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Master's Programme in Chemical and Process Engineering

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**Novel methods for treatment of steelmaking slags**

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## **ABSTRACT**

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### **Novel methods for treatment of steelmaking slags**

Master's Thesis

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70 pages, 18 figures, 14 tables and 3 appendices

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The demand for iron and steel is constantly increasing as infrastructure and society is developing. In addition to their primary products, iron and steelmaking industries produce slags containing mainly CaO, FeO, MgO and Al<sub>2</sub>O<sub>3</sub> which are still partly landfilled. The aim of this study was to find novel methods for treatment of steelmaking slags.

According to the literature survey, CaCO<sub>3</sub> is the most researched calcium product developed from steel slags with the aid of ammonium salts as the agent. The most important variables to take into consideration are particle size, sufficient mixing and solid-to-liquid ratio. The target of the experimental work was to find treatment methods for blast furnace, desulfurization, basic oxygen furnace and ladle slag.

Alkali metal salts of low and high molecular weight organic acids were selected as examined products by their novelty, possible markets and environmental impact. Experiments were carried out in a batch reactor with online pH and temperature measurements. GC and + ICP-MS were the main analytical methods. Differences in treatment medium pH, molarity and temperature were studied.

Synthesis of each product was first successfully conducted using commercial reagents. Depending on the type of the slag, 34% to 97% conversion was reached. The yield varied greatly (31% ... 84%) depending on the synthesis route even for a given slag.

The Thesis accomplished to prove the concept for four novel treatment methods for steel slags. The methods studied require further examination in commercial, analytical and process optimization point of views.

## TIIVISTELMÄ

Lappeenrannan- Lahden Teknillinen yliopisto, LUT

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LUT Chemical Engineering

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### Uusia menetelmiä teräskuonien käsittelyyn

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Jatkuvasti kehittyvä yhteiskunta pitää raudan sekä teräksen tarpeen korkealla. Rauta- ja terästeollisuus tuottavat kuonia sivutuotteena ensisijaisten tuotteidensa lisäksi. Kuonat sisältävät pääasiassa kalsiumin, raudan, magnesiumin ja alumiinin oksideja. Mineraalirikkaita kuonia ei ole kokonaan hyötykäytetty vaan ne läjitetään. Tämän työn tarkoituksena oli löytää uusia keinoja hyödyntää kuonia.

Kalsiumkarbonaatti on eniten tutkittu teräksenvalmistuskuonista jalostettu kalsiumtuote, jota tyypillisesti valmistetaan eristämällä kalsium kuonasta ammoniumsuolan vesiliuoksella. Teräskuonien käsittelyssä tärkeimpiä parametrejä ovat riittävä sekoitus, partikkelikoko ja kiintoaineen suhde liuoksen määrään. Kokeellisessa osuudessa käsiteltiin masuuni-, mikseri-, emäshappimellotus- ja senkkakuonaa. Tavoitteena oli kokeellisesti tuottaa kaupallisia tuotteita, joiden valmistamista teräksenvalmistuskuonista ei ole tutkittu. Panosreaktorissa tuotettiin suuri- ja pienimolekyylisten orgaanisten happojen alkalimetallien suoloja. Kokeiden lämpötilaa ja pH:ta seurattiin jatkuvasti, kun taas GC:llä ja ICP-MS:llä tutkittiin kvantitatiivisesti näytteiden koostumuksia.

Jokainen tuote syntetisoitiin onnistuneesti kaupallisella reagentilla. Teräksenvalmistuskuonasta riippuen, reaktion konversio vaihteli 34%:n ja 97%:n välillä. Syntetisointimenetelmästä riippuen, saanto vaihteli 31%:sta 97%:in.

Tutkimus onnistui todistamaan neljä mahdollista menetelmää kaupallisten tuotteiden valmistamiseksi teräksenvalmistuskuonasta. Jokainen menetelmä on esiasteella, joten ne vaativat kehitystä prosessiolosuhteisiin ja analyttisiin menetelmiin sekä laajaa kaupallista katsausta.

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## LIST OF ABBREVIATIONS

AOD	Argon-oxygen- decarburization
BF	Blast furnace
BOF	Basic oxygen furnace
CaFo <sub>2</sub>	Calcium formate
CSS	Converter slag solidification
DS	Desulfurization
FID	Flame ionization detector
FoA	Formic acid
GC	Gas chromatography
ICP-MS	Inductive coupled plasma mass spectrometry
LD	Linz- Donawitz
LF	Ladle furnace
LS	Ladle slag
MeFo	Methyl formate
MeOH	Methanol
PCC	Precipitated calcium carbonate
PSA	Paper sludge ash
PSD	Particle size distribution
TBP	Tributyl phosphate
TCD	Thermal conductivity detector
XRD	X-ray diffraction
XRF	X-ray fluorescence

## LIST OF SYMBOLS

$a$	Stoichiometric multiplier,	-
$d$	Diameter,	m
$p$	Pressure,	Pa
$pK_a$	Acid dissociation constant,	-
$SLR$	Solid to liquid ratio,	g/L
$t$	Time,	s, min, h
$T$	Temperature,	°C
$\omega$	Rotational speed,	rpm
$\Delta_r G_m^\theta$	Standard Gibbs free energy,	kJ/mol

## 1 Introduction

Steel is a central raw material in several sectors of everyday life. The consumption of steel is only anticipated to increase as the infrastructure and technology are developing. However, iron and steel production have high CO<sub>2</sub> emissions and partly landscaped side streams. These by-products are slags which are formed when iron and steel are smelted in furnaces or ladles. The purpose of slags is to improve the molten metal by removing impurities and controlling the properties of desired iron or steel grade. Slags mainly consist of calcium, magnesium, iron, phosphorus, aluminum with traces of other metals.

Steel production produces up to 200kg of slag per 1t of steel produced. Currently, steel slag is either landscaped, recycled back to the process or sold as a low value raw material for construction sites. Landscaping of the slag pollutes the soil as metals are slowly leached. Fully recycling of the slag is problematic as the metals accumulate in the process. Even utilization of slag as construction raw material has its difficulties. Due to the high content of calcium oxide and calcium silicate, slags are not volumetrically stable. The aim of this work is to derive a value-added calcium product from steelmaking slags by separating calcium from the slag.

The Thesis is divided in two sections. First, in the literature review, steel production, slag properties and current utilization of slags are presented. The literature review also finds the most important factors to take into consideration during selective leaching of calcium from steelmaking slags and gathers calcium products synthesized from slags in laboratory or pilot scale. In addition, production and utilization of three potential calcium products are taken into closer examination. The three products are; 1) calcium formate, 2) calcium soap (calcium salt of fatty acid) and 3) a calcium salt of a hydroxy acid. In the experimental section, each calcium product is synthesized with pure calcium oxide as reference before experimental testing with steelmaking slag. First, a novel technique where steelmaking slag is utilized as a catalyst and complexing agent in alkyl ester hydrolysis reaction is studied. Herein, the example reaction is hydrolysis of methyl formate for formic acid production. In addition, the same calcium salt is produced with direct leaching by the corresponding acid. Second, steelmaking slag dissolution is carried out with a salt of a hydroxy acid which could be separated from waste green liquor from pulp industry. The calcium is separated in alkaline conditions and sodium lactate serves as a leaching agent. This potential process route would combine the potential of an industrial waste and an unutilized by-product. Third, CaO in

steelmaking slag is leached and converted into a calcium soap which has potential in being an additive in animal feed.

## **2 Steelmaking process and slag formation**

Steel has set foot on several sectors, such as agriculture, construction, power generation and distribution, machinery and equipment manufacture, households and pharmaceutical (Remus, Aguado Monsonet, Roudier, & Delgado Sancho, 2012). In 2017, the total production of crude steel in the world, Europe and Finland were 1 690 000, 210 000 and 4000 thousand tonnes, respectively. Typical steelmaking processes are electric arc furnace (EAF) and basic oxygen furnace (BOF) also known as Linz-Donawitz (LD) converter. In the EU, BOF covers 60.5% of the total crude steel production whereas EAF 39.5% (Worldsteel, 2018). Figure 1 presents a simplified scheme of steelmaking processes (Yildirim & Prezzi, 2011).

Steelmaking starts with iron production in a blast furnace (BF). BF converts iron ore into crude iron which is mainly used as a molten raw material for steel. Iron ore is charged on top of the BF with ~20 wt-% of coke as a reduction agent. Air mixed with oxygen, carbon dust and oil are injected through a tuyere from the bottom of the furnace. Iron oxide (FeO), hematite (Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>) loses oxygen for carbon monoxide, hydrogen and carbon which are formed from coke, carbon dust and oil. The gases carry the oxygen out of the furnace through top vents. The temperature in the furnace varies from 2300°C at the bottom to 100°C at the top. Some of the impurities (phosphorus, manganese, silicon oxides) in the veinstone are reduced by carbon and mixed with crude iron. Fluxes (limestone or lime) are added to reduce remaining impurities and form a slag on top of the iron which can be tapped out of the furnace easily. Thus, the slag typically consists of CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and FeO (Metallinjalostajat ry, 2014; Y. Yang, Raipala, & Holappa, 2014). Depending on the cooling method, the BF slag can be granulated, expanded, pelletized or air cooled (Said, Mattila, Järvinen, & Zevenhoven, 2013).

In between the BF and BOF may be a desulfurization (DS) treatment where the sulfur content of the hot molten iron is reduced in ladles. The hot iron contains 0.025 to 0.050% of sulfur (FeS) which is typically removed with the aid of Na<sub>2</sub>CO<sub>3</sub>, CaO, magnesium, CaC<sub>2</sub> or a mixture of these (Y. Yang et al., 2014).

Hot molten iron is the main raw material of basic oxygen furnace. In addition to hot molten iron, 10-20% of steel scrap can be charged to the BOF to control the temperature (Brandt & Warner, 1999; Yildirim & Prezzi, 2011). A water cooled oxygen lance is inserted in to the BOF, right above the surface of the metal. The mixture of metals is ignited, and 99% pure oxygen is blown at supersonic speed. After the ignition, fluxes, such as lime (CaO) or dolomite ( $\text{MgCa}(\text{CO}_3)_2$ ), are added to the BOF for pH control. The carbon and impurity contents (silica, manganese, phosphorus) of the steel are oxidized and a slag forms on top of the hot molten steel. Temperatures up to 1650°C are reached. The chemical reactions take 20-25 minutes and then, the oxygen lance is lifted. The hot molten steel is poured into a large ladle where it can be further treated with additional alloys to produce the desired steel type. The slag formed is poured into another ladle (Brandt & Warner, 1999; Remus et al., 2012; Yildirim & Prezzi, 2011).

On contrary to BOF –process, the EAF utilizes high power electric arcs instead of gaseous fuels to produce the heat and the main raw material is steel scrap instead of iron from BF. After the EAF is charged with scrap, electrodes are lowered over the metal. The electricity flow (over 800kW) is turned on. The electricity bounces through one electrode to metal and back to another electrode. The resistance of the metal and the electricity flow itself generate heat which melts the scrap. Then, molten iron can be introduced to the EAF in small amounts. Fluxes, CaO or  $\text{MgCa}(\text{CO}_3)_2$ , are added before further refining of the steel. During the refining, an oxygen lance blows oxygen in the mixture and impurities are oxidized which form a slag with the flux agents. The refining step also includes addition of carbon powder if the carbon content is too low for carbon monoxide formation. The CO gas increases the thermal energy transfer by foaming the slag. When desired composition of the steel is achieved, steel and slag are poured into separate ladles (Brandt & Warner, 1999; Yildirim & Prezzi, 2011).

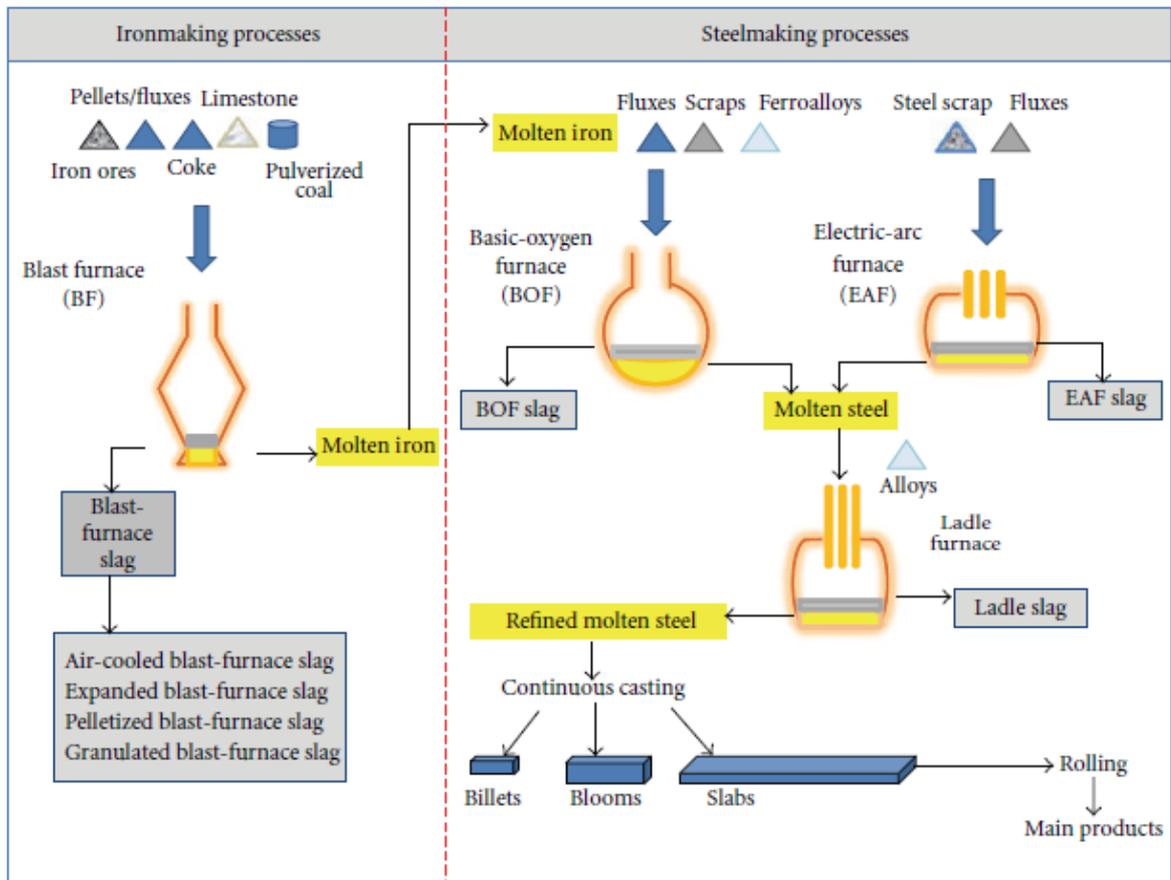


Figure 1 A simplified scheme of steelmaking process. Figure adapted from Yildirim and Prezzi, 2011.

The molten steel from primary steelmaking processes (BOF and EAF) can be further refined in secondary steelmaking processes. The primary objectives of secondary steelmaking are 1) final desulfurization, 2) deoxidation, 3) removal of other gases such as hydrogen and nitrogen, and 4) final decarburization (Yildirim & Prezzi, 2011). Secondary metallurgical slags include slags formed in ladle (LS) and ladle furnace treatment (LF), vacuum degassing (VD), argon oxygen decarburization (AOD) and in vacuum oxygen decarburization (VOD) (Euroslag, n.d.).

Figure 2 presents a typical LF process (Yildirim & Prezzi, 2011). Ladle furnaces are basically small EAFs. Electrodes are similarly used to produce the heat. A pipeline from the bottom blows argon gas to stir and homogenize the liquid steel. Desulfurization is carried out by adding desulfurizing agents (Ca, Mg, CaSi, and CaC<sub>2</sub>) through a lance. Deoxidation is accomplished with the addition of silicon and aluminum. The formed SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are absorbed in the ladle slag. To produce different steel types, alloying elements can be added in the ladle furnace (Yildirim & Prezzi, 2011). Different alloys, such as vanadium, nickel or

chromium, cover 2% or less of the steel and enhance, for example, the toughness, strength, corrosion resistance or hardenability of the steel (Brandt & Warner, 1999).

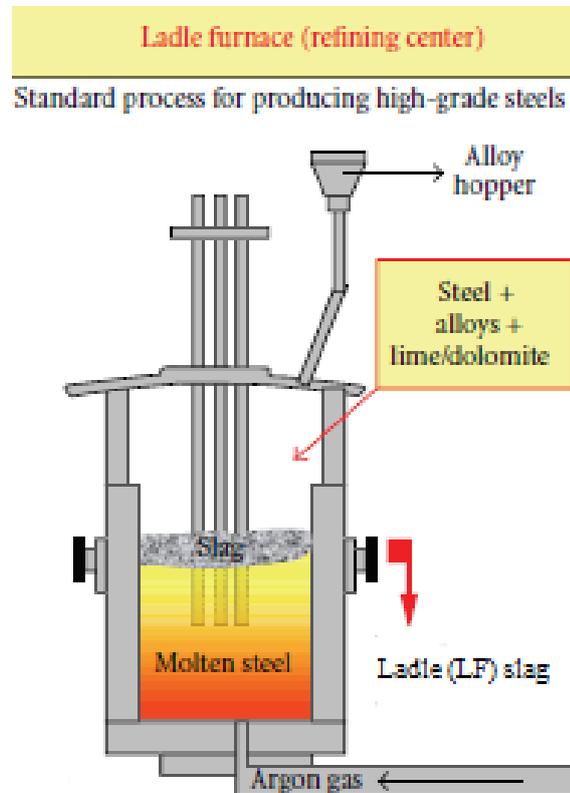


Figure 2 A simplified scheme of a ladle furnace. Figure adapted from Yildirim and Prezzi, 2011.

### 3 Properties of steelmaking slags

As presented in Figure 1, there are three main types of steelmaking slag: BOF, EAF and ladle slag. Table 1 presents a range for the amounts of each slag produced during steelmaking process. Secondary steelmaking produces significantly less slag than primary steelmaking processes.

Table 1 The amounts of slags generated in steelmaking processes (Pan, Adhikari, Chen, Li, & Chiang, 2016).

Source of the slag	Amount, kg/t-product
Basic oxygen furnace (BOF/LD)	50-200
Electric arc furnace (EAF)	70-200
Ladle furnace* (LF)	40-73
*Includes EAF reducing, AOD and DS slags.	

Table 2 presents chemical compositions of some steelmaking slags presented in research literature. BF slag typically contains smaller variety of elements than steelmaking slags and does not contain iron. The silicate ( $\text{SiO}_2$ ) content of the BF slag is 10–20 weight percentage points higher than in primary steelmaking slags.

The DS slag has approximately 1 wt-% higher  $\text{SO}_3$  content than other slags. Calcium oxide content is relatively high compared to BF slag and very similar with BOF and EAF slag. Besides sulfur content of DS slag, it does not contain significant amounts of heavy metals or other impurities.

Primary steelmaking slags (BOF and EAF) originating from carbon steel production are generally very similar with high CaO and FeO content (Yildirim & Prezzi, 2011). However, the chemical composition of EAF slag is dependent on the quality of the scrap metal fed in the furnace. On average, primary steelmaking slags contain less silicate than any other slags from steel production.

The chemical composition of LF slags is highly dependent on the steel type manufactured (Pan et al., 2016). Typically, it is higher in CaO and  $\text{Al}_2\text{O}_3$  and lower in FeO than EAF and BOF slags. Ladle slags do not typically contain free CaO (Eloneva et al., 2009; Iacobescu, Angelopoulos, Jones, Blanpain, & Pontikes, 2016).

Table 2 Chemical compositions of steelmaking slags. (BOF = Basic oxygen furnace, EAF = Electric arc furnace, LF = Ladle furnace, n.d. = not determined, ( ) = only one data point) Combined from (Adegoloye, Beaucour, Ortola, & Noumowe, 2016; Chen et al., 2017; Chen, Ko, Chang, & Lin, 2018; Euroslag, n.d.; Mineral Products Association, n.d.; Sheen, Le, & Sun, 2015; Tossavainen et al., 2007; Yildirim & Prezzi, 2011).

Weight percentage, wt-%	BF	DS	BOF	EAF	LF
<b>CaO</b>	35-42	40-48	40-60	24-60	30-60
<b>SiO<sub>2</sub></b>	33-38	15.4-18	8-20	14-20	2-35
<b>Al<sub>2</sub>O<sub>3</sub></b>	7-12	2.1-2.7	1-5	6.3-12.2	4.3-35
<b>MgO</b>	0-1	0.4-0.7	1-15	4-15	1-11.9
<b>FeO</b>	0-1	2.9-4.9	7-35	5.6-34.4	0-15
<b>Fe<sub>2</sub>O<sub>3</sub></b>	n.d.	n.d.	9-38	20-33	0.2-3.3
<b>SO<sub>3</sub></b>	n.d.	1.6	0-0.3	0.1-0.6	0.1-1
<b>MnO</b>	0-1	0.12	0.3-8	2.5-8	0-5
<b>TiO<sub>2</sub></b>	n.d.	n.d.	0.5-2	0.6-0.8	0-0.9
<b>P<sub>2</sub>O<sub>5</sub></b>	n.d.	n.d.	1.3-3.3	0-1.2	0-0.4
<b>Cr<sub>2</sub>O<sub>3</sub></b>	(<0.1)	0	0.2-2	0.3-2	n.d.
<b>free CaO</b>	n.d.	n.d.	2.5-10	0-0.5	2.5-19

A summary of typical phase compositions of steelmaking slags is presented in Table 3. Differences between mineral phases in steelmaking slags between steelmaking plants are due to differences in the furnace charges (scrap, ore, etc). Thus, phases identified vary between references. BF slag has the least complex mineral composition and second least complex is DS slag. As the steel is refined further, the mineral composition of slags formed becomes more complex.

