



Doctoral Thesis in Material Science and Engineering

Application of Wastes from Pulp and Paper Industries for Steelmaking Processes

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To my beloved family

ABSTRACT

Over the past several years, considerable efforts have been made to develop a more circular economy. The ambition to reuse, remanufacture and recycle materials is of great significance for the establishment of a sustainable society. An extended longevity of materials helps to decrease the amount of wastes in landfills, as well as to reduce the mining of natural assets. Pulp and paper industries and steel industries are two of the largest basic industries and export industrial sectors in Sweden. The pulp and paper industries generate large amounts of organic and inorganic wastes. A significant part of these wastes ends up in landfills. The deposit of wastes in landfills is becoming more costly and more challenging to employ, due to stronger regulations and demands with respect to the environment. During Electric Arc Furnace (EAF) and Argon Oxygen Decarburization (AOD) stainless steelmaking operations, burnt lime (primary lime) is charged together with other slag forming components in the furnace or converter to obtain a specific basicity of the slag and to attain purification from undesired elements by chemical reactions between the steel and slag. In blast furnace (BF) operations, fossil carbon is charged in the form of coke and injected as powder to provide heat to melt the iron ore and to reduce the iron oxides by separating iron from oxygen. The use of this primary lime and fossil carbon does not comply with the closing the loop idea that is being prioritized in modern society. This thesis presents results from preliminary experiments for examining the replacement of primary lime with recovered lime from pulp and paper production waste as slag formers in EAF and AOD converters and as neutralizing agents for acidic wastewaters, as well as hydrochar from organic sludges as a carbon source in BF. The gained results showed a possibility of partly replacing primary lime with recovered lime in the EAF without negative effects on the process. In the AOD process, the use of recovered lime didn't show any negative effects on the decarburization process nor on the reduction process. Moreover, the desulphurization function was similar when using recovered lime compared to when using the primary lime. However, the P content in the metal increased slightly. Thus, the

replacement ratio of the recovered lime will be limited by the acceptable P level in the final steel due to higher P content in the recovered lime materials from pulp and paper mills compared to that in primary lime. Furthermore, the obtained results of laboratory-scale trials using recovered lime materials as neutralizers showed that they can be successfully used instead of primary lime to significantly raise the pH level of the wastewaters as well as to decrease the concentrations of Cr, Fe, Ni, Mo and Zn. Also, the results from the industrial-scale experimental trials using hydrochar derived from mixed organic biosludge and from green waste showed that the production rate of hot metal, amount of dust, fuel rate and amount of injected coal, amount of slag, contents of FeO in slag and %C and %P in the hot metal of the BF process were very similar compared to the reference periods. Thus, it was proven that hydrochar derived from various types of organic residues could be used for metallurgical applications. However, the replacement ratio was very low and longer trial campaigns are needed to obtain more certain results. Moreover, it was revealed during this study that slags from AOD converters can be used as binding agents for briquetting of these recovered lime materials. In summary, these results show that waste materials/by-products from two of the most important Swedish base industries can unite two major industrial sectors in a circular symbiosis towards obtaining a more sustainable future.

SAMMANFATTNING

Under senare år har stora ansträngningar gjorts för att utveckla den cirkulära ekonomin. Ambitionen att återanvända, renovera och återvinna material är av stor vikt för att etablera ett hållbart samhälle. Ett utökat livsspann på material hjälper till att minska mängden avfall som hamnar på deponier, samt att minska utvinningen av naturtillgångar. Pappers- och massa industrin och stålindustrin är två av de största basindustrierna och viktiga exportsektorer i Sverige. Pappers- och massa industrin genererar stora mängder organiskt och oorganiskt avfall varje år, varav en stor del förvaras i deponier. Att deponera avfall blir svårare och dyrare på grund av hårdare regler och miljökrav. Vid tillverkning av rostfritt stål i ljusbågsugnar (EAF) och Argon Oxygen Decarburization (AOD) konverterar används bränd kalk (primärkalk) tillsammans med andra slaggbildare för att få rätt basicitet i slaggen och för att rena stålet från oönskade ämnen genom kemiska reaktioner mellan slaggbildare och stålmälta. Vid framställning av råjärn i en masugn chargerar fossilt kol i form av koks och injicerat kolpulver för att ge smältvärme till järnmalm och för att reducera järnoxiderna till järn genom att separera järn och syre. Användningen av primärkalk och fossilt kol gynnar inte den cirkulära ekonomi som eftersträvas idag. Den här avhandlingen presenterar resultat från försök att ersätta primärkalk med återvunnen kalk från pappers- och massa-produktionen som slaggbildare i ljusbågsugns- och konverterprocesserna, och för att neutralisera surt avfallsvatten, samt att använda hydrochar från organiska slam som kolkälla i masugnar. Resultaten visar att det är möjligt att delvis ersätta primärkalk med återvunnen kalk i ljusbågsugn utan negativa effekter på processen. I konverterprocessen har användning av återvunnen kalk inte visat några negativa effekter på kolfärsningen eller reduktionsprocessen, och den har motsvarande avsvavlningssfunktion som den primära kalken. Fosforhalten (P) i metallen ökades något, och möjligheten att ersätta primärkalken med återvunnen kalk kommer att begränsas av hur mycket P som kan tillåtas i stålet på grund av det högre P-innehållet i dessa återvunna kalkmaterial än i primärkalk. Vidare visar resultaten av försöken i laboratorieskala med neutralisering och rening av surt avfallsvatten att sekundära kalkmaterial framgångsrikt kan användas för att markant höja pH-värdet och minska halterna av Cr, Fe, Ni, Mo och Zn. Resultaten från de experimentella försöken i industriell skala med

användning av hydrochar från blandat organiskt bioslam och från grönt avfall visade att de flesta teknologiska parametrarna i masugnprocessen, såsom produktionshastighet för råjärn, mängd damm, bränsleåtgång, mängden injicerat kol, mängd slagg, FeO-halt i slagg och % C och % P i råjärnet i de experimentella försöken var väldigt lika jämfört med referensperioderna. Det bevisades således att hydrochar från olika typer av organiska rester kunde användas för metallurgiska tillämpningar även om ersättningsnivån var väldigt låg och längre försökskampanjer krävs för att få mer tillförlitliga resultat. Dessutom visar resultaten från den här studien att slagg från AOD-konvertrar kan användas som bindemedel för brikettering av dessa återvunna kalkmaterial. Sammanfattningsvis visar dessa resultat att avfall/biprodukter från två av de viktigaste svenska basindustrierna kan förena två stora industrisektorer i en cirkulär symbios mot en mer hållbar framtid.

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Stockholm, 2021

Tova Jarnerud

LIST OF SUPPLEMENTS

Supplement I:

Briquetting of Wastes from Pulp and Paper Industries by Using AOD

Converter Slag as Binders for Application in Metallurgy

Tova Jarnerud, Andrey V. Karasev, Pär G. Jönsson

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Application of fly ash from pulp and paper industries as slag formers in electric arc furnace stainless steel production

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Supplement III:

Utilization of fly ash and waste lime from pulp and paper mills in the Argon Oxygen Decarburization process

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Supplement IV:

Neutralization of acidic wastewater from a steel plant by using CaO-containing waste materials from pulp and paper industries

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Supplement V:

Utilization of organic mixed biosludge from pulp and paper industries and green waste as carbon sources in blast furnace hot metal production

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Tova Jarnerud, Andrey V. Karasev and Pär G. Jönsson

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Utilization of waste materials from the pulp and paper industry as raw materials in the steelmaking industries.

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- Supplement 2 Performed all of the literature survey, investigation, attended the trials and collected material samples and data, observations and analyses of the SEM work, data analysis, and major part of writing.
- Supplement 3 Investigation, attended the trials and collected material samples and data, writing, review, and editing.
- Supplement 4 Performed all of the literature survey and experimental work, data analysis, and major part of writing.
- Supplement 5 Performed all of the literature survey, investigation, attended the trials and collected data, data analysis, and major part of writing.

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LIST OF ABBREVIATIONS

AOD	– Argon oxygen decarburizer
BF	– Blast furnace
BR	– Briquettes
CF	– Cupola furnace
CRE	– Carbon removal efficiency
Dol	– Dolomite
EAF	– Electric arc furnace
EDS	– Energy dispersive spectroscopy
F or FA	– Fly ash
GHG	– Greenhouse gas
GrH	– Green waste hydrochar
HTC	– Hydrothermal carbonization
L, LM or WL	– Calcined lime mud
M	– Lime mud/Mesa
MJ	– Mega joules
MVA	– Megavolt-ampere
PCI	– Pulverized coal injection
pH	– Potential of hydrogen
PL	– Primary lime
PSH	– Paper sludge hydrochar
RW	– Retained weight
SEM	– Scanning electron microscopy
SF	– Slag formers
tHM	– Ton of Hot Metal
XRD	– X-ray powder diffraction
XRF	– X-ray fluorescence

1 INTRODUCTION

1.1 Background

1.1.1 The pulp and paper industries

Europe is a major pulp and paper-producing region in the world, with a production equivalent to 25% of the global production [1]. The pulp and paper industries are very important to Sweden, which has 69% of the land area covered with woodland [1], and where 58% of the land area consists of productive forestland that is suitable for forest production and not substantially used for other purposes [2]. Also, Sweden has the largest pulp production of any country in Europe [1]. Specifically, it corresponds to 31.7% of the total pulp production and 10.7% of the paper and board production in Europe [3]. In 2020, 9.3 million tons of paper were produced in Sweden, of which just over 90% was exported [4].

The pulp and paper industries in Sweden have made great efforts to reduce their environmental impacts. Since the 1970s, the effluent of organic materials to water has decreased by more than 90%, while the production has increased by 50%. One example of action taken is that chlorine gas bleaching ceased in the 1990s, due to major changes in the process technologies. Today, all wastewaters are purified in two or three steps before it is discharged [5]. Despite the great efforts from the pulp and paper industries to reduce their environmental impact, there is more to be done since the pulp and paper industries generate significant amounts of organic and inorganic wastes. The amount of waste produced in Sweden alone was 1.4 million metric tons in 2019, as can be seen in Figure 1. The Swedish pulp and paper mills sent 136,000 tons of various wastes to landfill in year 2019 [6]. Moreover, it is getting more difficult and more expensive to dispose waste materials in landfills due to stronger regulations and requirements with respect to the environmental impact [7]. According to the European council directive 1999/31/EC on the landfill of waste, prevention, recycling, and recovery of waste should be encouraged as should the use of recovered materials and energy, so as to safeguard natural resources and to obviate a wasteful use of land [8]. Therefore, the disposal of industrial paper mill sludge is an

important issue and it has great importance all over the world [9]. For instance, Europe hosts more than 500,000 landfills of which 80% essentially contain urban solid waste and 20% contain more specific industrial wastes and residues [10].

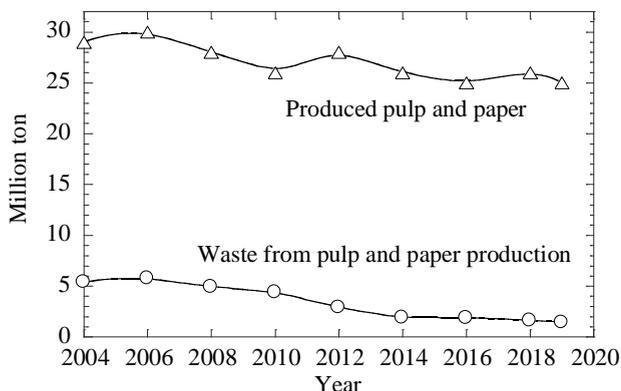


Figure 1– Amount of produced pulp and paper and waste from pulp and paper production in Sweden between the years 2004 and 2019 [7].

Up to now, the most common methods of sludge disposals are incineration and landfilling [11], where chemical leaching and greenhouse gas (GHG) emissions can cause significant environmental issues. However, Sweden has a ban on landfill of untreated organic waste since year 2001 [12]. The two dominating strategies for sludge handling at pulp and paper mills in Sweden are: i) mechanical dewatering followed by composting to make a landfill covering material or a soil amendment; ii) mechanical dewatering and incineration of the ashes [13]. Moreover, since April 2020 Sweden has a tax on incineration of wastes. It is 100 SEK/ton in year 2021 during a transitional period, with an increase in price over the coming years. However, tax exemptions have been introduced for biofuels [14]. The tax is expected to contribute to a more resource efficient waste handling to increase recycling and encourage to a fossil-free society [15]. This is an important step to reach Sweden’s goal of net zero GHG emissions in year 2045 [16], and to thereafter reach negative emissions. Negative emissions means that GHG emissions from

activities are less than for example the CO₂ absorbed by nature. Negative emissions can also be reached if Sweden helps to reduce the emissions abroad by participating in climate projects [17]. Several ongoing projects addresses the utilization of inorganic wastes from pulp and paper mills in various applications, for example; i) as alkaline fertilizers or soil amendments in the forest [18] (they contain nutrients such as N, P, K; ii) as supplementary cementitious materials or geopolymeric binders and mortars for construction applications to partially replace standard minerals [19]–[21]; iii) as stabilizers for engineering applications [22]; iv) as base materials for glass ceramic production [23]; and v) as adsorbents for environmental applications [24].

In general, biomass is a biological or organic material, which can act as a source of renewable energy through thermal or biochemical transformation processes [25]. In the view of tackling the global warming issue by minimizing methane from landfills and carbon dioxide emissions, the use of biomass as a substitute for fossil fuels combustion plays an important role. Sustainable managed biomass resources are considered green, as they do not contribute to net CO₂ emissions or global warming [26]. The uptake of carbon when the feedstock is grown is assumed to balance the release of carbon from a biomass combustion and it results in zero net emissions over some period [27], [28]. Some steps that need to be fulfilled for the utilization of biomass as a sustainable energy source were compiled by Sharma et al.: 1) sourcing locally to minimize CO₂ emissions during transportation and extraction of biomass; 2) making use of local waste such as waste wood, yard trimmings and other organic fraction of municipal solid waste that would have otherwise been sent to landfills; and 3) utilizing best energy efficient technologies [29]. An equation (Equation 1) for calculation of the net renewable power production which compares the total power supply chain energy consumption and conventional reference supply chain based on coal for energy production was developed by Miedema et al. [30]:

$$E_{\text{Renewable power}} (\%) = \frac{E_{\text{Biomass}} - (E_{\text{Supply chain}} - E_{\text{Reference chain}})}{E_{\text{Supply chain}}} \times 100\% \quad (\text{Eq. 1})$$

where E_{Biomass} is the energy contained in the biomass, $E_{\text{Supply chain}}$ is the energy consumption in the whole supply chain, and $E_{\text{Reference chain}}$ is the energy consumption in the coal reference chain.

It is clear that the efficiency of using biomass depends on the energy content of biomass and the energy consumption within the whole supply system.

Biosludge is a by-product of wastewater treatment. Due to its high contents of organic carbon and plant nutrients, it can be used as a raw feedstock for making organic fertilizers and building materials [31].

1.1.2 The steel industries

The production of steel is resource intensive and generates CO₂ emissions. In blast furnace (BF) operations, carbon is charged in the form of coke and pulverized coal to provide heat to melt the iron ore and to reduce the iron oxides to iron. The largest part of the total CO₂ emissions (85%) from the steel industry originates from the coal used to reduce iron ore [32]. 10% of the total CO₂ emissions in Sweden is generated by SSAB's BF's even though they are among the most efficient in the world in terms of minimizing emissions [33]. The use of renewable biomass resources are increasingly important to reduce greenhouse gas (GHG) emissions and to meet the increasing energy demand.

During electric arc furnace (EAF) and argon oxygen decarburization (AOD) steelmaking process, burnt lime is charged together with other slag forming materials to attain a specific basicity of the slag and to achieve purification by removing unwanted elements. The calcination of natural limestone (CaCO₃) generates large amount of CO₂ gas; 1 mole of CO₂ gas per mole of CaO, as seen in Equation 2. This corresponds to approximately 780 kg of CO₂ per ton of burnt primary lime (CaO).



The iron and metal industry is the single largest consumer of limestone in Sweden. Burnt lime and burnt dolomite are used in several steps of the production chain of iron and steel. Other process industries that use lime products include the cellulose industry and the paper mills. The consumption of burnt lime is approximately 30-45 kg per ton of steel for all types of steel except for stainless steel where the consumption is usually over 90 kg per ton. The production of lime products by the Swedish suppliers were 2 053 000 ton in year 2018, and 47% of the burnt lime products was used for iron, steel and metal production [34]. It should be pointed out that the requirements for the properties and chemistry of the lime differs for different steps of the steel production.

1.2 Sustainability

This thesis is a part of the VINNOVA, Sweden's innovation agency, Challenge-Driven Innovation (CDI) OSMET S2 project [35]. The project addresses Goal 12: Responsible consumption and production in the 2030 Agenda – for sustainable development. The project specifically addresses target 12.2: By 2030, achieve the sustainable management and efficient use of natural resources, and target 12.5: By 2030, substantially reduce waste generation through prevention, reduction, recycling and reuse [9]. The measures to reduce the environmental effects of landfilling in Sweden and the European Union can be divided into two main strategies. One is to reduce emissions from the landfills in the long term through how the landfills are designed. The second is to reduce the amount and dangerousness of the landfilled waste [36]. Furthermore, waste materials kept in landfills are a loss to society and represent a non-sustainable solution.

1.3 OSMET S2 project

The aim of the OSMET S2 project is to utilize sludges and other waste materials from pulp and paper industries as recovered materials within various metallurgical applications to reduce the climate impact

and avoid the needs for landfills. Some of the wastes contain high amounts of carbon, while some wastes contain high amounts of calcium oxide compounds. These waste materials can replace fossil fuels and natural raw limestone in metallurgical applications. The commonly used primary lime is produced by a calcination process, wherein most cases fossil fuels such as coal, oil, or natural gas are used. Also, CO_2 is emitted when the CaCO_3 from the limestone is separated into CaO and CO_2 in the calcination process. The use of recovered lime can reduce both the mining of natural limestone as well as the use of fossil fuels. However, today most of these wastes are kept in landfills [37]. This is costly and also has potential impacts on land and groundwater. One of the risks of putting inorganic residues in landfills is chemical leaching. Another risk is the formation of methane, CH_4 , from the organic landfilled residues. Methane has a global warming potential (GWP) significantly higher than that of CO_2 [38]. By the novel use of these materials in various metallurgical applications, valuable contents such as carbon and calcium oxides can be recovered, the amount of wastes in landfills, as well as the extraction of natural assets in Sweden, Europe, and the world can be decreased and the environmental impact can be reduced. The initial goal of the OSMET S2 project was to replace 5% of the fossil fuels, limestone, and lime traditionally used in metallurgical processes such as blast furnaces, cupola furnace, electric arc furnace and AOD converters with recovered material from pulp and paper mills. This innovative use of waste materials strives to keep resources in use for as long as possible. During the work in OSMET S2, new ideas were born, namely; the spin-off ideas of using AOD slags as binders in metallurgical briquettes, and CaO -rich wastes for neutralization of acidic wastewaters.

The OSMET S2 project was coordinated and led by SWERIM AB and the other partners were Outokumpu Stainless AB, SCA Obbola AB, RISE Processum, SSAB EMEA AB, SSAB Merox, Stora Enso AB, Swedish University of Agriculture (SLU), RISE, RISE IVF, Volvo Technology AB and KTH Royal Institute of Technology.

1.4 Residues from pulp and paper industries

Various types of sludges and wastes are generated from different process units within the pulp and paper mills. Two groups of wastes are considered in the OSMET S2 [35] project; namely wastes containing large amounts of carbon and wastes containing large amounts of calcium oxide compounds. A proper utilization of these residues can decrease the use of fossil carbon and natural limestone in the steel production processes.

1.4.1 Carbon-containing residues

A mixed biosludge is generated by mechanical biological methods in the primary and secondary wastewater treatment processes at a pulp and paper mill. It is a mixture of biosludge (sedimented bacteria) and pre-sedimentation sludge (fiber & sand) and it contains about 47% of C, 20% of O₂ and 8% of CaO. The amounts of sulphur (S) and phosphorus (P) are lower than 1%, which yet are considered to be high for metallurgical applications. The biosludge is usually first sent to an evaporator plant followed by incineration in a recovery boiler. The energy recovery from combustion is not beneficial, as it only has a net calorific value of 2–6 MJ/kg [13]. A compilation, made by Nwachukwu et al. [39], of the heating values for various fossil fuels used across the entire iron and steel production chain shows the range of 29–42 MJ/kg for sake of comparison.

Organic sludges have a high water content which makes an anaerobic digestion to biogas an attractive upgrading route to avoid an energy intensive dewatering process. However, many pulp and paper mill sludges are quite difficult to digest. The relatively low carbon concentration and high moisture content of organic sludges compared to fossil fuels are the major drawbacks of using them as carbon source and fuels in steelmaking. Drying of organic sludges is challenging since most of the water is contained within the cell walls of microorganisms. A pretreatment, such as a hydrothermal carbonization (HTC) is required to convert organic compounds into structured hydrochar. HTC is a thermochemical process for converting wet biomass into a carbon-enriched solid, commonly

referred to as hydrochar [40]. The HTC process is carried out in aqueous conditions at 180-250°C. The process water can be reduced to 50% by mechanical dewatering, and thermal drying can eliminate the water content to below 5%. The mechanical dewatering is much less energy consuming than thermal drying, since the water does not have to evaporate [41]. The HTC process is also referred to as a hydrothermal pretreatment, wet torrefaction, coalification or hot compressed water (HCW) treatment [42]. Various treatment options are available for biomass. The main advantage of the HTC process over dry conversion technologies (such as pyrolysis, gasification, and combustion) is its ability to convert the wet feedstock to a solid carbonaceous product (hydrochar) at relatively high yields without using prior dewatering and drying processes. Depending on the moisture content in the feedstock, the energy required to dry it can be significant [43]. The higher heating values for (HHV) of hydrochars from various feedstocks are among 24-30 MJ/kg, with an increase of 45-90% compared to the matching feedstock [44]. A comparative study of the fuel quality of pellets from raw biomass from woody biomass and agro-residues and corresponding hydrochar was done by Liu et al. [45]. The study concluded that hydrochar pellets were more suitable to be used for power generation than raw biomass pellets. Most of the hydrochar pellets had increased fixed carbon contents, higher heating values, improved combustion characteristics, decreased ash contents and higher mechanical strengths compared to the pellets made of raw biomass. Previous studies have investigated the possibilities to treat maize straw by using the HTC technology for production to produce bio coal for injection in a BF [46], and to use torrefied sawdust in a BF to reduce fossil carbon consumption and CO₂ emissions [47].

