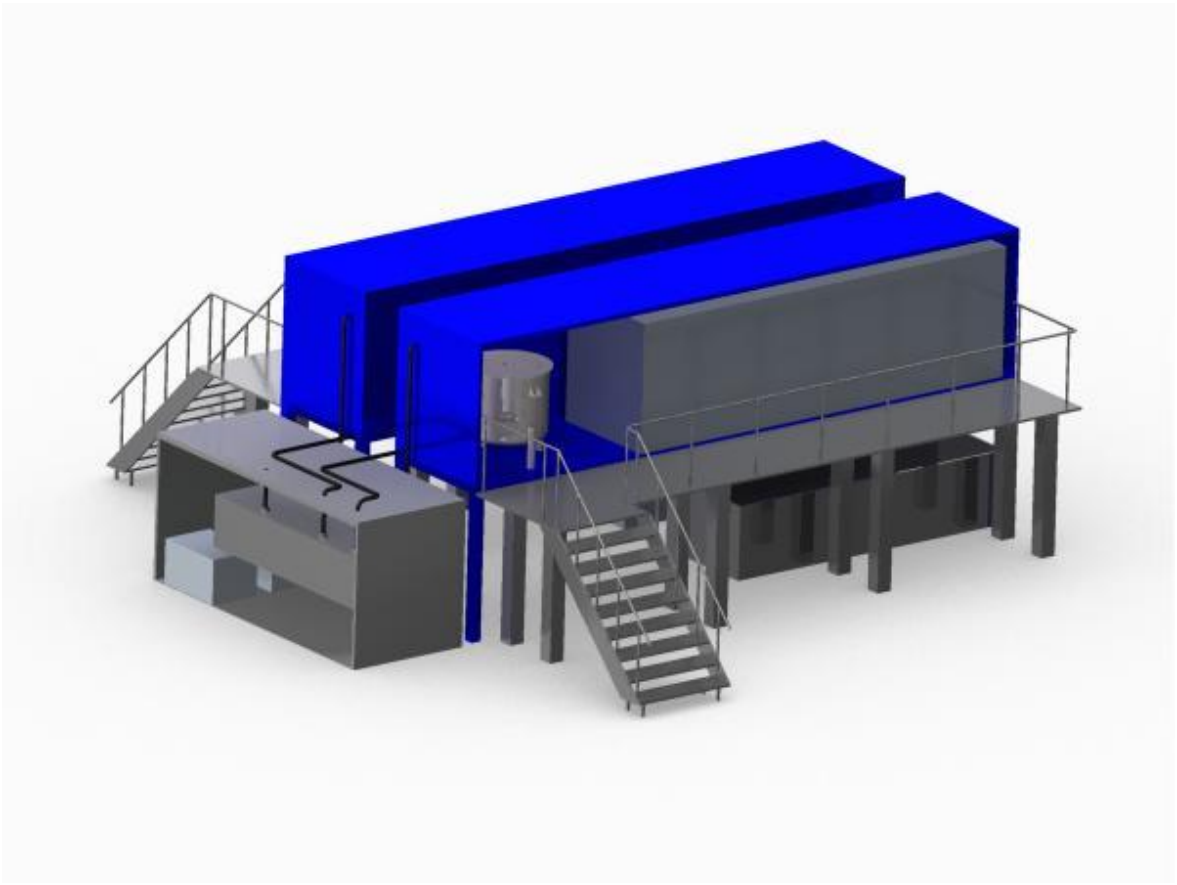


Figure 28. Demonstration plant layout sketch.

Figure 29 shows the flow chart of the demonstration plant. Reactor one, pump one and filter one are installed in the slag processing container. PCC processing container withholds reactor two, pump three, filter two and heat exchanger one. Holding tanks one and two, fresh solvent tank and also pumps four and two are mounted in chemical container. Dashed lines show borders of individual shipping containers.

Pumps four and two are liquid pumps for the solvent transportation from holding tanks to reactors. Pumps one and three are slurry pumps. These pumps feed slurry from the reactors to the filter presses.