Typically, the oxides (CaO, MgO and FeO) are in a silicate phase or in a complex e.g. (CaFeMnMg)O group of phases which decrease their reactivity (Hall, Large, Adderley, & West, 2014). The free lime in the steelmaking slag can be either grainy or spongy, slightly eluted residual free- CaO or precipitated free CaO in grain boundaries of iron-oxide complexes such as (CaFeMnMg)O (Pan et al., 2016). The Ca<sub>2</sub>SiO<sub>4</sub> phase (main phase in LS slags) is not volumetrically stable. It has four common polymorphs of which  $\beta$  starts to transform into  $\gamma$  at temperatures below 500°C. Therefore, the slag overcomes volumetric

expansion which causes the crystalline structure to break which results as dusting. Hence, LS slag is known as “self-dusting” slag (Yildirim & Prezzi, 2011).

Table 3 Phase compositions of steelmaking slags. (BOF = Basic oxygen furnace, EAF = Electric arc furnace, LF = Ladle furnace, SS = Stainless steel) ▲ = (Luxán, Sotolongo, Dorrego, & Herrero, 2000) ■ = (Tossavainen et al., 2007) ○ = (Eloneva, Teir, Salminen, Fogelholm, & Zevenhoven, 2008b) X = (Eloneva et al., 2009) ● = (Said, 2017) ▼ = (Yildirim & Prezzi, 2011) V = (Chen et al., 2018)

Mineral	BF	DS	BOF	EAF	LF
(FeMnMg)O			■	■	
Portlandite, Ca(OH) <sub>2</sub>		V	○, ●, ▼		
Calcite, CaCO <sub>3</sub>		V			
Mayenite, Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub>					■, ●
Bredigite, Ca <sub>14</sub> Mg <sub>2</sub> (SiO <sub>4</sub> ) <sub>8</sub>	■				■
Gehlenite, Ca <sub>2</sub> Al(Al,Si) <sub>2</sub> O <sub>7</sub>		V		▲	
Brownmillerite, Ca <sub>2</sub> (Al, Fe) <sub>2</sub> O <sub>5</sub>			○, X	■	
Ca <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub> Cl <sub>4</sub>					●
Magnetite, Fe <sub>3</sub> O <sub>4</sub>		V	●	■, ▲	
Srebrodol'skite, Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>			●, ▼		
Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub>					
Merwinite, Ca <sub>3</sub> Mg(SiO <sub>4</sub> ) <sub>2</sub>	■		▼		
Fluorite, CaF <sub>2</sub>		V			
Lime, CaO			■, ○, X, ●, ▼		
Larnite, CaSiO <sub>4</sub>		V	■, ○, X, ●, ▼	▲	●
Larnite, β-Ca <sub>2</sub> SiO <sub>4</sub>			■	■	■
Larnite, γ-Ca <sub>2</sub> SiO <sub>4</sub>					■
Magnesian ferrite, MgFe <sub>2</sub> O <sub>4</sub>				▲	
Periclase, MgO			■		■, ●
Manganese oxides, Mn <sub>3</sub> O <sub>4</sub> / MnO / MnO <sub>2</sub>				▲	
Wuestite, FeO			○, X, ●		
Mg <sub>0.1</sub> Ca <sub>0.9</sub> CO <sub>3</sub>					●
Quartz, SiO <sub>2</sub>		V	○		

The chemical composition and relatively low cooling rate are reasons for crystalline structure of steelmaking slags. Physical properties of steelmaking slags include high density, low impact value (toughness), high compressive strength, rough surface texture, good polishing and freezing resistance. Thus, they are widely applied in civil engineering (Euroslag, n.d.).

#### **4 Utilization of steelmaking slag**

Steelmaking slags are constantly increasing their popularity as a utilized side stream. Based on number of patents concerning steelmaking slag applications, China and Japan are leading the field (Dhoble & Ahmed, 2018). In 2016, 85.9% of the steelmaking slag generated in EU was utilized (Euroslag, n.d.). The corresponding values in Japan, China and US are 98.4, 29.5 and 84.4%, respectively (Guo, Bao, & Wang, 2018). Table 4 presents the utilization of steelmaking slags in Europe in 2016 (Euroslag, n.d.).

Steelmaking slag is typically treated in four different processes until further utilization. First, the hot molten slag is solidified and cooled (Horii, Kitano, Tsutsumi, & Kato, 2013). The structure of the slag depends on the cooling method. It can be 1) air cooled, 2) granulated or pelletized or 3) expanded (Said et al., 2013). The cooled solid slag is crushed, and metal iron is recovered with a magnetic separator. From there, the slag is fed to a crusher to obtain the desired grain size depending on the slag product. The magnetic separator and crusher can be one after the other repeatedly to obtain the efficient removal and recycling of Fe (Ashrit, Banerjee, Chatti, Rayasam, & Nair, 2015). Finally, the slag is introduced to aging treatment where the free CaO and MgO are hydrated to obtain volumetric stability (Horii et al., 2013; Pan et al., 2016). The aging treatment typically takes as long as 6 months and has potential of leaching of hazardous metals during landfill (Hall et al., 2014).

On the other hand, the Fe removed slag is rich in calcium silicate which makes it a suitable flux for iron sintering. The recycling of LD and EAF ladle slags back to the steelmaking process as a flux agent is the utilization method preferred by EU (Remus et al., 2012). However, steelmaking slags can not be fully recycled back to the process due to its phosphorus content ( $P_2O_5$ : 1.5-2%) (Ashrit et al., 2015; Hall et al., 2014; Remus et al., 2012). Conventional and novel utilization methods of steelmaking slags are collected in Figure 3 and discussed later in this chapter.

Table 4 Utilization of steelmaking slags\* in Europe in 2016. Data gathered by (Euroslag, n.d.)

Application	Percentage of total use, % **
Road construction	46.0
Metallurgical use	15.3
Final deposit	14.1
Interim storage	8.6
Others	6.6
Raw material for cement and concrete production	4.4
Fertilizer	2.7
Hydraulic Engineering	2.2

\*Steelmaking slags include LD, EAF and ladle slags

\*\*Data based on countries: AT, BE, BA, BG, CZ, FI, FR, DE, GR, LU, PL, PT, RO, SK, SI, ES, SE, NL and UK)

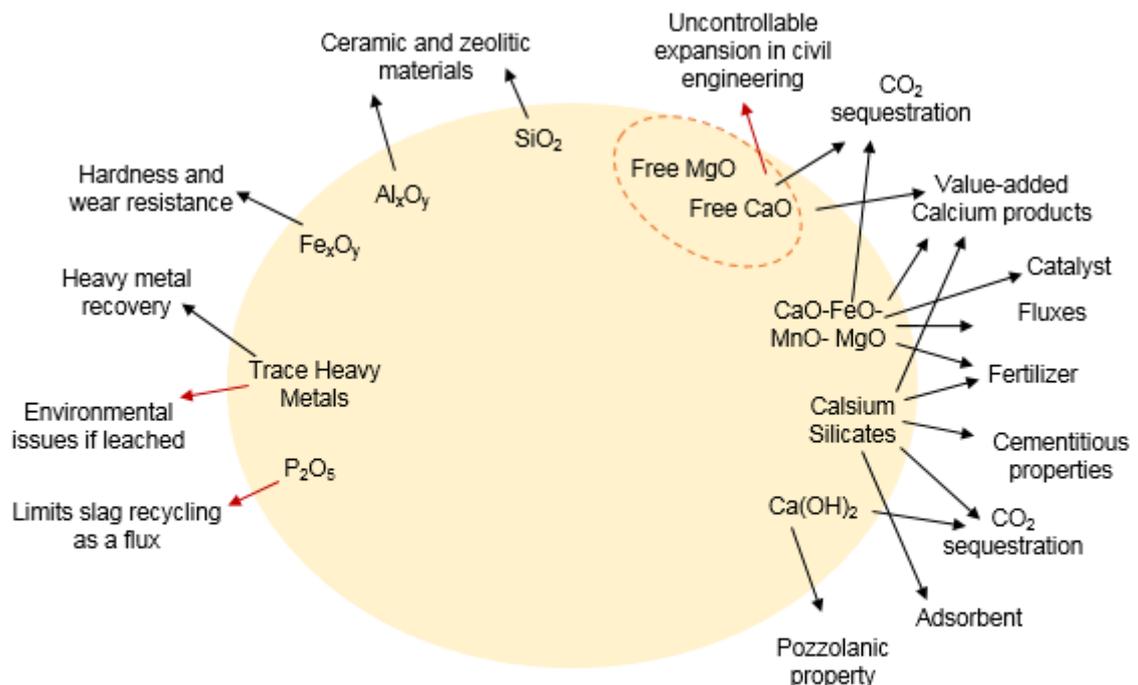


Figure 3 A summary of typical steelmaking slag properties and possible applications.

#### 4.1 Conventional methods

The most conventional utilization methods of steelmaking slag are as road base course material, construction raw material and in soil treatment (Dhoble & Ahmed, 2018; Hall et al., 2014; Horii et al., 2013; Pan et al., 2016; Remus et al., 2012). Iron and steelmaking slag are placed under the pavement surface which enhances the road's load-bearing capacity. In addition, steelmaking slag is utilized as an aggregate for asphalt mixtures and as railroad ballast (Dhoble & Ahmed, 2018; Horii et al., 2013). The mechanical properties of steelmaking slag include high level of strength, high binder adhesion and high frictional and abrasion resistance which especially make it an eligible raw material for civil engineering (Pan et al., 2016). When steelmaking slag is utilized as road base course material or a fine aggregate in concrete and cement (Pan et al., 2016), volumetric stability is essential which requires efficient removal or hydration of oxides (Huaiwei & Xin, 2011; Iacobescu et al., 2016; Salman et al., 2015). The utilization of LS and LF slags should be considered for each slag separately depending on its chemical and mineralogical composition (Pan et al., 2016).

Steelmaking slag stabilizes dispersive and/or acidic soil (Goodarzi & Salimi, 2015; Horii et al., 2013). Goodarzi and Salimi (2015) have found that 10% addition of steelmaking slag to dispersive clayey soil prohibits the soil dispersion. Steelmaking slag releases Ca<sup>2+</sup> ions and has a high pH (10-13 in contact with water) which activate pozzolanic reactions which form cementing products (Goodarzi & Salimi, 2015). In a similar manner, steelmaking slag is utilized as a ground improvement material in coastal regions of Japan to improve soft ground (Horii et al., 2013).

Favorable elements of BOF slag as a fertilizer are calcium, magnesium and silicates in addition to trace compounds such as FeO and MnO. Calcium guarantees a fast fix for acidity caused issues due to CaO and a slow fix through CaSiO<sub>2</sub>. Hence, BOF slag fertilizers are more durable than common fertilizers, such as dolomite lime or slaked lime. An affiliate of Nippon steel has sold BOF slag as a lime-based fertilizer since 1981 (Horii et al., 2013). However, the paper by Horii et al., (2013) does not discuss the potential of long time leaching of hazardous metals into the soil, such as vanadium, chromium, lead or barium (Hall et al., 2014), nor the pretreatments required to prevent it.

#### 4.2 Novel methods

Novel methods of steelmaking slag utilization mainly focus on environmental issues. Steelmaking slag has been studied for CO<sub>2</sub> sequestration, improving sea-areas and for waste

management. In addition, several methods for retrieving value-added products from steelmaking slag are under investigation. These include, for example, synthesis of zeolites, precipitated calcium carbonate (PCC) and recovery of heavy metals (Dhoble & Ahmed, 2018; Pan et al., 2016). This chapter provides information in different fields of study where steelmaking slag can be utilized with other than the above described conventional methods. Novel methods for steelmaking slag utilization which produce value-added calcium products are discussed later in Chapter 5.

#### 4.2.1 *CO<sub>2</sub> sequestration*

In order to enhance the suitability of steelmaking slag for civil engineering, different methods to accelerate the hydration of CaO have been studied. This has led to the development of CO<sub>2</sub> sequestration process, where the calcium oxide, calcium silicates and calcium hydroxide are directly carbonated with CO<sub>2</sub> from flue gases to form calcium carbonate CaCO<sub>3</sub> (Pan et al., 2016). The ability of steelmaking slag to capture CO<sub>2</sub> depends on the Ca –content of the slag. An estimation of the capacity is 0.25 kg of captured CO<sub>2</sub>/kg of steelmaking slag (Dhoble & Ahmed, 2018). CO<sub>2</sub> sequestration is studied for various steelmaking slag types such as, EAF and AOD slags from stainless steel manufacturing process (Baciacchi, Costa, Di Bartolomeo, Poletini, & Pomi, 2010) and BOF, EAF and LF slags from carbon steel production (Eloneva et al., 2009).

Advantage of direct carbonation of steelmaking slag is the requirement for only one processing step. However, the dry gas-solid carbonation requires high temperature and/or pressure ( $T=185^{\circ}\text{C}$  and  $p=150\text{kPa}$ ) (Hall et al., 2014) and has low carbonation conversion (Pan et al., 2016) as the highest achieved in  $T=600^{\circ}\text{C}$  and ambient pressure were 55% (Tian, Jiang, Chen, Yan, & Li, 2013). Direct carbonation also includes aqueous carbonation where alkali cations are first leached from solids to an aqueous solution. CO<sub>2</sub> is dissolved in the aqueous solution which forms carbonate and/or bicarbonate ions. Finally, the alkali carbonates precipitate (Pan et al., 2016). The drawback of this method is low purity of products (De Crom, Chiang, Van Gerven, & Santos, 2015). The product is typically an aqueous slurry which contains several by-products whereof carbonates are difficult to separate (Mun, Cho, & Kwon, 2017).

Indirect carbonation of steelmaking slag generates high purity PCC (Said, 2017). In indirect carbonation the alkali metals are first extracted from the solid matrix and the concentrated solution is carbonated (Pan et al., 2016; Said, 2017; Teir, Eloneva, Fogelholm, &

Zevenhoven, 2007). Indirect carbonation of steelmaking slag has gained great interest among researchers. Hence, it is described in detail later in 5.

#### 4.2.2 *Sea and coastal area treatment*

Utilization of steelmaking slag in creating artificial reefs have been studied. For example, a mixture of 50% steelmaking slag, 16% Portland cement clinker, 25% of sand and other additives have proven to have high density, strength and resistance for abrasion (Dhoble & Ahmed, 2018). In addition, Nippon Steel in Japan has commercialized Frontier Rock®, Frontier Stone® as a concrete block substitute that does not contain any natural aggregate such as sand or gravel. They also provide a Beverly® Block and Beverly® Rock derived from steelmaking slag for creating seaweed beds where the silicic acid and iron attracts seaweeds and benthic animals. The environmental impacts of the substitutes are compatible with environmental standards (Horii et al., 2013).

The soils in coastal areas of Italy are rich in sodium which decreases crop production and has disadvantageous effects on the soil structure. Treatment of the sodium rich soil with BOF slag resulted in 40% less sodium content than untreated and had higher tomato yield. Ion exchange occurred between slags  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and soils  $\text{Na}^+$ . However, the yield of wheat decreased which might be due to leaching of heavy metals (V and Cr). Thus, the BOF slag is not suitable for long term soil treatment as such (Pistocchi et al., 2017).

#### 4.2.3 *Waste management*

Water treatment, solid waste management and a daily landfill cover material are options for steelmaking slag utilization. Industrial acidic wastewaters often contain heavy metals (Pb, Cu, Cd) which can be treated with steelmaking slag as an adsorbent. The controlling mechanism has found to be chemisorption. The initial pH of the solution has shown to have significant effect on heavy metal recovery (Dhoble & Ahmed, 2018; Zhou, Richard, & Haynes, 2011). With initial pH over 4, Pb and Cu ions were removed completely and Cd by 85%. Metal ions form stable silicates and ferrites in contact with steelmaking slag. However, if the metal ions form carbonates, re-leaching in acidic conditions becomes an issue (L. Yang et al., 2019). EAF slag has been successfully used as an adsorbent for removal of Mn and Cd in basic conditions (Abd El-Azim, El-Sayed Seleman, & Saad, 2019). In addition to heavy metals, steelmaking slag is suitable for removing organic compounds such as 1,5-cyclo-octadiene and chloro compounds from wastewaters (Dhoble & Ahmed, 2018).

A mixture of 50% EAF slag and 50% cementitious LF slag is studied in large scale as a landfill daily cover material. The mixture meets the set infiltration criteria (Dhoble & Ahmed, 2018). Kim et al., (2005) have studied a novel technology called converter slag solidification (CSS) which utilizes BOF slag as the solidifying agent and CaO as the solidifying aid for sewage sludge. The CSS technology helps to prevent volatility, odors and heavy metal leaching of solidified sludge which is used as a daily cover material in municipal landfilling (E.-H. Kim, Cho, & Yim, 2005).

#### 4.2.4 Value-added products

In addition to Ca –based products, steelmaking slag derived zeolites, catalysts and recovery of heavy metals are applications which increase the value of the steelmaking slag compared to its use as a low value construction raw material. Steelmaking slag is a potential source of V, Mn, Cr, P, Cu and Mg. For example, Fe, Mn, V and Cr can be captured from steelmaking slag by feeding the slag through hollow electrode into a DC reactor. Different selective leaching techniques are also studied for heavy metal recovery from steelmaking slag (Aarabi-Karasgani, Rashchi, Mostoufi, & Vahidi, 2010; Dhoble & Ahmed, 2018).

Steelmaking slag is studied as a Ca –rich high basicity catalyst for different catalytic applications. Steelmaking slag is calcinated in high temperature ( $T > 700^{\circ}\text{C}$ ) and utilized in transesterification reactions of biodiesel and glycerol carbonate synthesis (Okoye, Abdullah, & Hameed, 2017; Shan, Zhao, Lv, Yuan, & Yao, 2016). However, the biodiesel is easily contaminated with calcium. If the process is contaminated with  $\text{CO}_2$  or  $\text{H}_2\text{O}$ , the calcium hydroxide and carbonate formed decrease the catalytic activity of the slag (Shan et al., 2016). Okoye et al. (2017) used LF slag for glycerol carbonate synthesis with a 97% yield. In addition, many organic compounds have been removed using Fenton or Fenton-like processes in the presence of slag as a heterogeneous catalyst (Matthaiou et al., 2019). For example, 81% of tetrachloroethylene is removed from ground water with BOF slag as an oxidative Fenton-like catalyst (Dhoble & Ahmed, 2018).

The residual slag after Ca- removal can be converted in to zeolitic materials (Chiang et al., 2014; Murakami, Sugano, Narushima, Iguchi, & Ouchi, 2011). The studies have focused on BF slag which contains the same main minerals as steelmaking slags ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , CaO and MgO). Zeolite synthesis is a hydrothermal conversion of the residual slag in basic conditions (NaOH added) to micro- and meso-porous zeolitic materials (Chiang et al., 2014). Typically,

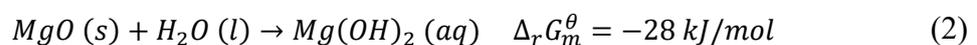
BF slag has higher silica content than steelmaking slags which is why it has been the focus on zeolite production.

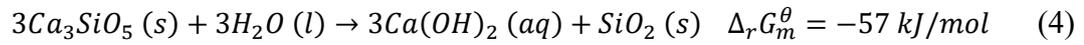
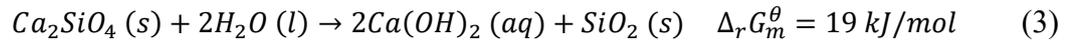
In a similar manner as zeolite production, the amorphous silica and alumina of steelmaking slag makes it a potential raw material for geopolymer production (Pan et al., 2016). Geopolymer is a substitute for concrete. It can be produced from silica and alumina rich mine tailings, dusts and slags without any addition of cement. Potential applications of geopolymers are as a high temperature insulator, structure of a catalyst, an absorbent or, for example, a sound barrier in the side of a high way. The main advantage of geopolymers over concrete is that the production is 80% less hazardous for environment and it utilizes industrial wastes and by-products in agreement with a vision of a circular economy (Tuominen, 2016). University of Oulu is currently working on a project called Geodesign which produces geopolymers from mineral side streams. For example, a copper producer Boliden Harjavalta Oy is in collaboration in the Geodesign project (Tuominen, 2016). However, as previously mentioned, Nippon steel in Japan has already produced the trademarked steelmaking slag derived substitutes for concrete block (Horii et al., 2013) which decreases the novelty of geopolymer applications for steelmaking slags.

## 5 Synthesis of value-added calcium products from steelmaking slags

The typical process route for formation of calcium products from steelmaking slag starts with selective extraction of calcium from the solid matrix. Hence, the leaching behavior of the steelmaking slag in aqueous media is presented before discussing the extraction agents studied. Potential calcium products are a carbonate, a hydroxide or a salt of given acid.