Moreover, the biomass char obtained from biosludge and green waste can be partially used in a BF process as a C-containing reagent instead of using conventional coke. In this project, hydrochar from HTC treated green waste was included in the blast furnace trials. The organic fraction in sludges does not contribute to net CO₂ emissions, since it is renewable [26].

1.4.2 Lime-containing residues

A number of residues from pulp and paper mills contain large amounts of calcium oxide compounds; lime mud/mesa (referred to as mesa in S1), calcined lime mud (referred to as lime mud in S1 and waste lime in S3) and fly ash. These residues can partially replace primary lime as slag formers during various stages in the steelmaking processes. These residues consist of powders of different size ranges. It is obvious that the natural lime can be saved by using these CaO compound-containing residues. As a result, effects on biodiversity, disruption of landscapes and other negative environmental impacts associated with mining of primary resources can be significantly decreased. Other benefits are the reduction of required energy and the reduced greenhouse gas emissions when recovered lime replaces natural limestone. These residues from the pulp and paper industries also contain impurities such as S, P and alkali metals. Thus, the effects of applications of these recovered lime sources in steelmaking processes on the technical parameters and the final steel quality should be evaluated with respect to the distribution of S and P between slag and liquid steel.

Lime mud consists of approximately 90 percent calcium carbonate (CaCO_3) and calcium hydroxide (Ca(OH)_2). It is the excess chemicals from the recovery boiler. The lime mud is formed in the Sulphate process, where wood chips breaks down into pulp when cooked in a mixture of chemicals called white liquor [48]. Calcined lime mud contains mainly CaO, since the CaCO_3 decomposes to CaO and CO_2 during the calcination process.

Fly ash contains approximately 60 percent of CaO compounds and it is formed by the combustion of internal and external fuels (sludge from the recycled paper and wood fuels) in the paper mill. The process used at the pulp and paper mill affects the chemical composition of the fly ash. Fly ash is commonly used in various applications especially in construction and civil engineering projects to partially replace cement in mortar and concrete [49]. However, the utilization of fly ash and lime mud represents only a small fraction, and the majority of these solid wastes are deposited in landfills. Today,

70% of the fly ash from pulp and paper mills in Sweden are kept in landfills [50].

1.5 Byproducts and residues from the steel industries

A material efficiency rate of 96.3% in the steel industry worldwide has been achieved by, for instance, the use of co-products. However, the overall goal is to reach a 100% efficient use of raw materials and zero-waste [51]. Almost two million tons of residues were produced by the iron and steel industries in Sweden in 2018. The residues (by-products and wastes) can be divided into three groups; 44% is used externally, for example sold as products, 34% is recirculated internally, for example as raw materials in the production processes, and 22% are wastes that are put to landfill [52]. Of the materials put to landfill, metallurgical slags accounted for ~70%, and 6% (approximately 120 000 metric tons) was AOD slags [52]. Slag is a non-metallic substance, a byproduct from the production of iron and steel. The primary contents of slags are oxides, such as calcium oxide and silica and they often contain low amounts of S and P. The characteristics, chemical composition and properties of the metallurgical slags differ significantly depending on the process they were produced in. The slag properties can be changed by changing the chemical compositions and cooling processes.

The steel industry aims to substitute some of the traditional raw materials with residues in various applications to ensure optimal use of the residues and thereby a decreased consumption of the natural raw materials [52]. However, how the steel slags can be re-used depends on the influence of their chemical compositions on the properties. Almost 100% of the slags from the blast furnace are reused, mostly for road constructions, as raw materials for cement production, and as cement-like binders [53].

Moreover, the use of some slags can be limited by swelling and disintegrating properties or by leaching of metals. Slags from the AOD converter typically have a ratio of lime and silica that promotes a formation of calcium silicates ($2\text{CaO}\cdot\text{SiO}_2$) during solidification. A phase inversion of the β -form of this phase can cause expansion during cooling through the temperature range of 400–500°C [54]. This, in

turn, leads to a volumetric expansion of the slag, which will break into a fine powder. Therefore, the textures, porosities and other physical properties are affected by the cooling rate [53]. The utilization scope of these slags are significantly reduced as this causes environmental deteriorations during storage in the slag yard [55].

A larger proportion of slags from the production of high-alloyed steels in EAF and AOD processes is put to landfills compared to the slags from the production of low-alloyed steels. One of the reasons why slags from stainless steel production are less used for road constructions and cement production is the higher contents of chromium oxides and the harmful effects caused by chromium that has to be considered [56]. This requires a careful process control to eliminate the risk of chromium leaching to the environment.

During the production chain of stainless steel, the steel undergoes a series of steps to reach the desired material properties and qualities. During treatments at high temperatures (such as hot rolling and annealing), alloying metals from the steel matrix diffuses to the surface and oxide layers are formed when the metals react with the surrounding air. When the chromium diffuses to the surface, some chromium-depleted zones are formed underneath the oxide layers. These zones have lower corrosion resistances and strengths [57]. Also, a pickling process can be applied to remove these chromium-depleted zones. It is a chemical cleaning process commonly used in a steel mill in various steelmaking processes for removal of impurities such as contaminants, corrosion products or scale from a steel surface. The aims of the treatment are to make the material more receptive to further processing or use. The pickle liquor usually contains strong acids such as sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) [58]. The pickling liquor gives rise to acidic wastewater streams. The wastewaters have to be neutralized and cleaned before they can be released to the recipient. In industrial practice, the acidic wastewater is usually neutralized by an addition of primary lime to raise the pH value up to normal neutral levels.

In several publications it was reported that steelmaking slags [59]–[64], waste limestone from the marble industry [65], and cement kiln dust [66] and other secondary lime sources can be used for neutralization of acidic wastewaters and for cleaning of industrial

waters. The content of CaO-compounds in the wastes from pulp and paper industries can reach 60-90%, which is comparable or significantly larger than that in steelmaking slags. Therefore, it was assumed that those wastes could be applied for neutralization of acidic wastewaters. Experimental results from utilization of lime mud and recovery boiler ash from pulp and paper industries to remove heavy metals from metal finishing wastewater was reported by Sthiannopkao et al. [67]. These wastes contain various carbonate compounds, which contribute to a high pH value. A direct precipitation of heavy metals by carbonate precipitation agents calcite and burkeite led to decreased residual metal concentration of chromium, copper, lead and zinc.

1.6 Overview and aim of the study

The specific aim of this study was to effectively employ residues from pulp and paper industries and thereby reduce the dependence on fossil carbon and nature limestone in the iron and steel industry. Moreover, utilization of these residues will reduce the amount of wastes in landfills. An overview of this thesis work can be seen in Figure 2 and the work presented in this thesis can be seen in Table 1. The carbon-containing materials were upgraded to hydrochar and tested as a carbon source in a production cupola furnace. The use of lime-rich residues for injection in a pilot electric arc furnaces was also tested. However, these results will not be further discussed in this thesis.

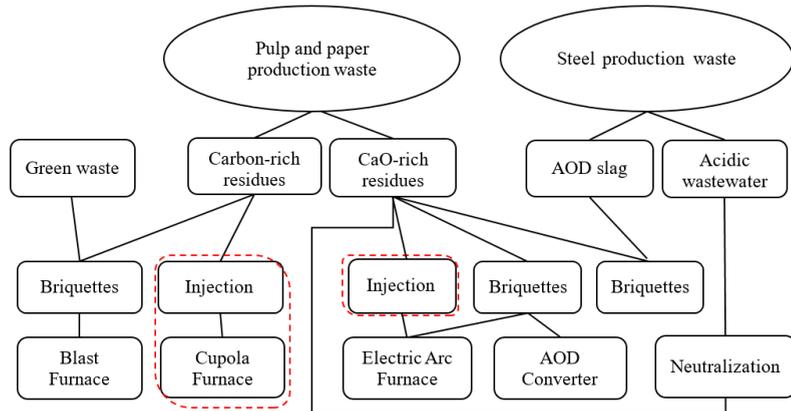


Figure 2 – An overview of identified possible applications of residues from pulp and paper industries in metallurgical processes. The parts marked with red are not further discussed in this thesis.

This thesis focuses on consideration of the results obtained from trials with these newly developed solutions in laboratory-scale, pilot-scale and industrial scale. In the industrial-scale trials in a production blast furnace, organic sludges and green waste were upgraded to hydrochar and charged into the BF. The aims of these trials were to test the possibilities: i) to utilize the organic mixed biosludge from pulp and paper industries and green wastes as hydrochar pellets after a hydrothermal carbonization in the BF process instead of incineration and landfilling; ii) to use these hydrochar pellets as a part of conventional briquettes containing in-plant fines (such as fines from pellets and scrap, dust, etc.) used for the BF process; iii) to use briquettes containing hydrochar pellets as a small part of the carbon source in a BF; and iv) to control and compare technological parameters and conditions of the BF process by conventional reference charging and experimental charging by using different amount of various briquettes.

Moreover, pilot EAF and AOD converter trials were conducted at SWERIM AB. Here, recovered lime-containing waste materials in the form of briquettes were tested to partly replace the primary lime as slag formers in different stages of stainless steel production. The study focused on considerations of how the processes,

steel quality with respect to the chemical composition and slag properties such as slag amount, P and S content and basicity were affected.

In addition, the possibilities to use recovered lime materials as neutralizing agents for acidic wastewaters from the pickling processes in a steel mill were tested in extensive laboratory-scale trials. The main aim was to determine the proper amount of different secondary lime materials and methods of addition to raise the “potential of hydrogen” (pH) to a value of 9 during a selected maximum process time of 30 min. Regular water has a pH value of 7, but the absorption of some elements (such as Ni) from the reactants are maximized at high pH levels [59]. Moreover, flocculants added in industrial applications will lower the pH value significantly of the treated water. Furthermore, the efficiency of neutralization of the acidic wastewaters was evaluated as a function of the chemical compositions of the neutralized waters and added wastes.

Moreover, laboratory tests were conducted at KTH to evaluate the possibilities to the use AOD slags as a binding agent for the lime-rich residues, and if further processing by heat-treatments or storage time would affect the strength of the briquettes.

Table 1 – Overview of the supplements (S) in this thesis.

S	Study	Objective	Approach	Parameters
I	Application of AOD converter slags as binders in metallurgical briquettes.	Decision of recipes. Method to produce metallurgical briquettes. Improvement of mechanical strength. Determination of impact strength of briquettes.	Production of laboratory-scale briquettes. Modification of chemical compositions (% AOD slag). Storage time in air (days). Heat-treatment T (°C). Drop tests. SEM-EDS studies.	Chemical compositions. Impact strength in drop tests. Retained weight after drop testing (RW). Phase changes, sintering performance.
II	Application of recovered lime-containing materials as slag formers in EAF.	Chemical compositions of metal and slag. Steel quality in the aspects of S and P. Impacts on the EAF process. The slag properties; amount, P and S content, basicity, fluidity.	Pilot-scale trials. Chemical compositions of metal, slag and dust. Mass balance calculations for main components. SEM-EDS investigations.	S and P content of steel and slag. Viscosity of slag (by visual inspection). Amount of slag and dust. Dissolution of charged slag forming materials.
III	Application of recovered CaO-containing materials as slag formers in AOD converters.	Impacts on the AOD processes; Decarburization, reduction and desulphurization.	Pilot-scale trials. Chemical composition determinations of metal, slag and dust. Mass balance calculations for main components.	Amount of slag. Carbon removal efficiency (CRE). Reduction and desulphurization efficiency. Chemical compositions with focus on S and P.
IV	Application of recovered CaO-containing materials as neutralizing agents for acidic wastewaters.	Neutralization efficiency and water cleaning ability.	Laboratory-scale trials. pH measurements and determinations of Cr, Fe, Ni, Mo and Zn levels in waters.	The efficiency of neutralization of the acidic wastewaters. Level of some metals.
V	Application of organic sludges and green wastes as part of the carbon sources in blast furnace (BF) operations.	Impact on the BF process; Productivity, fuel rate, chemical composition of hot metal and slag.	Industrial-scale trials. Data interpretation of process parameters.	Chemical composition of hot metal and slag. Impact on productivity.

2 MATERIALS AND METHODS

2.1 Materials

The recovered lime-containing materials, which are studied in this thesis, are; lime mud/mesa (M), calcined lime mud (L), fly ash (F) and AOD slag, as shown in Figure 3.

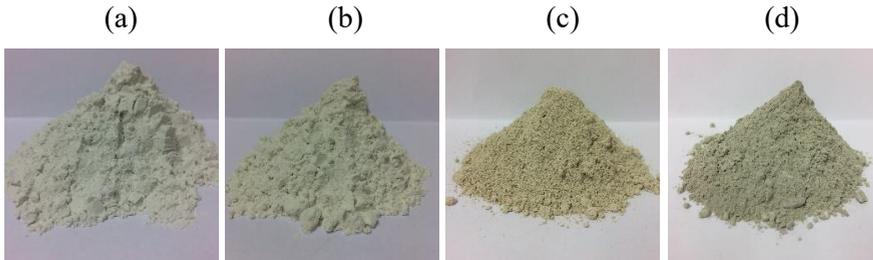


Figure 3 – Samples of lime mud/mesa (a), calcined lime mud (b), fly ash (c), and milled AOD slag (d).

2.1.1 CaO-containing residues used for briquetting trials

Determinations of the chemical composition of the materials were made by using Thermo finnigan element 1 Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) according to SS EN ISO 17294-1, 2 [68], [69] and the Environmental Protection Agency (EPA) method 200.8 [70]. The chemical composition determinations were made by ALS Scandinavia AB. The values from the determinations were recalculated to normalized values after subtracting the Lost On Ignition (LOI) value at 1000°C, which is the mass of the volatiles lost during heating of the material up to 1000°C (organic matter, carbonates, moisture etc.). The main components are shown in Table 2. Other than the main components, lime mud and calcined lime mud contains MgO (<1%) and the fly ash contains approximately 9% Al₂O₃, 3% MgO and <1% Fe₂O₃ and TiO₂.

Table 2 – Contents of main components (in wt %) after calcination at 1000°C of lime rich residues used in metallurgical briquettes.

Material	CaO	Na ₂ O	P	SiO ₂	K ₂ O	S	Balance	LOI 1000°C
Lime mud/mesa	95.9	1.5	0.4	0.2	0.2	0.1	1.7	40.6
Calcined lime mud	95.9	1.5	0.4	0.1	0.1	0.2	1.8	6.1
Fly ash	63.2	0.6	0.1	21.0	0.5	0.4	14.2	6.6

The residues consists of fine powders, and a briquetting operation is often required in order to facilitate handling, transportation and charging of these materials in the steel mills. Also, an AOD slag with the main components CaO, SiO₂, Al₂O₃, MgO, and FeO was used as a binding agent in the briquettes.

2.1.2 Fly ash and calcined lime mud used in EAF and AOD converter trials

Fly ash from Stora Enso, calcined lime mud from SCA Obbola and primary lime from SMA minerals were used as slag formers, together with commercial grades of dolomite, ferrosilicon (FeSi75) and fluorspar. In Table 3, the chemical compositions of the slag forming materials that were used in the pilot trials can be seen. The primary lime refers to the commercial lime commonly used in the EAF and AOD processes. Therefore, it was used as the reference material in this study.

Table 3 – Contents of main components in the lime-containing materials (wt%).

Materials	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	MgO	P ₂ O ₅	S	Others
Fly ash	61.5	15.8	8.9	0.6	0.07	0.08	3.1	0.26	0.40	9.29
Calcined lime mud	90.6	0.18	0.07	0.04	0.1	0.48	1.05	0.75	0.11	6.62
Primary lime	95.2	1.0	0.5	0.2	0.04	0.04	1.7	0.01	0.08	1.23
Dolomite	57.3	0.9	0.2	0.2	0.04	0	38.4	0.05	0.02	2.89

The results from X-ray powder diffraction (XRD) determinations of fly ash, calcined lime mud and primary lime can be seen in Figure 4. The calcined lime mud contains 90.6% CaO, and CaO was identified as the main phase. The fly ash contains 61.5% of CaO, where CaO was one phase, but other CaO-containing phases such as; calcium silicate (Ca_2SiO_4) and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) were also present. These results indicate that the free CaO content in the fly ash is less than 61.5%.

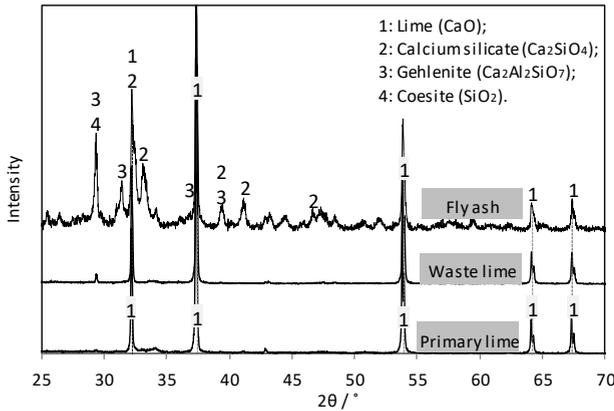


Figure 4 – XRD determinations of the fly ash, waste lime (calcined lime mud) and primary lime used in the pilot trials.

The briquetting of fly ash and calcined lime mud was carried out by using a roller press (Model Komarec B220B), with a briquetting force of 40 kN/cm² and a rate of 200 kg/h by SWERIM AB. In pre-trials of the briquette making, different compositions were tested and a recipe of 50% primary lime fines (<0.5 mm), and 50% fly ash or recovered lime (< 0.5 mm), with an addition of 0.5% calcium stearate as a lubricant was decided upon. The decision was based on tests results from the splitting tension test and drop test methods of the briquettes made in the pre-trials. Five briquettes were used for each test in the crush test and an average value was calculated as the force corresponding to when a breakage (kg) occur, according to Equation 3.

$$F = P_{at\ breakage} \frac{100\ 000 \times 0.00145}{9.81} \text{ (kg)} \quad (Eq.3)$$

The drops test were conducted by dropping 5 briquettes 2 times from a 2 meters height. The briquettes including broken material were then sieved. The result was briquettes with a mass fraction of < 11.2 mm.

These briquettes had a satisfying cold strength of 90 kg in the splitting force/crush strength test. This should be compared to 60 kg when 10% of fly ash or recovered lime was combined with 90% of primary lime fines. Moreover, the briquettes with the chosen recipe had a lower drop test index of 30% compared to that of briquettes with 10% of fly ash or recovered lime being 35-50% [71].

The produced ellipsoidal shaped briquettes (Figure 5) had a volume of 13 cm³. The briquettes (BR) were used to replace primary lime lumps as slag formers in EAF and AOD converter operations. As the fly ash contains 61.5 % CaO and primary lime contains 95.2% CaO-compounds, briquettes with a 50/50 ratio of these two powders will contain 39% CaO from fly ash and 61% CaO from primary lime. The other materials used in the trials also include commercial grades of primary lime lumps (PL), dolomite (Dol), ferrosilicon (FeSi75) and fluorspar.

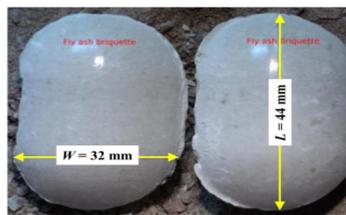


Figure 5 – Photograph of fly ash briquettes used in the experimental trials in the pilot-scale EAF and AOD converter trials.

2.1.3 Acidic wastewaters

Four batches of acidic wastewaters (AWW, BWW, CWW and DWW) from two steel plants were used in the trials. The chemical composition of the different batches of wastewaters differed significantly, depending on the mixture of acids used for the pickling

of different steel grades. The initial pH values of the wastewater batches in this study were on average 1.92 ± 0.14 for AWW, 2.08 ± 0.14 for BWW, 1.53 ± 0.15 for CWW, and 2.21 ± 0.11 for DWW.

2.1.4 Organic mixed biosludge and green waste

The biomass came from two types of feedstocks; organic mixed biosludge and organic residues of green waste. The sludges and wastes were treated by using the hydrothermal carbonization (HTC) technology to convert biomass into a carbon-enriched solid, referred to as hydrochar [40]. The hydrochar was pressed into small size pellets. In Figure 6, typical photographs of samples of carbon-rich organic biosludge, pellets made of HTC treated biosludge and briquettes containing green waste are shown. The hydrochar pellets from green waste is a standard material produced by the Ingelia HTC plant, and the values in Table 4 and 5 are typical values from chemical determinations. The values for mixed biosludge are from the specific batch of material used in the given trials. The ash content was analyzed according to the UNE 32004:1984 standard [69], whereas the sample was heated to 815°C and kept at this temperature for one hour. Thereafter, inductively coupled plasma (ICP) was used for determinations of the ash compositions. The volatiles were determined according to the UNE 32019:1984 standard [72], where the samples were heated up to 900°C for 7 minutes, without the presence of air. The elemental composition determinations were made by using a Fisons EA 1108 CHNS-O instrument. Approximately 4.5 tons of hydrochar from mixed biosludge, and 4 tons of hydrochar from green waste were produced by the Ingelia HTC plant.



