TOCANEM

TOWARDS CARBON NEUTRAL METALS

2020–
2023

TOCANEM

– TOWARDS CARBON NEUTRAL METALS

CONTENTS

TOCANEM IN A NUTSHELL

Key values

Time period:	2.9.2020–31.12.2023
Total budget:	18.28 million
Research institutes' budget:	8.28 million
Companies' budget:	10.00 million
Number of publications:	31 journal papers, 18 conference papers
Theses:	3 doctoral, 23 master's, 6 bachelor's.

The TOCANEM consortium

The TOCANEM project gathered partners from five tiers of metals production: five research institutes for the facilitation of research and dissemination of results, four technology and service providers for the application environment and technology development, six metals producers to provide the application environment and for process development, three small-to-medium size enterprises for the implementation and commercialization of research, and two energy and material suppliers who play a role in the production of materials that support the development of carbon neutral metals processing. Figure 1. illustrates an overview of the TOCANEM consortium.
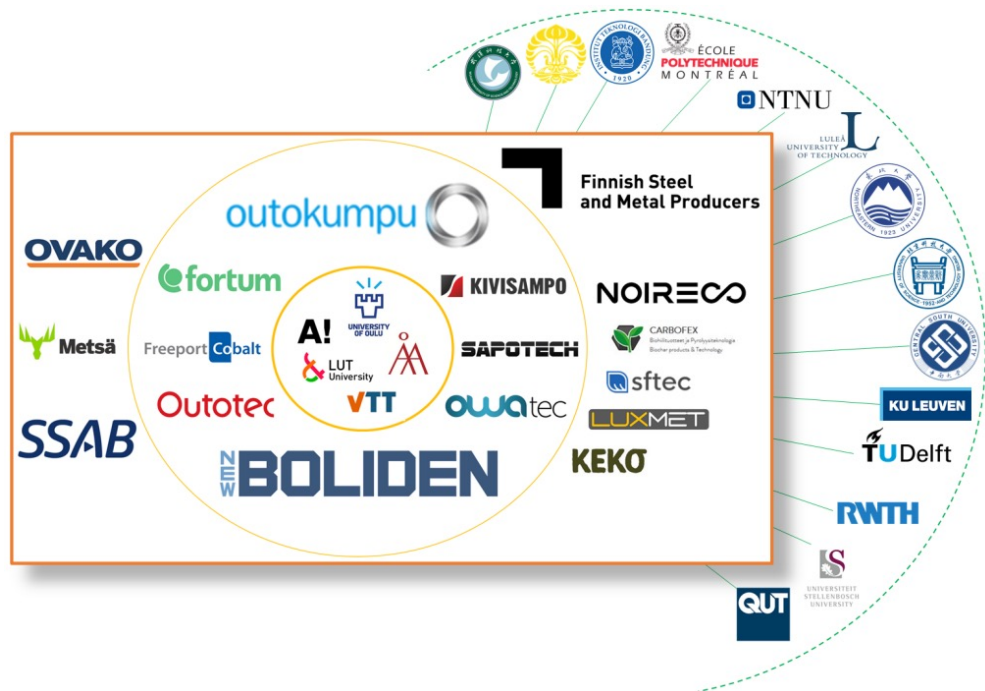
Figure 1. Overview of the TOCANEM consortium.

Project structure

The research activities are organized in cross-sectorial work packages, which focus on Direct Carbon Avoidance (WP1), Smart Carbon Usage (WP2), and the Circular Economy (WP3). As shown in Figure 2, two additional work packages were dedicated for international collaboration (WP4), as well as for coordination and dissemination of results (WP5).
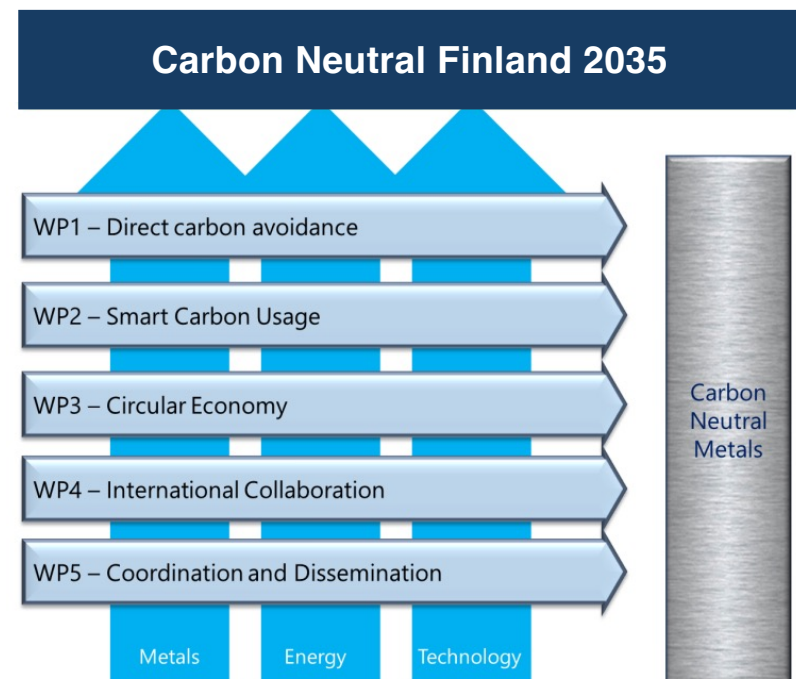
Figure 2. Schematic of the TOCANEM project structure.

COMPANY OVERVIEW

Synergy for Sustainability: Fundamental Research, Novel Solutions and Collective Commitment

The metal production industry is responsible for a major part of the total carbon emissions produced in Finland. The reduction of carbon releases is mandatory not only to lower the environmental load and support the national low-carbon roadmap to reach carbon neutrality by 2035, but also to ensure the competitiveness of domestic companies. As a result of the most ideal outcome, both cost-effectiveness and carbon footprint levels will be improved. As the name of the program states, TOCANEM promoted a shift towards carbon-neutral metal production by connecting joint research work between universities, companies, and research institutes to create innovative and new solutions to reach common and ambitious targets.

The technical readiness of the topics addressed during TOCANEM widely ranged from laboratory-scale research to commercially viable technological solutions. For example, the reduction of chromite ore using green electricity or bio-based reductants, which was widely covered by TOCANEM, might require years of development before full industrial-scale utilization but can be justified by its enormous CO_2 saving potential. On the other hand, quicker but smaller-scale CO_2 reductions can be achieved by using technology already available on the market to improve the performance of existing production processes and by rethinking the old ways of working. As an example, the utilization of optimized processing routes at Outokumpu's stainless steel production led to an 11% reduction in the carbon footprint (Scope 1 & 2) and brought significant cost-saving impacts, reflecting positively on competitiveness and customer relations. Similarly, smelting of direct reduced iron (DRI) investigated by Metso still requires dedicated research but has the potential of saving 80% of CO_2 emissions of carbon steel production. In a shorter period, Metso's customers can reduce their CO_2 emissions by using alternative reductants. All this work and results were enabled by high-level knowledge and the seamless contribution provided by Finnish universities and research units.
Now, after the hard efforts, the next crucial step is to ensure the continuity of the work that has begun. Ensure that the interesting ideas, promising demos, and successful pilots will eventually be upscaled step-by-step from laboratories to everyday production and full-scale production environments. This responsibility is in the hands of the industry partners.

We wish to extend our sincere gratitude to Business Finland and the Association of Finnish Steel and Metal Producers for being the key enablers in forming such an effective and competent consortium and making it possible to initiate significant steps toward the industrialization of the innovative ideas born before or during the TOCANEM program.

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UNIVERSITY OVERVIEW

The preparation of the Towards Carbon Neutral Metals (TOCANEM) was initiated as a follow-up project to the previous Symbiosis of Metals Production and Nature (SYMMET) project, continuing topics related to the circular economy. However, based on discussions with companies it was soon realized that completely new, CO_2-lean or preferably completely CO_2-free technology for metals production was crucially needed to meet the ambitious targets for CO_2 reductions. We thus embarked on a quest to study new processes and operating practices based on the use of hydrogen, electricity, and non-fossil reductants to replace conventional fossil reductants.

The onset of the COVID-19 pandemic brought about unprecedented challenges and limitations to research work, but it did not deter our commitment to the aims of the project. Limitations to the gathering of people were put into force so rapidly that new remote working practices had to be devised on the go and refined later. Travel limitations not only hindered collaboration within the consortium but also put a severe constraint on international collaboration, leading to delays and cancellations of planned research visits. Despite these setbacks, our commitment to tackling one of the most pressing global issues—reducing carbon emissions—remained unwavering. This final report offers a glimpse into our journey and achievements.

The TOCANEM project has enabled universities to develop new expertise and laboratory infrastructure specifically for CO_2-free metal production. This expertise and infrastructure are now available for further studies toward higher levels of technological readiness and piloting in the planned follow-up project. One example of the fundamental work initiated in the TOCANEM project is the study of CO_2-free technologies to produce ferrochrome. During the planning phase, several potential technologies were shortlisted on a conceptual level but there was virtually no knowledge of whether they would work in practice. In the end, two different technologies (molten salt electrolysis and molten oxide electrolysis) were tested by the project partners, while collaboration on a third technology (hydrogen plasma smelting reduction) was initiated together with German and Austrian research institutes. Of these technologies, hydrogen plasma smelting reduction was established as the most potential candidate. An exceptionally strong consortium has formed around the topic and is expected to form a global spearhead of research in this area. One example of the projects pursued by the consortium is the EU Horizon Europe project "H2PlasmaRed", which focuses on the reduction of iron ores and steelmaking side streams.

The sustainable use of mineral raw materials for non-ferrous metal production requires even more accurate recovery of metals from the side streams in the processes, such as slag and leach residues. The prevailing practice is to use coke as the reductant for metal oxides, resulting in CO_2 emissions. In TOCANEM, breakthrough results were obtained by replacing coke with different biochar (carbon neutral solution) and hydrogen gas (carbon-free solution). Both appeared to be more efficient reductants than coke, but there is still a considerable way to go before industrial implementation. The research infra and knowledge are now available, and new initiatives with industrial partners have been planned and launched.

Another important outcome of the project is the renewal of the workforce through new professionals with new skills. To this end, TOCANEM has served as the framework for several finished and ongoing doctoral theses as well as for about twenty master's theses. These professionals provide the metals industry with qualified personnel resources, which form an essential competitiveness factor for the Finnish metals industry.

Despite being a considerable undertaking, TOCANEM is by no means an end to the research and development work but rather a jump-start for the alignment of concrete research actions and the ambitious goals required by the green transition. It must be stressed that substantial public and private R&D expenditure is also required in the future to keep up with the long-term objectives. The research activities of the upcoming years will play a pivotal role in what kind of technology will be available in the 2030s, 2040s, and 2050s. Our journey continues, fueled by the determination to meet these goals and to be a global forerunner in technology related to CO_2-neutral metals production.

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WP 1

CARBON DIRECT AVOIDANCE

SUMMARY AND HIGHLIGHTS

Summary of the project's motivation and achievements based on industrial partners' point of view

outokumpu

Outokumpu scoped potential technologies to produce ferrochrome without carbon or direct CO_2 emissions on a laboratory scale and chose the most promising technology for further studies. Additionally, the company evaluated the chosen technology further and analyzed the technological feasibility to be utilized in a full-scale FeCr production environment. A feasibility study was conducted on replacing fossil fuel reheating processes with induction technology in stainless steel production. Additionally, Outokumpu explored the possibility of increasing scale removal efficiency by utilizing the rapid induction treatment concept.

The goal was to find new and alternative scrap melting technologies for EAFs (electric arc furnace) and conduct a proof-of-concept study of the most promising technologies identified. The company wanted to reduce natural gas consumption and direct CO_2 emissions by implementing furnace models allowing optimal process control on annealing and pickling lines in stainless steel production. Outokumpu wanted to study, implement and optimize novel processing routes leading to lower fossil fuel consumption and a reduced CO_2 footprint for traditional high-volume ferritic and austenitic stainless steel cold rolled products.

BOLIDEN

Boliden Harjavalta

The primary sources of direct CO_2 emissions in copper and nickel smelting processes stem from the external heating of furnaces and the reductants employed in processing. In the context of the TOCANEM project's Work Package 1 (WP1), our focus was on exploring alternatives to mitigate or reduce CO_2 emissions associated with furnace heating. During WP1, we conducted a comprehensive assessment of various alternatives aimed at either avoiding or minimizing CO_2 emissions during furnace heating. These alternatives ranged in terms of their technical readiness levels. To evaluate their potential impact on the gas treatment system and sulfuric acid plants of the smelting facility, we performed simulations. The simulations allowed us to quantify the potential effects on the smelter's gas treatment system if implementing these alternatives for furnace heating. Throughout the TOCANEM project, we identified the need for fine-tuning and validation of the existing simulation system. This was a critical step in ensuring the accuracy and reliability of our assessments. As a result, we conducted the necessary fine-tuning and validation procedures.

Boliden Kokkola

Boliden Kokkola participated actively in TOCANEM WP1 – Direct carbon avoidance.
The activities were focused on three tasks:
- Task 1.2 Pyrometallurgical zinc leach residue treatment with non-fossil reductants
- Task 1.3 Non-ferrous metal slag reduction with alternative reductants, and
- Tasks 1.8 and 1.13 on Extractive metallurgy.

Large pyrometallurgical experimental work was carried out in WP1 at Aalto University. The smelting and fuming characteristics were studied with test furnaces using alternative reducing agents including biochar and hydrogen. Biochar made in the University of Oulu in WP2 was also used for the test works. In addition, advanced thermodynamic modeling was carried out systematically for volatile metal recovery, as well as slag and speiss formation. The distribution of elements in smelting and fuming conditions at 1200–1400 °C (Zn, Pb, Ag, Au, In, Ga, Ge, Cu, Ni, Co, As, Sb, Cd, Bi, Te, Tl, Hg, F, Cl, S, Fe, Mg, Mn, Na, K, O) were evaluated and examined against experimental results and industrial experience. In the models, fossil carbon, biochar (made in WP2), methane, and hydrogen were used as reducing agents. In extractive metallurgy tasks, impurity handling was studied for manganese purification and arsenic removal.

KIVISAMPO

KIVISAMPO's primary objective is to advance the technology for utilizing organic waste in the form of briquettes as a source of renewable carbon. The underlying motives for this goal are driven by the need to promote sustainability, reduce waste, and contribute to eco-friendly practices.