As previously stated, typical steelmaking slag mainly consists of calcium-, ferrous- and magnesiumoxides (CaO: 40-52 wt-%, FeO: 10-40 wt-% and MgO: 5-10 wt-%) which often are in a silicate phase (*Federal Highway Administration Research and Technology, 2016*) Formulas (1)-(4) present the dissolution reactions of the CaO and MgO in an aqueous solution (Luan et al., 2012; Xu et al., 2012). The pH of an aqueous solution, which contains steelmaking slag, is in the range of 10-13 due to the released OH<sup>-</sup>.





Due to  $\Delta_r G_m^\theta < 0$ , reactions 1,2 and 4 are suggested to occur spontaneously in atmospheric pressure and 25 °C. However, the found  $\Delta_r G_m^\theta$  of reactions 2 and 3 are in the range of -40 and 40 kJ/mol which make the spontaneous nature of the reactions ambiguous (Xu et al., 2012).

Mineral leaching in water is a good benchmark when comparing different leaching agents for Ca extraction from steelmaking slag. Dissolution of 0.5g of BOF slag with grain sizes between 53 and 75 $\mu$ m in 25°C temperature and atmospheric pressure into 300mL of pure water over 50 hours yields: Ca: 28, Si: 8.5, Mg: 2.5, Fe: 0.31, Al: 0.72, K:1.4 and Na: 0.8mg/L. The initial mineral composition of the slag was: Al<sub>2</sub>O<sub>3</sub>: 6.1, CaO: 34.3, MgO: 6.3, SiO<sub>2</sub>: 16.1 and FeO: 31.6 wt-% (Yadav & Mehra, 2017). When the results are calculated as leached weight percentages, the results are: Ca: 4.9, Si: 3.2, Mg: 2.4, Fe: 0.1 and Al: 0.7 wt-%. In order to increase the yield, extraction agents should be used. These are discussed later in this chapter.

After the calcium is selectively extracted of the steelmaking slag, further utilization for the solid residue is important to be in place for waste minimization. The solid residue after carbonation releases significantly less heavy metals (Cr and V) than untreated steelmaking slag (Navarro, Díaz, & Villa-García, 2010). Thus, further utilization in for example, civil engineering is possible. In addition, the harmful volumetric instability is avoided when the oxide content of the steelmaking slag is minimized. Of course, utilization methods, e.g. soil treatment which exploits the calcium oxide and silicate groups, are prevented. Utilization of the solid residue is another, yet important, study itself. However, it is out of the scope of this work.

## 5.1 Processes based on organic acids

Organic acids are known to dissolve alkaline metals from silicate (Mun et al., 2017). Murakami et al. (2011) used BF slag as a source to produce zeolite A and calcium salts as by-products. First, different organic acids were tested for selective leaching of calcium. This study was the only one found in literature which utilizes formic and citric acids. The solid to

liquid ratio (*SLR*) was 1g/30mL and initial pH of the solution was 2.0. The leaching was conducted at room temperature for 2h. Figure 4 presents the extraction results with various leaching agents. Citric and formic acid showed superior leaching of Ca compared to hydrochloric acid. Treatment with formic acid produced 0.38g of white calcium formate powder ( $\text{Ca}(\text{CO}_2)_2$ ) from 1g sample of BF slag and leachate showed only minor dissolution of Si and Al. The calcium formate was recovered by evaporation of water. However, the purity of the calcium formate is not presented in the paper nor are the concentrations of other elements (V, Cr, Mg) in the leachate. The study also included the effect of ball milling which is why no stirring was adjusted for the static experiments (Murakami et al., 2011). The effect of ball milling is discussed later in Chapter Methods and factors affecting process efficiency and selectivity. Main focus of current research is on PCC production. Therefore, potential precipitation of calcium formate or calcium citrate have been a disadvantage.

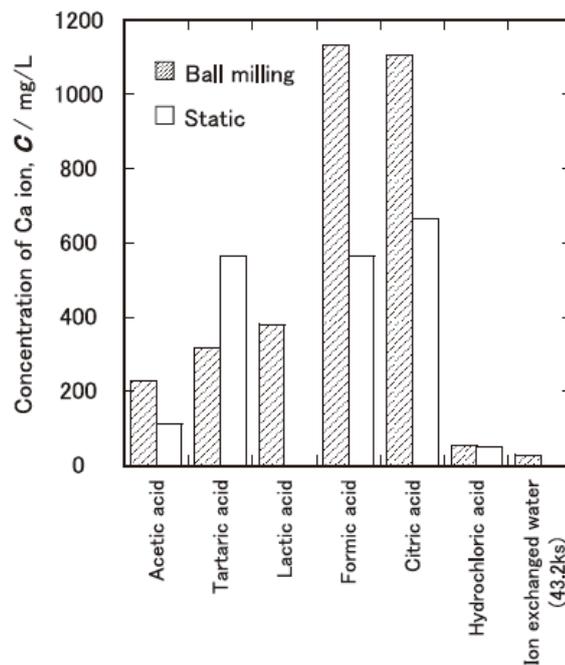


Figure 4 Concentration of extracted calcium from 1 g BF slag sample with 30 mL of leaching agent in room temperature within 2 hours (Murakami et al., 2011).

The process route for indirect carbonation with organic or inorganic acids as a leaching agent is typically as follows (Eloneva, Teir, Salminen, Fogelholm, & Zevenhoven, 2008a):

1. Extraction of Ca from the solid matrix to a leaching solution (e.g. acetic acid) in an extraction reactor with continuous stirring.
2. Solid liquid separation step: Filtration to separate the leachate from the solid residue.

3. Carbonation in a reactor by bubbling CO<sub>2</sub> through the leachate and pH adjustment (e.g. NaOH).
4. Second solid liquid separation step: Separation of solid PCC from the aqueous salt solution (e.g. sodium acetate).

The main differences with indirect PCC production processes come within step 1. Different leaching solutions are studied as the yield of PCC and the amount of CO<sub>2</sub> captured are dependent on the amount of leached Ca ions in the solution. The solid residue after carbonation is suitable for civil engineering due to enhanced volumetric stability and decreased leaching of trace elements (Bacocchi et al., 2010). However, Teir et al. (2015) has not noted similar decrease in leaching of other elements from stainless steelmaking slag residues after carbonation.

Eloneva et al. (2009) studied the dissolution of BOF slag with various leaching agents to produce PCC. These included two organic acids: acetic acid (CH<sub>3</sub>COOH) and propionic acid (CH<sub>3</sub>CH<sub>2</sub>COOH). The batch experiment had temperature of 20°C, solid to liquid ratio of 1g/50mL and 100rpm stirring. As presented in Figure 5, with 1M solutions, acetic acid extracted close to 98% of the Ca, and propionic acid 91%. Further addition to acid concentration did not enhance the extraction. However, strong concentrations of acids (1-2M) increased the leaching of Si, Fe and Mn whereas weak solutions (0.1-0.2M) of acetic acid remained selective towards Ca (Eloneva et al., 2009).

For leaching of Ca excess acid is favorable. Excess H<sup>+</sup> concentration is neutralized by the dissolved OH<sup>-</sup> which increases the pH during the leaching (Eloneva et al., 2009; L. Yang et al., 2019). Hence, each previously described experiment by Eloneva et al. (2009) had final pH over 7. If the acidic solution after Ca extraction is carbonated without any additional base, the acid regenerates which prevents the formation of PCC. Thus, the production of PCC requires addition of a base, e.g. NaOH, during the bubbling of CO<sub>2</sub> through the leachate (step 3) (Eloneva et al., 2008b). In addition, it is suggested that precipitation of calcium carbonate increases as the acid dissociation constant increases. Therefore, carbonation is more effective with, for example, acetic acid ( $pK_a=4.76$ ) than with formic acid ( $pK_a=3.75$ ) (Chiang et al., 2014).

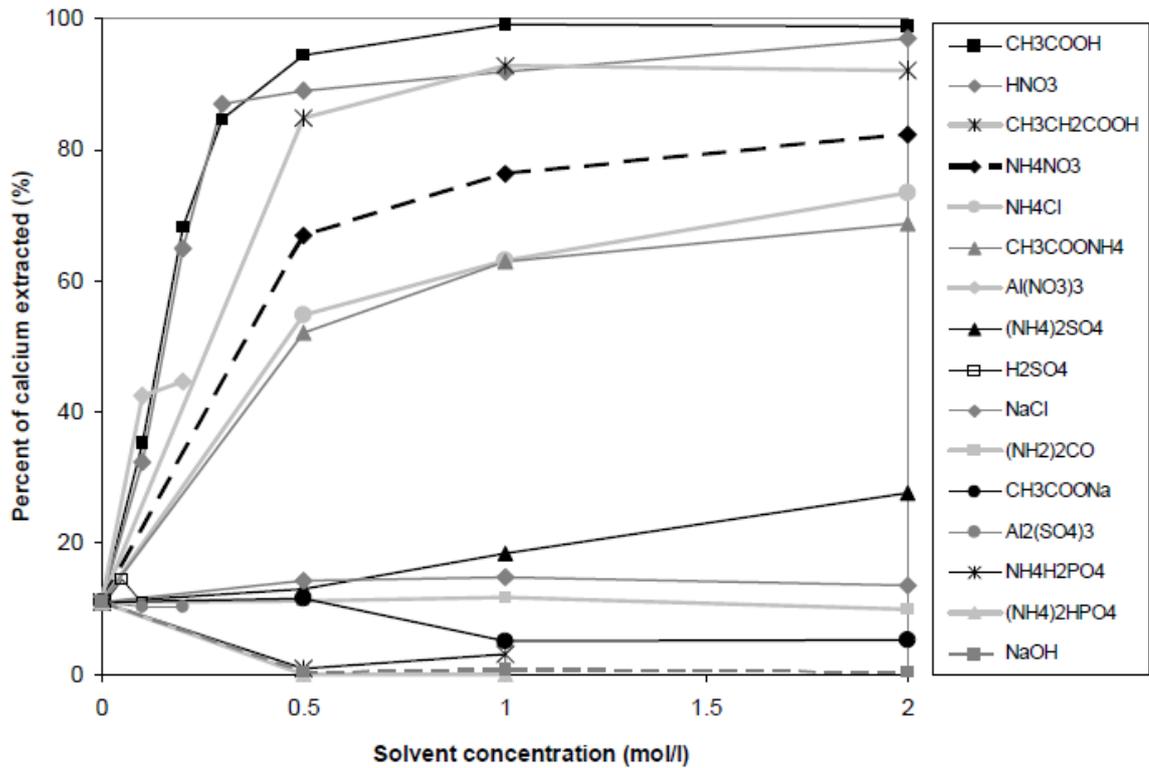


Figure 5 Calcium extracted from BOF slag in various concentrations with different leaching agents. ( $SLR = 1 \text{ g}/50\text{mL}$ ,  $T=20^\circ\text{C}$ ,  $\omega=100 \text{ rpm}$ ) (Eloneva et al., 2009)

Bao et al. studied a different process route for PCC production. Here selective leaching of Ca leaching from steelmaking slag was carried out with a solvent mixture which included organic solvent tributyl phosphate (TBP), acetic acid and water. When the mixture of TBP and acetic acid contacted water, acetic acid was partly stripped to the water phase. The acid in the water phase took part on the leaching reactions. The importance of the organic phase came within the second step, carbonation. The carbonation process is improved with addition of TBP as a part of the regenerated acetic acid is extracted to the organic phase instead of remaining in the water phase and lowering the pH of the solution which is not favorable for the precipitation of  $\text{CaCO}_3$ . However, the recovery of TBP and acetic acid are yet to be considered (Bao, Li, & Yi, 2010).

Santos et al. (2014) aimed to produce PCC by leaching the calcium from BF slag with acetic and succinic acids but ended up with precipitated calcium succinate. The extraction had two steps in which first was conducted with fresh slag and second with the residual solids from the first step. The experimental setup was as follows:  $SLR=100\text{g}/731 \text{ mL}$ ,  $C_0=0.5\text{M}$ ,  $T=80^\circ\text{C}$ ,  $\omega=1000\text{rpm}$  and  $t=60\text{min}$ . Succinic acid  $(\text{CH}_2)_2(\text{COOH})_2$  performed with higher extraction efficiency than acetic acid (30% and 21%, respectively). However, extraction efficiency

towards magnesium was as high as for calcium with both acids. With the aid of alkaline solutions (NaOH or NaHCO<sub>3</sub>), high temperature and pressure (120°C and 4000kPa) 69-74% of calcium in the leachate precipitated as calcium succinate (Ca(C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>)). In addition, disadvantageous precipitation of Al and Si were noted (Santos *et al.*, 2014). With optimization, succinic acid could have potential for significant increase in calcium extraction efficiency.

## 5.2 Processes based on mineral acids

Three mineral acids have been in the scope of steelmaking slag treatment – nitric acid (HNO<sub>3</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrochloride acid (HCl). Eloneva *et al.* (2009) studied the dissolution of steelmaking slag with various leaching agents with the aim of producing PCC. These included two mineral acids: nitric acid and sulfuric acid. The experimental setup was the same batch reactor set up as with organic acids ( $SLR=1\text{g}/50\text{mL}$ ,  $T=20^\circ\text{C}$ ,  $\omega=100\text{rpm}$ ,  $C_0=0.1\text{--}2\text{M}$ ). Figure 5 presents the amount of calcium extracted with different leaching agents. 1M nitric acid extracted 90% of calcium which is 1-8% less than with organic acids. 0.1–0.2M solutions of nitric acid were selective towards calcium. However, sulfuric acid did not show extraction towards calcium based on the calcium content of the leachate (Eloneva *et al.*, 2009) which is due to calcium sulfate precipitation. For example, Tata Steel Ltd. has applied a patent for treating BOF slag with sulfuric acid to produce yellow gypsum (calcium sulfate in the presence of iron) (“Tata Steel Ltd Files Patent Application for a Method of Producing Yellow Calcium Sulphate from LD Slag Waste Produced During the Recovery of Metallic Iron From LD Slag - ProQuest,” 2016).

In Tata Steel Ltd., Ashrit *et al.* (2015) conducted the yellow gypsum synthesis from BOF slag with  $SLR=10\text{g}/100\text{ mL}$  and 14% sulfuric acid in  $T=105^\circ\text{C}$  for 2 hours. Calcium and silica precipitated during the treatment. The slurry was neutralized with 20% lime solution and then filtered. The obtained yellow gypsum had purity of 87.98% and Fe<sub>2</sub>O<sub>3</sub> content of 5.04% which results as the yellow color of calcium sulfate. (Ashrit *et al.*, 2015) However, the paper does not discuss extraction efficiencies of the sulfuric acid, composition of the residual slag nor the volume/mass of the yellow gypsum produced. In addition, the leaching agent recycling is not considered. The acid is solely neutralized and sent to waste treatment. Aarabi -Karasgani *et al.* (2010) studied selective leaching of vanadium from BOF slag with sulfuric acid. The leachate contained only 5.6% of calcium due to calcium sulfate precipitation. However, the amount and purity of the calcium sulfate are yet undiscussed

(Aarabi-Karasgani et al., 2010). Consequently, determination of the leaching behavior of sulfuric acid towards calcium remains incoherent.

Kim and Kim (2018) conducted extraction experiments for paper sludge ash (PSA) with various leaching agents. PSA has a very similar chemical composition as steelmaking slag: CaO: 67.21, SiO<sub>2</sub>: 15.02, Al<sub>2</sub>O<sub>3</sub>: 6.62, MgO: 4.37; Fe<sub>2</sub>O<sub>3</sub>: 1.77, SO<sub>3</sub>: 2.72 and P<sub>2</sub>O<sub>5</sub>: 0.53 wt-%. Thus, the results can be used to consider which of the leaching agents could be the most efficient for Ca extraction from steelmaking slag. Acetic acid and HCl with initial concentration ( $C_0$ ) 0.7M and  $SLR$  0.04g/L gave 54 and 51% calcium extraction efficiencies whereas maximum extraction efficiencies with ammonium chloride and acetate are 33 and 30%, respectively. Table 5 presents the XRF analysis results of the remaining PSA after extraction. HCl extracts more Fe and Mg than acetic acid whereas less Ca, Si and Al (D. Kim & Kim, 2018). Si and Al are important to remain in the solid phase if it is desired to be utilized for zeolitic or geopolymer purposes.

Table 5 XRF analysis results of PSA after calcium extraction with  $SLR$  0.04g/L (D. Kim & Kim, 2018).

Component	Content (%)			
	Acetic acid	Hydrochloric acid	Ammonium chloride	Ammonium acetate
<b>CaO</b>	22.45	30.65	51.74	52.44
<b>SiO<sub>2</sub></b>	33.21	35.86	23.25	22.97
<b>Al<sub>2</sub>O<sub>3</sub></b>	10.43	18.73	11.06	10.89
<b>MgO</b>	5.51	5.07	6.27	6.12
<b>Fe<sub>2</sub>O<sub>3</sub></b>	5.53	4.68	3.01	3.18
<b>SO<sub>3</sub></b>	0.68	0.86	1.91	1.77
<b>P<sub>2</sub>O<sub>5</sub></b>	1.6	1.63	0.93	0.94
<b>TiO<sub>2</sub></b>	1.94	1.47	0.78	0.96
<b>Cl</b>	17.12	-	0.56	0.13

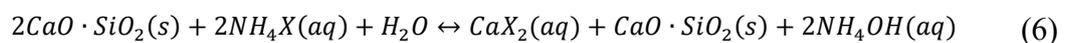
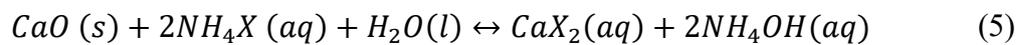
Kunzler et al. (2011) managed to extract over 85% of Ca from steelmaking slag with HCl with the purpose of CO<sub>2</sub> sequestration by the indirect carbonation process route described earlier. The result achieved with another mineral acid agrees with the results by Eloneva et al. (2009) with H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>. The  $SLR$  was 1:50,  $C_0=0.58M$ ,  $PSD$  (*particle size distribution*)=250 – 425 $\mu$ m,  $T=25^\circ C$  and  $t=30$  min with constant stirring. Different alkaline additives (KOH, NaOH or LiOH) were used to adjust the pH for carbonation (Kunzler et al., 2011) as in the case of organic acids. Höllen et al. (2018) conducted similar indirect

carbonation experiment for stainless steel production EAF slag with a mineral acid as a leaching agent. The results agree with other studies, ~90% of Ca is extracted. However, depending on the slag batch, Fe is leached in significant amounts. The concentration of Fe in the leachate can be higher than Ca which is problematic when considering the purity of desired product. Advantageously, HCl does not leach Cr or F from the slag. Due to significant leaching of other elements, pH of the leachate was increased before carbonation. Addition of aqueous solution of NH<sub>3</sub> caused Si, Fe and Al to precipitate at pH 9. However, it caused a minor loss of Ca from the leachate (Höllen et al., 2018). Thus, a process with several precipitation steps decreases the yield of final product.

All in all, mineral acids do not leach Ca of steelmaking slag effectively compared to organic acids at same pH (Eloneva et al., 2009; D. Kim & Kim, 2018; Murakami et al., 2011). In addition, the regeneration of mineral acids is typically energy intensive. Even in low concentrations, inorganic acids are not selective towards calcium (Chiang et al., 2014) which requires additional purification steps for the leaching agent and makes the production of pure Ca product difficult.

### 5.3 Processes based on ammonium salts

Ammonium salts in aqueous solutions, such as ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) and ammonium chloride (NH<sub>4</sub>Cl), extract calcium selectively from the steelmaking slag (Eloneva et al., 2009; Said et al., 2013). Formulas (5) and (6) present the extraction reactions where X presents the salt (Mattila, Grigaliu-naite, & Zevenhoven, 2012).



Eloneva et al. (2009) studied the dissolution of BOF slag with various leaching agents to produce PCC. These included six ammonium salts: ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>), ammonium chloride (NH<sub>4</sub>Cl), ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), ammonium di-hydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) and diammonium hydrogen phosphate ((NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>). The experimental setup was identical with the mineral and organic acid experiments (*SLR*=1g/50mL, *T*=20°C, *ω*=100rpm, *C*<sub>0</sub>=(0.1-2 M)). Among the salts, the

most promising results were obtained with ammonium nitrate, ammonium chloride and ammonium acetate. (Figure 5) In 1M solutions, calcium were extracted 74%, 61% and 60%, respectively (Eloneva et al., 2009). Teir et al. (2009) have filed a patent for calcium and vanadium extraction from alkaline industrial waste and by-products with ammonium salts.

Extraction with ammonium salts results in higher final pH of the solution than with acid (Yadav & Mehra, 2017) which is favorable to carbonation (Eloneva *et al.*, 2009; Yang *et al.*, 2019). Thus, the indirect carbonation process step 3 (carbonation) does not require addition of a base when ammonium salts are used as leaching agents and the leaching agent is regenerated during carbonation without formation of a by-product. Ammonium salt solutions do not extract Al, Cr, Mg, V, Mn or Fe from the steelmaking slag. Therefore, ammonium salts are selected as leaching agents for selective calcium extraction when producing PCC. (Eloneva et al., 2009; Said, 2017) However, Kim and Kim (2018) noticed leaching of Fe, Ti and Si from PSA to be higher than with acids (Table 5) (Kim & Kim, 2018) This may be due to mineralogical differences between PSA and steelmaking slag.