Figure 6 –Mixed biosludge (a), green waste (b), pellets produced by Ingelias HTC process (c), and bio briquettes containing green waste hydrochar produced at SSAB Merox (d).

Table 4 – Main elements of hydrochar pellets, dry and ash free base [wt% daf [72].

Feed stock	C*	H*	N*	S*	Ash content (%dry)**	Volatiles (%dry)**	Fixed C (%dry)**
Mixed biosludge	62.0	N/A	N/A	0.3	16.0	65.0	20.0
Green waste	61.4 ±1.6	6.3 ±0.3	1.3 ±0.09	0.1 ±0.1	10.2 ±2.3	64.7 ±5.6	25.0 ±5.1

*Values referring to dry basis and without ashes, **values referring to dry basis, N/A: Not Available

Table 5 – Ash composition of hydrochar pellets [wt%] of ashes [72].

Feed stock	Na ₂ O	K ₂ O	MgO	CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	P ₂ O ₅
Mixed biosludge	1.3	5.8	1.3	12.9	10.7	2.5	52.4	4.5
Green waste	0.9 ±0.4	4.3 ±1.7	3.9 ±0.5	42.7 ±4.9	6.3 ±1.0	4.6 ±0.7	31.5 ±1.9	4.6 ±0.7

2.2 Methods

2.2.1 Briquetting of residues from pulp and paper industries by using AOD converter slags as binders

In this study, CaO-containing rest materials obtained from pulp and paper production and an AOD converter slag with binding properties from a steel plant were combined to create metallurgical briquettes for stainless steelmaking, as illustrated in Figure 7. For CaO materials, water-containing binders cannot be used, since it would hydrate the CaO.

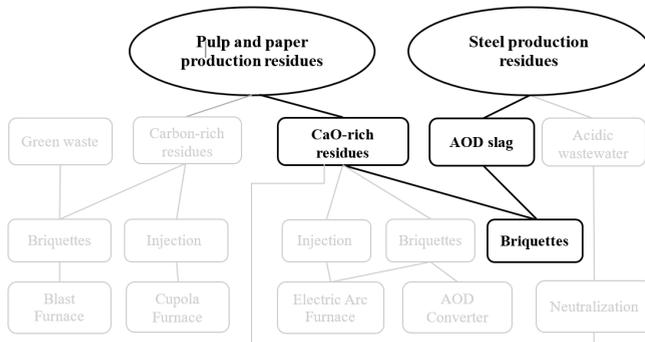


Figure 7 – Combination of two waste/by- materials to create metallurgical briquettes for iron and steelmaking; CaO-rich residues from pulp and paper production with AOD slags as binding agents.

One of the three CaO-rich residues used in this study (lime mud/meal – M, calcined lime mud – L and fly ash – F), was used as base material and mixed with various amounts of AOD slag and thereafter pressed into tablet shaped briquettes using a 18 MPa pressure. The dimensions of the briquettes were: 33 mm in diameter and 18 mm thick, and they consisted of:

- 1) 100% base material (referred to as M100, L100 and F100)
- 2) 90% base material and 10% AOD slag (referred to as M90, L90 and F90)
- 3) 80% base material and 20% AOD slag (referred to as M80, L80 and F80).

The original lime materials used in steel making are shown in Figures 8a and b, and the laboratory-scale briquettes can be seen in Figure 8c. In Figure 8d, industrial-scale briquettes are shown for sake of comparison.

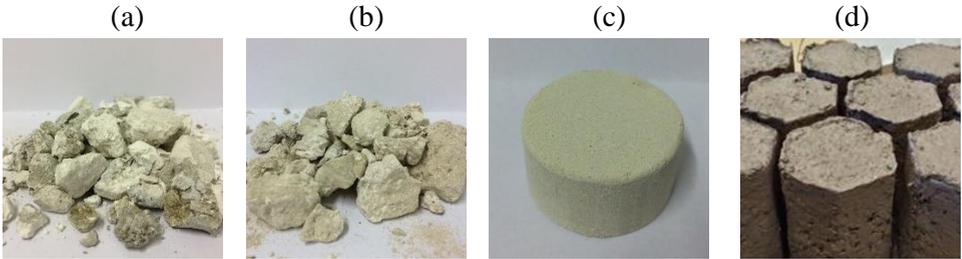


Figure 8 – Primary lime: AOD lime lumps 3–15mm (a) and EAF lime lumps 15–40 mm (b) and briquettes: laboratory-scale (c) and industrial-scale (d).

To evaluate how the impact strength of the briquettes are affected by storage time in air, some of the briquettes were stored during 7, 20 and 35 days before testing. The aim was to see if storage in air can be used as a curing method and to study how the briquettes can be stored for future industrial use. Also, heat-treatments at a 500°C or a 850°C temperature were applied to some of the briquettes to see if it can improve the impact strength of the briquettes. Totally, 90 briquettes were prepared and tested in this study, as shown in Table 6.

Table 6 – Compilation of produced briquettes for each set of test.

Base material	Comp. ref.	Base material [%]	AOD slag [%]	Number of briquettes					
				No add. treatm.	Stored [days]			Heat treated [°C]	
					7	20	35	500	850
Lime mud/ Mesa	M100	100	0	3					3
	M90	90	10	3			3	3	3
	M80	80	20	3					3
Calcined lime mud	L100	100	0	3					3
	L90	90	10	3			3	3	3
	L80	80	20	3					3
Fly ash	F100	100	0	3	3	3	3		4
	F90	90	10	3	3	3	3	3	4
	F80	80	20	3					4

Drop testing was the chosen method for evaluation of the impact strength of the laboratory-scale briquettes. Various methods can be used for drop tests and one is described by Mousa et al. [74]. For the purpose of this study, another method was used. It can be described as follows:

The briquettes were dropped with the flat face down, one at a time, from a distance of 1.0 m, onto a steel plate. After a completed test, the largest piece of the briquette was collected and the weight was recorded. The steel plate was cleaned and then the largest piece of the briquette was dropped again. The procedure was repeated until less than 1% of the initial weight of the briquette retained, or until a maximum of 15 drops were completed. It was assumed that the briquettes have to withstand 5–7 drops when used in industrial processes, during loading, transportation and unloading without causing a fast destruction into powder. The numbers are based on the production routes for the briquettes as follows in Figure 9.

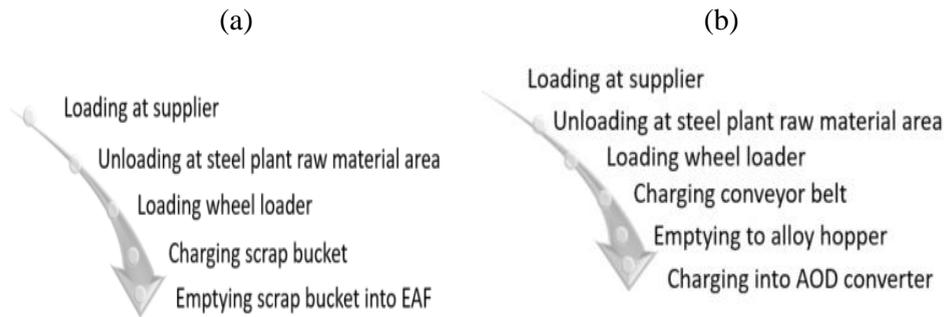


Figure 9 – Routes of briquette [74] for EAF (a) and AOD converter (b).

To evaluate the effect of the chemical composition and heat treatment of the briquettes on their mechanical properties, detailed investigations of the main compounds of the base materials and briquettes were done by using scanning electron microscopy (SEM) in combination with energy dispersive spectroscopy (EDS). The SEM imaging was done using a 10–11mm working distance and a 15 kV acceleration voltage. The composition of each main compound in different materials was determined based on 5 to 8 measurements by using an "area" mode analysis and based on 10–15 measurements by using point analyzers in different zones of samples.

2.2.2 Using fly ash as slag formers in EAF stainless steel production

In this study, CaO-rich fly ash was used as slag formers in an EAF, as illustrated in Figure 10. The charge materials used in the EAF pilot trials include scrap (5–7 ton) of a 304 stainless steel grade, alloying materials (Fe-75%Si ferrosilicon and anthracite), and slag forming materials such as primary lime, dolomite and briquettes containing recovered lime.

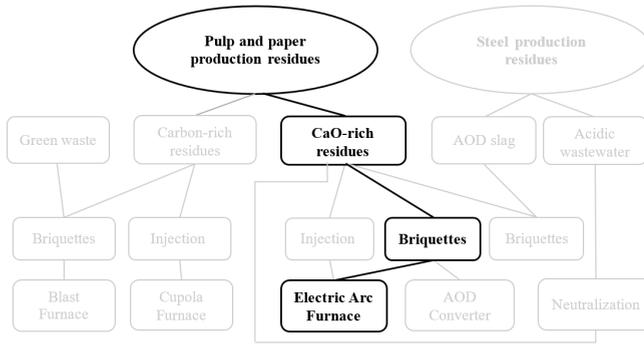


Figure 10 – Pilot trials using fly ash briquettes as slag formers in an EAF stainless steel making process.

The EAF input and output materials are shown in a schematic illustration in Figure 11, and Figure 12 shows a picture of the pilot EAF used for the trials in this study. The aim of the EAF melting was to reach a steel alloy content of up to 0.35% Si and 1.0–1.3% C, before the steel melt was transferred to the pilot AOD converter. The steel scrap, which was used for these pilot trials, contained 0.05% C, 0.40% Si, 18% Cr, 8% Ni, ~0.02% S, and ~0.034% P.

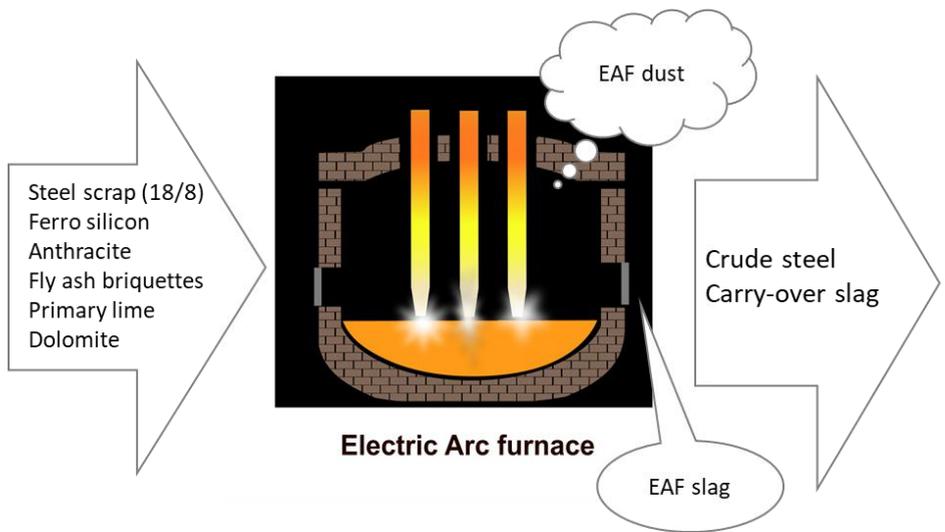


Figure 11 – Schematic illustration of the EAF process, including input and output materials.

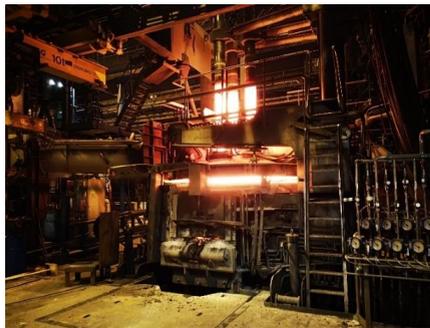


Figure 12 – The pilot EAF used in the trials. Photo: Chuan Wang.

Five pilot-scale trials were successfully carried out in a 10-ton EAF. It is used for melting of steel scrap and adjustment of composition. The first heat, (A) was a reference heat to obtain reference parameters of the specific experimental equipment used in these trials. Thereafter, four heats with gradually increased additions of briquettes as a replacement for primary lime were made. In these heats, the ratios of primary lime and fly ash, which were added as slag forming components, were 85/15 (B), 70/30 (C), 60/40 (D) and 50/50 (E). The charge materials were steel scrap, ferrosilicon, anthracite and

slag forming materials. When the charge materials were melted in the EAF, the temperature of the melt was measured. In addition, a steel sample and a slag sample were taken. Thereafter, the melt was heated up to 1650°C and the final samples of liquid steel and slag were taken just before tapping from the EAF. After that, about 0.25–0.48 t of slag was tapped from the slag door of the EAF and ~5 t of steel melt were tapped into a transfer ladle to enable the following decarburization process in the pilot AOD converter. Moreover, some amount of steel melt (about 2 t) and slag were kept after some pilot trials as hot-heat metal (HHMe) and slag (HHSI) in the EAF to be used in the following heat (as from heats A, C and E) or tapped into a mold for scrap (as from heats B and D). Moreover, the off-gas dust from each heat was collected in a separate barrel and a sample was taken when the heat was finished. The added input (such as scrap, slag formers, ferrosilicon and anthracite) and output (such as metal, slag and dust) materials were weighted.

2.2.2.1 Mass balance calculations

Conventional mass balance calculations were performed using a Microsoft excel spreadsheet for the following main components of slag and steel: CaO, MgO, Cr, Ni, Si, S and P, to estimate the effect of using fly ash as slag formers, on some parameter of the EAF pilot trials. The mass balance for the input and output materials is described as follows in Equations 4-6:

$$\Sigma m_{in} = \Sigma p_{out} \quad (Eq.4)$$

$$\Sigma m_{in} = m_1^i + m_2^i + m_3^i \dots = \text{Total component } i \text{ in all materials in} \quad (Eq.5)$$

$$\Sigma p_{out} = p_1^i + p_2^i + p_3^i \dots = \text{Total component } i \text{ in all products out} \quad (Eq.6)$$

Where Σ denotes the sum of all terms.

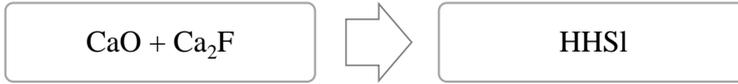
The input and output materials are listed in Table 7. The mass of some materials were measured, and the mass of some materials were calculated based on the mass balance described below. Table 7 shows which data that was known in the mass balance calculations.

Table 7 – Measured and calculated input and output data for mass balance calculations.

Input (measured data)	Chemical composition	Mass
Scrap	✓	✓
Primary lime	✓	✓
Briquettes	✓	✓
Dolomite	✓	✓
FeSi	✓	✓
Anthracite	✓	✓
Hot-heal Metal ($HHMe_{input}$)	-*	-
Hot-heal Slag ($HHSI_{input}$)	-*	-
Refractory	-**	-
Output		
Tapping metal	✓	✓
Tapping slag	✓	✓
Dust	✓	✓
Gas	-	-
Metal in slag	-	-
Hot-heal Metal ($HHMe_{output}$)	-	-
Hot-heal Slag ($HHSI_{output}$)	-	-

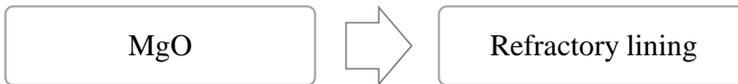
*assumed to be equal to obtained metal and slag from previous heat
**assumed to be pure MgO

- Since a rest slag in EAF after tapping of steel and slag cannot be weighted, a mass balance for CaO (including CaF₂ from added fluorspar) was used to determine the weight of the hot-heal slag ($HHSI_{output}$) in the EAF, after tapping of slag into the slag ladle. It was assumed that a difference between the amounts of CaO in the OUTPUT-materials (slag and dust) and INPUT-materials (briquettes and dolomite) in heats A, C and E (without using $HHSI_{input}$ and $HHMe_{input}$ in the charge) corresponds to the CaO amount in hot-heal slag for next heat in the EAF. This value can easily be recalculated into an amount of the $HHSI_{output}$ in the respective heat, based on the known CaO content in the obtained slag. Then, by using the amounts of hot-heal slags kept in the EAF and determined from previous heat, the amounts of the $HHSI_{input}$ contents in the heats B and D were calculated.



- A mass balance for MgO was used to evaluate the weight of the MgO refractory lining of pilot furnace, which was dissolved during the EAF process to become part of the slag. In this case, it was assumed that a difference between the amounts of MgO in the OUTPUT-materials (slag, dust and hot-heal slag) and the INPUT-materials (briquettes, dolomite and hot-heal slag from previous heat) completely correspond to the amount of MgO from the refractory lining (pure MgO), which was dissolved during the EAF process, as described in Equation 7.

$$\Delta MgO_{refr.}^{IN} = MgO^{OUT} - MgO^{IN} \rightarrow reference \text{ (Eq. 7)}$$



- Since a rest of metal in the EAF after tapping into the transfer ladle of steel melt cannot be weighted, the weight of the hot-heal metal (HHMe_{output}) in the EAF furnace after each heat was calculated, based on the Cr and Ni mass balances. In this case, the differences between amounts of Cr and Ni in OUTPUT-materials (metal, slag, dust and calculated hot-heal slag) and INPUT-materials (scrap and hot-heal slag from previous heat) were used to calculate the amounts of Cr and Ni in the HHMe and weight of the hot-heal metal kept in the EAF.



- The mass balance for Si was used for calculation of the weight of Si from the added FeSi, which was oxidized to SiO₂ during EAF melting and ended up in the slag.

- The mass balances for S and P were calculated to evaluate the effect of added briquettes with fly ash on the distributions of S and P, respectively, between metal and slag.
- The mass balance for C was used for evaluation of the weight of C in off-gas, which was partially oxidized to CO/CO₂ after addition of anthracite into the melt in EAF.

2.2.2.2 Thermodynamical calculations for melting behavior of slag

The melting behavior of the main oxides of the slags for heats A-E based on the ratio of PL/FA were determined using thermodynamic calculations. The oxide system CaO-SiO₂-Al₂O₃-Fe₂O₃-MgO was calculated using the Factsage 7.1 software and using the FToxid database, based on normalized values for the oxide system of added slag formers, as shown in Table 8.

Table 8 –Normalized values of main oxides in added slag forming materials.

Heat PL/FA, wt%	A	B	C	D	E
CaO	96.6	92.7	88.6	85.9	83.1
SiO ₂	1.0	3.3	5.7	7.3	8.9
Al ₂ O ₃	0.5	1.8	3.2	4.1	5.0
Fe ₂ O ₃	0.2	0.3	0.3	0.4	0.4
MgO	1.7	2.0	2.2	2.4	2.6

2.2.2.3 SEM-EDS investigations of slag samples

To evaluate the dissolution of fly ash and primary lime from briquettes in the formed slag during the EAF pilot trials, slag samples were taken from heat A, (0% Fly ash), heat C, (30% fly ash), and heat E, (50% fly ash). A picture of some slag samples can be seen in Figure 13. The samples were prepared and analyzed more in depth using SEM in combination with EDS to investigate the structures and compositions of the main components.



Figure 13 – Picture of typical slag samples.

2.2.3 Using fly ash and calcined lime mud as lime source in AOD converter

Briquettes containing recovered lime materials such as calcined lime mud and fly ash were used as slag formers in AOD converter trials, as illustrated in Figure 14. The crude stainless steel used in these AOD converter pilot trials was melted in a pilot EAF before it was transported to the AOD converter. The target contents of C, Si, Cr and Ni from the EAF were 1.0%, 0.35%, 18% and 8%, respectively. When the steel and slag were melted, samples were taken from the steel and slag to determine the chemical compositions. C and S were determined by using LECO combustion analysis and the other elements were determined by XRF (X-ray fluorescence) analysis. When the target chemical composition was reached, the temperature was increased to 1650°C. After the trial, the slag was tapped from the slag door, and the steel melt was tapped into a transfer ladle. About five tons of the steel melt was then charged into the AOD converter. An overview of the trial procedures is illustrated in Figure 15.

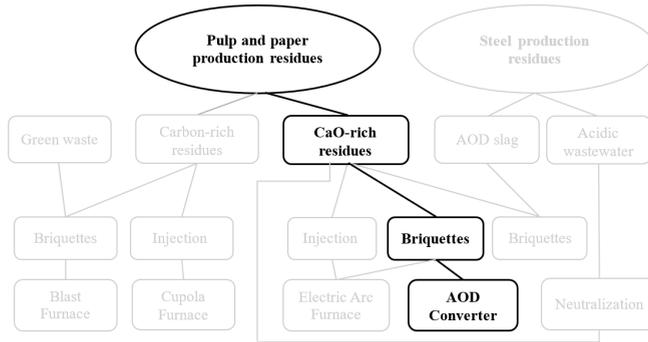


Figure 14 – Pilot trials using fly ash and calcined lime mud as lime source in AOD converter stainless steel making process.