These goals were achieved by:
1. Testing Biochar Coals: The company initiated a comprehensive test campaign that involved assessing biochar coals sourced from different companies. This enabled the evaluation of various biochar materials for their suitability in briquetting technology.
2. Development of Organic Waste-to-Biochar Technology: The company successfully trialed a technology for the preparation of wood charcoal using a test stand. This process encompasses the following steps: grinding, sieving, and milling organic waste materials to produce biochar. Chemical compositions were evaluated.
3. Customer Testing: The company provided several test campaigns for customers both within Finland and internationally. These campaigns incorporated the use of Electric Arc Furnace (EAF) dust and biochar coal as reduction agents and employing auger pressing briquetting technology. Notable elements of the testing campaign included:
   - A visit from a team from the University of Oulu, which entailed the delivery of a diverse range of samples.
   - Collaboration with the AMCOM GROUP on the technological aspects of the auger pressing technology, including binder development and biochar selection.

Metso

Metso's motivation is to help its customers decrease their carbon footprint in metals production by using alternative reductants. This requires knowledge of reductant properties and performance that was generated during the project. This allows Metso to design and deliver processes and technology with lower CO_2 emissions to global customers

KEY RESULTS AND IMPACTS
Summary of the key results and impacts based on industrial partners' point of view

outokumpu

Three potential upcoming technologies to produce ferrochrome without carbon and direct CO_2 emissions were validated in laboratory demonstrations. As a result of a techno-economical evaluation, HPSR technology was selected as the most promising technology for the next development phase (small-scale piloting). Additionally, a novel cost-effective production route was established for stabilized ferritic stainless-steel grades. 29 kilotons of material was already produced to end customers leading to ~1300 tons lower CO_2 emissions and over 800 k€ direct cost savings by the end of 2023. This equals 11% less released CO_2 emissions per produced steel ton. Outokumpu also gained new knowledge about the impact of omitting hot strip annealing of ferritic stainless steels on recrystallization and texture. This enabled the optimization of the product properties produced via novel process routes and ensured end-user customer satisfaction.

The relationship between processing practices, scale morphology, and descalability was clarified and laboratory tests of multiple mechanical and chemical descaling methods provided guidelines for technological solutions needed to effectively process type 304L austenitic stainless steel. Accelerated induction heating scale removal concepts were also studied in a laboratory environment for various austenitic and duplex stainless steels and the technical feasibility was simulated by modeling a full-scale production setup based on the laboratory results providing a basis for an investment project in the future. Fast slag composition analysis using laser OES was tested on both the laboratory scale and in an industrial electric arc furnace (EAF). The accuracy was successfully validated in the laboratory and online tests proved that the system can be used in slag composition control. After full implementation, significant savings in added raw materials and reduced refractory wear are expected.

A three-dimensional finite element model was developed to simulate the strip annealing process on Outokumpu's annealing and pickling lines. The influence of different features, such as the strip width and the radiative properties of furnace walls, on the heat transfer was studied using computer simulations. Computer simulations can be used for virtual production trials in process development without disturbing production. The simulator has also been converted into a web-based service running on the Azure cloud. The first web-based simulation tools have been released for testing by pilot users. Additionally, an improved heat transfer model was developed for model-based control of strip annealing at Outokumpu's continuous annealing and pickling lines. The added features reduce process variation in the annealing process and enable the reduction of safety margins, energy consumption, and direct CO_2 emissions. The new heat transfer model has been successfully implemented in the line automaton system of Tornio's annealing and pickling line number four.

BOLIDEN

Boliden Harjavalta

It is imperative to consider the surplus water generated during the combustion of hydrogen or bio-methane when assessing their suitability as fuels for furnace heating. This surplus water significantly influences the capacity and operational efficiency of the gas section within the sulfuric acid plant. As a result of the TOCANEM project, the roadmap for reducing CO_2 emissions in Boliden Harjavalta's smelting operations has now solidified and gained greater clarity.

Boliden Kokkola
Several diploma thesis works were carried out in these tasks as well as doctoral studies and licentiate thesis works. Several peer-reviewed articles were published. The collaboration with the universities (Aalto, OU, LUT) was very good and we kept regular research meetings within these tasks. The experimental and modeling works showed good agreement with industrial experience and gave new knowledge of near carbon-neutral processing of zinc residues. There is a high potential for using slag processed from landfilled zinc residues making the circular economy more closed. It was concluded that over 90% of the current landfilled waste, iron-rich sludges could be turned into metals and usable slag for cement making (in WP3) with significantly less Scope 1 and Scope 2 carbon dioxide emissions.

KIVISAMPO

The company's endeavors and testing initiatives have yielded valuable, detailed insights into the behavior of briquettes produced from organic waste, particularly wood charcoal, within metallurgical briquetting processes. These results have practical applications that encompass industrial implementations. The knowledge acquired from these experiments is currently in the negotiation phase for integration into industrial settings. Conversations are ongoing regarding the deployment of this technology within metallurgical operations, which has the potential to lead to significant advancements in carbon utilization and waste reduction.

In conclusion, KIVISAMPO's dedication to the development of organic waste utilization through briquetting, with a focus on renewable carbon sources, has resulted in substantial progress. Extensive testing and collaboration with research institutions and partners have yielded valuable knowledge, with practical applications now on the horizon. This initiative is in alignment with broader sustainability goals and represents a positive step toward environmental responsibility.

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TASK
1.1
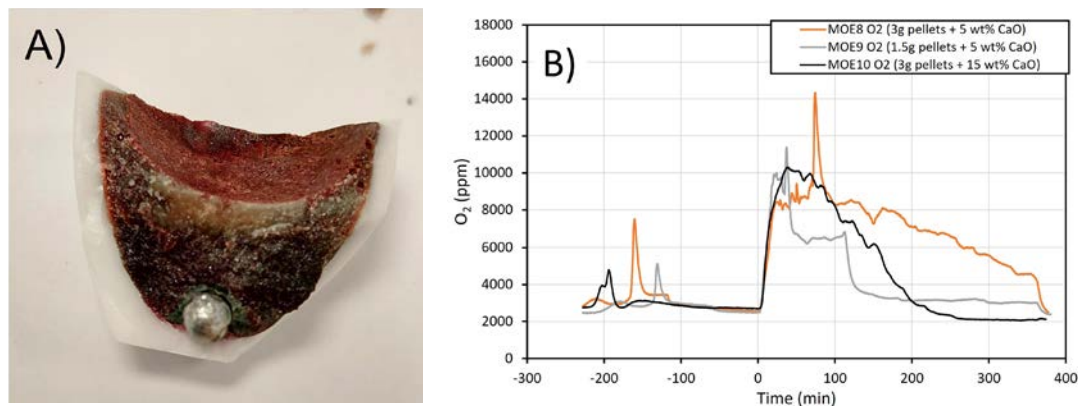## MOLTEN OXIDE ELECTROLYSIS FOR FERROCHROME PRODUCTION

Figure 3 A) Photograph of a sample after high-temperature electrolysis showing the crucible, electrolyte, and the formed metal alloy. B) Oxygen evolution during the high-temperature molten oxide electrolysis in 3 experiments.

INTRODUCTION

To mitigate the effects of climate change, our society must be able to drastically reduce its CO_2 emissions. As the metallurgical industry is a considerable producer of these emissions, new greener technologies must be invented and developed. One option could be the production of metals using renewable electricity. The aim of this task was to investigate the possibility of using high-temperature molten oxide electrolysis (MOE) for ferrochrome production. Subgoals were to study suitable electrolyte compositions as well as functioning anode and cathode materials. Additionally, suitable materials and the set-up for other parts of the experimental system (crucible, support materials, furnace) were investigated. The final goal was to produce ferrochromium using laboratory-scale high-temperature molten oxide electrolysis.

MATERIALS AND METHODS

Pre-experiments for determining relevant phase equilibria were initiated with two ternary systems. The first system was MgO-Al_2O_3-SiO_2 in small alumina or magnesia crucibles at 1600 °C in an air atmosphere. The second system was SiO_2-Cr_2O_3-CrO in silica crucibles at 1600 °C in $p_{O2} = 10^{-10} – 10^{-11.5}$atm. Samples were prepared from pure oxide powders, weighed, pelletized, placed in the crucibles and lifted into a hot furnace using platinum wire. After the desired equilibration time, the samples were rapidly quenched in icy water. These phase equilibria studies related to electrolyte composition were later expanded to other relevant systems using the same experimental technique, see publication list. Based on the results of the pre-experiments, the actual MOE experiments were conducted in larger alumina crucibles (Figure 3). The electrolyte was composed of SiO_2, Al_2O_3, MgO (and CaO). The sources of Fe and Cr were either pure Fe_2O_3/FeO and Cr_2O_3 powders or industrial chromite pellets from Outokumpu. Approximately 16 g of the electrolyte-pellet powder mixture was weighed in the alumina crucible, which was then lifted into a cold furnace using an alumina rod.

Once the electrolysis cell containing the sample was inside the furnace, the furnace was heated to 1550–1600 °C in an argon atmosphere. Platinum (0.5 mm diameter) and iridium (0.5 mm diameter) wires were used as the anode and cathode, respectively, in most experiments. After reaching the experimental temperature, constant voltage was applied to the cell and the resulting current was measured. Additionally, the concentration of oxygen in the off-gas was monitored. After the experiments, the samples were cast into epoxy, polished, carbon coated and analyzed with SEM-EDS. In the MOE experiments, the weight of the formed metal alloy droplet was recorded whenever possible.

RESULTS AND DISCUSSION

Thirteen MOE experiments were conducted, and the investigated parameters included the electrolyte composition, electrode material and size, cell voltage, and source of Fe and Cr (and temperature). The voltage applied to the cell was 6 V in most cases, which is high enough to reduce iron and chromium. Generally, the reduction of iron was not an issue, however, the maximum chromium content in the metal alloy formed was 10 at%. This is at least partially due to the low solubility of chromium oxide in the electrolyte, resulting in most of the chromium deporting to a solid spinel phase. From the spinel, Cr dissolution to the liquid electrolyte was very slow. Additionally, in every experiment, a significant amount of iridium (from the cathode wire) was dissolved in the alloy. Figure 4 shows the effect of CaO addition to the electrolyte on the composition of the reduced metal alloy. Even though the iridium dissolution was the most significant with the highest CaO addition, the Fe/Cr atomic ratio was also closest to industrial requirements. However, the weight of the reduced metal droplet with the highest CaO addition was only approximately 1/3 of the

Figure 4. Composition of metal alloy as a function of CaO addition in the electrolyte

weight without CaO. Therefore, the total amounts of Fe and Cr reduced were the highest without CaO addition to the electrolyte. Based on the conducted experiments, the optimal amount of chromite pellets (source of Fe and Cr) was approximately 19% of the total mass in the electrolysis cell. The highest reduction efficiencies obtained were approximately 30% for Fe and < 3% for Cr. The biggest challenges in producing ferrochrome on a laboratory scale seemed to be finding the optimal electrolyte composition (relatively high CrO_x solubility, not too aggressive towards the crucible material) and electrode materials (an inert, affordable, and carbon-free anode as well as a cathode which does not dissolve significantly in FeCr alloy).

PUBLICATIONS

Chen, M., Taskinen, P., Sukhomlinov, D., Lindberg, D., Michallik, R. M., Jokilaakso, A., (2023), Phase equilibria of the Al2O3-SiO2-CrOx system at 1600 °C and pO2 of 10-10–10-11 atm, Journal of the European Ceramic Society, 43(14): 6527–6535.

Chen, M., Sukhomlinov, D., Taskinen, P., Tiljander, M., Lindberg, D., Jokilaakso, A., (2023), Phase relations of the MgO-SiO2-CrOx system at 1600 °C in air and reducing atmospheres, Journal of the American Ceramic Society, 106(10): 6230–6243.

Chen, M., et al., Phase equilibrium study of the CaO-SiO2-CrOx system at 1600 °C in reducing atmospheres, Journal of the American Ceramic Society, accepted.

Sukhomlinov, D., et al., Phase equilibria of the MgO-SiO2-Al2O3 system, manuscript under preparation.

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TASK
1.2 PYROMETALLURGICAL ZINC LEACH RESIDUE TREATMENT
WITH NON-FOSSIL REDUCTANTS
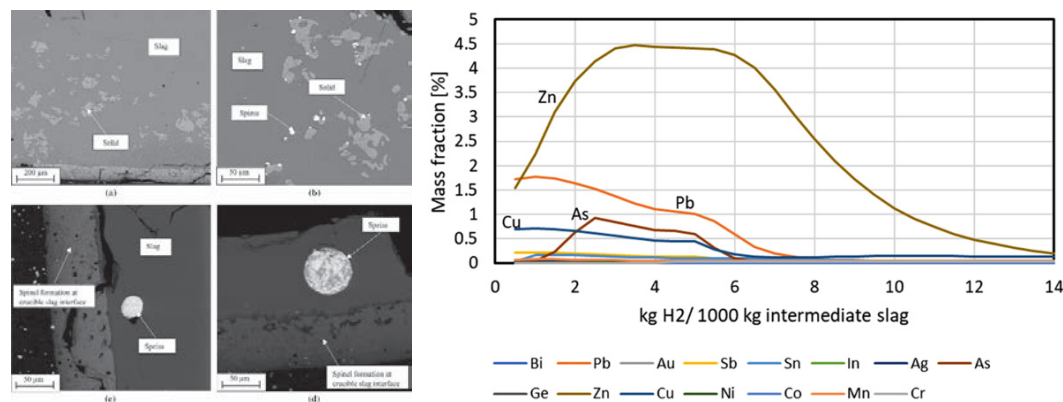
Figure 5. Micrographs of quenched iron residue post reduction at 1200 °C after (a) 5, (b) 10, (c) 15, and (d) 20 minutes (left) and the composition of slag as a function of hydrogen additions showing the elements of interest (right).

INTRODUCTION

Currently, iron-rich leach residue from zinc production is mainly landfilled. However, to reduce the amounts of residues landfilled, the residues can be treated to recover valuable metals, harmful elements can be separated, and valuable products can be produced from the residues. In this task a pyrometallurgical route to produce a clean iron-rich slag and metal alloy was studied using carbon-free and non-fossil reducing agents (hydrogen and biochar) for the leach residue treatment. One goal is for trace element values and precious metals—such as Ag (150 g/t), Au (0.5 g/t), Zn (2%) and Pb (3%)—to be recovered as saleable products in the metal industry. A high-temperature process for jarosite leach residue treatment was studied in this task. The investigation in this task focuses on the processing option of jarosite to determine what kinds of process conditions are favorable for jarosite operations when using hydrogen and other alternative reductants, and to determine the process parameters, and process chemistry. At the same time, the levels of impurities must be minimized in the resulting slag with acceptable environmental quality; for example, new Pb levels will be stricter allowing only 0.3% of lead in the bulk material and 0.03% in powder form for recycled materials. Laboratory-scale experiments and thermodynamic modeling were carried out to understand the element distribution between different phases and their reaction kinetics at high temperatures as a function of the process parameters and slag compositions with hydrogen and other alternative reductants.