In addition to BOF slag, Eloneva et al. (2009) studied calcium extraction from BF, DS and LF slag with ammonium salts. Only 10% of calcium from BF slag, 25% from LF and over 50% from DS slag was dissolved. The result is reasoned with free lime content of the slags. LF and BF slag do not contain any free CaO which is why the extraction results are poor (Eloneva et al., 2009).

#### **5.4 Methods and factors affecting process efficiency and selectivity**

The controlling mechanism of calcium extraction from steelmaking slag is the chemical reaction at first (Lekakh, Rawlins, Robertson, Richards, & Peaslee, 2008). During the leaching of the solid slag, a thin impurity layer forms on the surface which limits the reaction between the leaching agent and Ca- containing phases in the unreacted core (Aarabi-Karasgani et al., 2010; Said, 2017) which is the main issue with efficient extraction from the solid slag. Hence, diffusion through the porous layer becomes the rate controlling mechanism (Lekakh et al., 2008). Thus, methods such as sonication, ball milling and heat treatment have been studied to overcome this issue by breaking the layer of impurities during the leaching (Lee et al., 2017; Murakami et al., 2011; Said, et al., 2015).

Ball milling treatment of BF slag for selective Ca recovery was studied with various leaching agents by Murakami et al. (2011). One gram of BF slag powder, 30mL of acid solution and

30 SiC balls ( $d=10\text{mm}$ ) were placed in a rotating vessel ( $\omega=75\text{rpm}$ ) at room temperature. The treatment was repeated for the solid slag residue. Ball milling enhanced the extraction of calcium by almost twofold for acetic, tartaric, formic and citric acid compared to static experiments (Figure 4). Lactic acid extracted calcium only with ball milling treatment whereas improvement in calcium extraction did not occur with HCl (Murakami et al., 2011). However, the study does not compare ball milling treatment with continuous stirring with an impeller. Ball milling during the leaching guarantee efficient mixing and reduces the particle size which increases the reactive surface area.

Lee et al. (2017) studied ball milling and heat treatment as a method to improve selective calcium extraction with  $\text{NH}_4\text{Cl}$  as a leaching agent. Ball milling ( $\omega=360\text{rpm}$ ,  $t=72\text{h}$ ) reduced the particle size and calcium extraction rate improved. The results of ball milling agreed with the study with acids by Murakami et al. (2011) presented earlier in Figure 4. Within two minutes, the ball milled samples had released a twofold amount of calcium compared to the raw samples. However, the effect of ball milling was not noted after 5 minutes of leaching. The heat treatment ( $T=650^\circ\text{C}$ ,  $t=5\text{min}$ ), did not enhance the calcium extraction efficiency nor the initial extraction rate (Lee et al., 2017).

Said et al. (2015) used ultrasound to improve calcium dissolution from steelmaking slag to  $\text{NH}_4\text{Cl}$  solution. The  $SLR$  was  $20\text{g/L}$  and  $C_0$  was  $1\text{M}$ . As previously stated, silica and other remaining species in the steelmaking slag form a thin porous layer on the steelmaking slag particle surface during Ca leaching. The aim of the study was to remove the layer which prevents Ca leaching with ultrasound and compare the results with extraction efficiencies achieved with mechanical agitation. The treatment with ultrasound enhanced calcium extraction from  $50\text{-}74\mu\text{m}$  and  $500\text{-}1000\mu\text{m}$  steelmaking slag particles by 31 and 20%, respectively. The highest extraction efficiency (96%) was achieved for small particles whereas highest efficiency for large particles was 38%. In addition, ultrasound improved the initial extraction rate. However, the sonication treatment has high energy consumption which would make it feasible only if it would require the same amount of energy as mechanical agitation (Said et al., 2015). In addition, sonication increases the average rate of carbonation (R. Santos, Ceulemans, Francois, & Van Gerven, 2011).

As the presented methods state, grain size and  $SLR$  have significant effect on the extraction efficiency. Optimization of these factors increase the reactive surface area and enhances the mass transfer (Lee et al., 2017; Said et al., 2013; Xu et al., 2012). Low  $SLR$  shows higher

extraction efficiency (Hall et al., 2014; Kunzler et al., 2011; Said, 2017) which increases the extraction reactor's volume and decreases the economic feasibility. For efficient Ca extraction, *SLR* of 100g/L is a sufficient optimization with reactor volume (Eloneva, Said, Fogelholm, & Zevenhoven, 2010; Hall et al., 2014). As presented in Figure 6, increase in particle size decreases dissolution of minerals from steelmaking slag. However, the influence is greater for Ca as it is for Mg, Si or Fe (Kunzler et al., 2011; Yadav & Mehra, 2017). The optimum PSD is 250 – 425 $\mu\text{m}$  (Kunzler et al., 2011). The grain sizes should not exceed 500 $\mu\text{m}$  for efficient Ca extraction (Eloneva et al., 2010). Due to enhanced Ca extraction, smaller grain size results in higher pH of the leachate after slag treatment (Eloneva et al., 2010; Said et al., 2013).

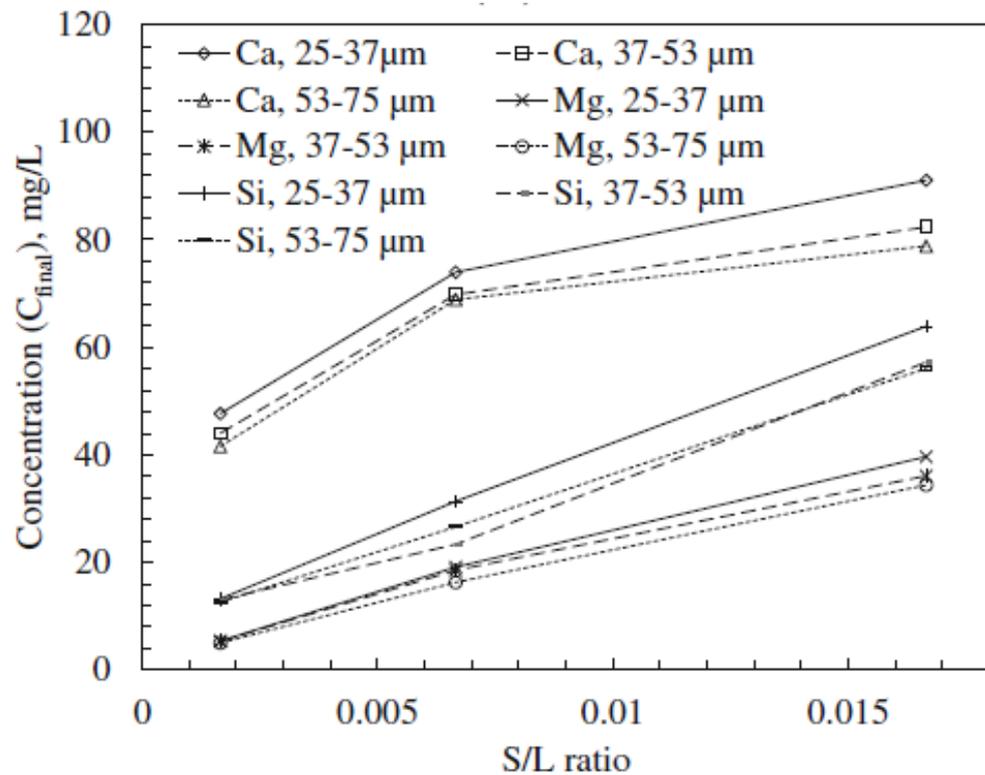


Figure 6 Effect of solid to liquid ratio and grain size on aqueous dissolution of BOF slag (Yadav & Mehra, 2017).

Chiang et al. (2014) and Teir et al. (2007) have studied calcium extraction from steelmaking slag with acetic acid in different concentrations. Teir et al. (2007) concluded that solution of 10 wt-% (~1.7M) of acetic acid extracts calcium as efficiently as 33.3 wt-% (~5.5M) acetic acid. Chiang et al. (2014) found that the extraction efficiency is higher with initial solution concentration of 2.0M compared to 1.0 and 0.5M. However, the lower pH of the solution made the extraction less selective towards calcium (Bao et al., 2010; Chiang et al., 2014). In

the case of ammonium salts, extraction efficiency is significantly improved from 0.1 to 2M. However, further increase from 2 to 6M does not show improvement in extraction (Figure 7) (Lee et al., 2017). Ammonium salt concentration over 1M, increases the leaching of other elements from the slag (Said et al., 2015) especially magnesium (Lee et al., 2017).

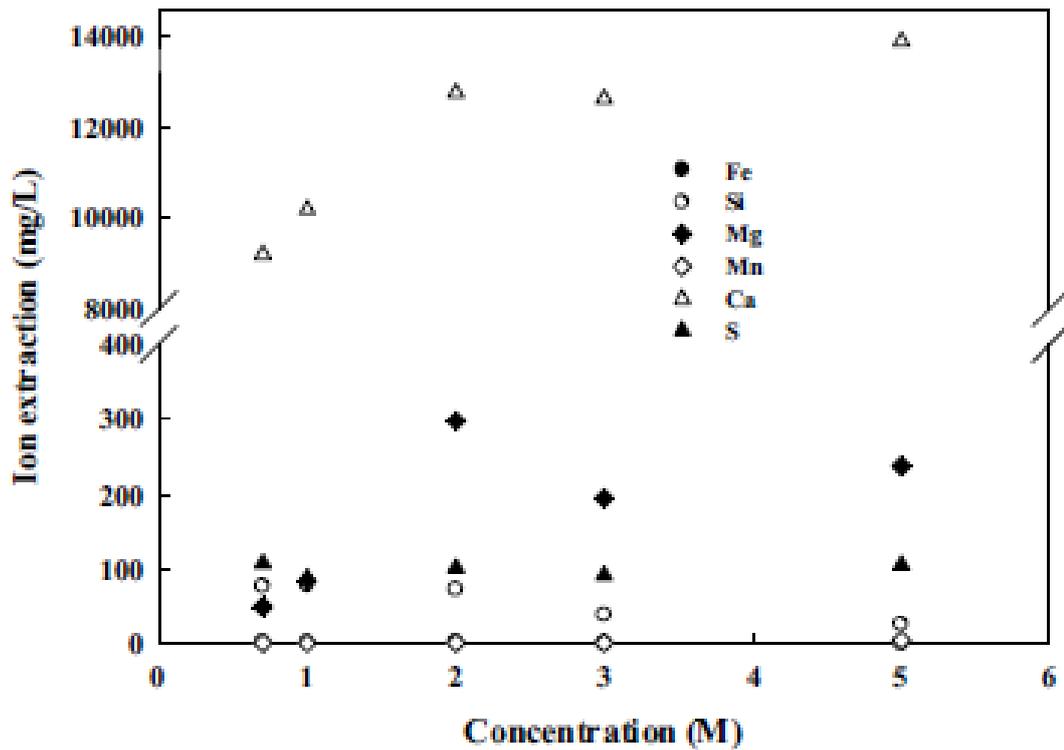


Figure 7 Effect of leaching agent concentration on steelmaking slag leaching. ( $SLR = 100\text{g/L}$ ,  $C_0(\text{NH}_4\text{Cl})=2\text{M}$ ,  $= 45^\circ\text{C}$ ) (Lee et al., 2017)

The effect of temperature and reaction time on the extraction of Ca have also been studied. Dissolution of Ca is an exothermic reaction which increases the reaction temperature slightly ( $<1^\circ\text{C}$ ) (Eloneva et al., 2010). Teir et al. (2007) conducted extraction experiments with acetic acid in different temperatures ( $30^\circ\text{C}$ ,  $50^\circ\text{C}$  and  $70^\circ\text{C}$ ). The study showed that Ca extraction becomes faster and results in lower Ca extraction as temperature increases. This indicated that rise in temperature decreases the dissolution of BF slag (Teir et al., 2007). Increase in temperature have found to enhance the dissolution of heavy metals from steelmaking slag in aqueous media (Yadav & Mehra, 2017). With acid solutions, increase in temperature ( $25$  to  $70^\circ\text{C}$ ) does not have an effect on Ca leaching whereas the leaching of Mg and Fe increases ( $85$  to  $88\%$ ,  $36$  to  $84\%$  and  $10$  to  $38\%$ , respectively) (Kunzler et al., 2011). Most of the calcium leaches rapidly. After the first 20-30 minutes, no significant increase in calcium extraction is noted during the next 30 minutes (Said et al., 2015).

## 6 Comparison of calcium leaching methods from steelmaking slags

The selective leaching of calcium from steelmaking slag is studied with various leaching agents, such as mineral acids, organic acids and salt solutions. Ammonium salts are the most efficient leaching agents among different salts. Organic acids obtain the highest calcium extraction efficiency, then mineral acids and finally ammonium salts. High acidity improves the Ca extraction. However, solutions with high acidity does not remain as selective towards calcium and an increase in Mg, Si and Al concentrations in the leachate are noted.

The optimum conditions for selective leaching of Ca from steelmaking slag are not significantly dependent on the leaching agent used. Studies with various leaching agents are in agreement that particle size should be under 500 $\mu\text{m}$ , temperature and pressure may remain uncontrolled, reaction time of 30-60minutes is sufficient, solid to liquid ratio of 100g/L is the maximum, initial concentration of the leaching agent is between 1 and 2M and constant stirring must be applied.

The suitable leaching agent for selective Ca recovery from steelmaking slag is also dependent on the desired product. Ammonium chloride ( $\text{NH}_4\text{Cl}$ ) has proven to be well recyclable leaching agent to produce precipitated calcium carbonate. Carbonation favors high pH, which requires addition of a strong base such as NaOH if the leaching agent used is acid. Hence, a salt of the acid used is formed as a by-product. The PCC production process does not require an addition of a base when ammonium salts are used as the leaching agent. If the aim is to produce PCC, ammonium salts are the obvious choice. If the goal is to remove as much calcium as possible from the steelmaking slag, organic acids have shown the most promising results. Herein, the obtained products would be calcium salts of given acids. The purity of the salt, and the conditions required for efficient leachate purification require further research.

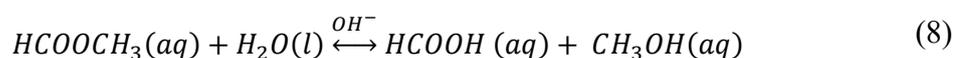
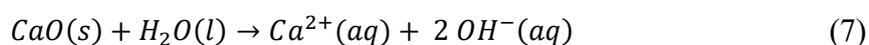
Current research for production of value-added calcium products have mainly focused on BF and BOF slag. Literature concerning LS and DS slag are limited. In addition, wider product range is required. The current research focuses almost solely to PCC. The goal of the experimental section is to find and prove of concept for other possible value-added calcium products.

## 7 Potential calcium products from steelmaking slags

In this Master's Thesis, synthesis of three potential novel value-added calcium products are studied experimentally. Theory and background of these; calcium formate, calcium salt of a hydroxy acid and calcium soap are discussed in this chapter.

### 7.1 Production routes of calcium formate

Different slag samples are tested to catalyze alkyl ester hydrolysis reaction to produce calcium salt of corresponding acid as a stable intermediate. Herein, the hydrolysis of methyl formate is studied as presented in the following reaction steps (Equation (7)-(9)).



First, the calcium oxide (CaO) is leached into the aqueous phase. The released hydroxide ions (OH<sup>-</sup>) catalyze the hydrolysis reaction of methyl formate to produce formic acid (HCOOH) and methanol (CH<sub>3</sub>OH). Finally, the free hydroxide ions neutralize the acid to water and calcium ions (Ca<sup>2+</sup>) form calcium formate with formate ions (HCOO<sup>-</sup>).

#### 7.1.1 Formic acid synthesis

Global production of formic acid (methanoic acid; HCOOH) was 621 000t in 2012. The main producers in Europe are BASF and Kemira which produce formic acid by hydrolysis of methyl formate. Another significant method is through acidolysis of formate salts (Hietala et al., 2016).

Since 1980's, formic acid has been commercially produced through a two-step process. First methanol is carbonated with the aid of a basic catalyst, typically sodium or potassium methoxide (NaOCH<sub>3</sub> or KOCH<sub>3</sub>) as presented in equation (10). The product, methyl formate, is then hydrolyzed to form formic acid and methanol according to equation (11). The reaction is typically autocatalysed by the formic acid. The methanol from the second step (equation (11)) is circulated back to the first step (equation (10)) (Hietala et al., 2016).

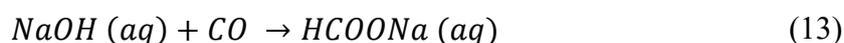


Hydrolysis of methyl formate has low conversion ( $K_c$  around 0.2) (Jogunola et al., 2012). Thus, different methods for improving the yield of the process are studied. The most common method is to include an excess of water which creates problems with energy efficient concentrating method for the product (Hietala et al., 2016). Another is to add a complexing agent (e.g. imidazole or tertiary amine) which forms a salt-like compound with formic acid, thus driving the reaction forward (WO2014082845A1, n.d.; Jogunola et al., 2017). A third method, currently being industrially utilized by Kemira, to overcome the low conversion issue is conducting the hydrolysis reaction in a chromatographic reactor. The bed is packed with ion exchange material which simultaneously catalyzes the hydrolysis reaction and separates the products (US6,429,333 B1, 2002).

Perstorp in Sweden is the largest formic acid producer which produces formic acid from formate salts. Formate salts (sodium, potassium and calcium formate) reacts with mineral acids to produce formic acid and salt of given acid (equation (12)). The disadvantages of this process route are the consumption of mineral acid (e.g. sulfuric acid) and the formation of the byproduct (Hietala et al., 2016).



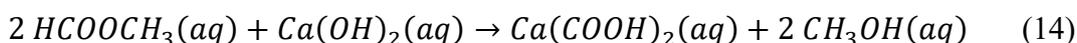
There are Chinese patents where formic acid is produced from carbon monoxide (CO) and alkali metal or alkali earth metal hydroxides when the resulting alkali metal salt is then acidified with phosphoric acid. The byproduct, phosphate salt, can be utilized as a fertilizer. In addition, formate salts can be produced with direct reaction between a base (e.g. NaOH or KOH) and CO (example reaction presented in equation (13)) (Hietala et al., 2016).



As steelmaking slags have a high calcium content, a combination of these methods may be viable to increase the yield of formic acid by producing a formate salt as an intermediate. Of course, the formate salt can be considered as a product instead of an intermediate if it is not further acidified.

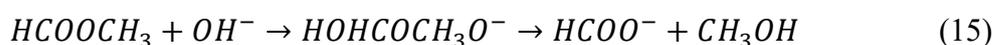
### 7.1.2 *Synthesis of calcium formate*

Calcium formate can be produced directly by dissolution calcium into formic acid or from aqueous solution of calcium hydroxide and methyl formate (equation (14)). First, as in reaction (7), the solid CaO from steelmaking slag is released in the aqueous phase. Second, the formed hydroxide catalyzes methyl formate hydrolysis to produce formic acid and methanol (equation (8)). Formate anions react with leached calcium cations to calcium formate (equation (9)). Ideally, the decreasing content of Ca(OH)<sub>2</sub> in the solution would increase the dissolution of calcium from the slag and would increase the yield of calcium formate. The total reaction is presented as:



Producing calcium formate from methyl formate and calcium hydroxide has an open patent by Evonik Degussa GmbH. As methyl formate is added, the temperature of the solution warms to 70°C spontaneously and the product obtained is precipitated with small pH adjustments (DE4007665C1, 1990). In addition, in a Chinese patent a method has been presented to produce calcium formate from calcium hydroxide and CO in a similar manner as presented earlier in equation (13) for sodium (CN201325936Y, 2008).

The reaction of an alkyl ester and a base is commonly known as a saponification reaction. Reaction mechanism of methyl formate saponification reaction has a tertiary oxidized intermediate. The formation of the intermediate is the rate limiting step. The dominant reaction mechanism (B<sub>AC</sub>2) of methyl formate saponification is presented in equation (15) (Pliego, Jr. & Riveros, 2002).



## 7.2 Calcium salt of hydroxy acids

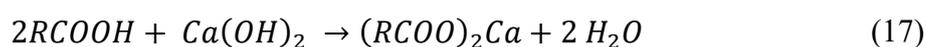
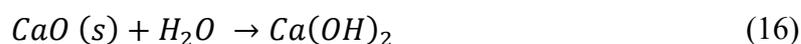
Hydroxyacids, or hydroxycarboxylic acids, are common substances in all living in nature. Aliphatic hydroxyacids have one or more hydroxyl group in addition to one or several carboxyl group. Depending on the skeletal structure of the hydroxyacids, they can be divided into three groups: 1) 2- or  $\alpha$ - hydroxycarboxylic acid, 2) 3- or  $\beta$ -hydroxycarboxylic acid or 3) hydroxycarboxylic acid which has the hydroxyl group located further than the fourth carbon atom. Familiar examples of hydroxyacids are citric acid, lactic acid and glycolic acid. Due to the proximity and polarity of the hydroxyl group, hydroxy acids are stronger acids than similar carboxyl acids. The highly acidic nature could benefit the leaching of calcium from steelmaking slag (Miltenberger, 2000).

The process has potential in combining circular economy of pulp and steel industries. Heinonen and Sainio (2019) have successfully separated hydroxy carboxylic acids from spent soda and kraft black liquors. These contain isosaccharinic, glycolic, lactic and 2-hydroxybutanoic acids which are separated in different fractions with 99 wt-% purity. For example, calcium salt of glycolic acid has commercial use in leather industry (Miltenberger, 2000). Commercial glycolic acid is efficient in leaching calcium carbonate, which increases the interest of its use for leaching calcium also from steelmaking slag (Chemours, 2016).