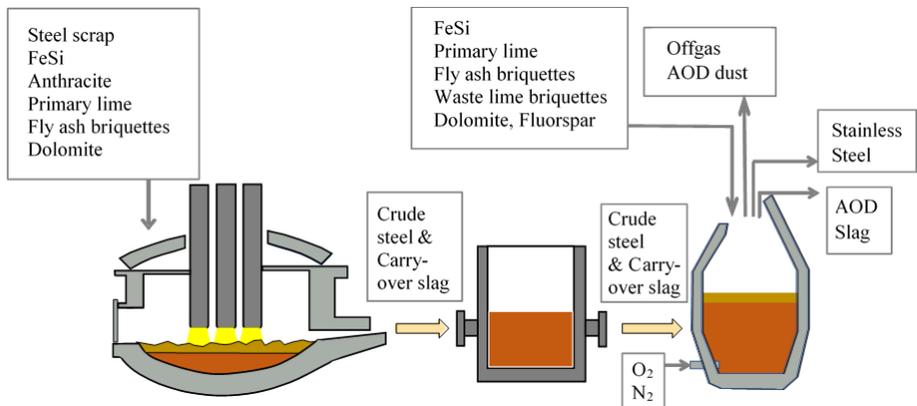


Figure 15 – Overview of the pilot EAF-AOD trials: crude stainless steel melt preparation in the EAF, transfer of the steel melt and further processing of the steel melt in the AOD converter.

In this study, six heats were conducted in a pilot universal converter, which was conditioned to be an AOD converter operated using sidewall blowing. The first heat (H1) was conducted as a reference heat to get reference parameters of the specific experimental equipment used in these trials. In this experiment, only primary lime was used. The other five heats (H2–H6) represented the testing heats, in which the primary lime was gradually replaced by fly ash and calcined lime mud in the form of briquettes. The replacing ratios of

CaO from the fly ash briquettes and calcined lime mud briquettes are listed in the detailed charge plan, as shown in Table 9.

Table 9 – Charge plan for the lime-containing materials in the AOD trials (FA, WL and PL refers to fly ash, waste lime (calcined lime mud) and primary lime, respectively).

Heat ID	CaO% from FA	CaO% from WL	CaO% from PL
H1	0.0	0.0	100.0
H2	4.4	4.9	90.7
H3	0.0	14.0	86.0
H4	7.8	8.2	84.0
H5	4.4	16.1	79.5
H6	5.1	14.9	80.0

When the steel melt and slag were transferred into the AOD converter, the materials were charged at the three consecutive stages included in the AOD process, i.e. the decarburization, reduction and desulphurization stages, as shown in Table 10. It is seen that the recovered lime-containing materials (fly ash briquettes and calcined lime mud briquettes) were mainly charged into the AOD converter during the decarburization stage. Only during the trial for heat H4, 85 kg recovered lime-containing materials (calcined lime mud briquettes) were charged into the AOD converter during the reduction stage.

The first stage was the decarburization stage, which started with the charging of lime-containing materials (calcined lime mud briquettes, fly ash briquettes and primary lime) and dolomite into the converter. In the next step, mixtures of O₂ and an inert gas (N₂ in this case) were injected through a submerged sidewall nozzle. For each heat, four decarburization steps with various O₂ to N₂ flow rate ratios (4:1, 1:1, 3:7 and 2:9) were planned. However, according to the limitations in the process control system, one or two blowing steps were skipped during the decarburization stage. The decarburization stage lasted approximately 25–30 minutes, when using a fixed gas blowing intensity (sum of O₂ and N₂ flow rate being 5 m³/min). The reduction stage started with a charging of FeSi75 together with lime (primary lime, and in H4 also calcined lime mud briquettes) and fluorspar into the converter. The purpose of the reduction stage was to reduce, especially the oxidized chromium and nickel in the slag back

to the steel melt. The reduction stage lasted for approximately five minutes and N₂ was injected at a flow rate of 5 m³/min. At the end of the reduction stage, the slag in the converter was removed.

The final step was a desulphurization stage that was implemented in four selected heats by adding slag formers consisting of primary lime and fluorspar into the converter. The desulphurization stage took approximately three minutes and N₂ was injected at a flow rate of 5 m³/min. After the desulphurization stage (or in two heats directly after the reduction stage), the slag and the steel melt were tapped into a sand box.

The temperature of the steel melt was measured by using a non-splash thermocouple during the trials. Also, samples of metal and slag were taken several times during the process. This was done by using an automatic sampling tool when the converter was in the upright position or by manual sampling when the converter was tilted.

The chemical compositions of the samples were determined by using XRF analysis and LECO analysis. A mass spectrometer was used to analyze the CO and CO₂ contents in the off gas continuously. The CO and CO₂ contents, the flow rates of O₂, N₂ and off gas were measured and logged automatically in a computer at an interval of 10 seconds. All the other solid or liquid materials charged in the converter and tapped from the converter were logged manually.

Table 10 – Charged materials (in kg) during various stages of the AOD process (FA, WL and PL indicate fly ash, waste lime (calcined lime mud) and primary lime, respectively).

Heat ID	Transferred from EAF		Decarburization stage				Reduction stage				Desulphurization stage	
	Steel melt	*Slag	Dol.	FA	WL	PL	PL	WL	FeSi-75	Fluor-spar	PL	Fluor-spar
H1	4951	20	85	–	–	175	70	–	112	70	–	–
H2	5020	20	90	40	30	100	90	–	116	67	40	20
H3	4900	30	85	–	60	100	45	–	103	60	–	–
H4	4960	30	85	70	50	60	–	85	110	65	40	20
H5	4950	30	85	40	100	35	90	–	115	67	40	20
H6	4955	20	85	50	100	50	90	–	100	73	40	20

*The slag was carried over from the EAF; the amount is estimated according to visual observations.

2.2.4 Using fly ash and calcined lime mud as neutralizing agent in acidic wastewaters

This part of the study focused on investigating the possibilities to use fly ash and calcined lime mud to replace the commonly used primary lime to neutralize and clean acidic wastewaters from steel mills, as illustrated in Figure 16. The main aim of the laboratory wastewater trials was to determine the proper amount of fly ash and calcined lime mud, and method of addition to raise the pH of the solution to a level of 9 during a maximum process time of 30 minutes. The initial pH values of the investigated wastewaters varied in the interval of 1.3 to 2.4. As mentioned before, the aim was to raise pH to a value of 9 since the absorption of some element, such as Ni, from the reactants are maximized at high pH levels [59]. Moreover, flocculants added in industrial applications will significantly lower the pH of the treated wastewaters.

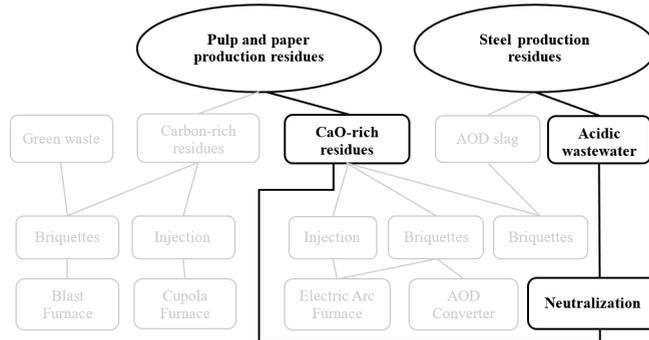


Figure 16 – Laboratory trials using fly ash and calcined lime mud as lime source in the neutralization process of acidic wastewaters.

Also, an industrial primary lime (PL) that is usually applied in the wastewater treatment process in a steel mill was tested in the same experimental set up for the sake of comparison. The fly ash, calcined lime mud and primary lime were used in the form of powders, as they were delivered from the pulp and paper mills, and from the steel mill. Moreover, for some trials, the powders were additionally calcined at 1050°C during 60 minutes to enable a comparison of their efficiencies as neutralizing agents.

When the experiments were started, 210 ml acidic wastewater was poured into a glass beaker. Thereafter, stirring was done during 5 minutes by magnetic stirring for homogenization of the liquid. When the stirring was stopped, the pH value of the wastewater was measured. The chosen amount of recovered or primary lime material powder was added into the beaker containing wastewater. Thereafter, the mixture was stirred for 5 minutes between the stops for measurements of the pH value of the solution. As the pH value did not increase during the stirring stops for measurement, only the stirring time was taken into account. The last two steps of the procedure were repeated until reaching almost constant values of pH, as illustrated in Figure 17, or until a pH value of 9 was reached. Every time the pH value was checked, three measurements were completed before a mean value was calculated.

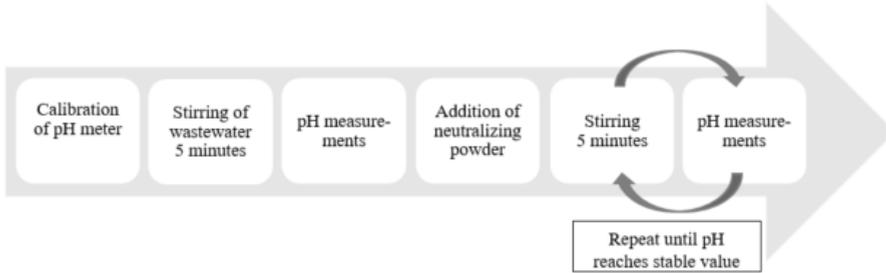


Figure 17 – Workflow for neutralization experiments.

The stirring device was run at approximately a constant speed of 500 rpm for most trials, but a stirring speed of 200 and 1000 rpm were also tested in some trials. In total, 88 neutralizing experiments were completed.

2.2.5 Organic mixed biosludge and green waste as carbon sources in blast furnace hot metal production

This part of the thesis focused on a six days trial in a production blast furnace where biomass were used in small amounts as carbon sources, as illustrated in Figure 18.

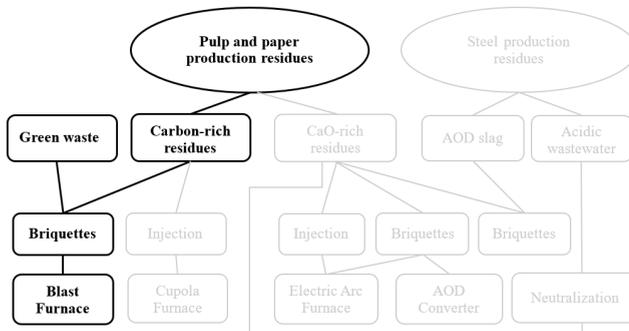


Figure 18 – Use of organic mixed biosludge and green waste as carbon source in blast furnace operations.

The hydrochar pellets cannot be charged as a separate charging material in the BF, due to its relatively low strength. Therefore, the hydrochar pellets were briquetted together with commonly used briquetting materials (in-plant fines such as fines from pellets and scrap, dust, etc. generated from the steel plant and cement) by SSAB Merox. The briquettes contained 2% hydrochar from mixed biosludge or green waste, 12% cement and 86% in-plant fines. It should be pointed out that the composition of the normally used briquettes is 8% cement and 92% in-plant fines. The amount of cement in the hydrochar-containing briquettes was increased, due to difficulties to get the briquettes to stick together and due to their lower mechanical properties. In total, 418 tons of hydrochar briquettes were produced. The briquettes were stored outside for 5 weeks.

Paper sludge hydrochar briquettes (PSH) refers to the briquettes containing organic mixed biosludge and green waste hydrochar briquettes (GrH) refers to the briquettes containing hydrochar from green waste in this study. As the strength of the briquettes are important for the BF operations, a determination of the tumbler handling strength (TTH) was made according to ISO 3271 [76]. TTH measures the cold strength of the briquettes, and it is the main quality index in the iron and steel making industry [77].

Hydrochar-containing briquettes from each type of feedstock were top charged into the blast furnace along with conventional briquettes for three days in a production blast furnace. Day 1; the charging rate was 10% PSH (10% of total amount of charged briquettes), day 2; 20% PSH, and day 3; 40% PSH. On day 4; 10% GrH was charged, day 5; 20% GrH and day 6; 22% GrH was charged. The total charge of briquettes in the blast furnace (containing low Mn briquettes, high Mn briquettes, and briquettes with hydrochar) was 301.35 ton/day. The hydrochar briquettes partly replaced the briquettes containing low amounts of Mn.

Samples of raw material, dust and sludge were collected during the reference periods and during the experimental trials. The charging rate and chemical analysis of all charged burden and injected materials were collected to evaluate and compare the trials. Moreover, the production rate of hot metal, slag, dust and sludge, and the

chemical composition of top gas and heat losses were recorded and collected during the experiments.

The aim of the trials was to investigate the stability and productivity of the blast furnace during charging of these experimental briquettes.

3 RESULTS AND DISCUSSION

3.1 Briquetting of residues from pulp and paper industries by using AOD converter slags as binders

It was revealed during this study, that most of the metallurgical briquettes cannot be transported and used in metallurgical processes without any additional treatment, due to their low impact strengths. The briquettes based on lime mud/mesa and calcined lime mud were almost completely destroyed after 2–6 drops in the drop tests. The fly ash briquettes without AOD slag (F100), with 10% AOD slag (F90) and with 20% AOD slag (F80) retained 33, 17 and 3% of their initial weight after seven drops, respectively.

Storage in air atmosphere during 7, 20 or 35 days did not improve the impact strength of the briquettes based on lime mud/mesa or calcined lime mud. The lime mud briquettes were destroyed during storage, while the lime mud/mesa briquettes were destroyed after six repeated drops in the drop tests. However, storage of fly ash briquettes without AOD slag (F100), and with 10% AOD slag (F90), in air during 20–35 days can significantly increase the impact strength. As an example, the retained weights of the largest briquette after seven drops in the drop tests are ~2–3 times larger compared to those for the F100 and F90 samples, which have not been stored before being tested (60–68% and 57–59% after holding during 20 and 35 days, respectively).

It was found that a heat treatment of the calcium-containing briquettes can significantly increase their impact strengths. Figure 19, and Table 11, shows the effect of heat treatment at a 500°C temperature (for 10% AOD slag) and at an 850°C temperature (0–20% AOD slag) on the retained weight after seven drops in drop tests, as well as the effect of 7, 20 and 35 days holding time for briquettes containing 10% AOD slag.

It should be pointed out that values shown in Figure 19 and Table 11 represent average values obtained from drop tests for three briquettes of each type of experimental briquette.

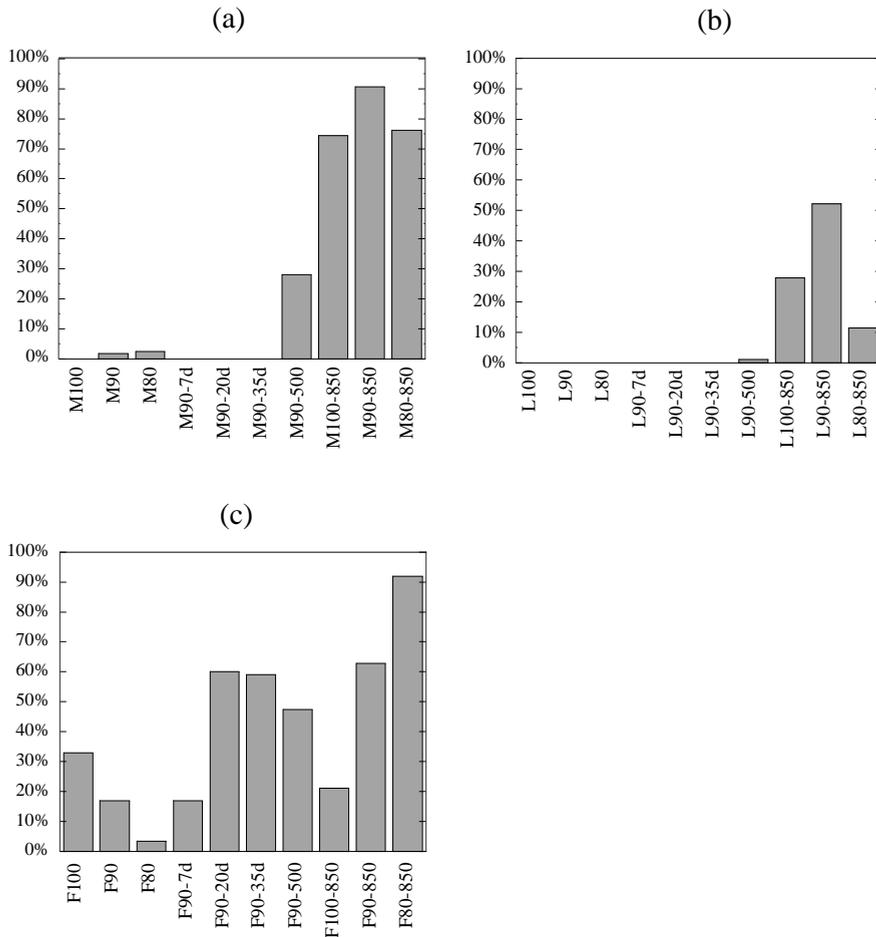


Figure 19 – The retained weight (in%) after seven drops in drop tests for briquettes containing lime mud/ mesa (a) calcined lime mud (b) and fly ash (c) as base material, and with different additional treatments.

For lime mud/ mesa briquettes, it can be seen that a heat treatment at temperatures of 500 and 850°C increased the retained weight of briquettes after the seventh drop test from 1–2% before heat treatment up to 28% for the M90-500 briquettes and up to 74%–91% for the M100-850, M90-850 and M80-850 briquettes. The largest improvement of the impact strength for the lime mud/ mesa briquettes was obtained for M90-850 briquettes (RW ~ 91%) after heat-treatment at a 850°C temperature.

Table 11 – Compilation of retained weights (%RW) of metallurgical briquettes and original lime lumps, after seven drops in drop test.

Composition reference	No additional treatment	Holding time in air [days]			Heat treatment T [°C]	
		7	20	35	500	850
M100	0	-	-	-	-	74
M90	2	-	-	1	28	91
M80	2	-	-	-	-	76
L100	0	-	-	-	-	28
L90	0	-	-	X*	1	52
L80	0	-	-	-	-	11
F100	33	60	68	57	-	21
F90	17	17	60	59	47	63
F80	3	-	-	-	-	92
EAF Lime	60					
AOD Lime	23					

* The briquettes were destroyed during storage and therefore drop tests could not be applied.

The impact strength of calcined lime mud briquettes cannot be improved by heat treatment at a 500°C temperature. However, when the heat treatment temperature was increased to 850°C, the impact strengths were improved. As an example, the retained weight of briquettes was increased from 0% (L90) up to 52% (L90-850), as seen in Figure 19b.

Heat treatment at a 500°C temperature of fly ash briquettes can significantly increase the retained weight of the briquettes after seven drops in a drop test, namely from 17% before a heat treatment (F90) up to 47% for F90-500 briquettes. The heat treatment at an 850°C temperature of most fly ash briquettes increases the retained weight of the briquettes by up to 63% in F90-850 and 92% in F80-850 briquettes. However, the impact strength for the fly ash briquettes without AOD slag does not improve after a heat treatment at a 850°C temperature (F100-850 RW ~ 21%).

Nevertheless, the impact strengths for the briquettes that are heat treated and contains 10% AOD slag can be significantly increased, as are the case for briquettes made based on lime mud/mesa and calcined lime mud. The largest improvement of the impact strength for the fly ash briquettes was obtained for F80-850 briquettes containing 20% of AOD slag (RW ~ 92%).

The metallurgical briquettes with the best impact strengths are compared to typical lime lumps used for usual steelmaking operations in EAF and AOD in Figure 20. The retained weight of the briquettes after seven drops for M90-850 and F80-850 briquettes is much larger than that for AOD-lime and EAF-lime. Moreover, the L90-850 briquettes and EAF-lime lumps have similar mechanical properties. These results indicate that these metallurgical briquettes have a sufficient impact strength.

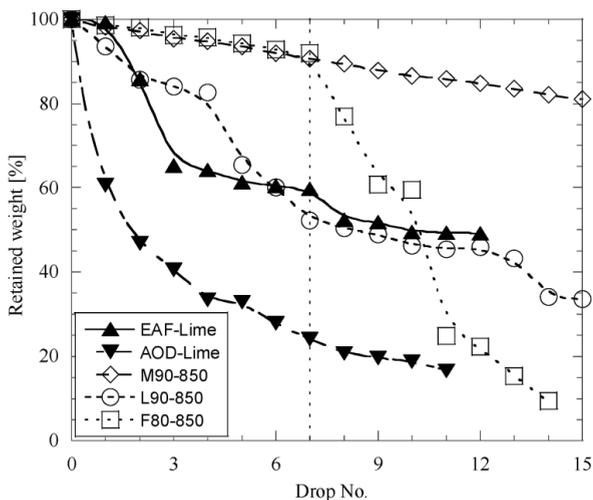


Figure 20 – Comparison of drop test results for the best metallurgical briquettes of each base material (M90-850, L90-850 and F80-850) and lime lumps used in EAF and AOD converters.

It should be pointed out that all the metallurgical briquettes based on lime mud/mesa (M100-850, M90-850 and M80-850) have significantly better impact strengths after heat treatments at a 850°C

temperature, compared to the briquettes based on fly ash and calcined lime mud. This may be explained as follows: though no water was added during briquetting, the lime mud/mesa powder used for preparation of metallurgical briquettes contained slightly more moisture than the calcined lime mud and fly ash powders. Water promotes the formation of a calcium silicate hydrate glue ($3\text{CaO}\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O}$), which gives a binding effect. Moreover, dicalcium silicate, $2\text{CaO}\cdot \text{SiO}_2$, starts to form when CaO and SiO_2 are heated up to temperatures of around 700°C in a strongly alkaline environment. This can also attribute to the binding effects. In this case, a better binding in the lime mud/mesa-based briquettes can be obtained during heat treatment of the briquettes at a 850°C temperature, as was confirmed by the obtained results shown in Figure 19. As for in all dry chemical reactions, the reaction is promoted by a fine size and a close contact of particles in briquettes [21].