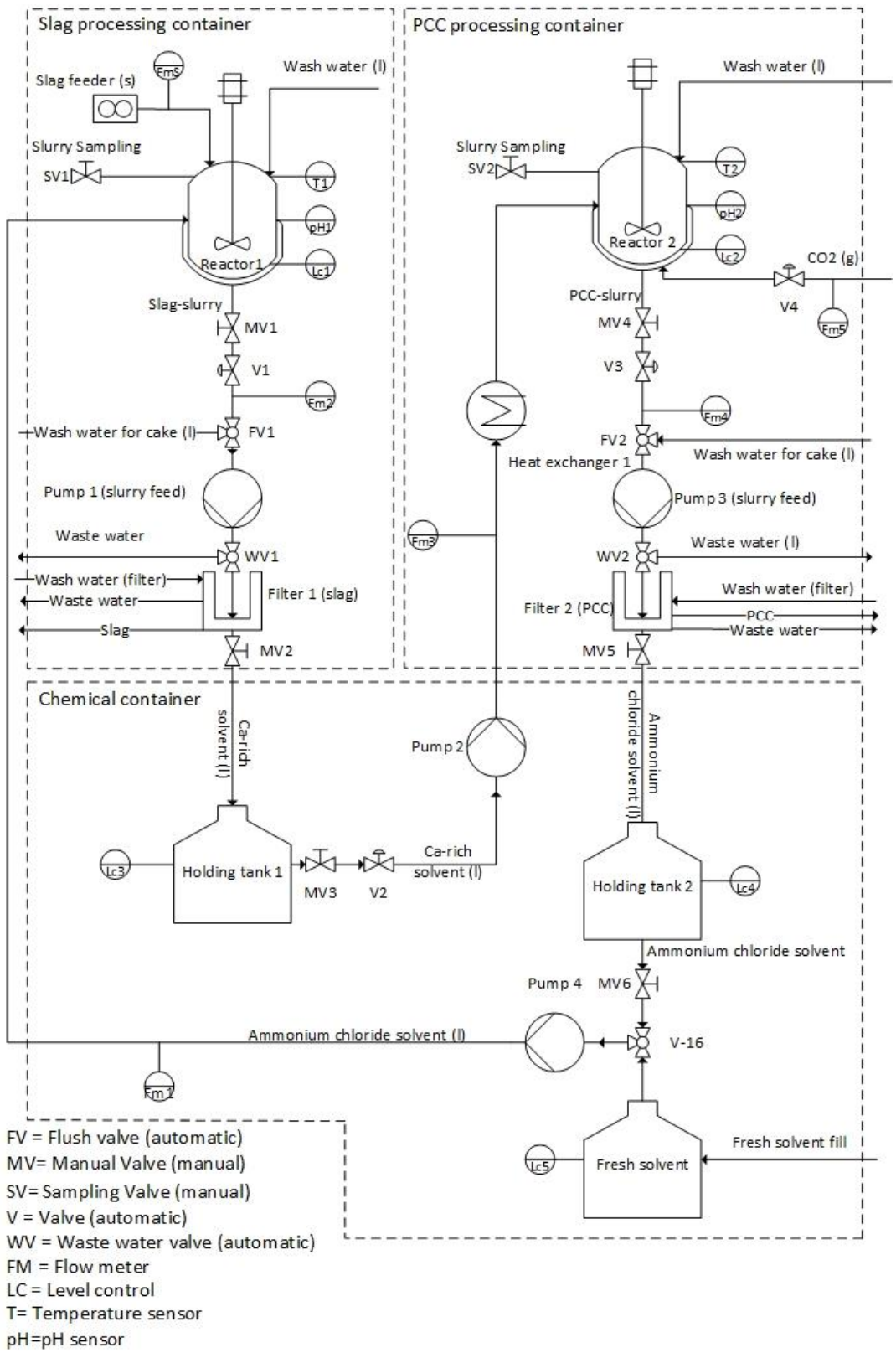


Figure 29. Demo plant flow chart.

4.6 Demo-plants general process description

Figure 29 demonstrates the flow chart of the demonstration plant. Process will start by loading a batch to reactor 1. Pump 4 pumps required solvent volume to reactor 1 which is the extraction reactor. This solvent will be taken from the holding tank 2, which is the recycled solvent tank. Pump 4 is also connected to fresh solvent container, if holding tank 2 doesn't have required amount of solvent for full patch, missing solvent will be pumped from fresh solvent container. Slag feeder and mixer will be started after liquid level has reached impeller level inside the reactor. After batch is loaded into reactor pump 4 and slag feeder will stop.

Mixer will be running through whole extraction reaction. Reactor ones temperature sensor and pH sensor measure and log reactor temperature and pH. After reactor pH reaches end value, drain valve in bottom of the reactor one is opened and pump 1 will start to pump slag-slurry to slurry filter. Reactor mixer is stopped when slurry level drops under impeller height. Pump 1 is stopped when reactor one is empty or if pumps pressure reaches slag filters maximum feed pressure.

After slurry batch has been loaded to filter press, filtration sequence is started. Filter will mechanically press cake and squish filtrate out. Filtrate flows to holding tank 1. After first pressing, pressure is released and wash water is pumped through the cake. Wash water will replace remaining filtrate in filter cake and waste water is led to waste water collection. Second pressing will force wash water out from the cake. Dewatered and washed cake is removed from the plate press and cake drops out from the filter container.