Lactic acid and the salts of lactic acids are mainly used in food industry, which makes difficulties in combining it with a metal containing by-product from steel industry. The directives and laws concerning industrial side-stream derived products suitable for feed are strict and make additional waiting periods to get the product on the market. However, lactic acid is cheap and easily available and has only one carbon atom more than glycolic acid, it is further studied in experimental part of this Thesis.

## 7.3 Calcium soap

Calcium soaps are commonly formed from pure calcium chloride, calcium hydroxide or lime in a direct reaction between straight chained saturated aliphatic acids and/or unsaturated carboxylic acids. The direct reaction typically has a minor aqueous media and the two step reaction is as follows: (Nora & Koenen, 2010)



As a novel utilization, calcium soap benefits ruminants milk productivity and fertility (Handojo et al., 2018). However, the material derived from steel industry process fluid must be far developed before utilization as a feed for cattle. Calcium stearate ( $\text{Ca}(\text{C}_{18})_2$ ) is the most widely used calcium soap. It is used for example in plastic production as lubricant. Interestingly, common cooking oil has a high content (almost 70%) of 18- carbon length substances. Thus, the idea presented in this Thesis could combine a waste from food industry with a potential, yet inefficiently utilized by-product from steel industry.

The novelty of this product lies on the source of calcium oxide being steelmaking slag. There is a US patent application concerning production of calcium soap from calcium oxide in which 1–2.5 equivalents of calcium oxide is added per one equivalent of unsaturated raw material and 2–5 equivalents of water per one equivalent of calcium oxide (US6392075, 2000). With similar reaction conditions, calcium soap is also patented to be produced from animal or vegetable fats and utilized as animal feed (EP 1 800 546 A1, 2007).

## 8 Experimental procedures

The aim of the experimental research was to utilize steelmaking slag to produce a calcium product. Three calcium salts were synthesized: 1) calcium formate, 2) calcium salt of hydroxy acid and 3) calcium soap. Preliminary experiments of each reaction were carried out with pure CaO for reference. Selectivity of the slag leaching experiments and yield of the CaO leached are defined as:

$$\text{Selectivity} = \frac{m(\text{leached CaO})}{m(\text{total of leached elements})} \times 100\% \quad (18)$$

$$\text{Yield}_{\text{CaO}} = \frac{m(\text{CaO})_{\text{initial slag}} - m(\text{CaO})_{\text{residue slag}}}{m(\text{CaO})_{\text{initial slag}}} \times 100\% \quad (19)$$

For calcium formate, two process routes were examined. In the second case, calcium formate was produced through methyl formate hydrolysis in which case the yield and conversion of the reaction were determined as:

$$\text{Yield}_{\text{MeOH}} = \frac{n(\text{product})_{\text{out}}}{n(\text{product})_{\text{calc.max}}} \times 100\% \quad (20)$$

$$Conversion = \frac{n(reactant)_{in} - n(reactant)_{out}}{n(reactant)_{in}} \times 100\% \quad (21)$$

### 8.1 Steelmaking slag characterization

SSAB Raahe provided four slag samples:

1. Granulated Blast Furnace (BF) slag
2. Desulfurization (DS) slag
3. Converter (LD) slag
4. Ladle slag (LS)

Steelmaking slags were crushed (Rotor mill/Hammer mill (Retsch SK300)) and sieved (HAVER&BOECKER, EML DIGITAL PLUS, Test sieve shaker) to a particle size of <math><500\mu\text{m}</math> to achieve efficient leaching of calcium based on the literature survey.

Single Reaction Chamber Microwave digestion system (Milestone, UltraWAVE) was used to dissolve 50mg of the slag sample to aqua regia (3mL HCl + 1mL HNO<sub>3</sub>) for determination of the chemical composition after the experiment. After microwave digestion, each sample was diluted with pure water to a volume of 50mL. The chemical composition was analyzed with ICP-MS.

Leached elements of the samples were determined by Inductive Coupled Plasma Mass Spectrometry (ICP-MS) Agilent Technologies 7900. Each sample was diluted with 1% HNO<sub>3</sub> (ROMIL-SpA, 67-69%) + 1% HCl (ROMIL-SpA, 34-37%).

### 8.2 Synthesis of calcium formate

Calcium formate was synthesized by two different process routes, direct leaching with formic acid and through methyl formate hydrolysis. The methyl formate hydrolysis reactions were carried out with commercial methyl formate even though it could be produced from methanol and carbon monoxide as earlier presented.

Constant variables in each calcium formate production experiment were *SLR* and particle size which are chosen according to the literature survey. Efficient leaching of calcium from steelmaking slag were found to be achieved with *SLR* =100g/kg and grain size<math><500\mu\text{m}</math> in the literature. The effect of leaching agent strength and temperature are studied and results between different slags are compared. The effect of leaching agent strength is examined by

three different reaction conditions; 1) FoA was 1.5 times stoichiometric excess, 2) FoA and CaO were stoichiometric equal and 3) CaO was 1.5 times stoichiometric excess. The amount of substance of the leaching agent is determined based on initial characterization of the steelmaking slag samples according to equation (22). The initial conditions of each calcium formate experiment are presented in Tables 6 and 7. For example, the calculation of initial masses of experiment 1 with BF slag and formic acid: the *SLR* is constant 100g/L. Hence, when the total mass of the leaching agent is 0.5kg, amount of the solid is 50g. If the initial CaO content of BF slag is 38.5%, according to equations (7)-(9), required amount of FoA/MeFo is  $(0.385 \times 50\text{g})/M(\text{CaO}) \times 3 \times M(\text{FoA}) = 48.42\text{g}$ . The amount of water is determined from total mass of the liquid phase being 0.5kg.

$$m(\text{solvent}) = \frac{\text{wt}\% \text{ of CaO} \times m(\text{slag})}{M(\text{CaO})} \times a \times M(\text{solvent}) \quad (22)$$

Where,  $a$  stoichiometric multiplier

### 8.2.1 Materials and methods

Desired amount of deionized water was weighted in which weighted amount of formic acid (FoA) (Riedel-de Haën, 98-100%) was added according to the experimental plan of reaction conditions (Table 6). The diluted FoA was poured into the reactor and thermostated into desired temperature. The reactor setup included 1L jacketed glass reactor (Syrris Orb) which contained two baffles, an impeller and a reflux, a thermostat (Lauda E300), an online thermometer (Omega HH374) and an online pH recording (Consort C3010 plugged into PC). Depending on the experiment, either pure CaO (ACROS, >97%) or steelmaking slag sample was weighted and added to the reactor. The mixture was under constant stirring (800rpm). All four slag samples were tested giving total of 16 experiments. Each experiment was carried out for 2 hours. Total of 16 samples by volume of 2mL were collected and immediately filtered with a membrane syringe RC 0.45 $\mu\text{m}$ .

Table 6 The reaction conditions for formic acid leaching experiments. The labeled reaction conditions were 1) FoA = 1.5x stoichiometric excess, 2) FoA and CaO = Stoichiometric equal, 3) CaO = 1.5x stoichiometric excess and 4) condition 2 in higher temperature.

	<b>-FoA-1</b>	<b>-FoA-2</b>	<b>-FoA-3</b>	<b>-FoA-4</b>	<b>CaO-FoA-3</b>
<b>T, °C</b>	25	25	25	70	25
<b>SLR, g/kg</b>	100	100	100	100	100
<b>m(liquid), g</b>	500	500	500	500	450
<b>m(solid), g</b>	50	50	50	50	44
<b>n(CaO)/n(FoA), -</b>	0.33	0.50	1	0.50	1

In the case of methyl formate (MeFo) hydrolysis experiments, the setup was identical as in the FoA experiments. The experimental procedure differed slightly as only the pure water was thermostated before the experiments due to the rapid nature of the reaction between MeFo and water. After the pure water had reached the desired temperature, the weighted amount of CaO or steelmaking slag was added to the reaction. The mixture was under constant stirring (800rpm). Directly after the addition of CaO source, weighted amount of methyl formate (Merck KGaA, 95-97%) was added to the reactor. Total of 6-11 samples by volume of 2mL were collected and immediately filtered with a membrane syringe RC 0.45 $\mu$ m. The experiments were carried out 30min. The experimental conditions, which are presented in Table 7, were selected to correspond with the FoA experiments. The possible amount of FoA formed in the MeFo experiments is the same amount of substance as in the initial leaching experiments with FoA. The first reaction condition 1, where MeFo was as an excess was studied with all four slag samples. Reaction conditions 2-4 were studied only with BOF slag.

Table 7 The reaction conditions for CaO catalyzed methyl formate hydrolysis experiments. The reaction conditions were 1) MeFo = 1.5x stoichiometric excess, 2) MeFo and CaO = Stoichiometric equal, 3) CaO = 1.5x stoichiometric excess and 4) condition 2 in higher temperature.

	<b>-MeFo-1</b>	<b>-MeFo- 2</b>	<b>-MeFo-3</b>	<b>-MeFo-4</b>	<b>CaO-MeFo-3</b>
<b>T, °C</b>	25	25	25	50	25
<b>SLR, g/kg</b>	100	100	100	100	92
<b>m(liquid), g</b>	500	500	500	500	460
<b>m(solid), g</b>	50	50	50	50	40
<b>n(CaO)/MeFo), -</b>	0.33	0.50	1.00	0.50	1

### 8.3 Calcium salt of hydroxy acids

The leaching of CaO from steel slags with organic acids is already comprehensively researched by Eloneva et al. (2009). However, hydroxy acids are cheaply available as unpurified salts, for example as basic sodium salt solutions. Thus, sodium lactate in a specified pH of 12 was studied here. Figure 8 presents the skeletal formula of lactic acid. It is an  $\alpha$ -hydroxy acid due to the position of the hydroxyl group from the carboxyl group.

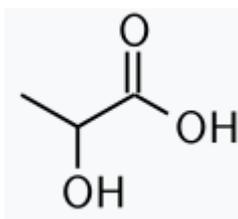


Figure 8 Skeletal formula of lactic acid.

#### 8.3.1 Materials and methods

Lactic acid (VWR Chemicals GPR Rectapur 90% aqueous solution) was diluted with pure water and pH was adjusted to 12 with NaOH (EMSURE, >99%). Total mass of the solution was 500g. The solution was thermostated to 25 °C. The experiment started with addition of CaO/steelmaking slag to the solution as such, that the amount of substance was equal with CaO and lactic acid. Hence, according to stoichiometry, CaO was in excess. The mixture was under constant stirring (800rpm). Total of 11 samples were collected and immediately filtered with a membrane syringe RC 0.45 $\mu$ m during the 30min experiment. Initial reaction conditions are gathered in Table 8. Experiments with pure CaO had slightly lower *SLR* as the amount of CaO was not 100% in the slags. However, both pure CaO and BOF slag experiment are comparable with the FoA leaching experiments. The experimental setup was also identical with the FoA leaching experiment. BOF slag was selected based on its high CaO content the possibility of containing free CaO.

Table 8 Initial reaction conditions for leaching CaO with a hydroxy acid. Both experiments were carried out with lactic acid which is set to pH 12 with NaOH. SL stands for sodium lactate.

	<b>CaO-SL</b>	<b>BOF-SL</b>
<b>T, °C</b>	25	25
<b>pH</b>	12	12
<b>SLR, g/kg</b>	84.38	100
<b>m(liquid), g</b>	500	500
<b>m(solid), g</b>	42.19	50
<b>n(CaO)/(Lactic acid), -</b>	1	1

## 8.4 Calcium soap

Commercial rapeseed oil was chosen for the saponification reaction as the goal was prove of concept. Later, for example waste cooking oil could serve the purpose to enhance the circular economy of both, steel and food industry.

### 8.4.1 Materials and methods

Commercial rapeseed oil (Rainbow) and pure water (20% of the mass of oil) were weighted and added to the reactor to thermostate according to experimental conditions presented in Table 9. The experiment started when weighted amount of pure CaO or BOF slag was added so that the molar ratio between CaO and oil is 2. Ratios between all three substances were chosen based on literature (Handojo et al., 2018; Mata-Segreda\*, 2002; EP 1 800 546 A1, 2007). The amount of substance of rapeseed oil was determined with the aid of Komers et al., 2001 where molar masses of different glycerides are quantified. The experimental setup for the saponification was the same as in previous leaching experiments. However, pH is not measured due to the small volume of the aqueous phase. The mixture was under constant stirring (500rpm).

The pure CaO saponification experiment was kept going for 1.5 hours and a total of 16 (7-10 mL) samples was collected. The samples were centrifuged for phase separation.

In the saponification reaction between BOF slag and rapeseed oil-water mixture, a total of 5 samples was collected with a siphon for 2 minutes during a 2-hour experiment. The volumes of the samples varied between 30 and 40mL.

Table 9 Initial experiment conditions for production of calcium salt of fatty acid.

Type of solid	CaO-F	BOF-F
T, °C	25	40
SLR, g/kg	106	105
m(liquid), g	481	455
m(solid), g	48	51
n(CaO)/n(Triglycerides), -	2	2

## 9 Analytical methods

Gas chromatography (GC) (Agilent Technologies 6890N) was used to determine the amount of reacted methyl formate and the amount of methanol formed. Helium was used as a carrier gas, TCD as detector, 1  $\mu$ L as the injection volume and Zebron ZB-WAXplus column which had 25m of length, 0.32mm inner diameter and 0.50  $\mu$ m film thickness. The calibration of MeFo was between 0.7 and 30.7 wt-% and the calibration of methanol (MeOH) (VWR Chemicals, 100%) between 0.7 and 17 wt-%. One standard was diluted for each analysis to determine the accuracy of the calibration. The pH's of the samples were measured before GC analysis due to the assumption that hydrolysis reaction was not fully quenched after the catalyst was removed in the sampling.

For the slag saponification experiment, GC was utilized to determine the amounts of di- and triglycerides. The analysis procedure had a FID detector, hydrogen as a carrier gas and an Agilent HP-1/SIMDIST column with a length of 15m, diameter of 0.530mm and film thickness of 0.15  $\mu$ m.

Inductive Coupled Plasma Mass Spectrometry (ICP-MS) Agilent Technologies 7900 was used to identify aqueous metals. Samples from FoA, MeFo and SL experiments were analyzed with ICP-MS. Each sample was diluted with 1% HNO<sub>3</sub> (ROMIL-SpA, 67-69%) + 1% HCl (ROMIL-SpA, 34-37%).

Single Reaction Chamber Microwave digestion system (Milestone, UltraWAVE) was used to dissolve 0.05g of the residue solid to a strong acid mixture (3mL HCl + 1mL HNO<sub>3</sub>) for determination of the chemical composition after the experiments. After microwave digestion, each sample was diluted with pure water to a volume of 50mL. The chemical composition was analyzed with ICP-MS. Slag residues were analyzed in all four calcium product syntheses.

In the case of pure CaO experiments, Leco CHN628 (Carbon, hydrogen & nitrogen) analyzer was deployed for determination of the carbon content of the solid residue. 100mg of the sample was weighted and fed to the analyzer. The amount of precipitated calcium salt was calculated based on the carbon content and stoichiometry.

## **10 Results and discussion**

The chapter begins with presentation of the steelmaking slag characteristics as it is the raw material studied. Each synthesis studied has results with both pure CaO and steelmaking slag. First in each chapter, which discuss the calcium products, is presented the results of the preliminary experiments with pure CaO. Second, experiments with steelmaking slag samples are presented and compared with each other and with pure CaO results.

### **10.1 Steelmaking slag characterization**

Analysis results are presented as oxides due to the knowledge of typical compositions of steelmaking slags. Table 10 presents the chemical compositions of <500 $\mu$ m steelmaking slag samples used in the following experiments. The highest calcium content was in the BOF slag (45 wt-%), second highest in the desulfurization slag (44 wt-%) and the lowest in BF and LF slags (~37 wt-%). These agree with literature findings presented earlier in Table 2.

The largest difference between literature and the analysis results (Table 10) are in the silicon dioxide content. The silicon dioxide should cover around 20 wt-% of steelmaking slags. Different silicates did not dissolve in microwave acid digestion. Due to the hazardous nature of stronger leaching agents (HF) they were not further dissolved. In addition, it was assumed that the silicates do not significantly dissolve during the leaching experiments as they did not dissolve in aqua regia and extreme reaction conditions. Thus, silicon is not discussed later in this work.

Other elements of the steelmaking slags were in a good agreement with literature findings. On one note, the Al<sub>2</sub>O<sub>3</sub> content of LF slag (24 wt-%) was significantly higher than in other slags. In the literature, Al<sub>2</sub>O<sub>3</sub> content of LF slag has a wide range probably due to differences in alloying elements and steel grades produced in different plants. As in the literature, BOF slag had the highest iron content (12 wt-%).

Table 10 Chemical composition of <500 $\mu$ m blast furnace, desulfurization, basic-oxygen furnace and ladle furnace slags diluted with microwave acid digestion and analyzed with ICP-MS.

wt-%	BF	DS	BOF	LS
CaO	36.48	43.64	45.33	37.21
Al <sub>2</sub> O <sub>3</sub>	11.66	1.66	1.21	24.46
SiO <sub>2</sub>	0.16	0.09	0.10	0.22
MgO	10.38	1.14	1.58	5.18
Fe	0.56	6.32	11.69	0.85
Mn	0.10	0.17	1.80	0.50
K <sub>2</sub> O	0.00	0.00	0.00	0.00
Na <sub>2</sub> O	0.40	2.17	0.70	0.57
V	0.02	0.11	1.66	0.03
Cr	0.00	0.00	0.18	0.02

## 10.2 Calcium formate

### *Pure calcium oxide powder*

Leaching behavior of pure CaO in formic acid (FoA) solution was studied prior to the steelmaking slag experiments. Figure 9 presents the online pH collected and the calculated hydroxide concentration based on it (self-ionization of water). At  $t=0$ , CaO powder was added which started to react with water immediately raising the pH of the solution to 10 within 5 minutes. Dissolution of CaO releases thermal energy by the formation of calcium hydroxide. During the first 5 minutes, temperature of the solution had increased up to 42°C from initial 25°C even though the thermostat cooled the solution if it exceeds 25°C. This demonstrated the rapidity of the dissolution reaction. After the FoA was added, temperature decreased 2 °C and an increase in the rate of pH increment was visible which implements that the rate of CaO dissolving had increased. However, before reaching 7 minutes the dissolution reaction had released enough thermal energy to reach a temperature of 55°C. Finally, at  $t=1440s$  (24min) the hydroxide concentration stays constant until the end of the experiment. This could be due to saturated solution where CaO has reacted until equilibrium, or the rate of CaO reaction and precipitation of calcium formate (CaFo<sub>2</sub>) are equal. Thus, 1800s (30min) was selected as a reaction time for the steelmaking slag experiments.

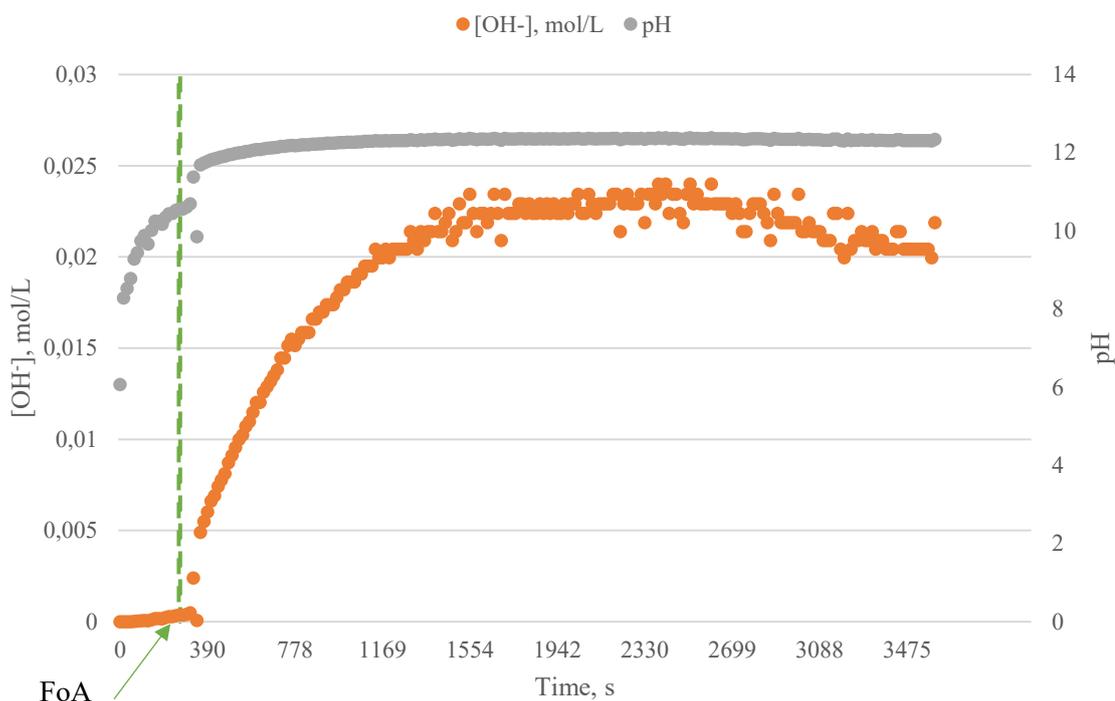


Figure 9 Online pH and calculated concentration of OH<sup>-</sup> ions during leaching of pure CaO with formic acid where CaO is an excess. Initial reaction conditions are presented in Table 6. Duration of the experiment was 1h.