Detailed investigations by using SEM in combination with EDS were performed to connect the effect of chemical composition of recipes and heat treatments, with the mechanical properties of the briquettes. The compositions of the main compounds and estimations of structures of powders of fly ash, AOD slag, as well as briquettes based on fly ash were analyzed before and after a heat treatment procedure. It was found that all investigated materials (powders and briquettes) contained small size particles ($0.5\text{--}10\ \mu\text{m}$) and large size blocks having different sizes from 10 up to $500\ \mu\text{m}$, as shown in Figure 21.

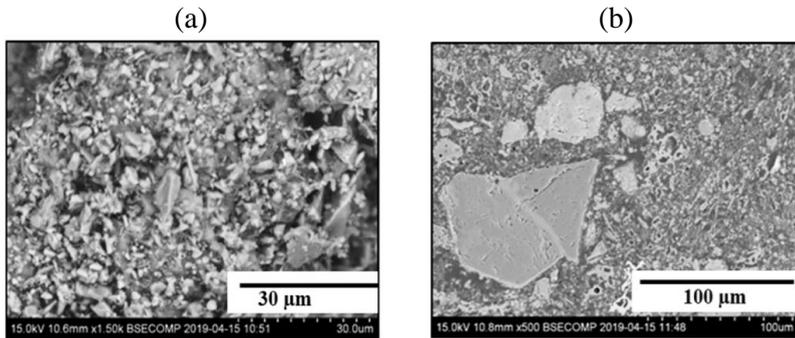


Figure 21 – Typical scanning electron microscopy (SEM) images of small particles (a) and large blocks (b) in investigated powders and briquettes.

All compounds in the investigated materials were classified into three main types, based on the chemical compositions. All three types of compounds were observed in the base materials (fly ash and AOD slag powders) and in all investigated briquettes. Furthermore, different size blocks and small particles from the same compound types have similar compositions. No clear relationship between the chemical compositions and the heat treatment procedure could be found. However, visual investigations of small particles in briquettes after a heat treatment at a 850°C temperature showed that most of the separate particles were sintered despite their different compositions, as seen in Figure 22. This could explain the better drop test results for heat treated briquettes compared to the other briquettes.

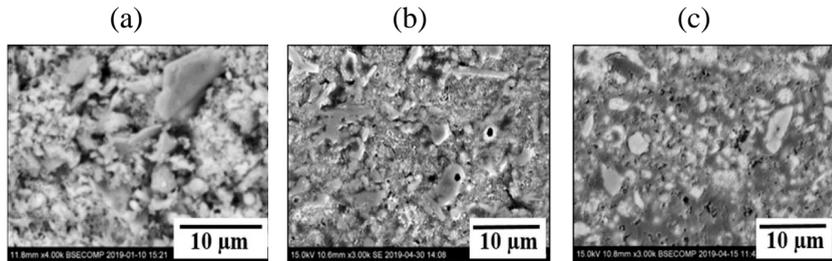


Figure 22 – Typical SEM images of small particles in fly ash powders (a) and in F80 briquettes before (b) and after (c) a heat treatment at an 850°C temperature.

3.2 Application of fly ash as slag formers in EAF stainless steel production

Fly ash briquettes were used to replace primary lime lumps as slag formers in EAF operations. The main results from the mass balance calculations for the EAF trials are summarized in Table 12. The obtained data were used to evaluate the effect of additions of briquettes containing fly ash and primary lime on the output materials. Since about 2 tons of hot-heal metal from previous heats were kept in the EAF, the weights of charged scrap and other materials in heats B and D varied significantly from those in heats A, C and E. Moreover, it should be noted that the amounts of added materials (slag formers, FeSi and anthracite) were decided for each experimental heat by the operator of the EAF depending on the amount of charged scrap, predicted amount of hot-heal metal kept in the EAF from previous heat and its composition. It may explain some variations of the INPUT data in the experimental trials.

The same mass balance calculations were used for all experimental heats. However, it should be pointed out that the results of the total mass balance for some elements, which was obtained by taking into account all above assumptions, showed some disagreements. The disagreements (average value and standard deviation in percentage from INPUT amount) for the main elements used in the given total mass balance calculations are given in Table 13. It can be seen that the disagreements for most components in the given mass balance are almost 0 (for CaO, MgO, Cr and C) or less than 5% for Ni, Si and P. However, although the average disagreement

for S in the mass balance is 1.25, the value of the standard deviation is about 10%. This big variation for S may be explained by the fact that some amount of S was removed with off-gases (as SO₂) during combustion of some amount of added anthracite (containing 0.76% of S). The latter is added for carburization of steel melt during the experimental trials in the EAF. The amount of off-gases was calculated from a mass balance of C present in the OUTPUT- and INPUT materials. However, the concentration of SO₂ in off-gases was not measured in the given pilot trials. Furthermore, some disagreements for several components can be explained also by some heterogeneity of compositions of the OUTPUT- and INPUT materials used in the given experimental heats.

Table 12 – Material balance results of experimental trials in the EAF (in kg).

EAF heats		A	B	C	D	E
INPUT materials						
Hot-heal metal*	(HHMe)	0	2023	0	2126	0
Hot-heal slag*	(HHSl)	0	86	0	91	0
Scrap		7060	5460	7060	5460	6210
Primary lime	(PL)	191	110	94	35	0
Briquettes (% of FA) **	(BR)	0 (0%)	46 (15%)	118 (30%)	137 (40%)	204 (50%)
Dolomite	(Dol)	71	55	71	55	62
FeSi		98	65	71	65	67
Anthracite	(Ant)	186	130	150	150	180
OUTPUT materials						
Metal	(Me)	5008	5015	4980	4960	4938
Slag		484	440	446	403	253
Dust		45.4	41.2	28.3	30.5	39.0
Rest of metal*	(RMe)	2023	2390	2126	2571	1307
Rest of slag*	(RSl)	86	74	91	67	106

* – value obtained from mass balance calculations;

** – % of fly ash used instead of primary lime in input materials (Equation 8)

$$\%FA = \frac{M(FA)}{[M(FA)+M(PL)]} \quad (Eq.8)$$

where M(FA) is the mass of fly ash and M(PL) is the mass of primary lime.

Table 13 – Disagreements (average value and standard deviation in percentage from INPUT amount) for main elements used in the given total mass balance calculations.

Component	CaO	MgO	Cr	Ni	Si	S	P	C
Disagree- ment (%)	~0	~0	0.05 ±0.13	2.27 ±1.71	0.17 ±3.74	1.25 ±9.79	0.33 ±4.06	~0

The effect of replacing primary lime with fly ash on the slag forming as well as on process parameters used in EAF melting, according to the obtained results from the mass balance calculations, are shown in the figures below: the amount of charged slag formers ($SF = PL + BR + Dol$), per ton of steel scrap in Figure 23 and the effect of added fly ash (FA) charged in briquettes to replace primary lime (PL) on the total amount of charged slag formers per ton of steel in Figure 24.

In these figures, and the text below, $M(FA)$ is the mass of fly ash, or respective component, in the input and output materials. The use of fly ash to replace primary lime increases the amount of slag formers per ton of steel scrap from 37.1 kg in heat A (0% FA), to 42.8 kg in heat E (50% FA). On the other hand, the total amount of slag per ton of steel melt in EAF can be decreased from 81.1 kg in heat A, to 57.6 kg in heat E. Fly ash contains ~15.8% SiO_2 and ~8.9% Al_2O_3 , which can lower the melting temperature of the slag. This, in turn, will lead to a faster formation of a liquid slag. This could lead to a better protection of the steel melt from the surrounding air, a decreased oxidation and a decreased transfer of elements such as Fe, Mn and Si from the steel melt to the slag. Furthermore, the liquid slag decreases the amount of dust, as seen in Table 12. When the replacement ratio was 40% FA, the amount of dust was decreased by 33% compared to the reference heat (A). Furthermore, when the replacement ratio was 50% FA, the dust was decreased by 14% compared to the reference heat (A). Moreover, increased additions of fly ash resulted in increased amounts of produced steel, while the final slag amounts decreased in the EAF pilot trials.

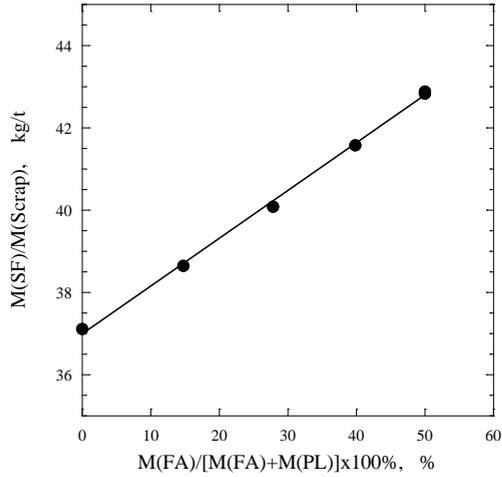


Figure 23 – Effect of added fly ash (FA) charged in briquettes to replace primary lime (PL) on the total amount of charged slag formers per ton of steel scrap.

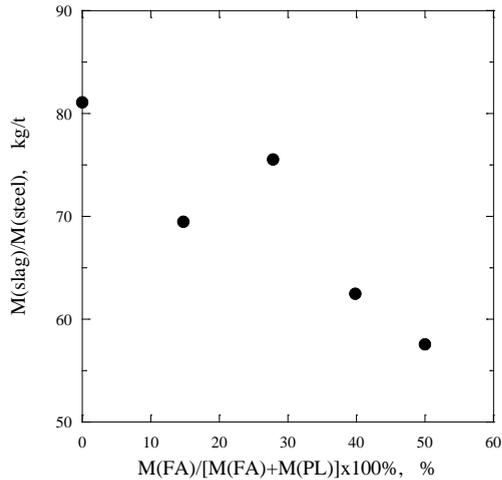


Figure 24 – Effect of added fly ash (FA) charged in briquettes to replace primary lime (PL) on the total amount of slag per ton of steel.

Ferro silicon (FeSi) is added in EAF steelmaking to enable a formation of an EAF slag with a proper concentration of SiO₂, as well as for alloying of steel with Si. Fly ash consist of ~15.8% SiO₂, and the amount of FeSi added in the EAF pilot trials was decreased from 13.9 kg/ton to 10.1 kg/ton of scrap with an increase of charged fly ash, as seen in Figure 25. Similar contents of Si in EAF steel can be obtained by different ratio of fly ash and FeSi, as seen in Figure 26. For instance, the similar contents of Si (0.48 and 0.42%) in the steels of heats A (0% FA), D (40% FA) and E (50% FA) were obtained when 13.9, 11.9 and 10.8 kg of FeSi was added per ton of scrap, respectively. The results show that, to reach the required concentrations of Si in the steel, and SiO₂ in the slag, the amount of added FeSi can be decreased by almost 3 kg/ton of scrap when 50% fly ash is charged together with primary lime instead of charging only primary lime.

Fly ash contains ~0.40% of S, meaning that the addition of fly ash as a slag former can increase the amount of S in the slag forming materials. Therefore, the S distributions in input and output materials were determined. The results of the chemical composition determinations for different fly ash additions are given in Table 14.

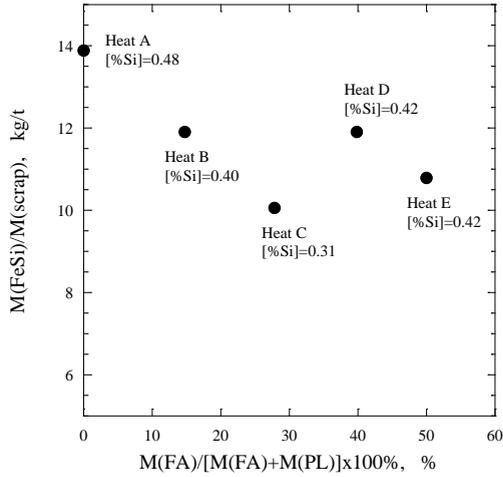


Figure 25 – Amount of FeSi added per ton of scrap as a function of the fractions of fly ash in the added slag formers.

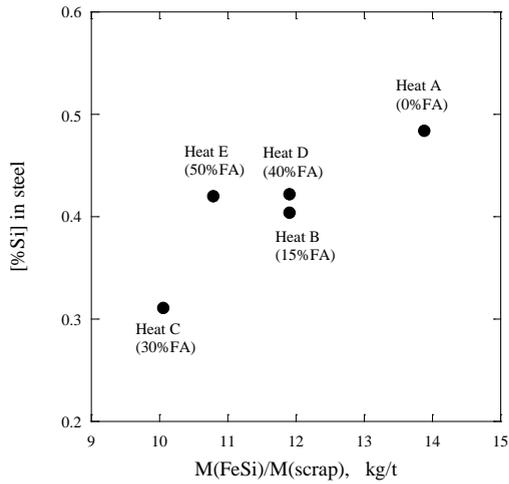


Figure 26 – Final concentration of Si in steel in different EAF pilot heats.

Table 14 – Frequency of S in input and output materials of experimental EAF trials.

EAF heats		A	B	C	D	E
INPUT (in %)						
S from metallic charge	S_{MeCh}	54	55	48	51	40
S from anthracite	$S_{Antr.}$	40	35	39	34	44
S from slag formers (from added FA in briquettes)	S_{SF}	6 (0)	10 (3.2)	13 (8.0)	15 (8.1)	16 (13.0)
OUTPUT (in %)						
S in metal	S_{Me}	62	58	61	47	38
S in slag	S_{Slag}	19	24	28	42	58
S in dust	S_{Dust}	19	18	11	11	4
$L_s=(\%S)/[\%S]$		4.00	6.13	6.07	14.47	16.39
Basicity of slag (= %CaO/%SiO ₂)	B_{Slag}	1.44	1.53	1.62	1.69	1.81
S content in slag, %	(%S)	0.092	0.098	0.170	0.275	0.459

As can be seen, the fraction of S charged with slag formers in heat A (0% FA) corresponds to only 6%, while in heat E (50% of FA) 16% of S were charged with the slag formers of the total amount of S in input materials. In heat E, 13% was derived from the fly ash additions. Moreover, it was found that the percentage of S in the final slag of output materials can be increased from 19% (heat A) up to 58% (heat E) with an increased amount of charged fly ash, as shown in Figure 27. This means that the amount of S in the slag can be significantly increased with an increased amount of fly ash to replace primary lime. In heat A, the S content in the slag was 0.092%, while in heat E, the S content was 0.459%, which corresponds to a ~500% increase of the S content in the slag. The actual distribution coefficient of S in the slag and steel ($L = (\%S)/[\%S]$) is shown in Figure 28 as a function of added fly ash and basicity of slag (B_{Slag}). As seen in the figure, the L value is four times larger for heat E than it is for heat A. Furthermore, it should

be pointed out that the basicity of the slag ($B_{\text{Slag}} = \% \text{CaO} / \% \text{SiO}_2$) increased from heat A ($B_{\text{Slag}}=1.4$) to heat E ($B_{\text{Slag}}=1.8$), and the FeO and MgO contents in the final slag decreased from 2.64 to 0.65% and from 1.80 to 0.42%, respectively with an increased amount of added fly ash. This indicates a significant improvement of desulphurization efficiency of the liquid steel in these EAF pilot trials. It can be explained by a faster formation of liquid slag during the EAF process with an increased amount of charged fly ash, as was mentioned above. As a result, the faster formation of liquid slag promotes a faster and more complete desulphurization process in the EAF.

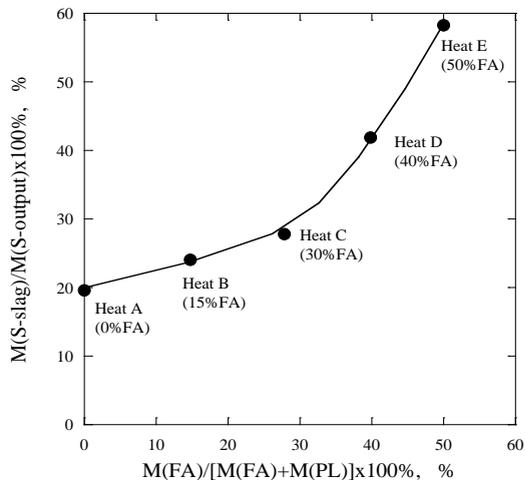


Figure 27 – Effect of replacing primary lime with fly ash in the EAF charge on the distribution of sulphur in the output slag and metal.

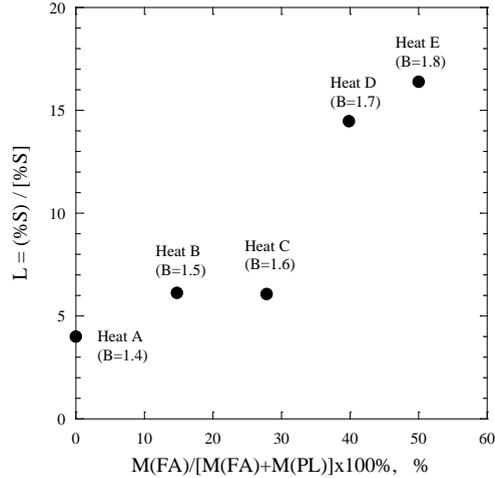


Figure 28 – Distribution coefficients of S in the slag and steel ($L = (\%S)/[\%S]$) in different EAF pilot heats as a function of the added fly ash content and basicity of slag (B_{slag}).

Fly ash contains on average 0.26% of P, which is much higher compared to that in the primary lime (0.01%) and dolomite (0.05%). Thus, the use of fly ash as slag formers to replace primary lime can significantly increase the amount of P in the input materials. The frequency of P distributions in input and output materials are given in Table 15 for the EAF pilot trials with various amounts of fly ash added.

Table 15 – Frequency of P in materials of experimental trials in the pilot EAF.

EAF heats		A	B	C	D	E
INPUT (in %)						
P from metallic charge	P _{MeCh}	98.0	96.3	95.4	94.6	92.7
P from anthracite	P _{Antr.}	1.0	1.0	1.1	1.0	1.5
P from slag formers (from added FA in briquettes)	P _{SF}	1.0 (0)	2.7 (1.0)	3.5 (2.6)	4.4 (2.8)	5.8 (5.0)
OUTPUT (in %)						
P in metal	P _{Me}	91.3	93.3	93.8	94.2	95.5
P in slag	P _{Slag}	7.7	5.8	5.9	5.4	4.3
P in dust	P _{Dust}	1.0	0.9	0.3	0.4	0.2
L _P =(%P)/[%P]		1.04	0.90	0.83	0.91	0.79
Content of P in steel, %	[%P]	0.032	0.034	0.036	0.034	0.033

As seen above, the fraction of P charged in heat A (0% fly ash) corresponds to only 1%, while in heat E (50% fly ash) it was 5.8% of the total P content in the input materials. In heat E, the amount of P that originate from fly ash is 5%. Thus, the main source of P in the input material is the metallic charge for all EAF pilot trials (from 98.0% in heat A to 92.8% in heat E). However, it was found that the P fraction in the slag in the output materials decreased from 7.7 to 4.3%, even though the contents of P₂O₅ in the final EAF slag are almost similar. This can be explained by the lower amounts of final slag per ton of steel, as discussed above. Furthermore, by the lower contents of FeO and MnO in the slag, which promotes a dephosphorization of the steel melt. Moreover, the content of P in the final steel increased slightly with additions of fly ash, as seen in Table 15. Hence, replacing primary lime with fly ash only slightly increases the content of P, from 0.032% P in heat A (0% FA) to 0.033% in heat E (50% FA), in the final EAF steel.

As was mentioned above, it is important to protect the steel melt from contact with the surrounding air to avoid reoxidation and to empower a desulphurization process of the liquid steel. This is facilitated by a fast formation of liquid slags. In order to study the slag, slag samples were taken at multiple times during the EAF process for all heats. The samples from heat A, C and E, taken before tapping were investigated by using SEM in combination with EDS analysis to

determinate to amounts of undissolved slag forming components as well as contents of S in different slag phases. The results from the investigations showed that the briquettes were completely dissolved in the molten slags in heats C and E. All slag samples contain the following main components: i) spherical metal droplets ($\text{\O} \sim 0.2\text{-}210 \mu\text{m}$), ii) irregular pieces of MgO refractory ($\sim 20\text{-}150 \mu\text{m}$), iii) regular and irregular $\text{Cr}_2\text{O}_3\text{-MgO-Al}_2\text{O}_3$ particles ($\sim 4\text{-}35 \mu\text{m}$), and iv) slag phases (Slag-1 and Slag-2) formed during a fast solidification of liquid slag samples.

The metal droplets contained 0.06 to 3.23% of S. The fast-solidified Slag-1 phase contained only low amounts of S (in the range 0–0.16% in heat A and of 0–0.31% in heat E). At the end of the solidification, a Slag-2 phase is formed. This can contain larger amounts of S, as shown in Table 16.

Table 16 – Main elements in slag phases of investigated slag samples.

Phase	CaO	SiO ₂	MgO	Al ₂ O ₃	S
Metal droplets					0.06–3.23%
Slag-1	47–55%	27–34%	9–13%	5–11%	0–0.31%
Slag-2	39–45%	28–31%	5–10%	13–24%	0–2.01%

In heat A, the S content in Slag-2 phase varies in the range of 0–0.21%, while in heat E, it varies in the range of 0–2.01%. It is important to point out that the S content increased over time in Slag-2 phase during desulphurization. The sample of the first melted slag in heat E contained 0.2–1.27% of S, while the sample taken just before tapping of the steel contained 0.56–2.01% of S.