MATERIALS AND METHODS

For hydrogen and biochar reduction, the iron-rich zinc leach residue was dried before pretreatment at 700 °C for 1 hour using a 65 mL/min air flow. Pretreated leach residue was mixed with silica sand to lower the melting point of the sample placed in an MgO and lifted into the furnace using a platinum wire which was hung from the top of the furnace. Oxidation was carried out using an oxygen flow for 60 minutes to remove sulfur present in the slag to mitigate the tendency of producing FeS or iron matte which traps valuable metals like Ag making it difficult to retrieve the valuable metal. After oxidation, reduction was performed for 5, 10, 15, or 20 min using H_2 and N_2 gases to form the reducing gas atmosphere at temperatures of 1200, 1250, and 1300 °C. Thermodynamic modeling of the hydrogen reduction was performed with the software Factsage to simulate the fuming of volatile metals, as well as the sequential formation of liquid metal and speiss.

RESULTS AND DISCUSSION

For the hydrogen experiments, after reduction, the results revealed that the reduction progressed far enough to form speiss droplets already after 10 minutes at all temperatures. Small speiss droplets were formed at different areas within the slag, and after some degree of coalescing, they settled towards the bottom of the crucible. The speiss consisted mainly of Pb, As, Sb, Ni, and Fe although the percentage of different species of speiss largely varied. For the biochar experiments, the results showed a trend towards enhanced slag cleaning with increasing treatment times for both biochar and coke, but systematically better results were achieved with biochar (Rämä et al. 2003). Thermodynamic modeling was also performed to simulate the reduction stage (Attah-Kyei et al. 2022, Pankka et al. 2023, Pankka 2022). Metal alloy formation was initially a lead rich-alloy as a function of added hydrogen, with subsequent formation of an arsenic-rich speiss phase. In general, the observed phases, and elemental compositions predicted from the thermodynamic modelling agree well with experimental results.

PUBLICATIONS

Attah-Kyei, D., Klemettinen, L., Michallik, R., Salminen, J., Taskinen, P., Lindberg, D., (2022), Hydrogen as carbon-free reducing agent in non-ferrous slag fuming, Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science, 53(6): 3775–3792.

Attah-Kyei, D., Klemettinen, L., Taskinen, P., Jokilaakso, A., Lindberg, D., (2021), Hydrogen as a carbon-free reducing agent in non-ferrous slag cleaning, EUROMAT 2021 (oral presentation).

Pankka, I., Taskinen, P., Salminen, J., Lindberg, D., (2023), Elemental distributions of trace elements in non-ferrous iron residue hydrogen reduction, JOM, 75(6): 2026–2033.

Rämä, M., Klemettinen, L., Rinne, M., Taskinen, P., Michallik, R., Salminen, J. Jokilaakso, A., (2023), Processing of a Zinc Leach Residue by a Non-Fossil Reductant, ACS Omega, 8(24): 21450–21463.

Pankka, I., (2022), Thermodynamic modeling of elemental distribution of non-ferrous iron residue with non-fossil reducing agents, master's thesis, Aalto University.

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TASK 1.3

NON-FERROUS METALS SLAGS REDUCTION WITH ALTERNATIVE REDUCTANTS
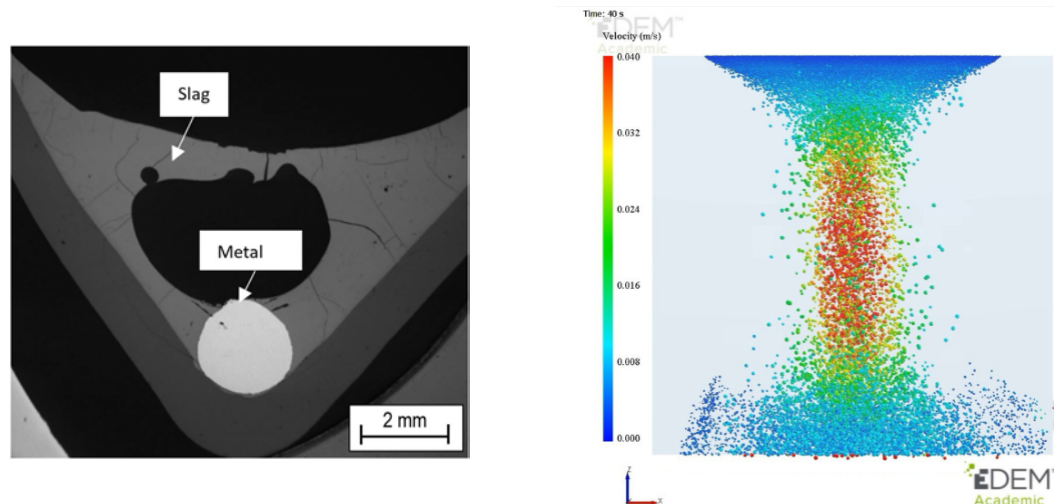

Figure 6. SEM micrographs of sample polished sections of nickel slag reduction with B600 for 15 minutes (left) and the channeling flow phenomenon colored according to droplet settling velocities (right).

INTRODUCTION

Non-ferrous metal production in pyrometallurgical processes includes significant amounts of slag which collects the unwanted impurities and gangue minerals. Valuable amounts of base metals copper, nickel, cobalt, lead, and tin, and precious metals gold, silver, platinum, etc. deport to the slag phase as chemically dissolved elements or mechanically entrained droplets which must subsequently be recovered. The commonly used current practice is to reduce coal/coke and settle to promote phase separation. In the current task, replacing fossil reductants with different biochars was studied to understand the effects of biochars produced from different sources and at different conditions. The reduction of non-ferrous slag with alternate reductants and hydrogen was investigated on a laboratory scale to examine basic phenomena, process feasibility, and kinetics. Additionally, the settling phenomenon in non-ferrous slag/matte-metal conditions was investigated in a modeling study. The effect of slag properties and different solid particles present in the slag (e.g. spinel or magnetite crystal, pieces of e-scrap) were investigated with coupled CFD-DEM modeling.

MATERIALS AND METHODS

Experimental studies were carried to examine the pyrometallurgical reduction of nickel and copper using different biochars and comparing these results with reduction using metallurgical coke. The biochars originated either from hydrolysis lignin or black pellet biomass and both were pyrolyzed at 600 and 1200 °C, meaning four different biochars were used as the reducing agents. Reduction tests were performed at temperatures between 1250 and 1400 °C for 15-, 30-, and 60-minutes reaction times under inert conditions. The CO and CO_2 concentration in

off-gas was analyzed using the FT-IR gas analyzer model in order to monitor the main reduction steps. The samples were quickly quenched, and the formed slag (molten oxides) and alloy phases were analyzed with a Scanning Electron microscope and Electron Probe X-ray Microanalysis. In the CFD-DEM work, Ansys Fluent and Altair EDEM were coupled with the plugin provided by EDEM. In this method, CFD is used to simulate a fluid medium (continuum) while DEM is used to simulate discrete particles in the medium. CFD simulations have DPM and DDPM models (discrete particle method and dense discrete particle method, respectively) but in this work, DDPM was used only by the CFD-DEM coupling plugin to obtain a two-way coupled simulation where the fluid flow affects the particles (in this work, droplets) and vice versa. DEM was used in the CFD-DEM software for simulating particle movement and interaction with geometry and other particles. Then collision frequency was used to determine the number of collisions between particles. Both CFD and DEM can be complemented with user-defined sub-models; for the matte–slag simulation, an in-house built coalescence model was used.

RESULTS AND DISCUSSION

The results showed that a metal alloy was obtained with every contacting time, which suggests that the contact between the slags and reductants was good, and the reactions proceeded rapidly. Figure 6 shows the SEM micrograph nickel slag reduction with B600 (Black pellet pyrolyzed at 600 °C). B600 appeared to be the most efficient biochar, although it has a lower carbon content compared to the other chars. The fast reaction kinetics is thought to be attributed to the relatively high content of volatiles in this biochar, leading to gas formation and thus mixing of the sample material. During the slag cleaning, biochars showed higher reactivity and faster reduction kinetics compared to coke. This, again, may be attributed to the high concentration of volatile matter present. The volatiles create pores upon moving into the gas phase, thus increasing the surface area for reaction. In addition, the CO_2 generated reacts with carbon (Boudouard reaction) resulting in more CO produced which takes part in the reduction reaction. Higher distribution coefficients between metal alloy and slag were obtained for Ni, Co, and Fe using any biochar, compared to using coke. Moreover, thermodynamic modeling was also performed using Factsage to simulate the reduction with different amounts of biochar. The results from thermodynamic modeling are in agreement with experimental results. In the CFD-DEM simulations, a channeling flow phenomenon was observed that significantly increased the settling velocity of droplets. As practical observations of settling in the flash smelting process cannot be made, an alternative method for validation of the modeling results was needed. Therefore, a matte–slag simulation was accompanied by a sphere–oil simulation, which was replicated as a physical experiment. The CFD-DEM models show factors improving settling efficiency (channeling flow, coalescence, and reaction kinetics-based changes to droplet properties [mostly change in density]) and can be used to optimize conditions for them. Based on the different CFD-DEM simulations together with the physical experiments with the sphere–oil model, the simulation method and results indicating the channeling settling flow phenomenon can be considered to be valid, and further investigations of the details of the copper matte settling behavior can be made.

PUBLICATIONS

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TASK
1.4   DIRECT REDUCTION PROCESS FOR CHROMITE
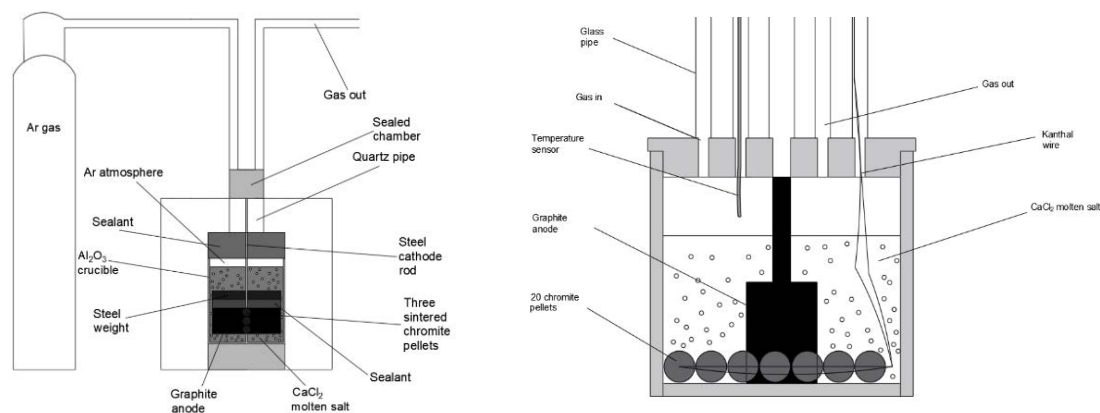
Figure 7. Examples of tested configurations with the FFC Cambridge method.

Figure 8. An example of EDS analysis (left), and voltage and current curves (right) from the third experiment.

INTRODUCTION

In the TOCANEM project, several technologies have been envisaged for CO_2-free reduction of chromite to ferrochrome. The FFC Cambridge method is a means of providing carbon-free ferrochrome by electrolysis in a molten salt electrolyte, providing the right cell configuration with an inert anode. This would open the possibility of producing ferrochrome with oxygen gas as the only emission to air. The aim of using the FFC Cambridge process in the production of ferrochrome is the replacement of carbon emission-generating coke and graphite, which are used in today's process as raw material and electrode material, respectively. The process also has benefits in reducing the energy required for reduction, as the temperature used in the FFC Cambridge process is usually around 850–950 °C.

MATERIALS AND METHODS

Chromite pellets are used as raw material for ferrochrome production with this method. The chromite is reduced in an airtight crucible in an argon atmosphere using molten salt as the electrolyte, which consists of $CaCl_2$ with or without added CaO. Graphite was employed as the anode material, while the welding rod and Kanthal wire were tested for the cathode. The experimental conditions that were used were a 2.8 V cell voltage, 900 °C temperature and 1 to 24 hours of electrolysis time. The argon flow used depends on the size of the tested cell configuration, ranging from 150 ml/min to 4000 ml/min. Before operating at the full voltage of 2.8 V, the cell was subjected to a 40-minute pre-electrolysis at 1.0 V to improve the efficiency of the electrolysis by preventing an overflow of different electrolytic reactions. After the electrolysis, the crucible is allowed to cool and the molten salt is removed by rinsing with water, and finally ethanol.

The pellets were analyzed with FESEM-EDS to identify the possibly reduced ferrochrome. An analysis with XRD will also be conducted after finding a suitable cell configuration.

RESULTS AND DISCUSSION

Thus far, ferrochrome has been produced at 2.8 V, 900 °C, and 8-hour electrolysis time with 0.8 wt-% CaO added. The FESEM-EDS analysis results, current versus time plot, and voltage versus time plot from this experiment are presented in the figure above. Various setups with 1 to 20 pellets were tested, but ferrochrome was found only with the 1-pellet setup. The corrosive nature of the cell has posed many challenges to making this method viable in use for ferrochrome production. For example, the chromite pellets were under a lot of stress and broke off the cathode rod. When the cathode material was changed to a slightly smaller diameter, the cathode wire itself was damaged. One solution to these problems has been covering the Kanthal cathode wire from contact with the electrolyte using alox piping. Ferrochrome was successfully produced at the edges of the chromite pellet in this cell configuration, and there are still ongoing experiments for optimizing the reduction of the whole pellet. A future challenge for making this process viable is the replacement of the graphite anode with an inert anode. If a solution is found, this method could produce carbon-free ferrochrome, as the only emission into the air would theoretically be oxygen gas. The protective gas, argon, also needs to be switched to a cheaper alternative. Industrial applications of this method would probably also require employing multiple cells in a large electrolysis hall.

PUBLICATIONS

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TASK
1.5

OXIDE SCALE FORMATION DURING INDUCTION HEATING

Figure 9. TG furnace setup.

INTRODUCTION

Induction heating of stainless steel slabs and strips is a potential method as an alternative to current combustion heating. Induction heating utilizes electricity and thus, the use of fossil fuels and CO_2 emissions would decrease. The method increases the heating rate of the steel and enables control of the furnace atmosphere compared to combustion heating. This affects the oxide scale formation of the stainless steels' surface and removal processes after high-temperature heating. In this task the oxide scale formation during induction heating is compared to the current natural gas combustion heating and the future H_2 fuel combustion heating methods.