The calcium ion concentration in the liquid samples decreased from 3 minute sample = 68g/kg to the 60 minute sample = 42g/kg which supports the theory of calcium formate or calcium hydroxide (Ca(OH)<sub>2</sub>) precipitation. Therefore, the carbon content of the residue solid was determined. Three samples were analyzed, and the carbon analyzer found that the residue solid contained 4.2 wt-% of carbon on average. Amount of dried residue solid was 30.05g which gives precipitated CaF<sub>2</sub> a total of 6.9g. The rest was assumed to be a mixture of unreacted CaO and precipitated Ca(OH)<sub>2</sub>. The solubility of CaF<sub>2</sub> is around 160g in a liter of water at 25°C. As the initial amount of FoA was 0.75mol and total volume 0.5L, the CaF<sub>2</sub> should have not precipitated (100% conversion gives 48g of CaF<sub>2</sub>). For further process design, it would be advantageous if the calcium formate would remain in liquid phase. Separation of residue CaO or steelmaking slag from the partial product and the product in liquid phase creates additional process steps.

Pure CaO powder was also used as a catalyst for methyl formate (MeFo) hydrolysis. Figure 10 presents the online pH recording of the experiment and the calculated concentration of hydroxide. The pH of the solution rose up to 13.5 before MeFo was added at  $t=375s$  (6.25min). The addition of MeFo dropped the pH significantly more than the addition of

FoA did. The solution was rapidly neutralized as MeFo was added and remains neutral for 20 minutes ( $[OH^-] = 0$ ). Thus, the rate of CaO dissolution and MeFo hydrolysis are equal. MeFo addition does not change the temperature of the solution. Prior to addition of MeFo, the thermostat had already started to steadily cool down the solution as it had risen to 46 °C from initial 25°C due to the dissolution reaction of CaO. As the concentration of MeFo is close to zero, CaO continues to rapidly dissolve. After approximately 1 hour, the solution had reached the same pH where previous experiment with FoA ended (~13).

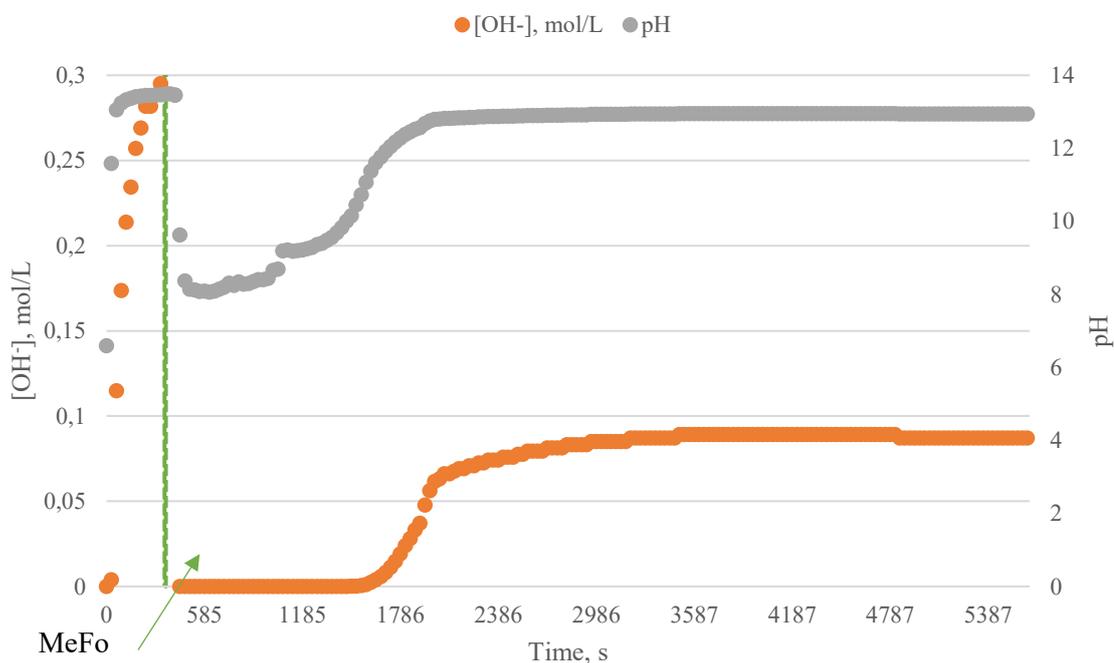


Figure 10 Online pH data and calculated concentration of  $OH^-$  -ions during pure CaO catalyzed methyl formate hydrolysis where CaO is an excess. Initial reaction conditions are presented in Table 7. Duration of the experiment was 1.5h.

In the GC analysis, MeFo and MeOH content of the samples were determined. Table 11 presents the main analysis results. Conversion of the reaction is 97% based on the MeOH concentration at the end and 100% based on the consumed MeFo. In addition, the analysis proved that the reaction goes over its equilibrium ( $K_c \approx 0.2$  (Jogunola et al., 2011)) when the CaO is an excess. The equilibrium constant is slightly dependent on the initial molar amounts of the reagents and temperature (Jogunola et al., 2011). The value of 0.2 is close to the reaction conditions studied here.

Table 11 Methyl formate (MeFo) and methanol (MeOH) concentrations of samples from pure CaO catalyzed methyl formate hydrolysis experiment determined with gas chromatography. Initial reaction conditions are presented in Table 7.

Sample, #	Time, s	MeFo, wt-%	MeOH, wt-%
1	435	1.5	3.9
2	455	1.0	4.1
3	975	0.8	4.4
4	3436	0.0	4.8
5	5477	0.0	5.0

According to the carbon content analysis, 11.2g of CaF<sub>2</sub> precipitated during MeFo hydrolysis. The amount of precipitated CaF<sub>2</sub> is 62% more than in FoA experiment which is caused by the formation of methanol. Calcium formate is practically insoluble in methanol and ethanol (~2.5g/L). As previously discussed, from process design point of view, partial precipitation of the product is not beneficial unless all the CaO has been reacted to yield pure CaF<sub>2</sub> precipitate. If the formed methanol could be removed during the reaction and for example recirculated to MeFo synthesis, the liquid phase would contain only CaF<sub>2</sub>. Separation of residue solid catalyst and liquid product would require less process steps than separating the product from both, solid and liquid phase.

### *Steelmaking slag*

Appendix II presents the online temperature curves of each steelmaking slag leaching with formic acid. The figures are divided into four; a), b), c) and d) which presents the four reaction conditions 1, 2, 3 and 4, respectively. With reaction conditions 1 to 3, DS and BOF slag experiments raise the reaction temperature the most. The result is obvious as the calcium oxide contents of these slags are the highest. With the higher initial temperature (70°C), LS slag has the highest increase in temperature (+14°C). Thus, it can be concluded that temperature increases the dissolution of calcium in the case of LS slag. Interestingly, with reaction conditions 1 and 2, the peak in temperature comes later with BF slag than with other slags. This indicates that the rate of the dissolution reaction is slower with BF slag which is most likely caused by the mineralogy of the slag or the cooling method of slag. The BF slag is granulated at the steel plant in contrast to the other slag samples.

Desulfurization (DS) slag showed superior leaching of calcium based on the online pH data (Appendix III). With reaction conditions 2-4, the final pH was significantly higher than in other experiments. The increase in pH is a sign of increasing concentration of hydroxide ion which is caused by the formation of calcium and two hydroxides during leaching of CaO. Thus, the pH and temperature data suggest that DS slag is leached most efficiently with formic acid compared to other slag samples.

Final pH's of the reaction mixtures show an interesting contrast between reaction conditions 2 and 4 (Appendix III, Figure 1, b) and d)). These two experiments have the same initial conditions except reaction temperature. However, in  $T=25^{\circ}\text{C}$ , the reached final pH for BF, DS, BOF and LS are 7, 5.1, 4.7 and 4.2, respectively whereas in  $T=70^{\circ}\text{C}$ , the final pH are 8, 4.7, 4 and 3.4, respectively. This indicates that only the leaching of CaO in BF slag benefits from the higher reaction temperature.

Appendix III, Figure 1, a), b) and c) shows that the strength of the leaching agent (initial concentration of FoA) influence the final pH of the solution as expected. If the final pH of the solution is under neutral, the solution contains unreacted acidic groups. This is strongly the case with reaction conditions 1 and 2 (FoA as an excess and stoichiometric equal). With condition 1, FoA is an excess and the final pH is purposely on the acidic side. Considering condition 2, the low pH already indicates that the calcium of the slag is not fully leached. Only DS slag reached final pH around neutral with reaction condition 2 where FoA and CaO are stoichiometric equals. This indicates almost total leaching of CaO. With condition 3, only BF slag stays under pH 7 which indicates inferior leaching of CaO compared to other slags.

Figure 11 presents the leached percentage of the compound compared to the content of the compound in initial slag. Thus, it does not give an overview of the residue solids chemical composition in weight percentages which is presented in Appendix I. However, when the purity of the product is desired to be high and the aim is to leach efficiently and selectively calcium, this figure gives a good view on reality of the leaching. Appendix I presents the calculated selectivity and yield of CaO removed in addition to residue slags chemical composition of each experiment. The conclusions based on online pH data have some conflict with the chemical composition analysis of the residue solids which is presented in Figure 11. For example, the high final pH (around 12) achieved with DS slag does not demonstrate major dissolution of CaO alone. The high final pH is a result of high overall

dissolution while CaO have not dissolved any more than in the case of BOF slag. The most selective leaching result with FoA is achieved with the highest concentration of FoA with DS, BOF and LS slags (94%). When FoA is an excess, it dissolves CaO significantly more than in other experiments but does not have a significant effect on the dissolution of other elements. Thus, the selectivity decreases when the strength of the leaching agent decreases. This is controversial to the literature study. However, the strength of the leaching agent is around 1M which is recommended by literature. The highest dissolution of CaO with FoA as the leaching agent is achieved from DS slag (83.7%). Second, from BF slag (80.6%). However, as expected, these are also the two experiments with the highest number of overall leached elements.

The effect of increase in initial reaction temperature from 25°C to 70°C to CaO leaching with FoA from steelmaking slags is: 1) BF slag 17.6% to 24.6%, 2) DS slag 50.7% to 53%, 3) BOF slag 44% to 57% and 4) LS slag 18.7% to 31.6% (Figure 11). For conclusion, the increase in temperature has significant effect on CaO leaching primarily in the case of BOF and LS slags which was already concluded based on the temperature curves presented in Appendix II. However, in the case of LS slag, the higher temperature decreases the selectivity from 92% to 81%. Interestingly, the similar effect is not observed with BOF slag. The selectivity slightly increases with higher initial temperature (~90% to 94%).

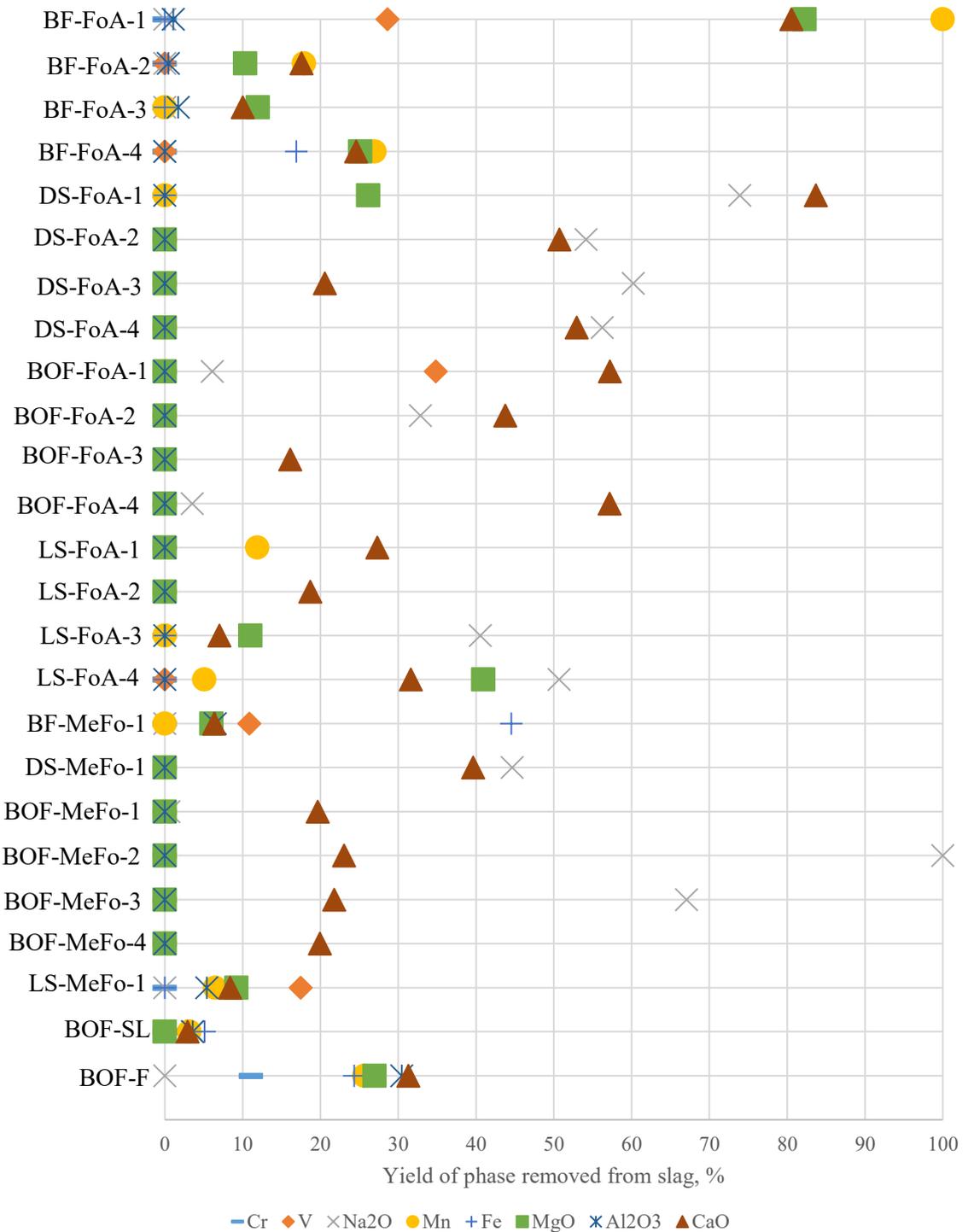


Figure 11 Yield of each experiment. Calculated based on Appendix I solid residue and Table 10 initial chemical compositions of steelmaking slags. Here, letters A-D represent slags BF, DS, BOF and LS, respectively. Numbers 1-4 correlates to reaction 1-4 described earlier in Chapter 8.2.1.

Steelmaking slag catalyzed methyl formate hydrolysis was experimentally tested in 7 different experiments. Each slag was tested to catalyze in reaction condition 1, where MeFo is as excess. Different process conditions were tested only for BOF slag. As in previous FoA

leaching experiments, in experiment 2) CaO and MeFo were stoichiometric equals, 3) CaO was an excess and 4) CaO and MeFo were stoichiometric equals but initial reaction temperature was higher (herein,  $T=50^{\circ}\text{C}$ ). The yield of each compound separated from initial slag is presented in Figure 11. The difference of steelmaking slag leaching with FoA and MeFo is similar between different slags. The amount of CaO leached in MeFo hydrolysis is 1) DS: 39.6%, 2) BOF: 19.6%, 3) LS: 8.4% and 4) BF: 6.4%. Thus, different slags behave relatively similar in each reaction. However, the CaO yield is half as much as with FoA leaching.

Figure 12 presents the online temperature data of each steelmaking slag catalyzed MeFo hydrolysis experiment. MeFo is added at  $t=0$  from which the temperature started to rise from initial temperature set based on reaction conditions presented in Table 7. In Figure 12 a) is presented each slag catalyzed MeFo hydrolysis with reaction condition 1. Based on it, DS reacts most in the hydrolysis reaction and second BOF slag which is similar with the result from FoA leaching. BF and LS show only minor dissolution based on the temperature curve. Dissolution of CaO is an exothermic reaction which releases thermal energy and there is no indication of such in the case of BF and LS slags. Thus, the dissolution of CaO is either slow or minimal. Based on the literature survey and the leaching experiments with FoA, CaO dissolution is typically a rapid reaction, Thus, the slow nature of the reaction in the case of BF and LS slags is unlikely. This conclusion agrees with the yield of CaO from BF and LS slags (6.4% and 8.4%, respectively). However, even in the case of DS and BOF slag, the raise in temperature is significantly lower than in the corresponding FoA experiments ( $+17^{\circ}\text{C}$  and  $+16^{\circ}\text{C} > +10.5^{\circ}\text{C}$  and  $+4.5^{\circ}\text{C}$ ). These differences agree with the yield of CaO presented in Figure 11 where FoA leaches almost half more CaO from DS and BOF slag than MeFo hydrolysis does. This implies that the steelmaking slag does not drive the MeFo hydrolysis further than its equilibrium ( $K_c$  around 0.2).

Figure 12 b) presents the effect of initial MeFo content and initial temperature to the reaction temperature development. The figure implies that the initial MeFo content does not have a significant effect on the leaching of CaO which is also witnessed from the slag residues (Appendix I). In the case of higher initial temperature, the effect of MeFo to the temperature is controversial. The boiling point of MeFo is around  $30^{\circ}\text{C}$  which makes the addition of MeFo to the vessel difficult. However, the hydrolysis of MeFo is also a rapid reaction which is why it can not be added to the water prior to setting the temperature. The vessel is well

sealed as the reaction is running, but during the addition of the alkyl ester some of it could have boiled out. However, adding the MeFo in room temperature decreases the reaction temperature momentarily.

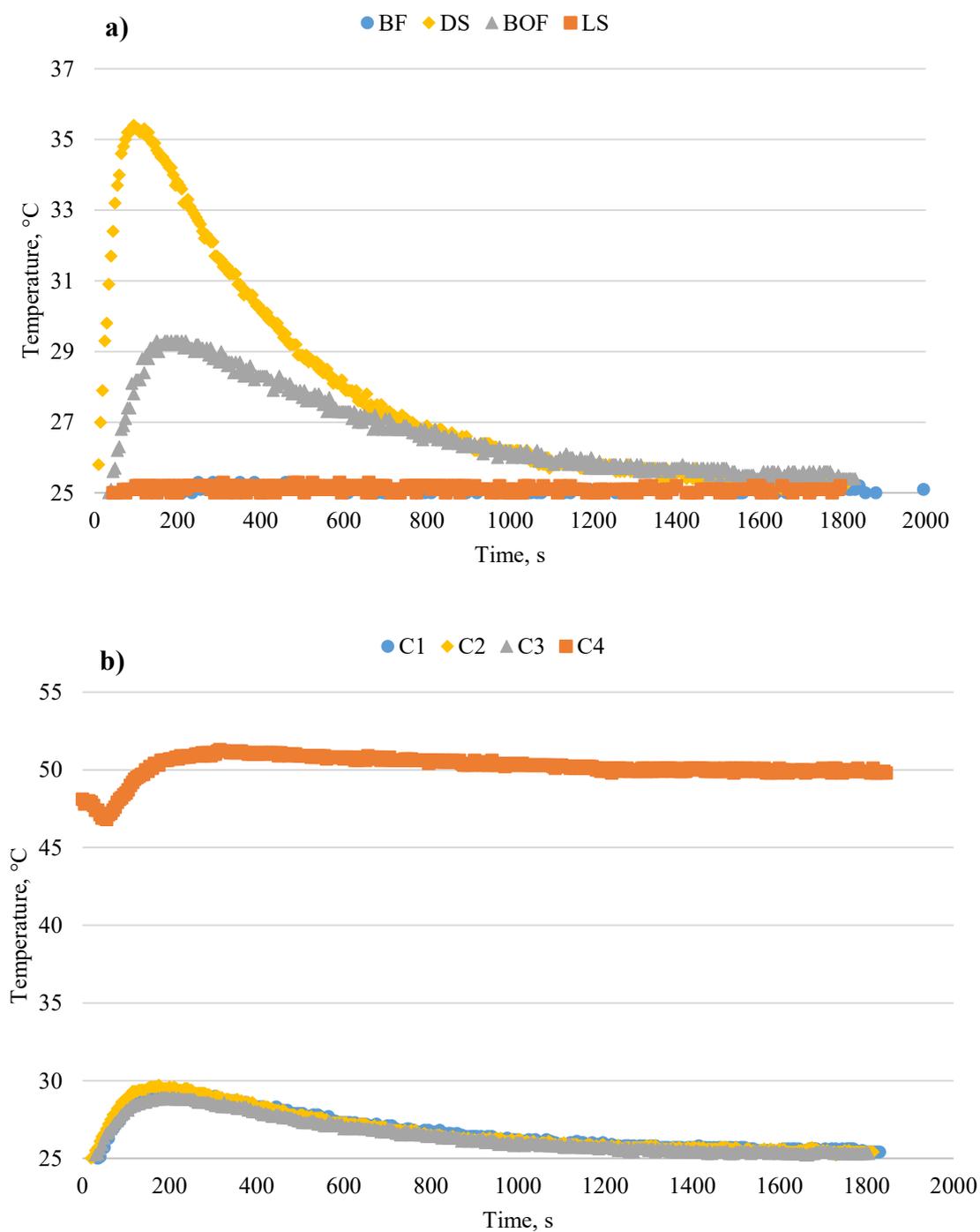


Figure 12 Online temperature data of steelmaking slag catalyzed methyl formate hydrolysis ( $t(0)$ =MeFo addition). Figure a) presents experiment 1 of each slag and b) experiments 1-4 of BOF slag. Initial reaction conditions are presented in Table 7.