A faster formation of liquid slag in the EAF, and better slag parameters regarding sulphur refining of steel, promotes a faster and more complete desulphurization process. This can explain the better desulphurization results of the steel in heat E (50% fly ash) compared to those in heats A and C. Thermodynamic calculations for the melting behavior of the main oxides ($\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MgO}$) of the slags for heat A–E depending on the ratio of PL/FA in slag formers are presented in Figure 29. The normalized values of the main oxides ($\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MgO}$) in the added slag forming materials (including briquettes), which were used for thermodynamic

calculations, are given in Table 8. It is clear that the theoretical melting temperature decreases with an increased FA ratio. At a 1700°C temperature, the share of molten oxides was 1% for a slag oxide composition corresponding to that of heat A (0% FA), 10% for heat B (15% FA); 19% for heat C (30% FA); 26% for heat D (40% FA) and 32% for heat E (50% FA). This supports the findings of a faster formation of a liquid slag when fly ash is used as a part of the slag formers.

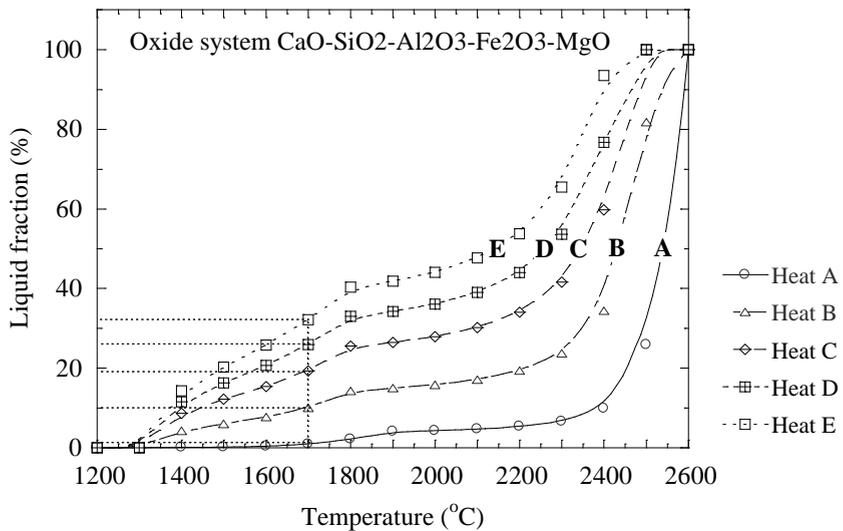


Figure 29 – Melting temperatures of oxide system $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MgO}$ for the various chemical compositions of slag formers in heats A-E.

3.3 Using fly ash and calcined lime mud as lime source in AOD converter

By considering the CaO amounts from the input materials (slag transferred from the EAF, the dolomite and the lime-containing materials) and the chemical compositions of slag after the reduction stage, the slag amount after the reduction stage can be calculated. The amount of steel after the reduction stage was calculated by considering the steel melt tapped into the AOD converter as well as the Cr and Ni balances before and after the reduction stage. The calculated amounts of the metal and slag after the reduction stage, as well as the slag/steel mass ratio for all the six AOD heats are shown in Table 17.

From the table below, it can be seen that there is an overall trend that an increased use of recovered lime result in an increased slag amount, especially when fly ash briquettes are used. This can be explained by the lower CaO content in the fly ash compared to that in primary lime. These results show that larger amounts of these materials are required to reach the desired basicity, which is ~1.5 in this study. Therefore, the acceptable slag amount in the AOD converter could limit the replacement ratio of calcined lime mud and fly ash.

Table 17 – Calculated amounts of metal and slag after the reduction stage as well as the slag/steel ratio.

Heat ID	Steel amount after reduction [kg]	Slag amount after reduction [kg]	Kg slag /ton steel
H1	4910	615	125
H2	4925	682	138
H3	4839	593	123
H4	4910	666	136
H5	4898	685	140
H6	4886	726	149

To characterize the speed of the decarburization process in the AOD converter, the Carbon Removal Efficiency (CRE) defined in Equation 9 was considered.

$$CRE = \left(\frac{m_C}{M_C} \times \frac{V_m}{2} \right) / V_{O_2}, \quad (Eq. 9)$$

where m_C is the amount of the carbon removed from the steel melt, which is equal to the sum of carbon in the emitted CO and CO₂; M_C is molar mass of carbon; V_m is molar volume of gas, being 22.4 L/mole at a standard temperature and pressure; V_{O_2} is the volume of blown oxygen during the decarburization stage.

The process time could be shortened, the use of injected gas decreased, and the oxidation of Cr lowered when the CRE value is high. Thus, this would improve the productivity and reduce the consumption of FeSi75 and lime [22], and vice versa. The CRE value for each heat can be calculated by using the logged data for CO and CO₂ gas and the accumulative injection volume of oxygen with time. To compare the CRE values among different heats with different replacement ratios of CaO from fly ash and calcined lime mud the heats H1, H3 and H4 were selected. The reason to select these heats for the comparison is that the initial conditions with respect to the silicon contents, carbon contents and temperatures are quite similar. Figure 30 shows the comparison results. It is seen that that the change of the CRE value with time follows a similar trend in the given three heats; the discrepancy is attributed to the slight differences in the initial conditions. In Figure 30, the carbon content decreases and the steel melt temperature increases with an increased treatment time; they are attributed to the sequentially combustion and oxidation of Si, C and Cr in the steel melt. By taking the heat H1 as the reference, it can be concluded that the use of recovered lime does not have any negative effects on the decarburization process in heats H3 and H4.

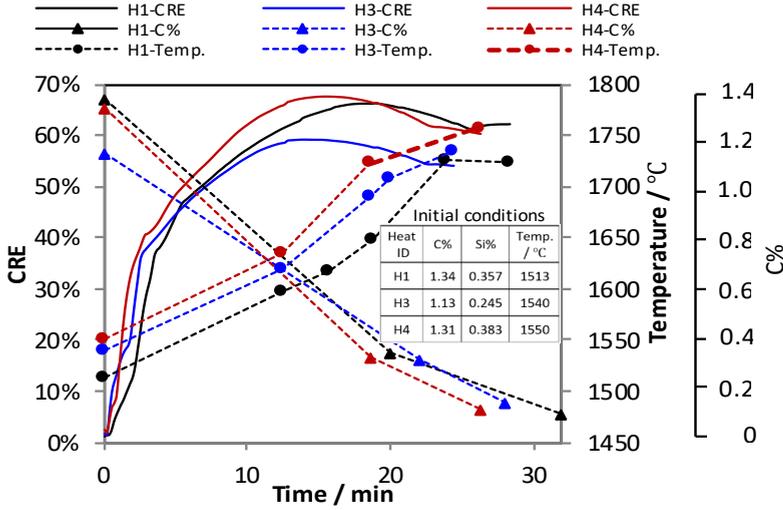


Figure 30 – Comparison of the Carbon Removal Efficiency (CRE), carbon content and temperature among heats H1 (reference heat), H3 and H4 during the decarburization stage.

The desulphurization efficiency can be defined as follows in Equation 10:

$$\eta = 1 - (m \times C_{[S]})/m_{(S)} \quad (Eq. 10)$$

where η is the desulphurization efficiency, m is the steel melt weight, $C_{[S]}$ is the sulphur content in the steel, and $m_{(S)}$ is the total input of sulphur from the materials charged into the AOD converter.

The mass balance of the sulphur distribution in the metal, and the sum of the ingoing sulphur contents from all charged materials by the end of the reduction process can be used to calculate the desulphurization efficiency for all six heats in the AOD converter. The results from the calculations are shown in Figure 31, along with the basicities and silicon contents. The desulphurization of the steel, the basicity and the oxygen potential are closely related. The oxygen potential of the liquid steel is a function of the silicon content and temperature of the steel bath. It can be seen that the desulphurization efficiency follows a similar trend, as that of the silicon content and especially the slag basicity.

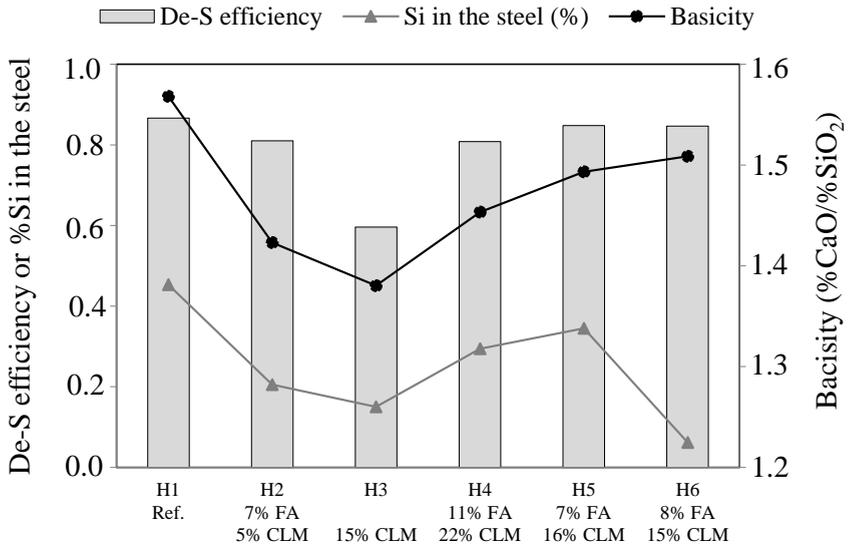


Figure 31 – Desulphurization efficiencies of different heats after the reduction stage.

The desulphurization efficiency in the reference heat reached 87%. In the two heats with comparable slag basicities, H5 and H6, the desulphurization efficiency reached 85%. This illustrates that the desulphurization process is as efficient when these recovered lime materials are used, as it is when primary lime is used. For the other heats, H2, H3 and H4, the differences in desulphurization efficiency may be explained by inequalities in slag basicities and silicon contents in the steel melt.

In this study, the S and P levels in the final steel are of particular importance. The input of S and P from the charge materials, as well as the S and P contents in the steel after the reduction stage sets the level for the final values of S and P. It is impractical to lower the levels of S and P after the desulphurization stage. This is why the levels are critical at this point.

The final desulphurization stage was carried out after the reduction stage in selected heats, (H2, H4, H5 and H6) by deslagging the reduction slag and by adding 40 kg of primary lime and 20 kg of

fluorspar. As seen in Figure 32, the S levels in the steel were reduced to concentrations of 20–40 ppm. On the other hand, the P contents in the steel increased after the desulphurization stage, as can be seen in Figure 33. This can be due to the reversal of P from the leftover reduction slag [77].

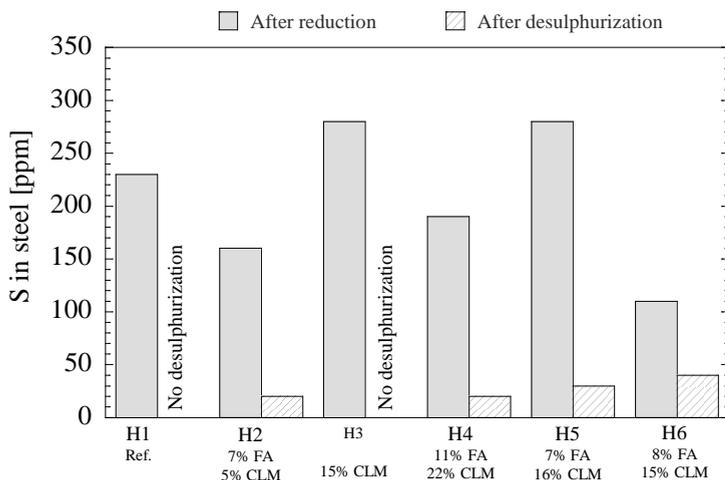


Figure 32 – S content in the steel after the reduction stage and after the desulphurization stage.

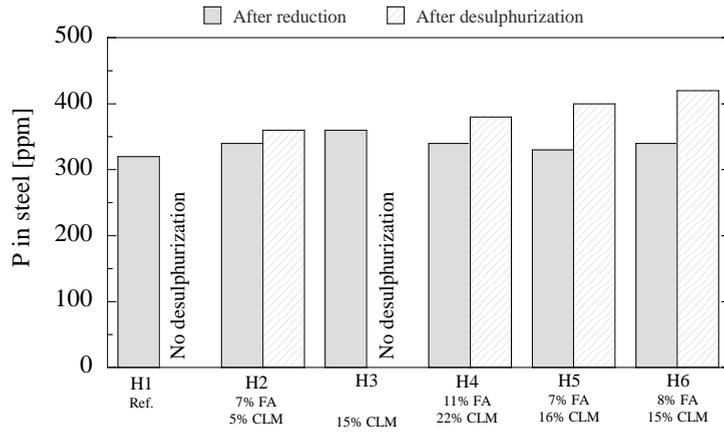


Figure 33 – P content in the steel after the reduction stage and after the desulphurization stage

3.4 Treatment of acidic wastewaters with fly ash and calcined lime mud

3.4.1 Neutralization of wastewater

The neutralization process is a type of replacement reaction: Acid + Base \rightarrow Salt + water. An acid-base reaction is a chemical reaction that involves the exchange of one or more hydrogen ions. When an acid is dissolved in water, the solution has a greater hydrogen ion activity than that of pure water. When a base is dissolved in water it can accept hydrogen ions. The choice and dosage of chemicals, the pH value and the mixing rate influences the neutralization process [57].

The acidity of an aqueous solution is determined by the concentration of hydrogen ions, and the acidity is quantified by the definition of potential of hydrogen (pH) as follows in Equation 11:

$$pH = -\log [H^+] \quad (Eq.11)$$

where $[H^+]$ is the number of moles of hydrogen ions per liter of solution [78].

A comparative study was conducted to determine the feasibility and efficiency of the use of limestone, dolomite and fly ash as pre-treatment agents based on their low cost for acid mine drainage in South Africa by S.S. Potgieter-Vermaak et al. [80]. They found that fly ash can be considered as a cost effective alternative for pre-treatment of acid mine drainage. Furthermore, that significant cost benefits can be derived from the use of pre-treatment agents before the widely practiced lime dosing of acid mine effluents are employed for increasing of the pH value and concomitantly precipitate heavy metals. It should be pointed out that the fly ash in the mentioned study had a severely different chemical composition (52.6% SiO₂, 34.6% Al₂O₃ and only 4.1% CaO) compared to the fly ash used in this study.

A process of increasing the pH value of acidic wastewaters by addition of CaO-containing materials is defined in this study as a

neutralization process. Furthermore, the reactivity is defined as the ability of the added material to increase the pH values of the wastewaters. The time boundaries of the experiments were arbitrary set to that the neutralization of wastewaters should be mostly finished during 30 minutes after addition of reagents. The final required value of pH should be equal to nine, because the following additions of industrial flocculants significantly decrease the final pH value of the water.

The cost and the amount of sediments need to be at the lowest possible level to attain an efficient process and still meet the required neutralization rate. Therefore, a ratio of neutralizer and wastewater for the prevailing circumstances needs to be established. It was found that the efficiency of the neutralization process depends significantly on the stirring intensity. Out of three tested stirring rates, the most efficient results were obtained when using a stirring rate of 500 RPM. In this case, the pH value 9 was reached after 25 minutes of stirring. The least efficient process was obtained when using the lowest stirring intensity (200 RPM). Finally, a batch stirred with a 1000 RPM speed reached a pH value of 8.8 after 45 minutes of stirring. However, the pH value did not reach the required pH level of 9 during 30 minutes, due to a less efficiency of the neutralization process at a high stirring rate. A similar tendency was found by Zinck and Aube [81] by evaluation of the effect of a mixing process on neutralization and cleanliness of wastewaters. They reported that the conditions of formation and growth of precipitated particles are less productive when the mixing rate is higher than the optimum value. Thus, all experimental trials discussed below were carried out using the same stirring rate of 500 RPM.

The different wastes used in these trials have different reactivities for the different batches of wastewaters (the chemical composition of the batches of wastewaters A, B, C and D varied). It is obvious that the obtained pH value increases with an increased amount of added CaO-containing materials. The neutralization effects obtained in wastewaters C and D after additions of fly ash (FA), calcined lime mud (LM) and primary lime (PL) in various amounts after 30 min of stirring (at 500 RPM) can be seen in Figure 34. It can be seen that the neutralization of wastewater C up to the given pH value of 9 required approximately a 2.2 times larger amount of fly ash (9.5 g/l) compared

to that of calcined lime mud (4.3 g/l). This can be explained by the significantly higher concentration of CaO in the LM compared to that in FA. Also, the original FA and PL powders consist of various complex CaO-containing components (such as CaCO_3 and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$), which can be more stable and resistant in contact with acidic water compared to pure CaO. The content of such stable components can significantly decrease the reactivity of the investigated materials. A similar effect was observed for wastewater D: the required weight of FA is almost 2.7 times larger than that of LM. Even though FA contains less free CaO than LM and PL, it contains 1.8 times more MgO than PL, and 3 times more than LM. MgO reacts with water to form magnesium hydroxide (Mg(OH)_2), which is known for its acid neutralizing capability [65]. However, the amounts of MgO are not very high in the materials: 3.1 wt% for FA, 1.05 wt% for LM and 1.7 wt% for PL).

Moreover, it was found that a further increase of the added material (~24 g/l of LM and ~66 g/l of PL in D-wastewater) larger than some specific value did not promote an increase of the obtained pH value larger than ~12–12.3, as shown in Figure 34b. It should be pointed out that an effect of the same amount of added powders on the pH values of different wastewaters can vary significantly.

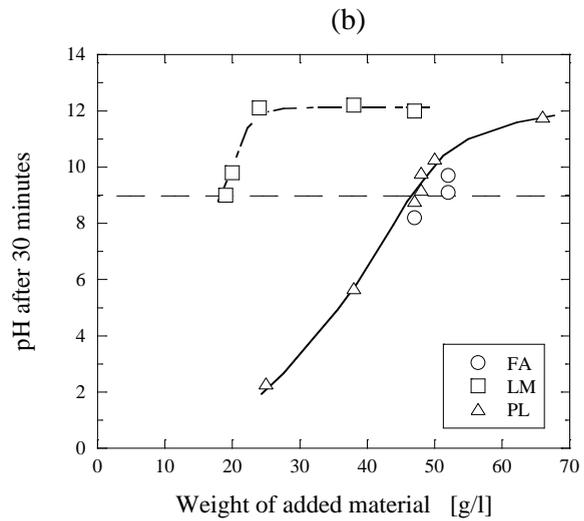
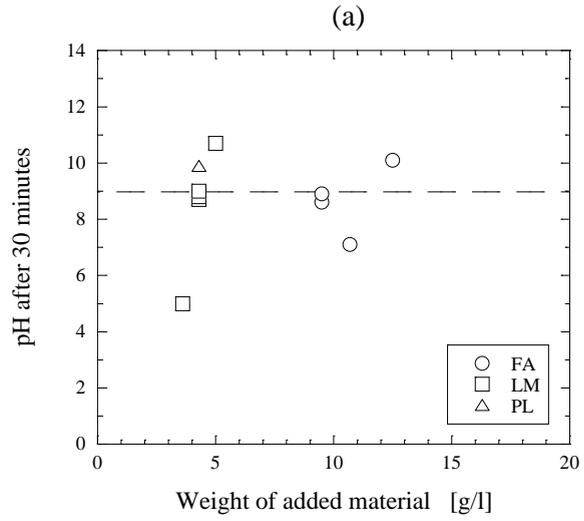


Figure 34 – Neutralization effects obtained 30 minutes after addition of fly ash (FA), lime mud (LM) and primary lime (PL) in to C (a) and D (b) acidic wastewaters.

In Figure 35, some results are plotted to compare the amounts of FA and LM needed to neutralize the different batches of wastewaters. It can be seen that wastewater D requires significantly more neutralizers than the other batches of wastewater (for FA 52 g/l in the D-wastewater compared to 9–11 g/l in other wastewaters and for LM 19 g/l in the D-wastewater compared to 4 g/l in the A- and C-wastewaters). Moreover, it was found that the C-wastewater requires only 4 g/l of primary lime, while the D-wastewater requires about 48 g/l of PL to reach similar results. Specifically, this amount is 12 times higher.

It is important to note that the neutralization effect of acidic wastewaters can significantly depend on both compositions and other characteristics of the added powder materials (such as size distribution of particles, moisture, etc.). For instance, small sizes of particles promote faster neutralization reactions. The particle size distribution of the FA and LM powders were done by using a sieve shaker range instrument. It was found that the particles of LM ($< 56 \mu\text{m}$) used in the present study are much smaller than those of FA powders (40~250 μm), which can also promote a higher efficiency of the LM compared to the FA due to the higher surface/volume ratio.

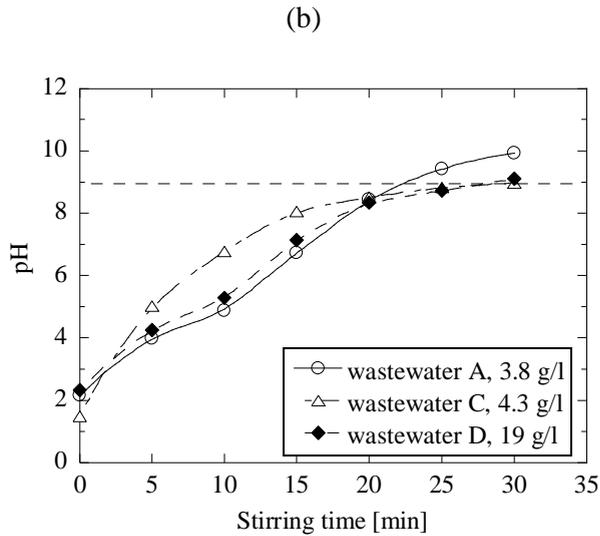
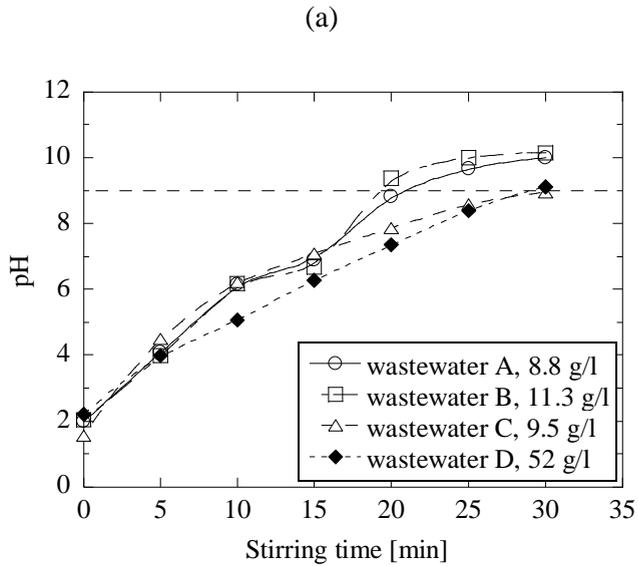


Figure 35 – Neutralization of wastewater A–D using fly ash (a) and wastewater A, C and D using calcined lime mud (b).