While filter press 1 is executing cake wash routine pump 2 can start to pump calcium rich filtrate from holding tank 1 to reactor 2. Calcium rich solvent is pumped through heat exchanger, solvent is heated to carbonation temperature and solvent flows to reactor 2. When holding tank 1 is empty, pump 2 stops and carbonation reaction can be started. This is done by starting the mixer and letting CO2 to flow into the reactor trough valve 4. Reactors temperature and pH are monitored and logged through whole carbonation reaction. Reaction will be stopped when reactor pH reaches goal value, this is done by cutting of CO2 flow.

Reactor 2 is emptied from PCC slurry with pump 3. Slurry is pumped to filter press 2, which mechanically separates solvent from the PCC cake. Filtrate flows to holding tank 2. After mechanical dewatering cake is washed with water, by pumping wash water through cake with pump 3. After washing cake is dewatered again mechanically and then removed from the filter press.

5 Discussion

This thesis aimed to produce concept designs for demonstration plant that produces calcium carbonite from steel making slag. Thesis gives good grounds for further developing steps, but some changes were made to initial requirements. Initial requirements at the start of this work were, that equipment should be mounted in 20' containers and reactors should have volume of $2m^3$. There was also a wish that demo plant could operate as continuous and patch process.

The wish of having two different process flows, continuous and patch, was dropped in the early state of design process to limit the scope of work. Also, the decision of having either patch or continuous process is one of the first decisions that are made in process equipment design. This decision effects the whole equipment chain. Reactor and container sizing also needed to be changed. 20' containers weren't large enough for filtration system and demonstration plant was instead designed for 1000kg slag patch.

There wasn't too much specific information available about Slag2PCC plant designing as process itself is quite new and is still in development phase. However literature research gave good idea about the mechanisms that caused problems in the pilot plant and information about possible solutions for problems in pilot sub functions. Pilot plants problems were resolved according literature references and observations made when working with pilot plant. Rest of this chapter go through the design chooses for sub functions in more detail.

From the two reactors, extraction and carbonation, extraction reactor is much more demanding when it comes to solid suspension. This is due to larger particles, higher solid concentration, denser solids and cooler liquid. Literature, observations made while working with the pilot plant and conclusions in this thesis agreed on this matter. It should be judged if completely suspended solid distribution is required in extraction reactor or if just suspended state is enough.

It also needs to be stated, that impeller speed calculations for carbonation reactor most likely give too low rotation speed. Specific speed increase wasn't found and literature states that models for solid, liquid gas mixing aren't as refined and precise as models for pure solid suspension. It was also stated that gas sparging reduces impellers power requirement, but increases the required rotation speed for solid suspension. Precipitation reaction might also require more even solid distribution in reactor than extraction reactor. It is advised that carbonation reactor impeller speed is dimensioned for uniform solid distribution. Research work usually states that tests were carried out in "vigorously mixed" vessel. Jet mixing technology was also discarded due to lack of information about its suitability for slag to PCC process.

Through the design process it became apparent that filtration system would be extremely critical and most challenging part of demonstration plant. This system will be technically most complicated and also most expensive system in demo plant. Filtration systems could make up as much as half of the plants investment costs. Pressure filtration also seems to be right technology choice for demonstration plant filtration system. The choice of filter press devices means that standard and best practices, introduced in literature, for slurry transportation can't be completely followed. Filter press system has unique requirements

that differ from requirements of slurry transportation i.e. continuous steady slurry flow with over critical flow velocity can't be attained trough whole filtering process.

However, the final choice of filter technology, medium and filtration parameters requires filtration tests. Filter manufacturers have laboratory equipment or even mobile test rigs for required tests. These test should be performed with real process materials. Meaning that solvent, solids and their portions are as close to reality of intended process as possible. Required slurry volume varies between companies. Slurry volume can be as small as few dozen liters or as high as few cubic meters. This depends on the scale of testing and equipment.

The suggested layout of two 40' processing containers and one 20' chemical container is based on initial filtration equipment dimensions given by manufacturer. However these dimensions might not be that accurate. This means that reactors might not fit in 40' material processing containers and require a separate 20' container that they are mounted in. However this shouldn't pose a problem as this extra reactor container could be mounted over chemical container and shipping containers make only miniscule portion of plant costs.

The key requirement that was given in the start of the concept design process, was that reactors need to be 2.5m^3. However this "reactor centric" design philosophy might not be the best starting point for demonstration plant design. It could be wiser to design demonstration plant around the filtration system, and mainly around extraction filter system as it requires more capacity. This would lead at least to three different shipping container mounted mobile plant designs paths which are:

- As large unit in shipping container as possible
- As mobile as possible
- Design for specific capacity

Third option is basically same approach that was given in the design assignment for this thesis. This requires the information of wanted trough put flow that plant needs to operate with. The draw back with this approach is that when plant is moved to new site the optimum plant capacity might not be the same. There was also conflict with initial requirement that demonstration plant would be mounted in to 20' DC shipping containers and that filtration equipment with enough trough put volume requires 40' HC containers. One design approach for demonstration plant capacity could be that capacity is defined by equipment that can be mounted in 20' containers. This would decrease production capacity, but improve mobility of the plant.