Figure 13 presents the online pH data of steelmaking slag catalyzed MeFo hydrolysis. As presented in Figure 13 a), the final pH with each slag in reaction condition 1 is around neutral. Thus, further dissolution of CaO could be expected as pH 13 was achieved with pure CaO (Figure 10). As seen in Figure 13 b), different initial concentrations of MeFo results as differences in final pH due to the amount of formic acid formed.

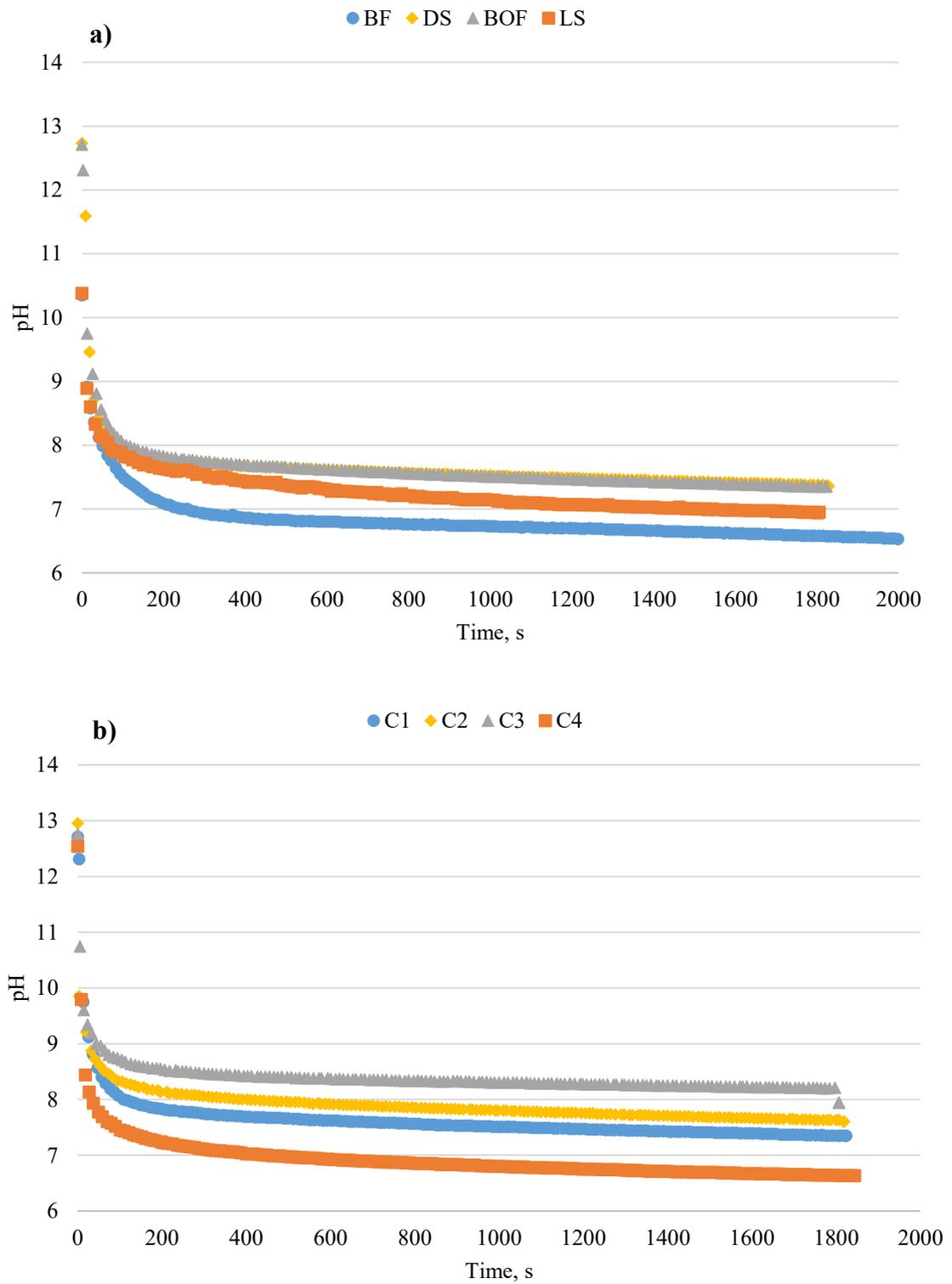


Figure 13 Online pH data of steelmaking slag catalyzed methyl formate hydrolysis experiments. ( $t(0)$ =MeFo addition). Figure a) presents experiment 1 of each slag and b) experiments 1-4 of BOF slag. Initial reaction conditions are presented in Table 7.

The GC analysis of the samples gives the yield and conversion of MeFo which are presented in Table 12. Highest yield (76.2%) is achieved with BOF slag and lowest MeFo concentration (reaction condition 3: CaO is an excess). The experiments with pure CaO powder showed that CaO must be as an excess in MeFo hydrolysis experiments (Yield 97%). Interestingly, the lowest initial MeFo concentration leaches CaO from steelmaking slag as efficiently as the highest, where the concentration of MeFo is three times higher. One possible reason could be the higher water content with the reaction condition 3. However, water is a major excess in both experiments which undermines the explanation. The yield which could be achieved with the initial reaction conditions (3) with the equilibrium constant found from literature is 40.2% which is almost half as much as achieved. The conversion is calculated based on GC analysis results of MeFo concentrations. These suggest a high conversion in each case even though the yield of leached elements, yield of methanol and pH of the samples proves otherwise. Thus, the GC analysis results of MeFo are not considered as reliable as yield of products and yield of CaO which support each other.

Table 12 The results of steelmaking slag catalyzed methyl formate hydrolysis experiments. Yield of CaO is determined from residue slag with microwave acid digestion and ICP-MS. Yield and conversion of the hydrolysis reaction is defined from gas chromatography analysis results of formed methanol and consumed methyl formate. The initial information of the experiments is found from Table 7.

	Yield <sub>CaO</sub> , %	Yield <sub>MeOH</sub> , %	Yield <sub>MeOH(Kc)</sub> , %	Conversion, %
<b>BF-MeFo-1</b>	6.4	42.8	42.4	92.5
<b>DS- MeFo-1</b>	39.6	22.9	40.0	89.8
<b>BOF -MeFo-1</b>	19.6	21.6	38.6	76.2
<b>LS- MeFo-1</b>	23.0	24.9	45.7	77.5
<b>BOF-MeFo-2</b>	21.8	73.8	33.2	80.0
<b>BOF-MeFo-3</b>	19.9	76.2	40.2	86.8
<b>BOF- MeFo-4</b>	8.4	41.3	31.2	92.7

### 10.3 Calcium salt of hydroxy acid

#### *Pure CaO powder*

In preliminary experiments of leaching pure CaO with sodium lactate at pH 12 the temperature of the solution rose to 39°C from initial 25°C. The peak in temperature occurred at  $t=270s$  where hydroxide concentration decreased from 0.13mol/L to 0.095mol/L. The changes in pH and hydroxide concentration are minute as expected. The solution already

contains hydroxide ions. However, the aim is to “capture” two lactate anions from the solution with calcium. Thus, two sodium ions are “released” and left to form an ionic bond with the two hydroxide ions which calcium has formed when reacting with water. However, the small electronegativity difference between sodium and calcium leaves room for doubt (0.9 and 1.0, respectively).

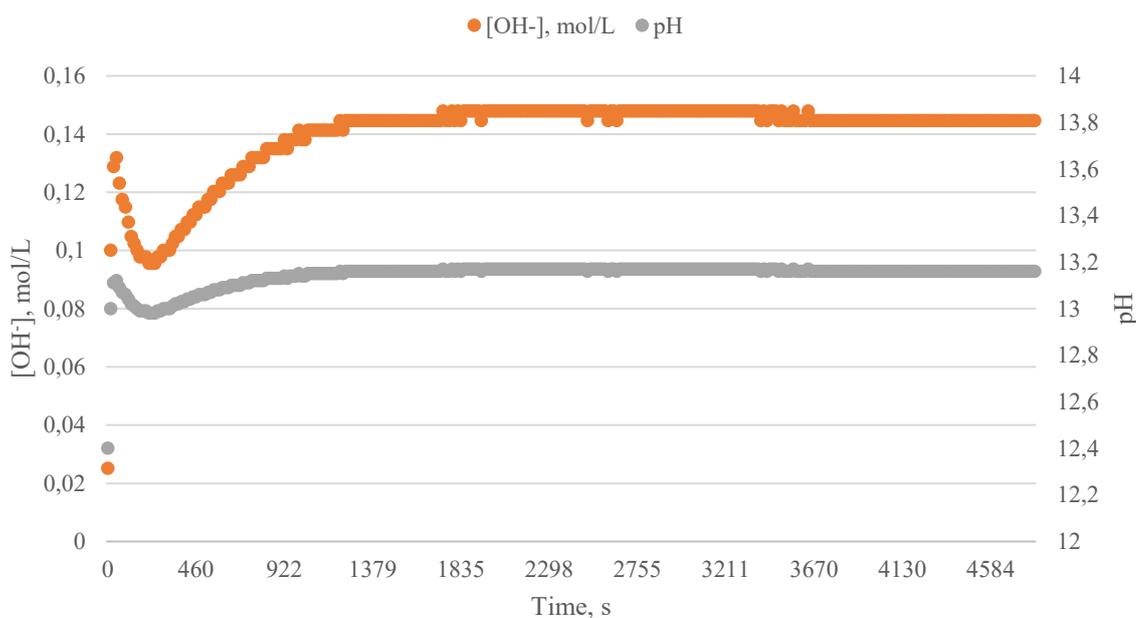


Figure 14 Online pH and calculated hydroxide concentration of pure CaO dissolution to aqueous sodium lactate solution (pH 12). Initial reaction conditions are presented in Table 8. Note, the second vertical axis (pH) begins at value 12.

The dry solid residue of the sodium lactate experiment weighted 50.1g. The carbon content analysis indicates that 10.3g of calcium lactate precipitated which is almost the same as in pure CaO+MeFo experiment (11.14g). However, lactate anions are larger than formate anions, which causes the larger mass of the precipitated product even though the precipitated mass of calcium is smaller ( $m(\text{Ca})_{\text{FoA}}=2.1$ ,  $m(\text{Ca})_{\text{MeFo}}=3.4\text{g}$  and  $m(\text{Ca})_{\text{sodium lactate}}=1.9\text{g}$ ). Yet, the difference between precipitated mass of calcium in FoA and sodium lactate leaching is not significant. Hence, the leaching effect of sodium lactate to CaO can not be concluded based on the carbon content analysis.

The ICP analysis results determine the calcium and sodium contents of the samples at different times. Table 13 presents the main results of ICP analysis. As Figure 14 and the 14°C release of thermal energy presents, the CaO leaches rapidly. Thus, the difference between calcium concentration of first and last sample is not significant (0.4g/L). However, the calcium content of the solution varies during the experiment and does not constantly increase

reaching its steady state. This may be due to precipitation of calcium hydroxide or calcium lactate. The last sample has calcium content of 5.1g/L which is over the limit of calcium hydroxide solubility (1.73g/L at 25°C).

Table 13 ICP-MS analysis results of pure CaO powder leaching with sodium lactate at pH 12. The initial reaction conditions are found in Table 8.

Sample, #	Time, s	c(Ca), g/L	c(Na), g/L
1	90	4.7	42.6
2	240	3.8	43.7
3	1200	5.0	45.6
4	2100	4.3	43.9
5	4800	5.1	44.9

### *Steelmaking slag*

The temperature of the reaction between sodium lactate at pH 12 and BOF slag did not show any change during the experiment. However, as presented in Figure 15 the hydroxide concentration reaches the same concentration (0.145mol/L) as in the experiment with pure CaO powder which is presented earlier in Figure 14. Due to the identical final pH, it is assumed that the reaction had already found equilibrium. Nevertheless, with pure CaO the temperature had a significant 14°C increase which indicates a more rapid reaction. In addition, the reaction between sodium lactate and pure CaO had a decrease in hydroxide concentration which was not achieved with BOF slag. This indicates that the reaction had low conversion.

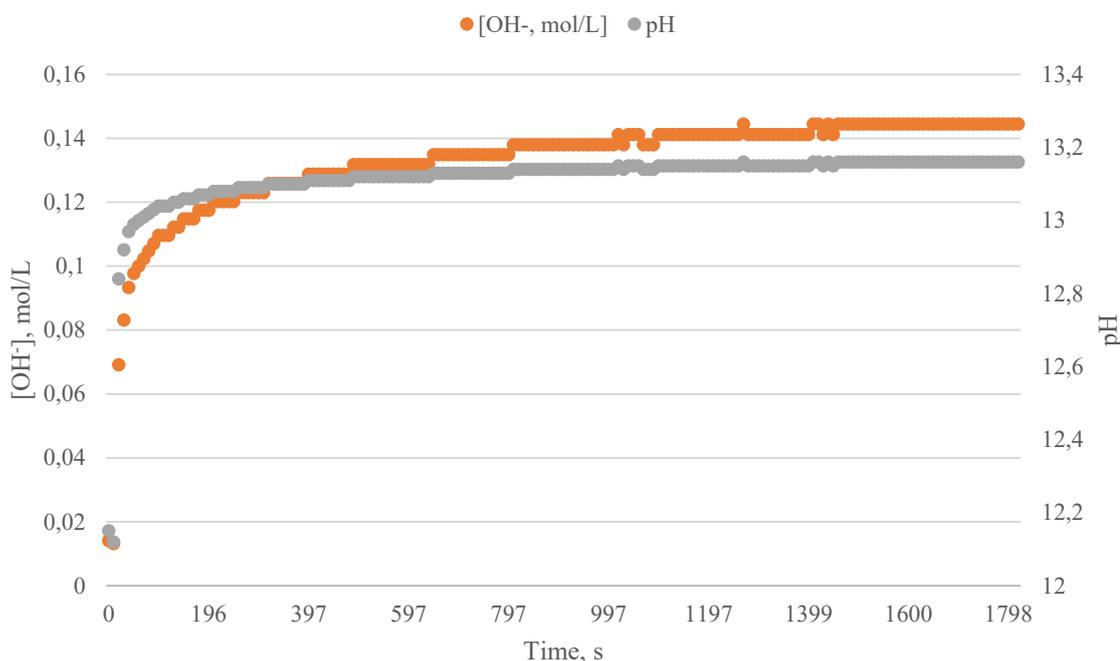


Figure 15 Online pH and calculated hydroxide concentration of BOF slag dissolution to aqueous sodium lactate solution (pH 12). Initial reaction conditions are presented in Table 8. Note, the second vertical axis (pH) begins at value 12.

Microwave assisted acid digested slag residues analyzed with ICP-MS proves the low conversion (Appendix I). Only 2.9% of the CaO in steelmaking slag is leached. With the same molar amount of acid and slag (0.42mol) and the same reaction mass (500g) and particle size of slag (<500 $\mu$ m), FoA leached 57.2% of the CaO in BOF slag. This proves the conclusion of the literature review, where it was found that low pH increases the leaching of calcium.

## 10.4 Calcium soap

### *Pure CaO powder*

The calcium soap experiment with pure CaO powder and rapeseed oil was monitored by temperature to obtain data of the progression of the saponification reaction. Figure 16 presents the temperature curve of the experiment. The thermostat was not able to decrease the temperature of the solution as the oil is a good insulator due to its dielectric properties. In the case of aqueous solutions such as formic acid and sodium lactate, the thermostat was able to cool down the solution rapidly. Thus, the wide temperature curve does not necessarily indicate long-term rapid CaO dissolution.

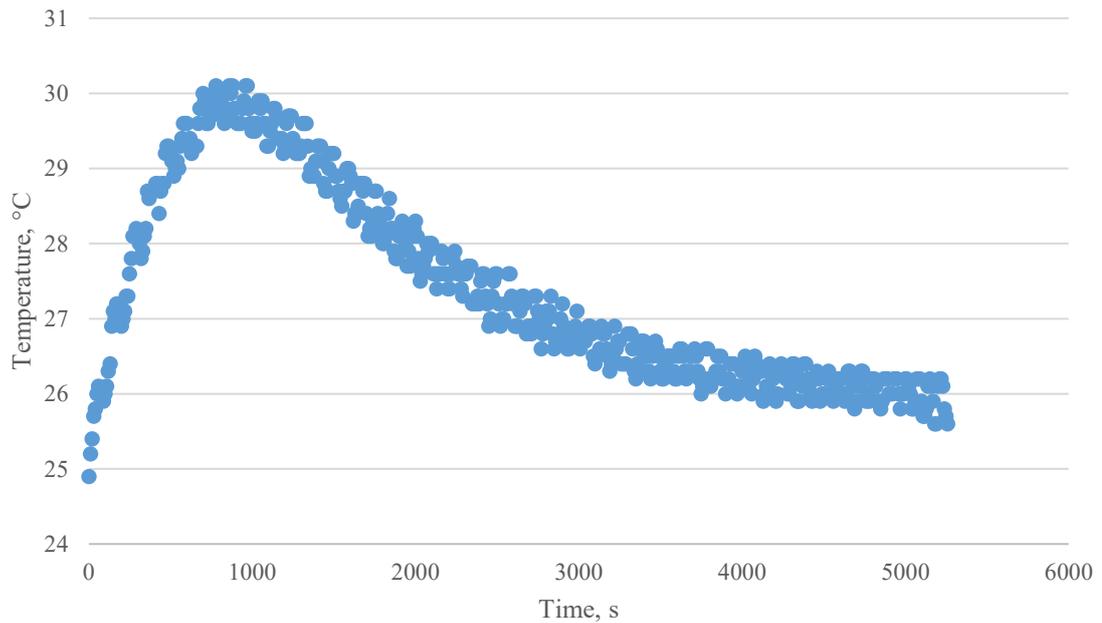


Figure 16 Temperature curve of pure CaO powder saponification experiment. The initial reaction conditions are presented in Table 9.

The carbon content of the soap was 44 wt-%. By eyesight, the volume of the calcium soap in the sample stayed constant through the experiment. An example of a sample is presented in Figure 17. After centrifuging, four phases were visible in the sample and they were assumably 1) aqueous glycerol, 2) fat, 3) calcium soap and 4) solid phase of precipitated  $\text{Ca}(\text{OH})_2$  and unreacted CaO.

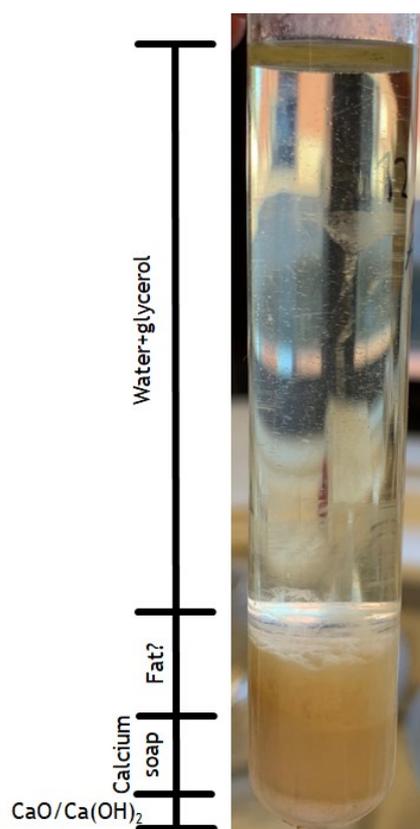


Figure 17 A centrifuged sample from pure CaO saponification experiment.

The experiment showed important practicality features for following steelmaking slag experiments. First, the calcium soap did not dissolve in any common leaching agents which creates analytical difficulties. The soap did not dissolve in kerosene, benzene, toluene, 75% isopropanol solution or in 5:4 isopropanol-hexane solution. In the case of pure CaO experiments, a clear residue rapeseed oil phase was not visible which created difficulties as gas chromatography was not a viable analysis method. Third, the sample volume could be bigger and the sampling rate more scattered. Sampling with a tube and syringe was not effective due to the viscosity of the solution. Thus, for later experiments, the temperature of the solution was increased.

### ***Steelmaking slag***

The steelmaking slag saponification experiment differs with the pure CaO powder experiment. The temperature of the steelmaking slag experiment did not increase more than one °C whereas in the pure CaO experiment it increased 5°C. This indicates slower and/or less leaching of calcium. However, the change in reaction temperature between the two experiments can explain the difference in released thermal energy. The thermostat can be

quicker to cool the solution back to 40°C than closer to room temperature which is nearly 25°C in the laboratory.

The main difference is visible in Figure 18 which presents the phase separated sample. On contrary to pure CaO experiments, the visible phases include only solid residue steelmaking slag phase mixed with calcium soap and an organic phase which includes unreacted glycerides. A clear aqueous phase is not visible. These differences can be due to the minor initial aqueous phase in the solution. In theory, the aqueous phase leaches the calcium from the steelmaking slag forming calcium hydroxide which reacts with the organic phase breaking ester bonds in triglycerides. The broken ester bond leaves the carboxyl group negatively charged and it forms an ionic bond with calcium. As the calcium transfers from aqueous to organic phase, it enhances the leaching of CaO from solid phase.