MATERIALS AND METHODS

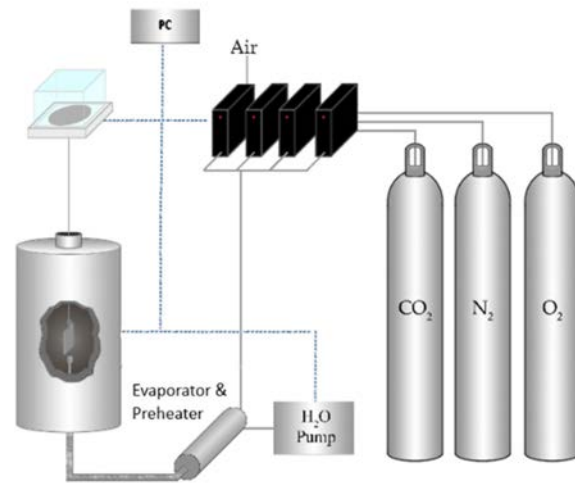For slab reheating, stainless steel grades AISI 301, AISI 304, and AISI 444 were used. The laboratory heating tests were performed in a vertical tube furnace equipped with a digital scale to produce thermogravimetry data. The simulated atmospheres for combustion heating were CH_4-air, CH_4-oxy, CH_4-oxy (lean), CH_4-H_2-oxy, and H_2-oxy. Respectively, air and N2 for induction heating. The characterization of oxide scales was performed using FESEM-EDS and GDOES. Cooling tests were performed by comparing the surface's oxide scale after four different cooling rates. For hot rolled strip annealing, grades AISI 304L and AISI 316L were used. The laboratory heating tests were performed without a digital scale, and the simulated atmospheres were CH_4-air and CH_4-oxy.
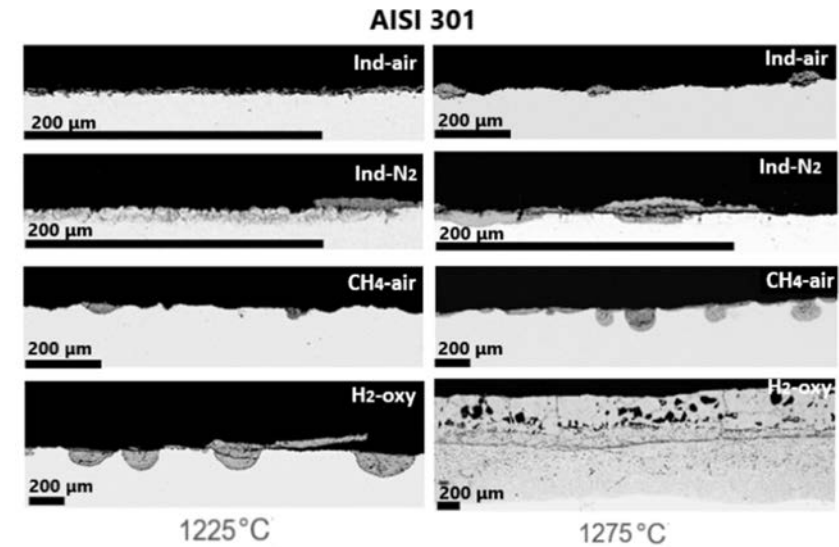
Figure 10. Effect of the heating method on oxide scale structure for AISI 301 stainless steel.

RESULTS AND DISCUSSION

Induction heating of slabs is a potential method for reducing oxide scale formation of austenitic stainless steels due to faster heating rates and better control of the furnace atmosphere compared to combustion heating. The progress of oxidation can be prevented even more by utilizing an N_2 atmosphere in the furnace. In combustion heating of AISI 304, switching the oxidizer of natural gas from air to oxyfuel increases the oxide scale formation similar amount than with a 25 °C temperature increase, whereas a lean-oxyfuel method without free oxygen in the atmosphere considerably decreases oxide scale formation. At a high target temperature, the effect of a high water vapor content from the H_2 oxyfuel method increases the oxidation of austenitic grades significantly compared to the CH_4-air method, while the change of heating method had only a minor effect on the oxidation of ferritic grade. For the annealing of hot rolled strips, high-temperature heating promotes chromium-enriched oxide layer formation in the oxide-steel interface for both austenitic steel grades, which would affect the removal of oxide scale by the pickling process.

PUBLICATIONS

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TASK
1.6

OPTIMIZING OXIDE SCALE MORPHOLOGY IN UNANNEALED HOT STRIP MANUFACTURING
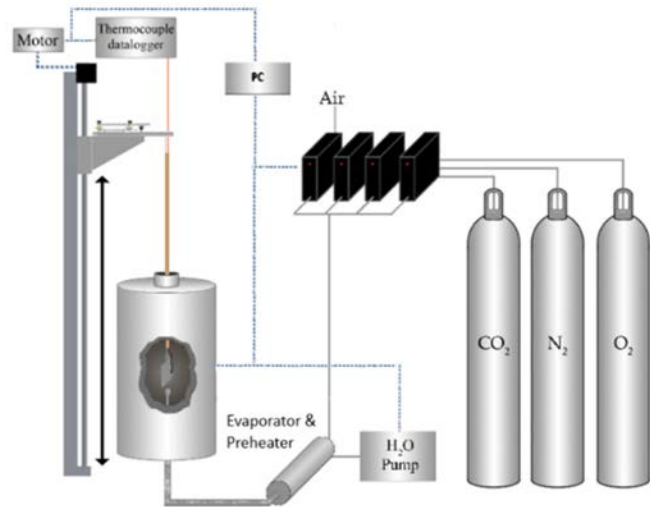
Figure 11. Annealing heating setup.

INTRODUCTION

The annealing of hot rolled stainless steel strips affects the homogeneity of the microstructure but also the pickling efficiency of the oxide scale layer. For some steel grades, omitting the annealing process before cold rolling would be possible if the microstructure of the steel is desired after hot rolling. The finished rolling and coiling temperatures in the hot-rolling process are the main factors for the development of the structure. Skipping the hot rolling process would reduce costs, time, and the CO_2 emissions formed in the heating of the furnace by fossil fuel combustion.

MATERIALS AND METHODS

Oxide scales of hot rolled stainless steel grade AISI 304L with different finish rolling temperatures and coiling temperatures were studied before and after annealing. Annealing was performed in a vertical tube laboratory furnace with vertical adjustment of the sample's position concerning hot spot of the furnace. For the annealing tests, three annealing temperatures and simulated methane-air or nitrogen atmospheres were used. Oxide scales were characterized by FESEM-EDS and pickled as presented in task 1.7.
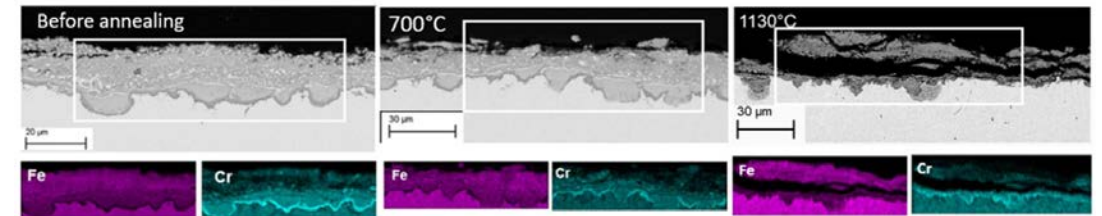
Figure 12. The effect of the annealing temperature on oxide scale for hot rolled AISI 304L.

RESULTS AND DISCUSSION

The oxide scale composition and structure of hot rolled stainless steel were observed to depend on the temperatures of the finish rolling and coiling. The oxide scales were composed mainly of Fe-oxides and Fe-Cr oxides, while the highest temperatures produced a chromium and manganese enriched layer on the oxide-steel interface. In addition, metallic phases inside the oxide scale were observed using the same temperature combination. After annealing at 700 °C, the oxide scale structure was similar to before annealing, while after annealing at 1130 °C, chromium enrichment in the oxide scale near the oxide-steel interface increased and the oxide scale layer became looser from the steel surface. Thus, annealing increased the efficiency of the oxide scale removal via the pickling process.

PUBLICATIONS

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TOCANEM
FINAL REPORT 01/2024

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TASK
1.7　　PICKLING OF UNANNEALED HOT-ROLLED STAINLESS STEEL

INTRODUCTION

Annealing stainless steel after hot-rolling improves the pickling efficiency but increases the costs as this is an energy-intensive process step. However, the mechanisms behind the pickling efficiency increase from black hot band annealing have not been studied. A deeper understanding of the mechanisms can help to customize the pickling processes so that this carbon emission-producing, and energy-consuming process step can be omitted without compromising product quality.

MATERIALS AND METHODS

Laboratory-scale pickling experiments were conducted for AISI 304L to determine the effect of hot rolling parameters and black hot band annealing on the electrolytic and mixed acid pickling efficiency. In total six combinations of finish rolling temperature (FRT) and coiling temperature (CT) were investigated. The short-term annealing was performed at 700°C, 950°C, and 1130°C in an oxidizing and inert atmosphere.
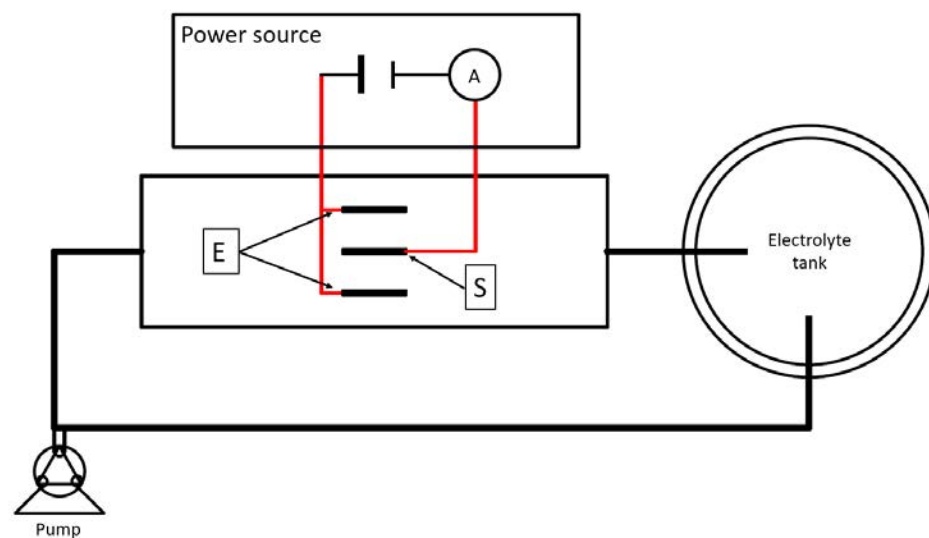
Figure 13. Laboratory-scale pickling device (Tuovinen et al. 2020).

RESULTS AND DISCUSSION

High coiling temperatures are preferred to obtain a rougher grain structure that favors the higher dissolution rate of oxide scales, thus leading to a higher pickling efficiency. However, no complete breakthrough was made and the root cause of the weakened pickling efficiency of laminar-cooled samples without pre-annealing remained unclear.

Lowering the annealing temperature and using an oxidizing atmosphere impairs the pickling results. High annealing temperatures result in easily dissolving chromium-rich oxide, while low annealing temperatures cause a layered structure of chromium and iron-rich oxide, hindering dissolution. An inert atmosphere is favorable for the formation of a porous and loose oxide layer allowing the pickling acid to enter the chromium-depleted layer. This is directly reflected in the enhanced pickling. In terms of pickleability, it is not possible to produce AISI 304L without pre-annealing with the electrolytic pickling technology and parameters currently used in the Tornio annealing and pickling lines without significantly reducing the line speed. The netlike oxide pockets and layered iron-rich oxide without a chromium-depleted layer impair the pickling efficiency of unannealed material. Additionally, the mixed acid pickling time required to dissolve silicon oxide from the oxide-metal interface increased significantly without annealing. However, omitting annealing is a better option than annealing at a reduced temperature.
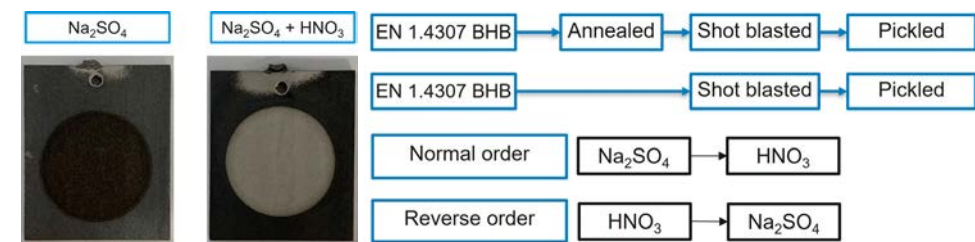
Figure 14. Picking efficiency studies for EN 1.4307 stainless steel.

The pickling efficiency of as-received material without pre-annealing can be improved via HNO_3 electrolytic pickling. HNO_3 electrolyte is remarkably more efficient for scale removal than Na_2SO_4 electrolyte and the pickling efficiency further increases as the charge density increases. However, the implementation on a production scale requires cost-effectiveness calculations, corrosion studies, and layout changes to the annealing and pickling line/lines.

PUBLICATIONS

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TASK
1.8

LIQUID-LIQUID EXTRACTION FOR REMOVAL OF HARMFUL IMPURITIES AND VALUABLE METALS FROM NON-FERROUS RESIDUES AND WASTE AND PROCESS STREAMS IN HYDROMETALLURGICAL INDUSTRY

INTRODUCTION

The performance of a chemical reactor at a given temperature and pressure depends on the chemical kinetics, residence time distribution (RTD), degree of segregation, and mixing efficiency. When the kinetics are known, it is possible to estimate the conversion for a chemical reaction in a continuous reactor if its RTD is also known. In continuous liquid–liquid extraction, the reactants spend a finite time (determined by the RTD) within a mixing zone, in which dispersion is created to enhance mass transfer. The mass transfer rates decrease quickly after coalescence and phase disengagement, which occur when the liquids are no longer under dispersive shear forces. When interfacial reactions with different rates take place simultaneously, the RTD will have an impact on selectivity. This kind of situation can be faced in hydrometallurgical liquid–liquid extraction processes, where metals are separated from multicomponent mixtures. It can be shown that the mean residence times are equal for both liquid phases when two immiscible liquids are mixed in an ideal CSTR without recycling. Furthermore, the assumption of perfect mixing leads to a theoretical conclusion that the RTDs should be equal for both phases. On the contrary, it is widely known that dispersions do not contain uniformly sized droplets, but the droplets have a size distribution. Droplets of different sizes may exhibit different hydrodynamic behavior, and thus migrate at different rates through the reactive zone. Additionally, phase continuity (aqueous or organic continuous) can significantly impact the phase disengagement rate. Nevertheless, an inert tracer is eventually collected in the bulk liquid phase after dispersion and coalescence. The time of the dispersion in the reactive zone is characterized by an RTD. Because of contingencies, the RTDs of a bench-scale mixer–settler unit were measured and compared against the RTDs of an ideal continuously stirred tank reactor (CSTR). Additionally, mathematical models were used to describe the measured RTDs.