First option would result in pretty similar plant as introduced in this thesis. The plant would have larger capacity, but it still would fit in to similar set up as suggested demonstration plant. Plant would be more expensive, but it would most likely have larger capacity per investment cost as it is more economical to increase the capacity of exiting plate press equipment to a certain extend.

Second design path would lead to most compact and mobile demonstration plant. Basically this plant would have quite similar reactor volumes as pilot plant has, but it could be assembled in single 20' shipping container. This design would strongly emphasize usability and mobility.

In future, research for demonstration plant should focus on filtration testing. Pressure filtration is most likely best technology choice for the plant, but choice of filter machine type requires precise testing and further consulting of manufacturers. There is also the research question of continuous slag to PCC process. This matter requires further research. Continuous process requires own reactor designs and also re-evaluation of sub functions technological implementation, focusing on filtration.

In addition, demonstration plant requires further work on fields of automation, electrical engineering and waste water management. Further work is also required on how well demo plant integrates on different process chains and is the dry slag as feed material the optimal choice or could extraction reaction be started in grinding mills that grind slag to fine powder.

6 Summary

Steel is widely used, versatile construction material. However steel manufacturing is energy intensive process and steel industry produces nearly 7 % of mankind's carbon dioxide emissions. Sustainable future requires means to reduce these emissions and slag to PCC process offers one way to degrease both the carbon emissions and solid waste quantity of steelmaking process. Reduction in carbon emotions is achieved by binding $CO2_2$ in calcium that is extracted from steelmaking slag. This reaction forms precipitated calcium carbonate.

This thesis introduced concept design for slag to PCC demonstration plant that works as patch process. Plant is designed as modular and mobile unit and its equipment is mounted in 2 40' high cargo shipping containers and one 20' high cargo shipping container. Plant reactors are patch stirred vessel reactor and semi patch reactor that are dimensioned according to "standard" stirred vessel guidelines. Plant uses filter press machines as solid/liquid separation system. Thesis also goes through initial calculations for reactor and pipeline dimensioning.

Further design work for demonstration plant should focus on automation, electrical engineering, waste water management and filtration system. Filtration system requires further filtration and cake washing test performed in co-operation with filter manufacturers.

Demonstration plant that this thesis describes operates as patch process. However in larger industrial scale continuous process could be more desirable. Current demo plant could be used as test platform for continuous process. Extraction reactor and carbonation reactor could be used as reserve tanks for plate press filter when carrying out continuous reactor test. This demonstration plant could also be used to test continuous filtration equipment as filter manufacturers have movable test rigs for some of their filtration equipment.

For further development, it is crucial that demonstration plant purpose is clear. If the plant is used to demonstrate process and as proof of concept, small, mobile and well-functioning pilot-scale plant could be good option. Or if plant is required to provide large enough production volumes for equipment and technology testing for larger industrial scale, it should be confirmed that demonstration plant capacity is sufficient for these purposes.

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Appendices

Appendix 1. Parameters for solids suspension in dished vessels

Parameters for solids suspension in dished vessels (Mak, 1992)

Impeller Geometry and Location	Zwietering Constant, S
A-310 (T/2.4)	
C = T/4	6.9
A-310 (T/2)	
C = T/4	7.1
30° PBT (T/3, D/2.5)	
C = T/4	6.4
C = T/6	7.1
C = T/8	7.2
45° PBT (T/3.3, D/2.1)	
C = T/4	4.5
C = T/8	4.3
45 PBT (T/3, D/3.5)	
C = T/4	4.8
C = T/6	4.6
C = T/8	4.2
45° PBT (T/2.5, D/2.8)	
C = T/4	4.7
C = T/8	3.4
45° PBT (T/2, D/3.5)	
C = T/4	5.2
C = T/6	4.2
C = T/8	3.7
45° PBT (T/2, D/6)	
C = T/4	5.5
C = T/8	
45° PBT (T/1.7, D/3.5)	
C = T/4	6.7
C = T/6	5.1
C = T/8	4.4
45° PBT (T/1.7, D/4.3)	
C = T/4	6.8
C = T/8	3.8
45° PBT (T/1.4, D/5.0)	
C = T/4	5.4
C = T/8	4.5
45° PBT (T/3, D/4)	
C = T/4	4.4
C = T/6	4.1
C = T/8	3.7
90° PBT (T/3, D/5)	
C = T/4	4.4
C = T/6	4.1
C = T/8	4.1