The effect of moisture in the powders on the reactivity were evaluated by performing an additional calcination at 1050°C during 60

minutes in a laboratory muffle furnace. The neutralization effects obtained 30 min after the addition of fly ash and primary lime without and with additional calcination (open and filled marks, respectively) into C and D wastewaters are shown in Figure 36. The volatile matter and moisture are removed from the powders by thermal degradation and vaporization. This, in turn, leads to a higher concentration of substances being active in the neutralization process. It is clear that the amount of powder can be significantly decreased for both the FA and PL samples when it is calcined. For instance, by using an additional calcination treatment, the amount of added powder can be decreased by ~1.6 time for FA (from 52 up to 33 g/l) and 2.4 time for PL (from 48 to 20 g/l) to reach a similar pH value of approximately 9 in the D-wastewater.

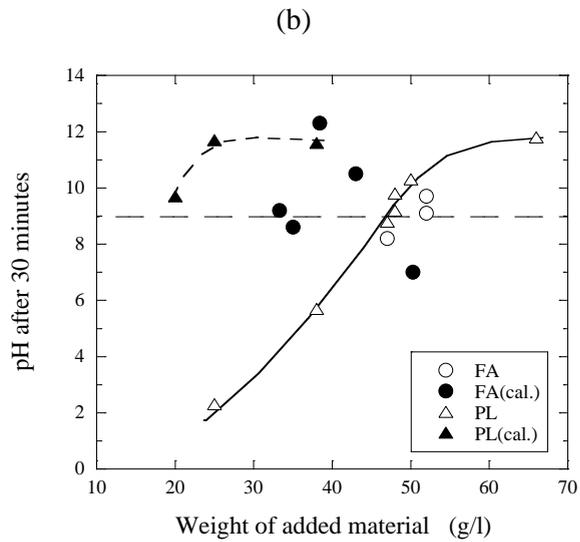
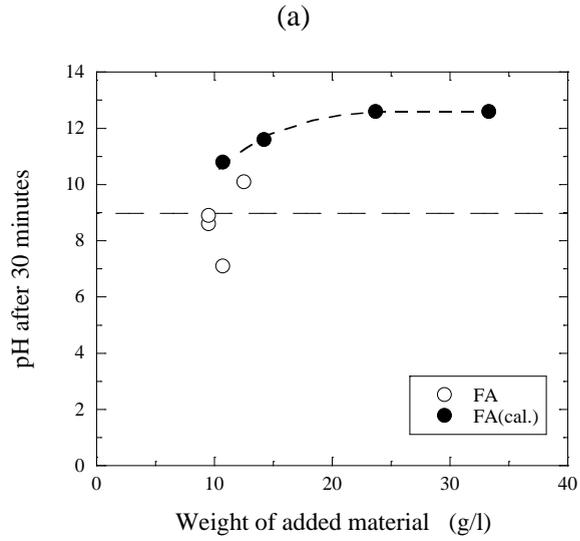


Figure 36 – Neutralization effects obtained after 30 min after the addition of fly ash (FA) and primary lime (PL) powders without and with additional calcination in to C (a) and D (b) acidic wastewater.

In Figure 37, it can be seen that LM (19 g/l) reaches a pH value of 9 in 30 min, while the original PL powder (38 g/l) reaches a pH value of 5.7 during the same time. The neutralization efficiency was dramatically improved when the PL powder was calcined prior to the trials. Specifically, the maximum pH value of approximately 12 is reached in less than 10 min by using the same amount of powder. However, an additional calcination of the materials means an additional technological process and an additional cost.

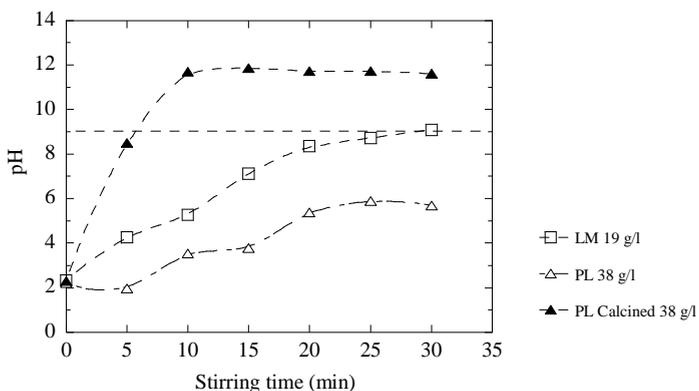
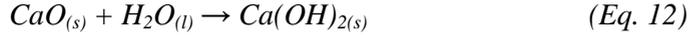


Figure 37 – Neutralization effects obtained after the addition of LM, PL and calcined PL into wastewater D.

3.4.2 Metal removal from wastewater

Varieties of chemical and physical means are generally accomplished to remove heavy metals from wastewaters. Some examples are; hydroxide precipitation, ion exchange, adsorption and membrane processes. The by far most widely used process to remove heavy metals from wastewaters in the industry is chemical precipitation [82]. The pH value is a major factor in neutralization and metal removal through precipitation. Neutralization and precipitation are double displacement reactions. The principle of neutralization of acidic wastewaters by using lime lies in the insolubility of heavy metals for alkaline conditions, resulting in precipitates of hydroxides of these

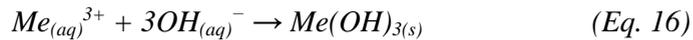
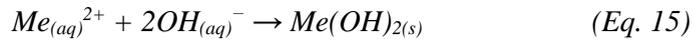
materials. If the pH value is high, the concentration of OH⁻ is high [83]. A pH value in the range of 8.0–11.0 minimizes the solubilities of metal hydroxides [84]. The neutralization and co-precipitation process starts with the hydrolysis of lime (Equation 12), the lime dissolution. The partial dissolution raises the pH value due to the formation of hydroxyl ions (Equation 13), which can be illustrated by the following reactions [85]:



When the pH value has increased, the hydroxide ions precipitate the metals. The precipitation reaction is shown with Zn as example in Equation 14 [86]:



The metals form insoluble hydroxides at higher pH values, which may be removed from the wastewater to the sediments [87]. The hydroxyl ions interact with the divalent and trivalent cations present in the solution, forming precipitates (Equations 15–16):



The solubility of metal hydroxides depends on the pH value of the solution as mentioned above, and metal ions will reach their minimum hydroxide solubility at different pH values.

The Pourbaix diagram [88] or potential-pH diagram is a kind of fully-equilibrium phase diagram, reproducing the dominant phases of a certain element in an aqueous electrochemical system. The Pourbaix diagram is a good tool for interpreting the dissolution of pure metals, even though it only reflects the most dominant phases in the system [64]. The phase boundaries in a Pourbaix diagram are shown

as a function of the acidity (pH) of the aqueous solution and a standard hydrogen electric potential (Eh) or the electrode potential (E) which is a measure of the electrochemical environment [89]. The diagrams are derived for selected temperatures, pressures, and selected concentrations of ionic species. Most Pourbaix diagrams consider pure substances only, such as pure iron in pure water [89], [90]. The pourbaix diagrams assumes that equilibrium conditions exist and give no information on reaction rates. In the passivation region of the pourbaix diagrams, the stable phases are insoluble metal oxides.

In Figure 38 by E. McCafferty [88] drawn by data from M. Pourbaix [87], it can be seen that the passivity region for zinc is at approximately a pH value between 8 and 12, and for chromium approximately at a pH value of 4–13 at a 1 atm pressure and a 25°C temperature.

In practice, however, it is not common to have such simple systems as are specified in the figures below. The water often contains dissolved substances that cause precipitation or complex formation. The presence of such substances can radically change the diagram [92].

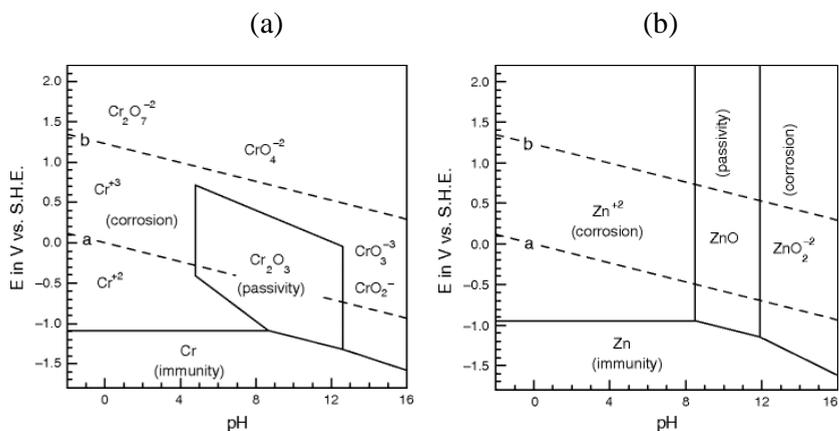


Figure 38 – Pourbaix diagrams for chromium (a), and zinc (b) at 25°C.

In this study, the concentrations of some metals (such as Cr, Fe, Ni, Zn and Mo) were determined in the C- and D-wastewaters (CWW and DWW, respectively) before and after neutralization by addition of FA, LM and PL. The element determination was carried out by using conventional optical emission spectrophotometers inductively coupled plasma (OES-ICP) using a SPECTRO ARCO AES-ICP model: FHX in an industrial laboratory. The obtained results are given in Table 18. First of all, it can be seen that the DWW samples contained significantly larger concentrations of these metal elements compared to those found in the CWW samples. More specifically, the concentrations of metals in D-wastewater are about 2.9–3.9 times larger with respect to the elements Cr, Fe and Mo, ~6.1 times for Ni, and more than 100 times for Zn. Furthermore, it was found that the concentrations of these metals in the wastewater decreased dramatically (except for Zn) during the neutralization process in all trials when using of PL as well as LM and FA. For instance, the concentrations of Cr after neutralization decreased approximately 450–1550 times in the CWW experiments and 1800–20600 times in the DWW experiments. This corresponds well to the Pourbaix diagram in Figure 38, showing that the dominant phase is Cr_2O_3 in the passivity region in the pH range of 4–13. The pH value of the treated wastewaters reached 8.6–12.6 for the waters that were analyzed for chemical composition determinations, as seen in Table 18. It should be pointed out that the reduction of concentrations of the given metals during neutralization of DWW is 4–60 times larger (depending on the metal) compared to the CWW results. It may be a reason why D-wastewater needs significantly larger amounts of added materials for neutralization up to similar pH level. Moreover, it can be seen that the LM sample has a purification effect in the acidic wastewaters from the given metals similar to the PL sample, while the FA has lower purification effect compared to the LM and PL samples.

Based on obtained results, it can be concluded that the fly ash and calcined lime mud, which were obtained as CaO-containing wastes from pulp and paper industry, can be successfully applied instead of the common primary lime for neutralization of acidic wastewaters in steelmaking.

Table 18 – Results from chemical composition determinations of some metals in wastewater C and D as received, and after addition of FA, LM and PL.

Sample	Added neutralizer [g/l]	pH after 30 min	Cr [mg/l]	Fe [mg/l]	Ni [mg/l]	Zn [mg/l]	Mo [mg/l]
CWW Before neutralization	0		202	609	179	<0.01	40.1
		12.6 in 5 min					
C + FA*	33		0.13	0.02	<0.01	0.04	3.48
C + LM	4.3	8.7	0.45	1.40	1.20	0.01	6.93
C + PL	4.3	9.9	0.43	0.53	0.29	<0.01	15.7
DWW Before neutralization	0		618	2350	1084	1.5	117
D + FA	52	9.1	0.08	0.10	0.04	<0.01	5.06
D + FA*	33	8.6	0.34	0.35	0.28	<0.01	4.66
D + LM	19	9.1	0.10	0.54	1.67	0.01	1.06
D + PL	47	8.8	0.11	0.45	156	0.47	0.17
D + PL	48	9.2	0.03	0.12	0.15	0.01	2.46

**powder used after additional calcination of FA at 1050°C during 60 minutes.*

The results obtained in the given study correspond well to the published results of other researchers. For instance, Sthiannopkao et al. presented in a study in 2009 that lime mud had a greater capability than recovery boiler ash for removing heavy metals contamination in metals finishing wastewater. This was found to be due to that lime mud contains mainly calcium carbonate, while recovery boiler ash comprises mainly salts, which can interfere with the process of metal precipitation [92]. It should be pointed out that the lime mud used in the present study was calcined, so it contained mainly CaO.

3.5 Organic mixed biosludge and green waste as carbon sources in blast furnace hot metal production

It is well known that the strength of the briquettes used in a BF is important, both at room temperature and at high temperatures. The main quality index in the iron and steel industry is the cold strength of the briquette, the tumbler handling strength (TTH) [77]. After the curing period of 5 weeks, determinations of the TTH of the briquettes resulted in values of 45% for the PSH and 63.5% for the GrH. The requirements for TTH may vary for different BF. For this specific BF, it should be at least 75%. However, even though the TTH values of the experimental briquettes were lower than the required parameters, the given briquettes were accepted for a short-term trial for preliminary evaluation of the possibility of industrial application in the BF process and effect on main production parameters. Also, the low strength of the briquettes led to a generation of fine particles. Therefore, the briquettes were sieved to separate the fines before charging the briquettes into the BF. The PSH generated 5% of fines and the GrH 20% of fines. The big difference between the amount of generated fines can possibly be at least partly explained by the fact that the fines were noticed when charging the PSH material. Therefore, more attention was given to the generation of fines from the GrH leading to more sieving of the GrH briquettes. Before the briquettes used in the trials were produced, a smaller batch of 5 ton of briquettes containing 2.2% hydrochar from sewage sludge, 10% cement and the rest was in-plant fines, were produced to ensure that the mechanical strength of the briquettes were sufficiently high. The TTH value was determined to be 75% after 2 weeks of storage and 71% after 4 weeks of storage. This indicates that the strength of the hydrochar-containing briquettes are not favored by a long storage time outdoors. The fines are a big threat to a stable BF operation as it can cause problems with the gas cleaning system and result in a higher counter pressure when they clog the porous bed in the BF. Therefore, the strength of the briquettes need to be improved by an optimization of the recipe and briquetting process in order to carry out a longer trial campaign in the future.

The average values for production rate and fuel rate, amount of injected powdered coal (PCI) and dust, temperature of the hot metal, amount and basicities (CaO/SiO_2) of slag and ratio of sulphur contents in slag/steel from the experimental trial campaign and the reference periods (two days before and two days after the trials) are shown as average values for each day in Table 19.

Table 19 – A compilation of the main production parameters during the trial campaign and the reference periods.

Test day	ton HM/day	Fuel rate (kg/tHM)	PCI (kg/tHM)	Dust (kg/tHM)	Temp.(HM) (°C)	Slag (kg/tHM)	CaO/ SiO ₂	(%S)/ [%S]
Ref-1	2845.0	477.2	103.6	20	1463	168.4	0.89	15.1
Ref-2	2909.2	470.6	99.2	13	1474	168.4	0.92	17.8
PSH-10	2913.6	472.8	96.4	18	1472	169.2	0.91	17.6
PSH-20	2842.2	472.5	101.3	16	1469	168.4	0.88	15.2
PSH-40	2894.9	473.2	100.0	14	1469	168.4	0.89	14.6
GrH-10	2860.7	475.3	101.0	15	1454	169.9	0.88	13.2
GrH-20	2855.9	480.2	99.6	12	1457	171.2	0.89	13.3
GrH-22	2811.9	488.0	104.8	15	1458	173.6	0.91	12.6
Ref-3	2835.7	483.2	100.1	12	1473	173.5	0.88	16.6
Ref-4	2787.0	488.7	102.4	20	1474	173.5	0.94	20.3

The production of hot metal (ton/day) was larger in the paper sludge hydrochar briquettes (PSH) trials (2883.6 tHM/day) and almost the same during the green waste hydrochar briquettes (GrH) trials (2842.8 tHM/day) compared to that in the reference days (2844.2 tHM/day). However, it should be pointed out that the production rate can differ by approximately 200 tHM/day without changing any process parameters during a conventional production. The average amount of produced dust was similar during the PSH trials (16.0 kg/tHM) and lower in the GrH trials (14.0 kg/tHM) in comparison to that in the reference trials (16.25 kg/tHM), as can be seen in Figure 39. In the figures below, the red dotted lines highlights the highest and lowest values during the reference days.

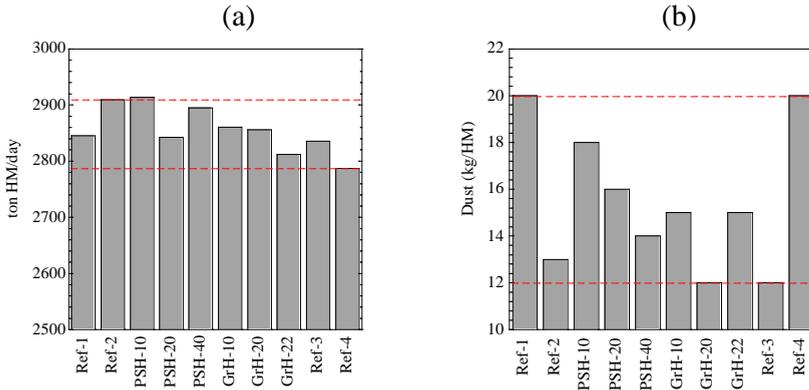


Figure 39–The production rate of hot metal (HM) (a), and average amount of dust (b) obtained during reference and experimental trials.

In Figure 40a it can be seen that the fuel rates during the PSH trials (on average 472.8 kg/tHM) were very similar to that in the Ref-1 and Ref-2 trials. In the GrH trials, the fuel rates were increased (up to 488.0 kg/tHM in GrH-22) as well as in the Ref-3 and Ref-4 trials. However, the highest fuel consumption (488.7 kg/tHM) was obtained during ref-4. Also, the amount of injected powdered coal (PCI) (Figure 40b) was lower in the PSH trials (99.2 kg/tHM) and almost the same as in the GrH trials (101.8 kg/tHM) in comparison to that in the reference trials (101.3 kg/tHM on average).

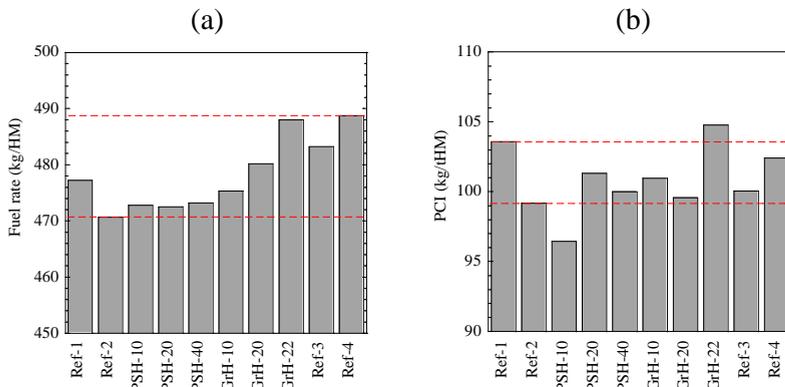


Figure 40– Average fuel rates (a), and injected PCI (b) obtained during reference and experimental trials.

Figure 41a shows the average carbon content in the HM obtained during the reference and experimental trials. The carbon content was slightly lower in the in the PSH and GrH trials (on average ~4.48% and 4.44% respectively) than it was in the reference trials (4.51%). However, it fluctuated significantly during the reference periods as well. Figure 41b shows the average temperatures of the hot metal during the reference days and the experimental trials. The temperature when using PSH briquettes were almost the same (1470 °C) as in the reference periods (1471 °C on average), while when using hydrochar from green waste (GrH trials), the temperatures were significantly lower (~1456 °C). In order to increase the HM temperature, additional coke was added during the trials.

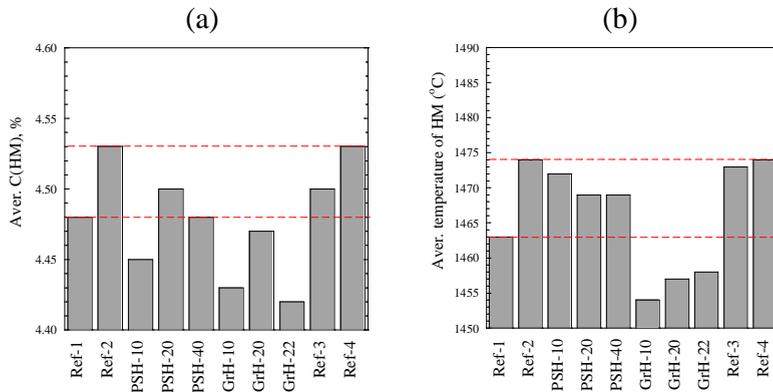


Figure 41 – Average contents of C in hot metal (%) (a), and average temperature of hot metal obtained during the reference and experimental trials (b).