MATERIALS AND METHODS

RTDs of an MSU0,5 mixer–settler (MEAB Metallextraktion AB, Askim, Gothenburg, Sweden) were determined by continuously measuring conductivities or pH values from the mixer and its outlet after injecting a known quantity of KCl or HCl solution. Pure water ($\kappa < 2\ \mu$S cm^{-1}) was used as the bulk aqueous solution. Both single- and two-phase measurements were performed, and Exxsol D80 dearomatized hydrocarbon solvent (ExxonMobil) was used as the bulk organic solution. Pulse injection and an off-line sample analysis by gas chromatography were attempted to measure the RTDs of the organic phase.

RESULTS AND DISCUSSION

The single-phase tracer measurements indicated that the RTDs of the mixer were close to the RTD of an ideal CSTR when the flow rate was 3–10 dm^3 h^{-1}. However, with flow rates less than 3 dm^3 h^{-1} there were significant deviations from the RTDs of an ideal CSTR. Parameters of the mathematical models suggested that the fraction of the bypassing flow increases with decreasing flow rates. The conductivity signals measured from the settler revealed minor back mixing in the settler. The spatial position of the conductivity probe significantly affected the measured residence time distributions in the settler side. When the conductivity probe was placed at 1 cm distance from the mixer outlet slit, the RTD already exhibited significant back mixing. Placing the tip of the conductivity probe 2.5 cm higher or lower compared to the outlet slit height, resulted in significantly different RTDs. The shape of the RTD was more sensitive to changes in the probe height than the horizontal distance from the slit. Placing the conductivity probe in the nearest vicinity of the outlet slit caused interference to the hydrodynamics of the mixer, and the interference is shown very clearly in the RTDs measured from the mixer. Based on these observations, it is not recommended to measure the RTDs from the vicinity of the mixer outlet slit on the settler side.

Conductivity measurements with the two-phase systems were difficult because the hydrocarbon solvent has negligible conductivity compared to the dilute KCl solution, and the small organic droplets disturb the measurement. Despite this challenge, RTDs could be determined reasonably well for the aqueous phase with total flow rates between 4.1–5.9 dm^3 h^{-1}, but the disturbances were too severe for a reliable measurement at higher flow rates. The aqueous phase RTDs measured from two-phase flows exhibited bypassing at higher than 6 dm^3 h^{-1} flows, whereas back mixing was observed at flow rates lower than 5 dm^3 h^{-1}.

PUBLICATIONS

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TOCANEM

FINAL REPORT 01/2024

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TASK
1.9 PREPARATION OF ORGANIC WASTE IN ORDER TO INCREASE C CONTENT AND REMOVE ASH

Microwave furnace

Experimental setup

Figure 15. Experimental setup for microwave treatments.

Figure 16. Pictures of briquettes and maps of the Zn content a) before and b) after microwave heating at 950 °C. A FESEM image after an experiment showing the formation of metallic iron is seen in c).

INTRODUCTION

New technologies are needed to promote the recycling of electric arc furnace (EAF) originated by-products, such as EAF dust, which is generally disposed of as waste. The reduction of zinc content in EAF dust is possible using microwave energy as a heat source with a reducing agent to accelerate the reduction rate of zinc oxide and zinc ferrite. Selective zinc removal from EAF dust has been previously studied at temperatures ranging between 750–1050 °C. However, agglomeration methods are often needed for recycling fine secondary raw materials to increase the particle size. Auger pressing briquetting technology based on the extrusion technique was applied to EAF dust to study the reduction of zinc from the finished briquettes.

MATERIALS AND METHODS

The EAF dust-based briquettes consisted of EAF dust (89%) rich in iron and zinc, anthracite (9%) which was used as a reducing agent, and a proprietary AMCOM binder (2%) consisting of harmless raw materials which were both organic and inorganic. The total Fe content in the finished briquette was 32.5% and the ZnO content was 23.4%. The diameter of the briquettes was 25 mm and the lengths varied between 60–120 mm due to the briquetting method used. For the experiments, the briquettes were sawn into 10 mm long pieces. The experiments were performed using a laboratory-scale multi-mode microwave furnace operating at 2.45 GHz with a maximum output power intensity of 4 kW. Air and N_2 atmospheres were tested at controlled temperatures of 950 °C and 1050 °C. The temperatures were measured using a thermocouple. The processing time was 20 min and the N_2 flow rate was 0.2 l/min. The evaporated zinc was pumped into a collector.

RESULTS AND DISCUSSION

Iron oxides are good microwave absorbers, and a sufficient content in the EAF dust briquette resulted in rapid and efficient heating throughout the sample. The temperature of 1000 °C was reached in less than 5 minutes. The temperature was kept at 950 °C until the end of the experiment. A significant amount of ZnO was captured in the collector. Based on the FESEM-EDS analysis, the ZnO content decreased to less than 3% in the residue of the microwave-treated briquette sample. Iron oxide in the briquette was reduced to metallic iron. Based on the laboratory-scale test results, zinc removal was rapid and selective, and it was affected by the reaction atmosphere and the briquette size. Carrying out similar additional experiments on whole briquettes and large sample masses would give information on the suitability of the method for industrial use.

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TASK 1.10

SUSTAINABILITY ASSESSMENT FOR INDUCTION HEATING

INTRODUCTION

This task aimed to evaluate the sustainability of induction heating at a general level. In the assessment, induction heating was compared with conventional furnace heating. Induction heating is a heating method that transfers contactless power to the workpiece, potentially with very high efficiency and speed. The heater consists of a coil that generates a varying magnetic field that induces currents in a workpiece. Resistive losses are the main heat generation mechanism, but for ferromagnetic materials, a minor part is also generated from magnetic hysteresis. Conventional heating is the dominant method, due to technical limitations in existing induction heating technology. Conventional heating is often performed in ovens or furnaces, powered by electricity or combustion of fossil fuels. Ovens and furnaces employ convection and radiation—either individually or in combination—to achieve the desired heating results.

MATERIALS AND METHODS

A sustainability assessment was conducted using Multicriteria Analysis (MCA) with an Analytical Hierarchy Process (AHP). Multicriteria Analysis (MCA) is a decision-making tool developed for complex multi-criteria problems that include qualitative and/or quantitative aspects of the problem in the decision-making process (Department for Communities and Local Government 2009). MCA provides a transparent sustainability assessment for an assessment target considering economic, environmental, and social sustainability issues. As its name indicates, MCA utilizes several criteria in the assessment. AHP represents a semi-objective approach for quantifying the weights and preferences

Economic criteria	Ranking	Weight%
Investment costs	1	21.2
Operational costs	1	21.2
Commercialization potential	4	4.4
Amount of references	5	3.6
Productivity	1	21.2
Capacity	3	7.8
Flexibility	3	7.8
Quality	2	12.8

Environmental criteria	Ranking	Weight%
CO_2 emissions	1	30
Other gaseous emissions	3	16.7
Dust emissions	3	16.7
Noise	3	16.7

Social criteria	Ranking	Weight%
Safety issues	1	31.3
Health issues	1	31.3
Ease of operation	3	11.9
Acceptability	3	11.9
Innovativeness	4	6.8
Imago issues	4	6.8

Table 1. Criteria and weights used in the assessment.

of decision criteria. Both systems (induction heating and conventional furnace heating) were screened against 18 relevant criteria (Table 1). There were 8 economic criteria, 4 environmental criteria, and 6 social criteria. All criteria were ranked and weighted according to the order of importance. For each criterion a numerical value between 1–7 was given (7 being the best and 1 being the worst). The reference case (the conventional heating) got a numerical value of 4 for each criterion. For induction heating numerical values were given with respect to the reference. The total score was the sum of products of numerical value and the weight.

RESULTS AND DISCUSSION

The total sustainability (all dimensions of sustainability are considered in the assessment) of the cases is presented in Figure 17. The higher the score the better in terms of sustainability.
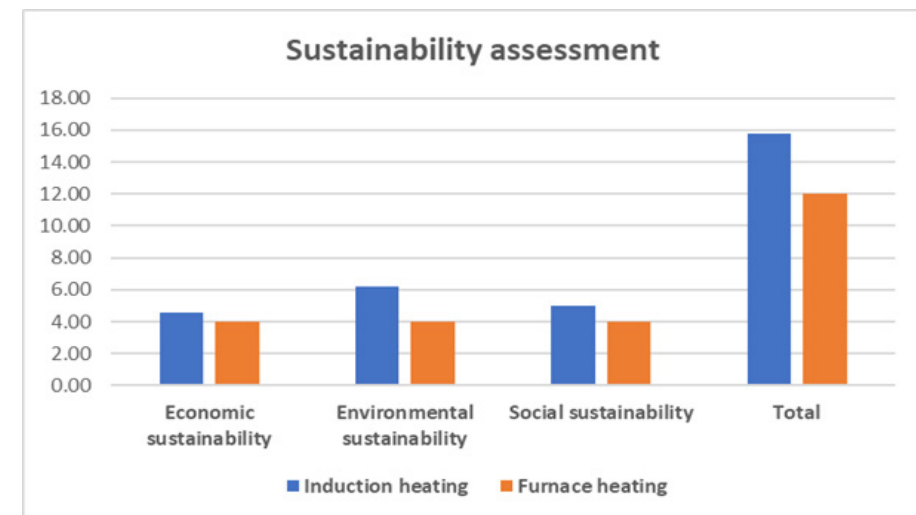
Figure 17. Results of sustainability assessment.

Economically, induction heating is slightly better than furnace heating. Environmentally, induction heating is superior to furnace heating. In the social assessment, the induction case is better in terms of sustainability as well. When all dimensions (economic, environmental, and social ones) are equally taken into consideration in the assessment, induction heating shows the most sustainable performance by a clear margin. It is 31.3% better than conventional furnace heating.

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TASK 1.11
STAINLESS STEEL STRIP EMISSIVITY CHANGE DURING ANNEALING OXIDE GROWTH

Figure 18. The emissivity measurement system.

INTRODUCTION

The surface emissivity of stainless steel is a monitoring parameter to control strip temperatures in the annealing furnace. The quality of temperature control is an important factor in producing the desired grain size of the steel strip, and thus, its formability, strength, and hardness. During annealing, an oxide scale is formed on the surface of the strip which affects the spectral emissivity of the steel and leads to inaccuracy in temperature measurements. The oxide scale formation is influenced by the temperature, annealing time, atmosphere, and chemical composition of the steel.

MATERIALS AND METHODS

The calibration of the emissivity device was done using black paint with a well-known emissivity value. The emissivity of cold and hot rolled strip materials was measured via a coupled system with a sample holder and 2-color pyrometer. The measurements were performed in the isothermal furnace by keeping the sample at a high temperature. The cold rolled materials were austenitic AISI 304 and AISI 316L and ferritic AISI 441, and the hot

rolled materials were austenitic AISI 304L, ferritic AISI 441, and duplex AISI 318LN. Comparative tests with oxide scale formation and emissivity were performed for AISI 304 and AISI 316L using simulated annealing heating 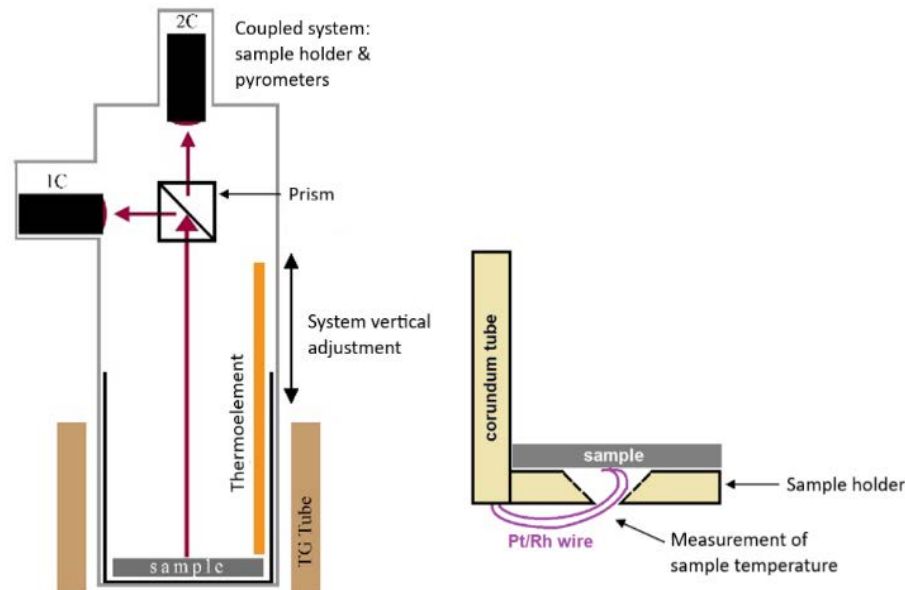curves by adjusting the sample's position in relation to the hot spot of the furnace. A model for strip emissivity change during annealing as a function of oxide scale layer thickness was created based on AISI 316L measurements.
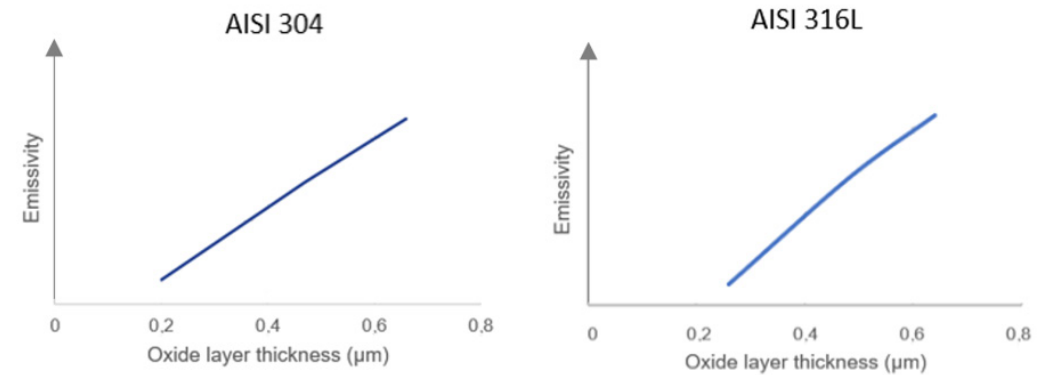
Figure 19. Emissivity compared to oxide layer thickness at 1100 °C.

RESULTS AND DISCUSSION

Calibration of the emissivity device was successful with the configuration of a 2C pyrometer without a prism. Differences between the development of the emissivity value were observed using different temperatures, atmosphere, and steel grades. Using an N_2 atmosphere, emissivity values were mainly lower than values in an oxidizing atmosphere, which correlated to higher oxidation of the surface in the oxidizing atmosphere. The created mathematical model was able to predict oxide scale growth during annealing well for AISI 316L at lower annealing temperatures and to predict emissivity reasonably well. However, more data is needed to develop this data-based model.