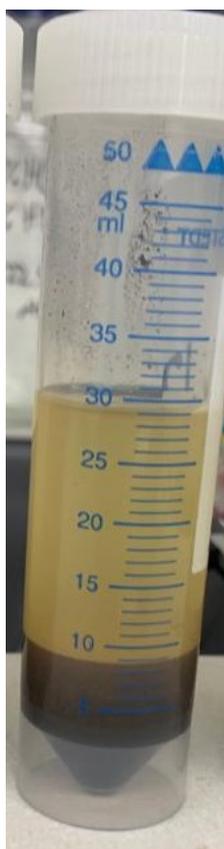


Figure 18 A BOF slag saponification sample.

The GC analysis of the samples determined the concentration of fatty acids, resin acids, diglycerides, sterols, steryl esters and triglycerides. Table 14 presents the GC analysis results of the rapeseed oil used in addition to the samples collected during the experiment. The rapeseed oil contains 77.9 wt-% of triglycerides, 2.75 wt-% of diglycerides and 2.39 wt-%

of steryl esters. The aim of saponification reaction is to break triglyceride into free fatty acids and glycerol. Herein, the fatty acid is not expected to be a free fatty acid but to form a calcium salt of fatty acid. Hence, the concentration of fatty acids is not expected to increase significantly. However, the decrease in triglyceride concentration suggests that only 0.018 mol of triglycerides breaks during the experiment. Thus, the yield of calcium soap was approximately 22.5g. However, the conversion was as low as 5.4% defined by the amount of triglyceride bonds broken.

Table 14 BOF slag saponification samples analysis results obtained by gas chromatography. Sample #0 is pure rapeseed oil (Rainbow).

Sample	0	1	2	3	4	5
<b>t, min</b>	<b>0</b>	<b>6-8</b>	<b>27.5-29.5</b>	<b>59.5-61.5</b>	<b>91-93</b>	<b>118-120</b>
<b>c(fatty acids), mg/g</b>	0.7	0.5	0.5	0.8	2.4	1.1
<b>c(resin acids), mg/g</b>	1.4	1.2	1.9	1.8	1.4	0.8
<b>c(diglycerides), mg/g</b>	27.5	35.7	31.3	24.3	29.7	19.8
<b>c(sterols), mg/g</b>	2.1	4.3	2.0	2.0	2.3	1.7
<b>c(steryl esters), mg/g</b>	23.9	35.4	28.6	26.2	27.5	23.2
<b>c(triglycerides), mg/g</b>	778.9	811.6	805.0	797.6	748.3	736.7

Appendix I shows in Table 1 the chemical composition of the residue slags. Based on the amount of leached calcium which was determined with microwave assisted acid digestion and ICP-MS, the conversion was 31%. In addition, Al<sub>2</sub>O<sub>3</sub>, MgO, Fe, Mn and V were leached significantly: 30, 27, 24, 26 and 26%, respectively. Due to low selectivity, the purity of the product is poor, and the process requires further optimization.

## 11 Summary and Conclusions

Steel is a central raw material in several sectors of everyday life. The consumption of steel is only anticipated to increase as the infrastructure and technology are developing. However, iron and steel production have high CO<sub>2</sub> emissions and partly landscaped side streams. These by-products are slags which are formed when iron and steel are smelted in furnaces or ladles. The purpose of slags is to improve the molten metal by removing impurities and controlling the properties of desired iron or steel grade. Slags mainly consist of calcium, magnesium, iron, phosphorus, aluminum with traces of other metals.

Steel production produces up to 200kg of slag per 1t of steel produced. Currently, steel slag is either landscaped, recycled back to the process or sold as a low value raw material for construction sites. Landscaping of the slag pollutes the soil as metals are slowly leached. Fully recycling of the slag is problematic as the metals accumulate in the process. Even utilization of slag as construction raw material has its difficulties. Due to the high content of calcium oxide and calcium silicate, slags are not volumetrically stable. The aim of this work was to derive a value-added calcium product from steelmaking slags by separating calcium from the slag.

According to the literature survey,  $\text{CaCO}_3$  is the most researched calcium product developed from steel slags with the aid of ammonium salts as leaching agent. The most important variables in process conditions are particle size, sufficient mixing and *SLR*. The target of the experimental section was to experimentally produce calcium products from blast furnace, desulfurization, basic oxygen furnace and ladle slag. Calcium formate, calcium soap and calcium salt of a hydroxy acid were selected as examined products by their novelty, possible markets and environmental impact.

The experimental section of the Thesis included three different products: calcium formate, calcium salt of a hydroxy acid and calcium soap. Calcium formate was produced with two different production routes: direct leaching with formic acid and CaO catalyzed methyl formate hydrolysis. Each product was first produced with pure CaO powder as a reference. Second, the same experiment was carried out with slag samples provided by SSAB Raahe, a Finnish steel plant.

CaO leaching with formic acid showed a rapid reaction between the two substances and unexpected precipitation of calcium formate in pure CaO experiments. The reaction temperature rose 30 °C and the reaction found equilibrium during the first 25min. In the case of steelmaking slag leaching with formic acid, DS and BOF slags showed superior dissolution compared to BF and LS slags. Initial temperature of the solution had an effect only in the leaching of CaO from BOF and LS slag (44% to 57% and 19% to 32%). The initial 70°C temperature did not have an effect on the selectivity of the leaching. The most selective leaching is achieved with the highest FoA concentration ( $c_0(\text{FoA})=1\text{M}$  and  $T=25^\circ\text{C}$ ) The highest obtained selectivity is 94%. The highest yield of separated CaO is also with the 1M FoA solution in temperature of 25°C, with BF and DS slags (80.6% and 83.7%, respectively). In the case of BF slag, the amount of CaO leached was significantly less than

the amount of CaO leached with DS slag as it has 7 wt-% higher initial content of CaO. The precipitation of calcium formate increases the required separation steps when it is partially in solid and liquid phase.

Calcium formate synthesis with pure CaO showed great promise towards CaO catalyzed methyl formate hydrolysis with a 97% yield of methanol. The precipitation of calcium formate increased as it is insoluble in methanol. However, in the case of steelmaking slag samples, the yield of CaO leached is half as much as in similar FoA leaching experiment. DS slag proved to be the best performing slag for catalyzing methyl formate hydrolysis (yield 34%). The initial concentration of MeFo did not have an effect on the yield of CaO removed - 22% versus 19.6% when initial concentration of MeFo was threefold. In addition, the lowest initial concentration of MeFo gave the highest yield of methanol 76.4% and thus, the highest yield of calcium formate. The effect of initial concentration of MeFo may be caused by the large excess of water in the reaction as it is one of the reactants. The CaO in steelmaking slag served its purpose as a catalyst to drive the methyl formate hydrolysis further. A better quantitative analysis method for calcium formate would benefit further research. Herein, the analysis relies on methanol quantification.

Calcium salt of hydroxy acid was experimentally produced in pH 12 with sodium lactate. The pure CaO experiment proved minor precipitation of calcium lactate and ICP-MS results showed the presence of calcium lactate in the solution. The initial pH of this experiment did not agree with literature findings of calcium leaching from steelmaking slags. In the literature, low pH was favored for CaO dissolution. The reaction between sodium lactate and BOF slag wasn't rapid based on temperature and pH curved of the reaction. The yield of CaO was only 2.9%. As a comparison, with the same initial reaction conditions, only different leaching agent, FoA leached 57.2% of CaO from BOF slag. As a conclusion for synthesis of calcium salt of hydroxy acid from steel slag, the next step for further study could be glycolic acid as a leaching agent due to shorter carbon chain and potential markets.

Calcium soap was successfully produced with pure CaO powder and cooking oil. The calcium soap was found to be insoluble in most of common leaching agents which caused analytical difficulties. In addition, the separation of soap from other phases (water+glycol, solid residue) requires further research. However, in the case of cooking oil and BOF slag experiment, only two phases were identified. Thus, the solid steelmaking slag residue was mixed with the soap formed which creates, yet again, separation difficulties as the soap nor

the steelmaking slag does not dissolve in common leaching agents. Analysis of the residue cooking oil phase mixed with water gives the conversion of the reaction being 5.4% which is relatively low. The samples collected did not show clear 4 phases as they did in the case of pure CaO experiments. The steelmaking slag experiment was conducted in higher temperature (40°C) than the pure CaO experiment (25°C) which could influence the result. Nevertheless, the yield of CaO was as high as 31.3% which is over 10% higher than the one achieved in MeFo hydrolysis experiments.

All in all, each of the four methods were shown to be feasible in producing calcium products from steel slags. However, every studied method requires further process development in terms of optimization of process conditions, analytical methods, separation of product from liquid or solid residue and a comprehensive market study. The most process optimization is required on the calcium salt of hydroxy acid but within the aid of this Thesis, adjustments are easier to conduct. The yields of calcium separated from the slags were lower than in the studies found from literature (up to 98 wt-%). However, the Thesis achieved prove of concept in all four methods studied. Each of the methods studied were novel and similar studies was not found from current literature. Thus, a commercial study on the products and improvement of analytical methods are suggested for the next steps.

## 12 Appendices

Appendix I, Chemical compositions of residue steelmaking slags and results	1 page
Appendix II, Online temperature data of steelmaking slag leaching with FoA	1 page
Appendix III, Online pH data of steelmaking slag leaching with FoA	1 page

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Table 1 Chemical composition of residue steelmaking slags and final results of each experiment from Chapter 8. Reaction conditions: 1=Leaching agent was as 1.5 times excess, 2=reagents were as stoichiometric equal, 3=CaO was as 1.5 times excess and 4=2 in higher initial temperature.

Leaching agent	Formic acid																Methyl formate								Sodium Lactate	Rape-seed oil
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	1	1	2	3	4	1			
Reaction condition	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	1	1	2	3	4	1			
Slag	BF				DS				BOF				LS				BF	DS	BOF				LS	BOF	BOF	
CaO	7.1	30.1	32.8	27.5	7.1	21.5	34.7	20.5	19.4	25.5	38.0	19.4	27.1	30.3	34.6	25.5	34.2	26.4	36.4	34.9	35.5	36.3	34.1	44.0	31.1	
Al <sub>2</sub> O <sub>3</sub>	11.5	11.6	11.5	12.6	3.4	2.8	2.1	2.5	2.3	2.2	1.9	2.1	29.3	27.2	27.4	28.2	10.9	2.8	1.5	1.5	1.6	1.6	23.1	1.2	0.8	
SiO <sub>2</sub>	0.1	0.2	0.3	0.2	0.2	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.4	0.4	0.3	0.2	0.0	0.3	0.1	0.3	0.2	0.2	0.4	0.1	0.3	
MgO	1.8	9.3	9.1	7.8	0.8	1.3	1.3	1.7	4.4	3.5	2.4	2.3	5.2	5.2	4.6	3.1	9.8	1.6	2.0	1.9	1.9	1.9	4.7	1.7	1.2	
Fe	0.7	1.0	1.9	0.5	13.4	22.7	24.4	21.3	31.3	26.9	17.6	21.4	1.9	2.8	1.9	6.2	0.3	23.3	14.5	14.3	13.5	14.7	1.1	11.1	8.8	
Mn	0.0	0.1	0.1	0.1	0.2	0.4	0.3	0.6	3.9	3.1	2.5	2.3	0.4	0.6	0.7	0.5	0.1	0.4	2.1	2.2	2.2	2.2	0.5	1.7	1.3	
K <sub>2</sub> O	0.0	0.0	0.2	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.6	1.6	0.6	1.4	1.1	0.0	1.3	
Na <sub>2</sub> O	0.6	0.7	0.8	0.5	0.6	1.0	0.9	1.0	0.7	0.5	0.7	0.7	1.1	1.4	0.3	0.3	0.7	1.2	0.7	0.0	0.2	1.3	2.0	0.7	1.4	
V	0.0	0.0	0.0	0.0	0.2	0.4	0.2	0.4	1.1	1.7	1.9	2.7	0.0	0.0	0.0	0.1	0.0	0.3	2.0	2.0	2.0	2.0	0.0	1.6	1.2	
Cr	0.0	0.0	0.0	0.0	0.1	0.3	0.1	0.1	0.6	0.5	0.3	0.4	0.3	0.1	0.1	0.1	0.0	0.0	0.3	0.3	0.2	0.3	0.0	0.2	0.2	
Yield <sub>CaO</sub> , %	80.6	17.6	10.0	24.6	83.7	50.7	20.6	52.9	57.2	43.7	16.1	57.2	27.3	18.7	7.0	31.6	6.4	39.6	19.6	23.0	21.8	19.9	8.4	2.9	31.3	
Selectivity, %	76.1	80.6	68.9	74.2	94.3	91.1	80.1	91.4	93.8	91.3	81.5	93.9	94.1	92.4	69.5	81.2	52.2	90.5	89.5	86.3	86.8	96.2	63.0	35.3	76.5	

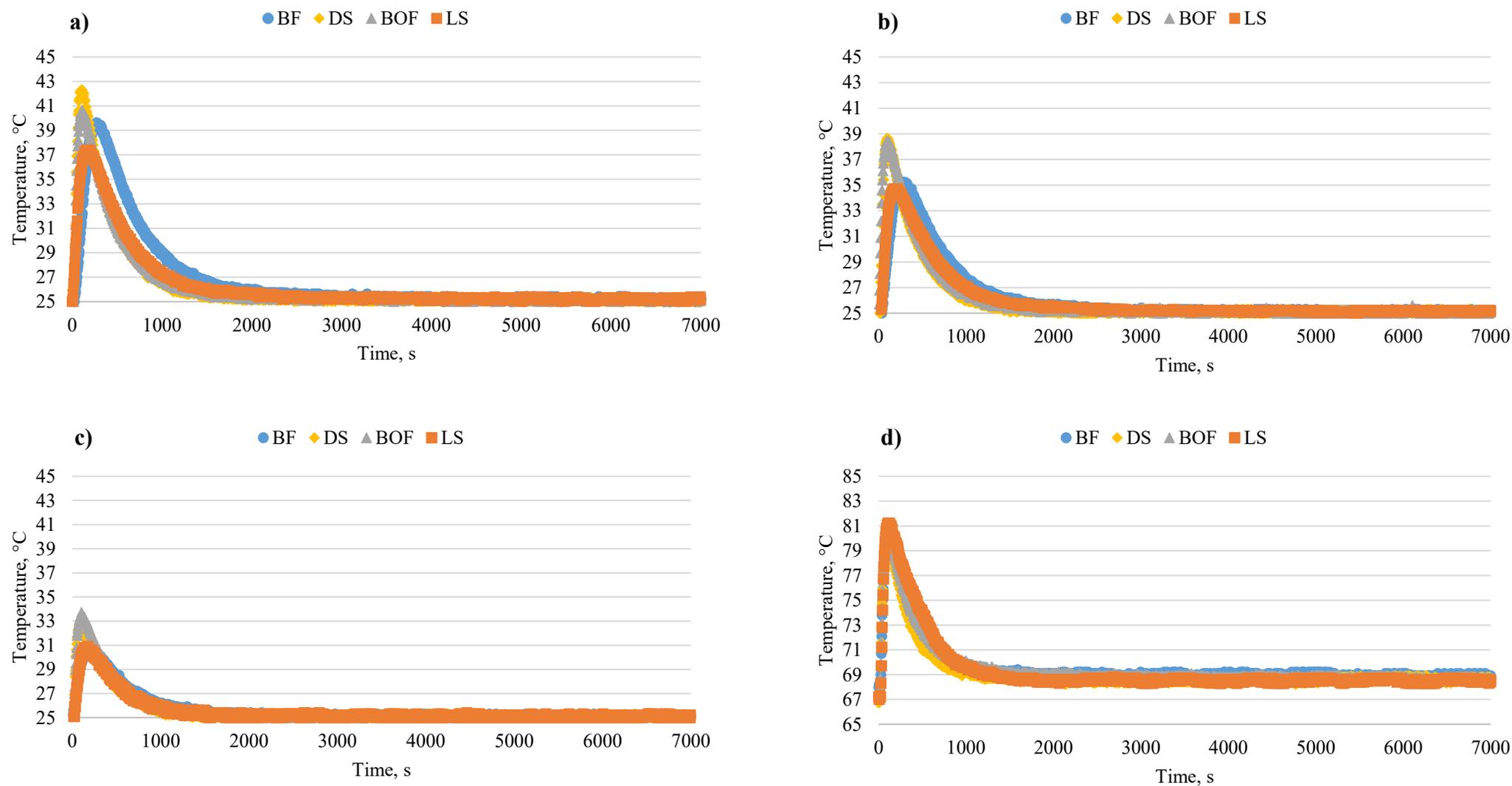


Figure 1 Online temperature data of steelmaking slag leaching with FoA. In a) FoA is an excess and  $T=25^{\circ}\text{C}$ , b) CaO and FoA are stoichiometric equal and  $T=25^{\circ}\text{C}$ , c) CaO is an excess and  $T=25^{\circ}\text{C}$  and d) CaO and FoA are stoichiometric equal and  $T=70^{\circ}\text{C}$ .

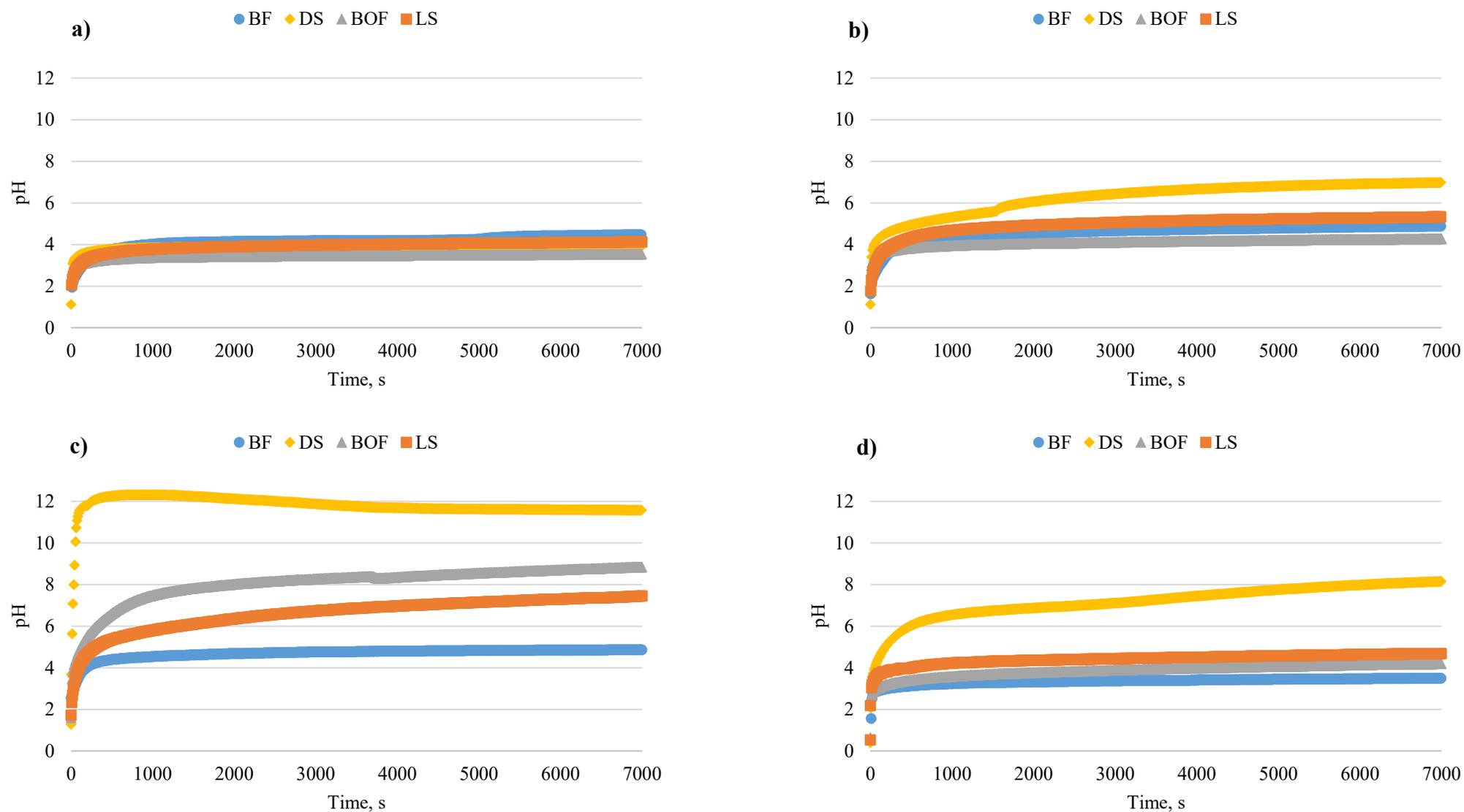


Figure 1 Online pH data of steelmaking slag leaching with FoA. In a) FoA is an excess and  $T=25^{\circ}\text{C}$ , b) CaO and FoA are stoichiometric equal and  $T=25^{\circ}\text{C}$ , c) CaO is an excess and  $T=25^{\circ}\text{C}$  and d) CaO and FoA are stoichiometric equal and  $T=70^{\circ}\text{C}$ .