The average values for calculated amounts and basicities (CaO/SiO_2) of the slag obtained during reference and experimental trials are given in Table 19. It was found that the slag amount in the PSH trials (on average 168.7 kg/tHM) was very similar as in the Ref-1 and Ref-2 periods (168.4 kg/tHM), while it was increased in the GrH trials (up to 173.6 kg/tHM in GrH-22) and in the Ref-3 and Ref-4 periods (up to 173.5 kg/tHM). The amount of slag was increased due to the additional amount of coke added to increase the HM

temperature. The slag basicities in all trials fluctuated significantly during the studied period, including the reference trials. One possible reason for that could be the moisture content of the top charged limestone during the trials, due to the high humidity. The higher moisture content in the limestone affected the charging system so that less limestone was charged. This in turn, led to a lower CaO content in the slag and large fluctuations of the slag basicity. Even so, the average values of slag basicities during the experimental trials (~0.89 in the PSH and GrH trials) were lower than that in the reference trials (~0.91). Moreover, the lower basicity of obtained slags in experimental trials may also be explained by relatively high concentrations of SiO₂ in both hydrochar pellets, which were used for preparation of PSH, and GrH experimental briquettes, as given in Table 5. Moreover, it was found that the S concentration (Figure 42a) in hot metal increased with an increased amount of added PSH and GrH briquettes. More specifically, the average content of S in hot metal increased from 0.072% in the reference trials up to 0.076% and 0.088% in the PSH and GrH trials, respectively. The largest concentration of S (0.094%) was obtained in the trial GrH-22. The lower basicities in most of the experimental trials can be an explanation for this. At the same time, the S average content in slag (Figure 42b) decreased from 1.24% in the reference trials up to 1.20 and 1.15% in the PSH and GrH trials, respectively. As a result, the coefficients of S distribution between slag and hot metal ($K_s = (\%S)/[\%S]$) decreased significantly from ~17.4 in the Ref trials up to 15.8 and 13.0 in the PSH and GrH trials, respectively, as shown in Figure 42d. One possible explanation could be the lower basicities of the slags in the experimental trials, caused by the relatively high concentrations of SiO₂ in the hydrochar pellets. However, another explanation could be the increased amount of charged Si-containing coke required due to the wet charge materials. Also, the charging of wet lime led to an impaired sulphur refining.

It should be pointed out that the S content in dust varied in all trials (from 0.32 up to 0.42%), as can be seen in Figure 42c. However, the average value of S content in dust were very similar: 0.36% in the Ref trials and 0.35 and 0.37% in the PSH and GrH trials, respectively.

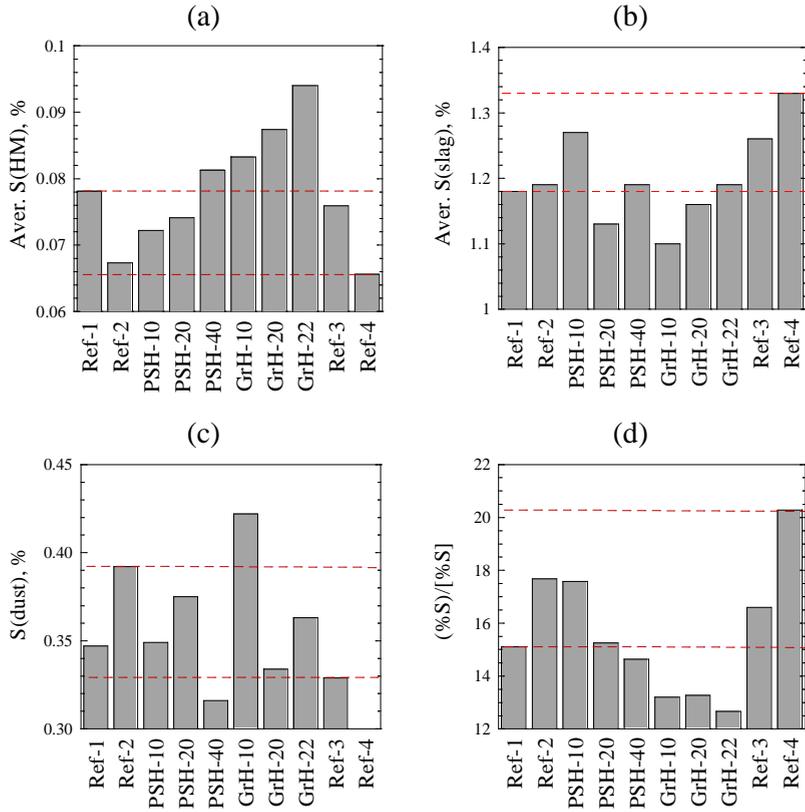


Figure 42 – Average contents of sulphur (%) in hot metal (a), in slag (b), in dust (c), and ratio of sulphur in slag/hot metal (d) obtained during reference and experimental trials.

The average concentrations of P in hot metal are quite stable and are almost the same (~0.029) in all trials and independent on the type and amount of experimental briquettes added during the BF process, as seen in Figure 43a. Moreover, though the concentration of FeO in slags showed a tendency to decrease during the trial period (Figure 43b), the average values of FeO content in slags were also

very similar for all trials, namely 0.51% in the reference periods and 0.52 and 0.49% in the PSH and GrH trials, respectively.

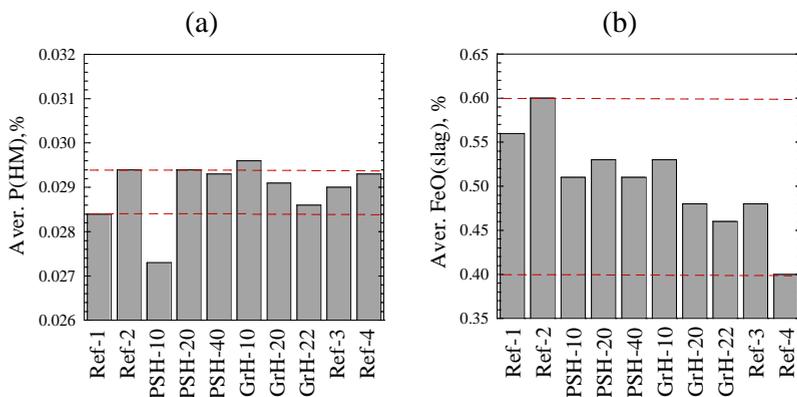


Figure 43 –Average concentrations of phosphorous (%) in hot metal (a), and of FeO in slag (b) in different trials.

The economical and environmental effects of using hydrochar briquettes in blast furnaces can be determined in a reliable manner if the BF operation is stable. An advantage of using bio-briquettes is that the bio carbon has a higher reactivity compared to that of conventional coke. This can be due to that biomass char has a larger gasification rate and a larger reduction rate of iron oxides in bio briquettes. In previous studies [93], [94], it was found that a mixture of fine powder coke and iron ore resulted in a much higher reduction reactivity due to a closer contact with each other compared to that of using a conventional layer-by-layer burden in the BF. Moreover, an increased gasification reaction in the carbon-iron ore mixture can significantly improve the reduction process in the BF and decrease the thermal reserve zone temperature [95]–[97]. Also, it was reported that the reactivity of biomass char obtained from the carbonization process is much higher than that of coke [97].

Overall, it was difficult to evaluate the economic and environmental effects of using different bio-briquettes in the BF during this short-term campaign due to the low strength of the briquettes and the small amount of hydrochar used. Therefore,

additional trials and investigations are necessary in the future for optimization of the properties of the bio-briquettes containing hydrochar pellets and the blast furnace process, when charging bio-briquettes containing hydrochar pellets at the top of the blast furnace. Another thing that has to be considered is the unpleasant smell of the hydrochar, which can be an issue for the people working with the materials.

4 CONCLUDING DISCUSSION

The thesis focuses on the evaluation of possibilities to partly replace primary lime and fossil coal and coke with recovered lime materials and carbon from pulp and paper production residues and green waste in metallurgical processes.

The CaO-containing residues (such as fly ash, lime mud, etc.) having more than 60% of CaO can partially be applied as slag formers instead of conventional natural primary lime in steelmaking processes in EAF and AOD converters. The implementation of this procedure can promote a decrease of the problem of landfill of CaO-containing wastes from pulp and paper industries and to reduce mining and preparation of natural assets (for instance limestone), which is important from an environmental point of view.

Usually the lime-containing waste materials from pulp and paper industries after drying are in a powder form. Therefore, they can be used in metallurgy as a powder for injection or as briquettes for charging into furnaces, converters or ladles. In this study, the CaO-containing materials (fly ash and waste lime) were used in a briquette form as slag forming materials instead of a part of the primary lime. Experimental trials were carried out in a pilot-scale Electric Arc Furnace and an Argon Oxygen Decarburization Converter. However, in steel making processes, it is very important to control the chemical composition of the steel and contents of impurities (such as S, P, etc.). High levels of phosphorus and sulphur lowers the corrosion resistance, decreases the weldability, and makes the final steel brittle. Therefore, the amount of waste materials used for steelmaking processes can be limited by the requirements to the concentrations of S and P in the final steel product.

This thesis consists of five supplements, which focuses on the possibilities to make briquettes of the recovered lime-containing residues from pulp and paper industries such as lime mud, calcined lime mud and fly ash, using AOD slags as binder (supplement I), as well as the effect of partly replacing primary lime with recovered lime in EAF (supplement II) and AOD converters (supplement III), the possibilities to use recovered lime to neutralize and clean acidic wastewaters (supplement IV). Furthermore, the use of hydrochar derived from

organic mixed biosludge and green waste as part of the carbon sources in a blast furnace (supplement V) was evaluated. The results and applications of the studies are summarized in Table 20.

Though the recipes of CaO-containing briquettes for experimental pilot trials in this project (OSMET S2) were developed and produced by SWERIM AB (Luleå, Sweden), an additional laboratory study was carried out in KTH (supplement I) for testing of possibility to use an AOD slag from steelmaking for briquetting as a binder (instead of cement, lignin or other binder materials commonly used for this purpose) for different wastes from pulp and paper industries. As was described above, three different CaO-rich residues (lime mud/mesa, calcined lime mud and fly ash) from pulp and paper production and pulverized AOD converter slag were pressed in different proportions into laboratory-scale briquettes at room temperature. Drop testing experiments were used to study the mechanical strength of briquettes with different chemical compositions and for comparison with that in conventional lime lumps usually used as slag formers in EAF and AOD operations. It was revealed that the use of AOD slags (up to 20%) as binders in metallurgical briquettes can effectively increase the impact strength of briquettes if a following heat treatment at a 850°C temperature of the briquettes is applied.

The strength of briquettes is influenced by many factors such as the shape, volume, mass, and density of the briquettes. Furthermore, by the briquetting device used and the pressure applied. In this study, the chemical composition of the briquettes was the only factor that was varied. In addition, different after-treatments were tested, namely; heat-treatment and storage time. It should be noted that there are more ways to test strengths of briquettes than was performed in this study. S. R. Richards [98] states that the resistance to crushing, impact, abrasion and water penetration are the most important to determine for fuel pellets. However, the drop testing method is a commonly used technique suitable for the industrial conditions of loading-unloading, transportation and charging of briquettes into furnaces in many steelmaking companies.

In supplement II, it was shown that when primary lime is partly replaced with fly ash (up to 50%) as slag formers in EAF operations, a faster formation of liquid slag, as well as a faster and full

desulphurization is achieved, and less FeSi alloying additions are needed. The briquettes were not too strong since the briquettes were dissolved in the melting processes, as is desired. Specifically, no undissolved pieces of fly ash or lime were detected in the slag samples taken after the melting of the charges in the EAF trials.

In supplement III, it was concluded that in the AOD converter trials, by referring to the S content in the steel after the reduction stage and the attainable S content in the steel after the desulphurization stage, the S content in the steel can be controlled. In addition, the S content from the recovered lime is not a big issue in the present study. However, the P content in the steel increases gradually with an increased input of P from the recovered lime as well as from the subsequent processing stages. To meet specific requirement of P in the steel, the replacement ratio of recovered lime is limited by the acceptable P level in the steel due to a high P content in the recovered lime.

As in the case for supplement I, the idea of treating two waste streams at once is appealing and resulted in the idea that the recovered lime materials could be used to neutralize acidic wastewaters from the pickling process in a steel mill. In supplement IV, it was shown that addition of calcined lime mud and fly ash to the wastewaters can raise the pH levels and lower the concentrations of some metals efficiently. However, more in-depth chemical determinations of the cleaned water and the sediments should be made. It should also be evaluated how the sediments from the cleaning process can come to their best use. As today, some steel mills recirculate the sediments as flux, while in some steel mills the sediments are put to landfill since they cannot be further used due the chemical composition [99].

In supplement V, it was revealed that briquettes containing hydrochar derived from mixed organic biosludge in a pulp and paper mill, and green waste can be partially used for charging in a production blast furnace together with conventional briquettes. During the trials, most of the technological parameters of the blast furnace process were very similar compared to those in the reference periods. It should be pointed out that the replacement ratio was very low, and additional trials and investigations are necessary for optimization of compositions and amount of added experimental residue-briquettes. Also, the

strength of the hydrochar-containing briquettes need to be improved before longer trials can be performed.

However, these positive results support our efforts to perform more in-depth investigations in this directions in the future. In the respective supplement, more detailed descriptions of the results can be found.

Table 20 – Overview of the results of the supplements (S).

S	Study	Objective	Main results
I	Application of AOD converter slags as binders in metallurgical briquettes.	Decision of recipes. Method to produce metallurgical briquettes. Improvement of mechanical strength. Determination of impact strength of briquettes.	An addition of AOD slag does not improve the impact strength of briquettes when no additional treatment is applied. An addition of 10-20% AOD slag in combination with heat-treatment at a 850°C T can significantly improve the impact strength of briquettes.
II	Application of recovered lime-containing materials as slag formers in EAF.	Chemical compositions of metal and slag. Steel quality in the aspects of S and P. Impacts on the EAF process. The slag properties; amount, P and S content, basicity, fluidity.	Slightly increased S and P contents in steel. Decreased need for FeSi alloying additions. Faster formation of liquid slag. Well dissolved lime material.
III	Application of recovered CaO-containing materials as slag formers in AOD converters.	Impacts on the AOD processes; Decarburization. Reduction and desulphurization capacity.	Larger amount of slag. No negative effect on decarburization nor reduction in AOD converter. As efficient desulphurization agents as primary lime. Increased S and P content in steel.
IV	Application of recovered CaO-containing materials as neutralizing agents for acidic wastewaters.	Neutralization efficiency and water cleaning ability.	The recovered lime materials can be used to successfully neutralize and clean acidic wastewaters.
V	Application of organic sludges and green wastes as part of the carbon sources in blast furnace (BF) operations.	Impact on the BF process; Productivity, fuel rate, chemical composition of hot metal and slag.	Main parameters very similar during the trials and the reference periods.

5 CONCLUSIONS

The thesis tested possibilities to partly replace primary lime and fossil coal and/or coke with recovered lime materials and carbon from pulp and paper production residues and green waste in metallurgical processes. The implementation of this aim can promote a decrease of the problem of landfill of wastes from pulp and paper industries and to reduce mining of natural assets, which is important from an environmental point of view. Based on the results obtained in this study, the following main conclusions can be formulated:

1. Based on the results obtained in laboratory-scale experiments (supplement I), it was found that the AOD slags (up to 10–20%) can be used as a binder component for briquetting of different wastes from pulp and paper industries such as lime mud/mesa (M), calcined lime mud (L) and fly ash (F). However, most of the briquettes, which were produced without using an additional heat treatment and were stored in open atmosphere (indoors) for 20–35 days, were destroyed before or during the drop tests. The mechanical impact strength of the obtained CaO-rich briquettes was significantly increased by the following heat treatment of the briquettes for 60 minutes at 850°C. The retained average weight (RW) after seven drop tests was used as a parameter for quantitative evaluations of the mechanical strengths of the different metallurgical briquettes and conventional lime lumps used as slag formers in EAF and AOD operations. For instance, the briquettes, which contained CaO-rich wastes from pulp and paper industries (such as lime mud, calcined lime mud and fly ash) and 10–20% of AOD slag, after a heat treatment at a 850°C temperature showed the largest values of RW parameter: 91% RW for M90–850 briquettes, 52% RW for L90-850 briquettes, 63% RW for F90-850 and 92% RW for F80-850 briquettes. The obtained RW values for these experimental briquettes after 7 drop tests are comparable or significantly larger compared to those for lime lumps used for EAF (60% RW) and for lime lumps used for AOD (23% RW) received from a steel plant.

2. Pilot experiments (5–7 t) in EAF (supplement II) showed that when primary lime is partly (up to 50%) replaced with fly ash as slag formers in EAF, a faster formation of liquid slag (because the FA contains about 16% SiO₂ and 9% Al₂O₃), as well as a faster and better desulphurization is achieved. As a result, less amount of FeSi alloying additions (~3 kg Fe-75%Si per ton of scrap by charging 50% FA) are needed because less part of added FeSi is used for oxidation and formation of liquid slag. It should be pointed out also that, although the increased amount of added fly ash (containing 0.4% of S) increases the initial S content in charged slag former materials, the concentration of S in the final EAF slag and an actual coefficient of S distribution in the slag and steel (L_S) increased more than 4 times at a charging level of 50% FA compared to the conventional reference trial. However, the actual coefficient of P distribution in the slag and steel (L_P) decreases by 10–20% with an increased charge of FA and the final concentration of P in the steel can be slightly increased because the FA contains on average 0.26% P.

3. Pilot trials in the 5 t AOD converter (supplement III) with using of briquettes, which contained 50% of primary lime (PL) and 50% of secondary lime: fly ash (FA) or calcined lime mud (LM), showed that the partial use of fly ash and calcined lime mud (up to 10–20% of total amount of added CaO) do not have negative effect on the decarburization process nor on the reduction process in the AOD converter. Moreover, the fly ash and calcined lime mud are as efficient desulphurization agents as primary lime. Therefore, although the S contents in steel melt can be significantly increased with an increased amount of added FA (contains 0.40% S) and LM (contains 0.11% S), the final S content in the steel can be decreased up to required level during the reduction and desulphurization in AOD converter. However, the amount of addition of secondary lime materials instead of conventional primary lime in the AOD converter process should be limited by the accepted phosphorus level in the final steel and by the amount of produced slag due to the much higher P

contents in the FA (0.26% P_2O_5) and LM (0.75% P_2O_5) compared to that in the PL (0.01% P_2O_5).

4. Additionally, the powders of CaO-containing residues (fly ash (FA) and calcined lime mud (LM)) from pulp and paper mills were successfully applied in lab-scale experiments (supplement IV) for neutralization of various industrial acidic wastewaters after the pickling process from two steelmaking companies instead of primary lime (PL). It was found that the neutralization of acidic wastewaters up to the required pH value (up to pH 9) during 30 minutes required about 2.2–2.7 times less LM compared to that of FA. This was found to be due to the significantly higher concentration of CaO in the LM (~91% CaO) and much smaller particle sizes compared to those in the FA. Almost same amounts of fly ash and primary lime should be added to reach the same neutralization levels of acidic wastewaters. However, an additional calcination of PL and FA powders (at 1050°C for 60 minutes) can increase the neutralization effect and decrease the required amount of FA and PL on 1.6 and 2.4 times, respectively. Moreover, both powders of LM and FA from pulp and paper mills can be applied for purification of wastewaters from Cr, Fe, Ni, Mo and Zn. For instance, the concentration of Cr in various wastewaters can be decreased 450–20600 times depending on initial concentration of Cr in the water. However, the purification effect of FA is lower compared to the LM and PL, which have similar purification effect for the given metals.
5. Carbon-containing wastes from a pulp and paper mill (organic mixed bio sludge) and green waste were used for production of hydrochar (HTC) pellets and bio briquettes (supplement V), which were tested as a part of the carbon sources in an industrial blast furnace (BF). The briquettes for experimental trials in the BF contained 86% common in-plant fines, 12% cement and 2% HTC pellets produced from mixed paper sludge hydrochar (PSH) or green waste hydrochar (GrH). However, the mechanical strength of the obtained briquettes was lower than the required

level for conventional briquettes used in BFs. Therefore, in this first step, the obtained briquettes were used for short industrial experimental campaign in a BF. Most of the technological parameters of BF process (such as the production rate of hot metal, fuel rate, amount of slag and dust, etc.) in the experimental trials with partial charging of PSH and GrH briquettes (10–40% of the total amount of charged briquettes) during a 6-day industrial trial campaign were very similar compared to the values in the reference trials before and after experimental trials. Overall, the addition of PSH briquettes show better operational results compared to when adding GrH briquettes. However, the strength of the experimental briquettes needs to be improved for future long–time trials in the industrial BF.

6 FUTURE WORK

The fundamental work of utilizing wastes from pulp and paper production as raw materials in iron and steelmaking have been investigated in this study. However, there are several aspects which need to be taken into account in the future research work towards industrial implementations of upgrading and using industrial residues for metallurgical applications and to contribute to net-zero fossil CO₂ emissions.

1. Scale-up trials of promising concepts are needed to evaluate their performance on a larger scale using both long-term industrial trials and pilot trials to test these new materials to provide a better understanding of the effect of addition of secondary materials on different process parameters.
2. Life cycle analysis (LCA) assessments should be made to quantify the environmental performance of the different studies in this thesis.
3. Spatial systems analysis assessments should be made to evaluate national capacity.
4. Business models should be made to further develop and maximize the value chains.
5. Energy aspects of utilization of these recovered materials should be considered.

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