PUBLICATIONS

Lassila, E., (2023), Effect of scale formation on the emissivity of austenitic stainless steels in an annealing furnace, master's thesis, University of Oulu.

TOCANEM
FINAL REPORT 01/2024

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TASK
1.12   COLD ROLLING WITHOUT HOT STRIP ANNEALING, OPTIMIZED
MICROSTRUCTURE AFTER HOT ROLLING

INTRODUCTION

The motivation for this task is to remove the hot strip annealing step before cold rolling to optimize the complete strip rolling process. The microstructural state of steel needs to be well-known to make such a drastic change to the process. The main point of interest is the metallurgical strain left on the strip after hot strip rolling. Static recrystallization (SRX) plays a key role here, as the newly formed grains effectively reset the metallurgical strain back to zero. In this task, SRX behavior is studied experimentally, with the eventual goal of creating a reliable SRX model that can be used to estimate the effect of hot rolling process parameters on the microstructural state of the hot strip.

MATERIALS AND METHODS

Ferritic stainless steels 4509 and 4512 were chosen for the task. All results presented here are with grade 4509. A Gleeble 3800 thermo-mechanical simulator, shown in Figure 20a), was used to conduct experiments for the recrystallization with the double-hit test method. In the double-hit test, test samples are heated, then compressed, then held for various inter-hit times, and then compressed again, as in Figure 20.b). The idea is that with an increasing inter-hit time, the test piece has more time to anneal, which shows a decline in the material deformation resistance during the second hit. Deformation resistance differences can be used to calculate recrystallization progression over time.
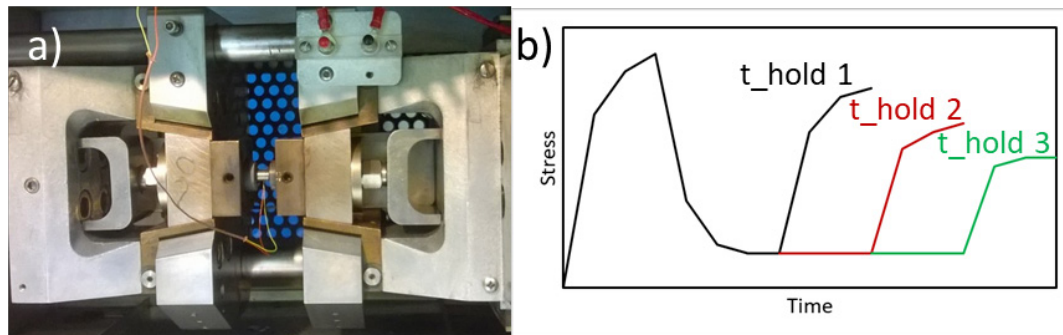
Figure 20. a) Gleeble 3800 test setup: compression jaws with the test piece in the middle. b) Double-hit test schematic illustration.

The double-hit test results require some processing to be comparable. First, the stress-strain data needs to be normalized, and then the first and second hits need to be fitted separately using the Hollomon equation. Figure 21 shows some example holding times for case: strain-rate 0.1 /s l temperature 950 °C l strain 0.2. The fitted data for various inter-hit times can be compared to see the softening that occurs during holding. The softening is presumably caused by recrystallization, so the stress differences can be used to estimate

recrystallization progression with the lever rule. KJMA equation is fitted to the experimental recrystallization progression.
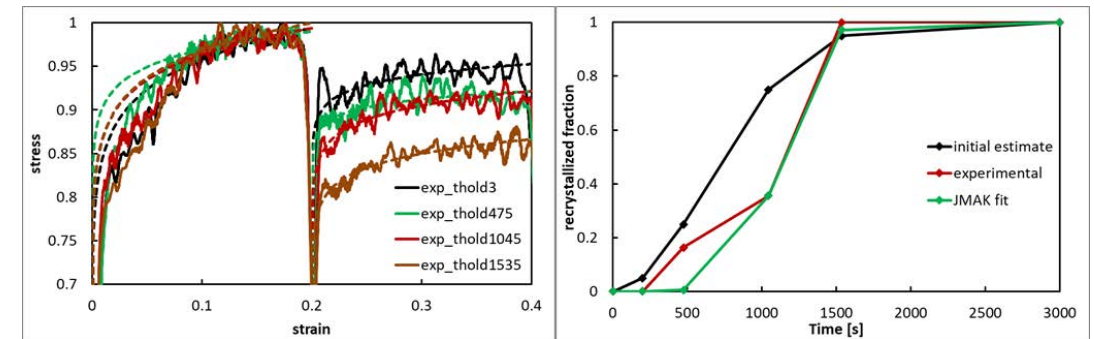
Figure 21. For case SR0.1 l T950 l S0.2 a) holding times with Hollomon equation fittings for double-hit tests and b) calculated SRX values and JMAK fitting result.

RESULTS AND DISCUSSION

Double-hit tests were performed with various temperatures, strains, and strain rates. Figure 22a) shows SRX values for various temperatures and Fig 22b) shows the strain rates. Experimental data are marked as crosses and solid lines are KJMA-fitted data.
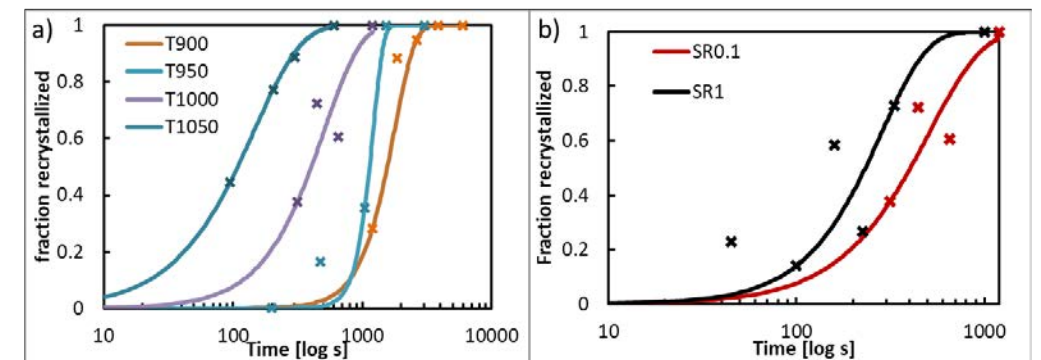
Figure 22. Fraction recrystallized with a) S0.2 l SR0.1 and various temperatures b) S0.2 l T1000 °C and various strain rates.

As a summary, the results obtained are quite promising and they can be used to conduct preliminary predictions of recrystallization behavior for the studied steel. A complete RX model can be developed with continued future work, and it can be used to estimate the effect of hot rolling process parameters on the material metallurgical behavior. Some unforeseen issues were encountered with the test methods that can be prevented in future studies. They are extensively reported in the full final report for future reference, where more recrystallization results and details regarding the methods and fitting techniques are also included. Future study possibilities are also discussed in the full final report.

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TASK
1.13   METALS RECOVERY FROM WASTE PROCESSING SLUDGES

INTRODUCTION

In waste processing, significant amounts of metal-containing side-streams are produced. In this task, the bottom ashes were treated in pyrometallurgical unit processes at high temperatures with bio-based reductants to separate and recover valuable as well as hazardous metals. The reduction of the ashes with alternate reductants was investigated on a laboratory scale to examine basic phenomena and process feasibility. The recovery of metals to the metal alloy phase and distribution between the alloy, slag, and gas phases was also studied with thermodynamic modeling. Special focus was placed on studying the feasibility of recovering rare earth elements (REEs) from waste incineration bottom ash, as well as alternative strategies by using phosphate additives to concentrate the REEs into different phases. This task involved close cooperation with tasks 1.3 and 3.15.

MATERIALS AND METHODS

A: The feasibility of metal value recovery from incinerator bottom ash (IBA) supplied by Fortum was investigated pyrometallurgically. The original 0–1 mm starting material was sieved in narrow-size fractions and characterized by ICP-MS and ICP-OES. Small samples (half a gram) placed in alumina crucibles were heat-treated for 1 hour in a protective atmosphere of Ar at 1400 °C with 1 wt% addition of <C> and without it. After the heat treatment, the samples were quenched in an ice-water mixture, and polished sections were prepared with a wet metallographic method for subsequent SEM-EDS examination.
B: The distribution of REEs between two oxide liquids was investigated as a function of temperature (1100 to 1300 °C) and oxygen partial pressure (10^{-11} to 10^{-7} atm). The selected composition of the samples was close to the industrial IBA, comprised of SiO_2, Fe_2O_3, CaO, Al_2O_3, MgO, and K_2O. In addition to that 15 wt% P_2O_5 was added. REE oxides (CeO_2, Pr_6O_{11}, Nd_2O_3, Yb_2O_3) were present in the system with 0.5 wt% each. Small samples (quarter a gram) placed on a Pt substrate were equilibrated with subsequent quenching and phase composition examination from polished sections with SEM-EDS and EPMA.

RESULTS AND DISCUSSION

The feasibility study on the metal value recovery from IBA showed that at 1400 °C a distinct metal and/or matte phase comprised of mainly Cu, Ni, Fe (and S) was formed within 1 hour even without the addition of <C>. Meanwhile, 1 wt% of <C> added to the IBA increased the mass fraction of the metal phase formed due to a substantial reduction of iron and even cobalt. This approach has great potential for recovering the listed non-ferrous metals from IBA, however, the REEs are deported to the oxide liquid phase in these conditions.
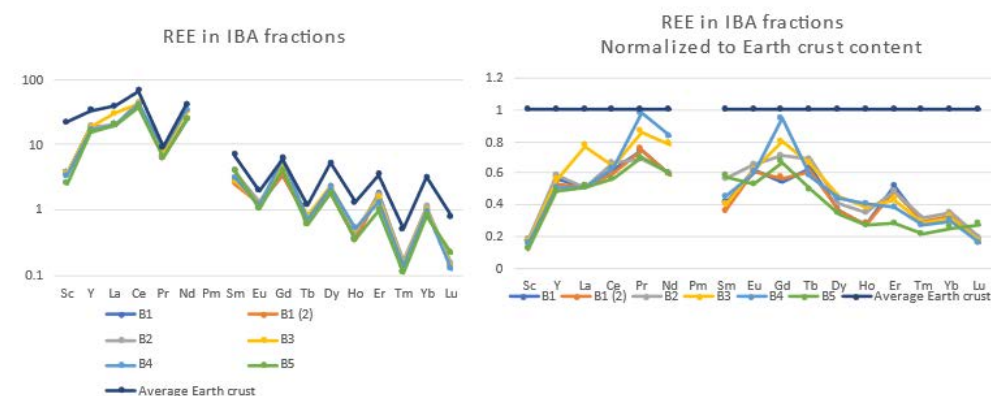
Figure 23. Rare earth elements in studied incineration bottom ash fractions: absolute values and normalized to earth crust levels.

An equilibrium study on synthetic samples simulating the composition of IBA with the addition of P_2O_5 revealed the prevailing distribution of REEs in the phosphate liquid phase and solid calcium phosphate. The distribution coefficients of Nd, Pr, Ce, and Yb between phosphate and silicate liquids are 3 to 5, depending on temperature on oxygen partial pressure. Meanwhile, their distribution coefficients between solid calcium phosphate and silicate liquid are from 10 to 42. These phase equilibrium data indicate a potential for REEs recovery from IBA pyrometallurgically. The separation of the REE-enriched phases can be performed by subsequent comminution of quenched material and beneficiation methods.

PUBLICATIONS

Sukhomlinov, D., Lindberg, D., (2023), Distribution of REE oxides between phosphate and silicate liquids, manuscript under preparation.

TASK 1.14	ALTERNATIVE PROCESS PRACTICES AND TECHNOLOGIES FOR STAINLESS STEELMAKING IN EAF

INTRODUCTION

Mathematical process models can be used in process control applications and to study the process without expensive and time-consuming process trials. For electric arc furnaces (EAFs) such models have previously been developed, however, a clear gap still exists within our field in the form of DRI-base EAF-process modeling. In the present work, the aim is to develop a complete EAF-process model, which can be used to model both the traditional processing routes and DRI-based processing routes. Previously developed submodules are being further developed and coupled with each other to form the complete EAF-process model. Significant progress is being made, despite the lack of good validation data.

MATERIALS AND METHODS

The EAF model was built of independent modules, which have been improved to consider new phenomena and to use the information produced by other modules for more accurate overall results. The work has so far focused on the scrap melting and heat transfer module, thermochemistry module, and equilibrium calculation module. The scrap melting and heat transfer module is used as the base for the rest of the model. This module is used to model heat transfer and melting in the furnace, using the explicit Runge-Kutta method. The thermochemistry module is used to calculate the thermochemical properties of materials and reactions. The module's thermochemistry database has been updated from a hardcoded format into a csv file reading format. This makes changes and additions to the database possible even if the code is not easily accessible, such as when it is compiled into an exec file. Additionally, the new structure of the database makes reading it much more efficient, improving computation times. The equilibrium calculation module uses the Gibbs free energy minimization method to find the equilibrium composition of a given starting composition. The module fetches the required thermochemical information from the previously described thermochemistry module. The module is used to model reactions occurring in the gas phase and in the burner, assuming that they are always in a state of equilibrium. Applying reaction kinetics to the model is planned for later stages. The gas phase is significantly affected by the gas flowing into and out of the furnace. To consider this, pressure-driven gas flow modeling, using Bernoulli's principle, is being introduced to the model. Using this module, we can introduce regions with different pressures, and then model the gas flow between these regions, based on the pressure differences, and model the dynamic pressure evolution of the furnace gas phase. This will allow us to model the effects of the furnace hood and leakage air on the gas phase composition and temperature. Some initial successes have been achieved in implementing this module with the rest of the EAF model, however, significant improvements are still needed, especially in the computational times.
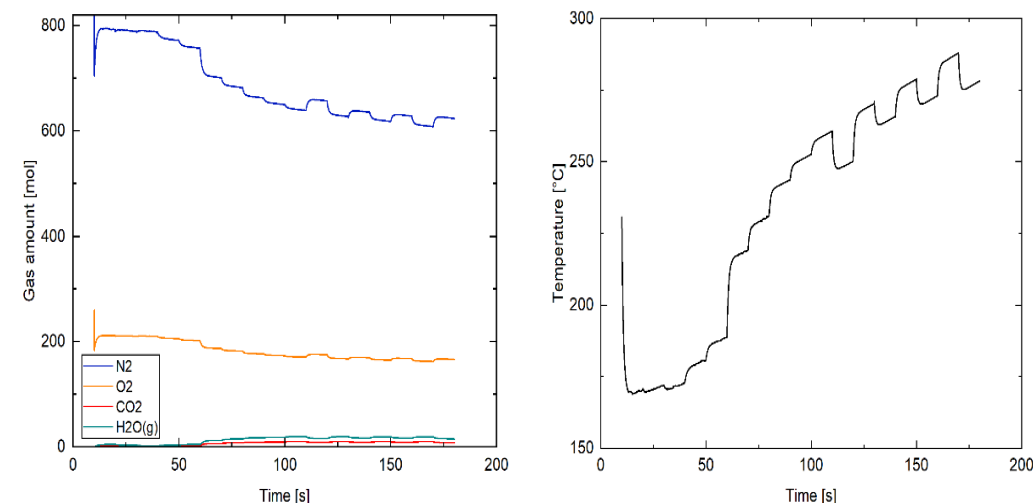
Figure 24. Simulated EAF gas phase composition and temperature evolution.

RESULTS AND DISCUSSION

The new implementation of the thermochemical database and coupling of the thermochemistry module have significantly improved the computation times of the model. Previously the scrap melting and heat transfer model could be expected to calculate 30 minutes of process in 402 s, but with these new changes, the computation time has been reduced to 201 s. Implementing the equilibrium calculation module and pressure-driven gas flow in the model has significantly improved the description of the gas phase. In Figure 24, a dynamically evolving gas phase composition and temperature are presented. It can be seen that the gas phase temperature quickly increases as the burners are turned on, indicated by the increase in CO_2 and water vapor. The step-like structure of the graphs is caused by the data used to simulate the burners, which use a static fuel feed rate for 10 seconds at a time. While these results look quite simple; the methods used to calculate them could be used to simulate more complex gas phase compositions and reactions. For instance, the current model does not consider lancing or metal-slag reactions in gas formation, but once models describing these phenomena have been developed, coupling them to the rest of the model should be quite straight forward, allowing us to model more complex scenarios. However, significant improvements need to be made to the computation times of the model. The current implementation of the pressure-driven gas flow calculation requires setting the error tolerances to be so small that a simple 15-minute timespan takes up to 36 hours of computation time on a laptop with an 11th Gen Intel® Core™ i5-1135G7 @ 2.40 GHz processor. Currently, the authors are looking for ways to implement the gas flow calculations in ways that improve the calculation times, while keeping the calculation error at reasonable levels. After these improvements have been made, the aim is to start working on the metal-slag reactions module and its coupling to the rest of the model.

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Justin Salminen, Boliden Kokkola Oy

WP 2

SMART CARBON USAGE

KEY RESULTS AND IMPACTS
Summary of the key results and impacts based on industrial partners' point of view

SUMMARY AND HIGHLIGHTS
Summary of the project's motivation and achievements based on industrial partners' point of view

outokumpu ◯

Outokumpu's goal was to develop biochar-based reductant with desired properties and suitability for chromite reduction in the submerged arc furnace process as a part of ferrochrome and stainless steel production. Additionally, it clarifies technical, environmental, and economic aspects caused by replacing metallurgical coke with bio-based reductant by conducting a life cycle assessment.

NEW BOLIDEN

Boliden Harjavalta
The research project under the work package "Smart Carbon Usage" was undertaken with the primary objectives of developing a conceptual framework for the industrial-scale testing of substitutes for metallurgical coke and advancing our understanding of slag cleaning furnace operations where coke is traditionally utilized. The project aimed to address this issue by exploring alternative reductants, with a focus on minimizing environmental impact and optimizing operational efficiency.

The project involved close collaboration with the University of Oulu and Aalto University, allowing us to tap into cutting-edge research on alternative reductants. Extensive laboratory experiments were conducted, involving gaseous reductants and biobased coke. A small batch of biobased coke was successfully tested in an industrial trial. This test confirmed its operational viability and yielded valuable guidelines for future experiments. The project also screened alternative reductants for use in the copper anode fire refining process, setting the stage for a concept study. This work is slated to continue beyond the TOCANEM project.

Boliden Kokkola
Boliden Kokkola participated actively in TOCANEM WP2 – Smart carbon usage. Justin Salminen from Boliden was the chairman of the WP2, the finest WP in the TOCANEM consortium. The following tasks were the main focus:
Task 2.1 Recycling of process residues in base metal production
• Task 2.2 Reductive treatment of slag from non-ferrous metals production with
  kraft lignin biochar
• Task 2.3 Value-added uses for the pyrolysis gases from biochar production
• Task 2.4 Sustainability assessment for biochar usage
Large biomass pyrolysis experimental work was carried out in WP2 at the University of Oulu. The smelting and fuming characteristics using biochar were studied with test furnaces at Aalto University (WP1). The thermal and mechanical properties of biochar were studied and compared to standard fossil coals. Thermochemical models were further applied to investigate the reducing conditions and fuming properties of metals when using fossil carbon, biochar, methane, and hydrogen as reducing agents.

outokumpu ◯

The technical suitability of biocoke for use as a reductant of chromite in a submerged arc furnace process was successfully proven in industrial scale ferrochrome production by Outokumpu Stainless. The current established technical capability can be compared to a **~90 kiloton reduction** in total annual direct CO_2 emissions related to the usage of metallurgical coke (vs. 2022 base level). Laboratory-scale production of bio-briquettes proceeded to pilot scale and the recipe was further tailored as a result of extensive research work to fit Outokumpu's production processes. In late 2023 Outokumpu announced to invest in a pelletizing plant to produce biocoke at its site in Tornio, Finland. The investment will be approximately EUR 30 million and the aim is to start production in mid-2025.

NEW BOLIDEN

Boliden Harjavalta
Alternatives for replacing fossil coke in nickel slag cleaning were identified and one was tested in an industrial process. The knowledge and insights gained from this work package will guide Boliden Harjavalta's efforts to transition towards more sustainable and environmentally friendly metallurgical practices.

Boliden Kokkola
Several diploma thesis works were carried out in these tasks as well as doctoral thesis works. Several peer-reviewed articles were published. The collaboration with the universities was very good and we held regular research meetings within these tasks. The experimental and modeling works showed promising results and gave new knowledge of the usage of alternative reducing agents. On an industrial scale, there is a definite potential for using responsibly sourced biomass-based carbon as a reducing agent in the non-ferrous industry.

Contact persons
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TASK
2.1   RECYCLING OF PROCESS RESIDUES IN BASE METAL PRODUCTION

INTRODUCTION

Base metal production streams, side streams, and residues contain a wide variety of valuable target metals but also trace metals and impurities. This task aimed at advanced impurity management in base metal production. The recovery of impurities is a necessity to prevent accumulation, and efficient impurity control also plays a crucial part in operating energy and material efficient production of the main metals. This task had two main aims: firstly, to improve impurity management based on an experimental investigation into the behavior of trace elements in base metal processes, and secondly to carry out process modeling and simulations to evaluate mass- and energy balances, and to perform a Life Cycle Analysis (LCA).

MATERIALS AND METHODS

In their work, Teimouri et al. (2022) proposed a new hydrometallurgical method for Zn, In, and Ga extraction, along with Fe as a common impurity, from electric arc furnace dust (EAFD), using ionic liquids. EAFD is a metal-containing waste fraction generated in significant amounts during steelmaking from scrap in an electric arc furnace. Currently, this side stream is heavily underutilized. Two ionic liquids, [Bmim+HSO$_4$-] and [Bmim+Cl-], were studied in conjunction with three oxidants: $Fe_2(SO_4)_3$, $KMnO_4$, and H_2O_2. The composition of the raw material was determined with AAS, ICP-OES, and a sulfur/carbon analyzer. The mineralogy was characterized by XRD and the particle size distribution was measured with a particle size distribution analyzer. SEM was used to capture the morphology of the EAFD. Rinne et al. (2022) evaluated and compared the technical and environmental aspects of treating EAFD using a novel process, including alkaline roasting and organic acid leaching, to the globally applied conventional Waelz process. Contribution analysis and sensitivity analysis were used as the primary methods for interpreting the results. The processes were modeled with HSC Sim 9 to obtain energy and mass balances. These values were then used as a basis for the life cycle inventories. A secondary goal of the study was to reveal issues in the novel process and to help prioritize them.

RESULTS AND DISCUSSION

The results by Teimouri et al. (2022) indicated that the best combination out of the tested ionic liquid–oxidant combinations was [Bmim+HSO$_4$-] with [$Fe_2(SO_4)_3$]. An experimental series demonstrated that the combination of 30% v/v [Bmim+HSO4-], 1 g of [$Fe_2(SO_4)_3$], S/L ratio = 1/20, a 240 min leaching time, and a temperature of 85 °C was optimal, resulting in maximum extractions of 92.7% Zn, 97.4% In, and 17.03% Ga. In addition, 80.2% of the impurity metal Fe was dissolved. The dissolution kinetics of these four elements over a temperature range of 55–85°C was found to be diffusion-controlled. The remaining phases present in the leached residue were low amounts of ZnO, Fe_3O_4, and $ZnFe_2O_4$ with traces of $Ca(OH)_2$ and MnO_2 and additional sharp peaks indicative of $PbSO_4$ and $CaSO_4$ appeared within the XRD pattern. The results demonstrate that [Bmim+HSO$_4$-] is able to extract the target metals due to its acidic properties. Rinne et al. (2022) determined that the
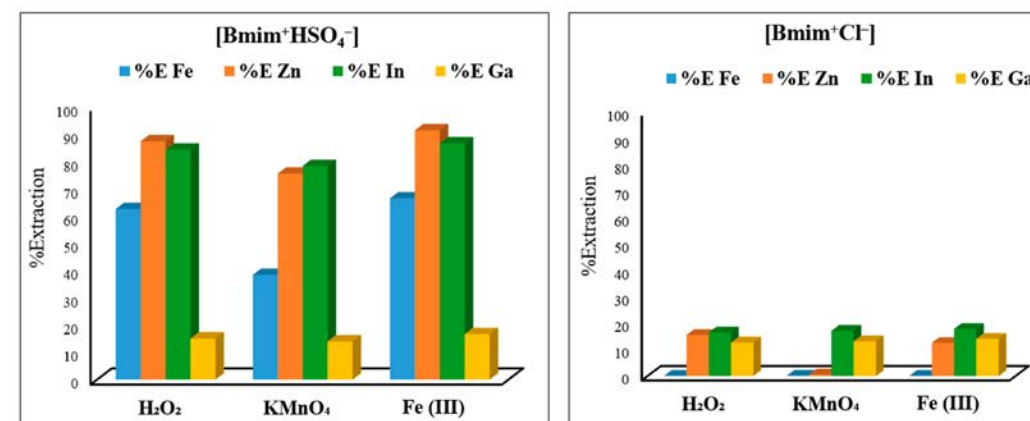

Figure 25. Extraction percentages achieved by ionic liquids and oxidizers. (Teimouri et al. 2022).

global warming potential (GWP) of the roasting–organic acid EAFD leaching process and the Waelz processes were 7.48 and 4.71 kg CO_2-eq with 33% Zn content in the feed material. With decreasing Zn content, the novel process became environmentally more competitive, and with 12% Zn, the corresponding GWP values were 6.31 and 9.26 kg CO_2-eq. Co-product recovery reduced the net environmental impacts from the processing of the dust, which brought some benefits to the new process. The Waelz process was observed to be energy intensive; however, the high consumption of leaching and roasting chemicals was the issue in the novel process. The excess caustic soda in the roasting step was observed to be a significant factor in the overconsumption of the organic acid in the leaching stage, and therefore, optimization of the roasting step was deemed crucial. In addition to these deliverables, a literature review on arsenic management in zinc and copper production has been compiled (Palomäki 2022). The motivation behind and future alternatives of arsenic, antimony, and bismuth removal processes was discussed. State-of-the-art impurity management techniques that are in use in the industry were reviewed and detailed. Experimental work on arsenic recovery electrochemically has been carried out, and a publication will be written on this topic, but as of writing this report, the experiments are still ongoing.

PUBLICATIONS

Rinne, M., Halli, P., Aromaa, J., Lundström, M., (2022), Alternative Method for Treating Electric Arc Furnace Dust: Simulation and Life Cycle Assessment, Journal of Sustainable Metallurgy, 8(2): 913–926. https://doi.org/10.1007/s40831-022-00531-x

Teimouri, S., Potgieter, J. H., Lundström, M., Billing, C., Wilson, B. P. (2022), A New Hydrometallurgical Process for Metal Extraction from Electric Arc Furnace Dust Using Ionic Liquids, Materials, 15(23), 8648. https://doi.org/10.3390/ma15238648

Palomäki, H., (2022), Arsenic, Antimony and Bismuth Management in Base Metal Production Processes: Literature Review on the State-of-the-Art, literature review for TOCANEM, 39 p.

Rinne M., Environmental impact assessment of electric arc furnace dust recycling by a novel method, 70th Zinc Expert Meeting (oral presenation), submitted.

Teimouri S., Potgieter J. H., Billing C., Conradie J., Lundström M., Wilson B. P., Indium and Gallium Extraction Using Ionic Liquids: Experimental and Theoretical Study, EMC2023, submitted.

TASK 2.2	REDUCTIVE TREATMENT OF SLAG FROM NON-FERROUS METALS PRODUCTION WITH KRAFT-LIGNIN BIOCHAR

INTRODUCTION

Kraft-lignin is a side product of the Kraft-pulping process in the pulp and paper industry. Currently, Kraft-lignin is utilized in heat and power generation. Kraft-lignin contains a considerable amount of sulfur due to the sulfate used in the pulping process. Nevertheless, Kraft-lignin could be utilized in the reduction of side streams in the non-ferrous metal production industry because the reduction process, for example, the electric furnace (EF) process, is not too sensitive to sulfur and the reducible materials also contain sulfur. Currently, the majority of the Kraft-lignin side streams worldwide end up being fuel in heat and power generation. By utilizing Kraft-lignin in biocarbon production and further as a reductant, additional value would be gained for Kraft-lignin in comparison to its contemporary use as a fuel.

Maybe the most important question concerning the substitution of fossil-based reductants with bio-based reductants is the high reactivity of the bio-based reductants. Additionally, the mechanical strength and apparent density of the bio-based carbon products are generally lower than those of fossil-based reductants. In this experimental work the main emphasis is on the kinetic analysis of different Kraft-lignin biocarbon gasification in a wide temperature range (1000–1350 °C), but also the mechanical strength and density of the produced biocarbon are investigated.

MATERIALS AND METHODS

The raw material Kraft-lignin was provided by UPM, and its commercial product name is "BioPiva 300". The reference material, metallurgical nut coke, was provided by Boliden Harjavalta. Nut coke was selected as a reference material because it is commonly used as a reductant in metallurgical processes and the main properties (reactivity, density and mechanical strength) of nut coke are quite high.

The choice of treatment methods of Kraft-lignin (high pyrolysis temperature and agglomeration) was made to improve the main properties that are required from reductants. The agglomeration was carried out before pyrolysis to promote carbon bridging and thus a denser and more organized structure. The pyrolysis temperatures of the briquetted Kraft-lignin were 600, 900 and 1200 °C for promoting higher carbon content and low volatile content. The pyrolysis method was slow pyrolysis in which the heating rate was 5 °C/min and the holding time 4 hours in the final temperature.

The mechanical strength (compression strength) of the biocarbon and reference material samples was measured with a Gleeble 3800 thermomechanical simulator, and the apparent density of the samples was determined by measuring the volume and the mass of the individual briquette samples.

The reaction kinetics of the gasification reaction of different Kraft-lignin biocarbons and reference nut coke was determined by fitting 12 different reaction models with the actual conversion data from the gasification experiments. The gasification experiments were

performed with a thermogravimetric analyzer (TGA, Netzsch STA 449 F3 Jupiter) at eight different temperatures in the range of 1000–1350 °C. The volumetric percentages of the gas components in the gasifying gas were: 25 vol.% of CO, 25 vol.% of CO_2, and 50 vol.% of N_2.
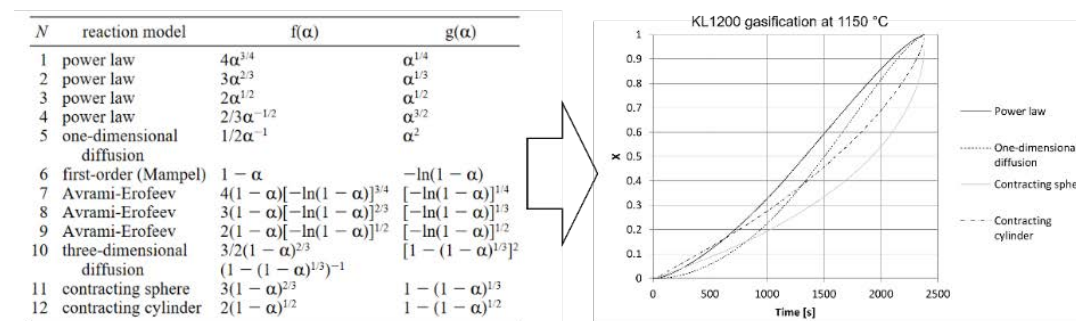
Figure 26. The choice of reaction model for describing biocarbon and nut coke gasification.

RESULTS AND DISCUSSION

The best models to describe the gasification of the samples were the power law, one-dimensional diffusion, contracting sphere, and contracting cylinder (Figure 26) models. When considering all the gasification data of every sample type, the contracting cylinder was found to have the highest linear correlation with the conversion data. It was found that a pyrolysis temperature of 1200 °C led to considerably higher activation energy (EA) throughout the temperature range of 1000–1350 °C (Table 2). As can be seen from Table 2, the EA and reaction rate constant (k0) changed considerably as the temperature was elevated. Moreover, there were three observable temperature ranges with their own EA and k0. Because of the clear threshold points of these different temperature ranges, the rate-controlling mechanism ought to be changed when moving from one temperature range to another.

Because of the low ash content of the samples, ash diffusion is not supposed to control the reaction. However, film diffusion can control the reaction in lower temperatures, while the significance of chemical reaction as a controlling mechanism increases as the temperature is elevated.

Sample	E_A [J/mol]			k_0 [1/s]		
	1000–1100 °C	1100–1200 °C	1250–1350 °C	1000–1100 °C	1100–1200 °C	1250–1350 °C
KL600	46330.6	12619.8	3980.49	0.08838	0.00457	0.00224
KL900	39895.6	11148.2	7937.71	0.05057	0.00404	0.00307
KL1200	86856.4	25941.3	12954.9	2.50703	0.01177	0.00394

Table 2. Activation energies and reaction rate constants of biocarbon samples.

PUBLICATIONS

Koskela, A., Tarkka, A., (2023), Reaction kinetics and mechanism of Kraft lignin-based biocarbon gasification in CO_2 containing gas atmosphere, manuscript.

Contact persons
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TASK
2.3
VALUE-ADDED USES FOR THE PYROLYSIS GASES FROM
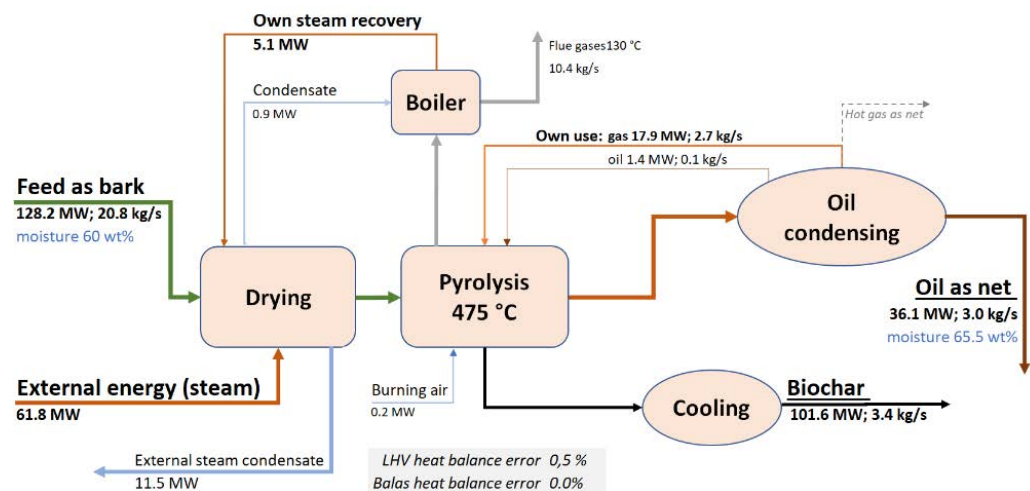BIOCHAR PRODUCTION

Figure 27. Schematical process diagram: Oil-producing scenario with LHV heat flows.

INTRODUCTION

The objectives of this work were to analyze and compare bark and saw dust behavior in slow pyrolysis, as both are available in large quantities within the forest industry, and which were readily available for experimental purposes. Both bark and saw dust provide ample raw material source for slow pyrolysis to produce biocarbon, pyrolysis gases, or oil. According to Hassan et al. (2019), in a survey estimating forest industry side-streams generated in Finland the bark was the largest solid woody side stream and saw dust was also notable (bark ca. 3.8, saw dust 0.7, and total solid woody side streams 7.9 million tonnes). Analyzed biocarbon, oil, and non-condensable pyrolysis gases enhanced the previous modeling work by Hakala et al. (2020). Of specific interest was to analyze the compounds in non-condensable pyrolysis gases and moisture content in the liquid fraction, resulting both from pyrolytic water formation and raw material moisture content. The new experimental data obtained were applied in a slow pyrolysis model for bark (yields, heating values, elementals, gas compounds, ash contents, and moisture). The experimental data obtained within this study improved the model relevancy notably.

MATERIALS AND METHODS

The slow pyrolysis experiments were performed for bark and saw dust at 475 or 600 °C using a 3 h carbonization time. The formed products from the slow pyrolysis experiments of these feedstocks (biocarbon, condensed oil, and non-condensable gases) were analyzed for their chemical compositions, yields, ash contents, heating values, and moisture. A

literature survey was carried out for further utilization options of the condensed pyrolysis oil. Selected raw material for modeling purposes to produce biocarbon was mixed bark (spruce and pine), providing a high yield of biocarbon (41.3 wt%) from dry bark. Mass and energy balances for the slow pyrolysis process were calculated using the BALAS process simulation software.

RESULTS AND DISCUSSION

The utilization of the condensed oil from slow pyrolysis for other applications than energy use is gaining attention due to the increasing number of biocarbon producers. Some research exists on increasing the biocarbon yield of biocarbon by carbonizing the oil together with biomass (Veksha et al. 2014) or by adding bentonite clay to the biomass to trap the gases already at the reactor (Russell et al. 2017). One other proposed use has included the replacement of traditional kiln tar as a wood preservative (Egenberg et al. 2003, Mazela 2007). Extracting valuable compounds from the oil is one additional possibility. A chemical analysis of the condensed oil fraction showed high water contents in samples collected from a heating range of 280 to 475 or 600 °C. Saw dust had lower water contents (65–70 wt-%) than bark (83–88 wt-%) at both temperatures, ash contents were at max 0.3 wt-%. Carbon contents (db) were 50 to 59 wt-% which suggests there is some potential for biocarbon production, but the water content of the oils is a challenge. Gas chromatography results showed a wide range of aromatic and aliphatic polar compounds with low concentrations but the differences between feedstocks and preparation temperatures indicate a possibility to control the produced amounts to some extent. Utilization of the condensed gases needs more experimental work to produce new commercial products outside energy use. The feasible solution for the production of biocarbon is a slow pyrolysis process integrated with an industrial plant with cheap low-temperature heat source(s) available for bark drying. Further, the feasibility is improved if the integration needs a high-temperature heat source, hot pyrolysis gases can be burned as such (assuming applicability) without condensing of pyrolysis oil, thus maximizing the heat contents of the products. Oil production is an option when the value in it is foreseen and/or integration has no suitable high-temperature heat source applicable for the direct burning of hot pyrolysis gases. Pyrolysis oil could provide added value as a fuel enabling storage and as a transportable product for other processing sites for further conversion processes or energy use. Re-pyrolyzing oil with biomass may provide a higher biocarbon yield, too. The heat content in the products (biocarbon and net oil) is less than for the previous case due to oil condensing and burning a small amount of the oil on the side of using all non-condensable pyrolysis gases for pyrolysis own energy needs. Additionally, further investment is required for oil condensing equipment. If there is added value in pyrolysis oil and/or gas products concerning their energetic value, on the side of biocarbon production, even higher production yields for pyrolysis oil/gases would be possible if the energy requirement for pyrolysis can be covered by some other fuel or heat source.

PUBLICATIONS

Hakala, J., Siipola, V., (2023-2024), Biocarbon from woody side-streams -Characterisation and modelling of slow pyrolysis focusing on process integration benefits, manuscript under preparation.

TOCANEM
FINAL REPORT 01/2024

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TASK
2.4 — SUSTAINABILITY ASSESSMENT FOR BIOCHAR USAGE

INTRODUCTION

The metallurgical industry and steel production are very energy and carbon-intensive industrial sectors, up to 5–10% of the global CO_2 emissions are formed by steel production. Most of these emissions are formed in power production and carbothermal reduction processes such as submerged arc furnaces (SAF), electric arc furnaces (EAF), and blast furnaces (BF) (Suopajärvi et al. 2017, Surup et al. 2020). In recent years, the substitution of fossil coke with bio-based reducing agents has emerged in many studies and one of the most promising reducing agents is charcoal (Suopajärvi et al. 2013, Surup et al. 2021). In this study, the sustainability of charcoal use in SAF is assessed based on environmental, economic, and social aspects.

MATERIALS AND METHODS

A sustainability assessment was carried out by using Multicriteria Analysis (MCA) and an Analytical Hierarchy Process (AHP). The SimaPro software was used in the evaluation of the environmental impacts of transport. A sustainability assessment was performed for charcoal replacement ratios of 100%, 50%, 25%, and 0% (reference case, 100% coke). All cases were screened against 26 relevant criteria and all criteria were ranked and weighted according to the order of importance. The main assumptions in the assessment were: 1) by-products (bark and sawdust) from the pulp and sawmills are used as raw material in the charcoal production, 2) charcoal is produced by slow pyrolysis at 600ºC close to pulp or sawmills 3) charcoal is pelletized before transportation, and 4) charcoal replaces coke with a ratio of 1:1.
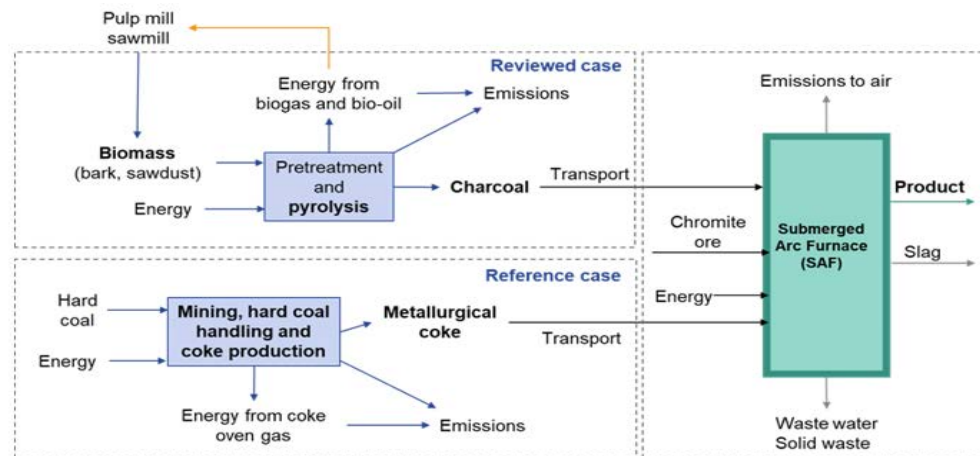

Figure 28. Charcoal usage in ferrochrome production.

RESULTS AND DISCUSSION

The assessment shows that replacing coke with charcoal improves environmental sustainability. When using charcoal in SAF, the most significant positive impact on environmental sustainability is the reduction of CO_2 emissions in the production of ferrochrome. The economic sustainability remains lower when charcoal is used, mainly due to higher operating costs, the price of charcoal, and the additional costs to the process caused by the properties of charcoal. However, the reduction of CO_2 emissions has a positive impact on economic sustainability. The overall differences in social sustainability are very small. The most significant indicators of social sustainability are the acceptability of the use of charcoal and health and safety issues related to the reductant and ferrochrome production. The highest sustainability was achieved with a 100% charcoal substitution rate. However, 100% replacement of coke with charcoal may pose technical challenges for the ferrochrome production process due to the different properties of charcoal compared to coke.
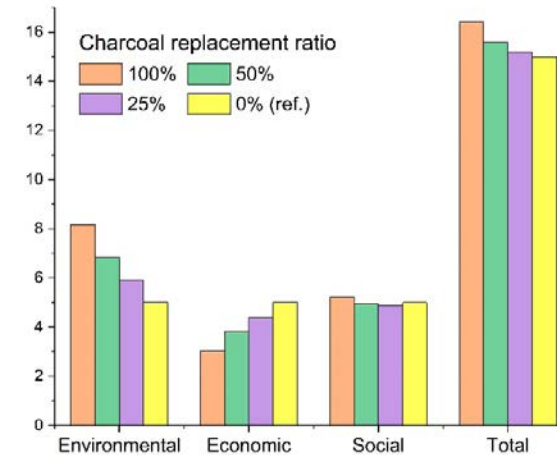
Figure 29. Overall sustainability of charcoal usage in ferrochrome production.

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WP 3

CIRCULAR ECONOMY

SUMMARY AND HIGHLIGHTS

Summary of the project's motivation and achievements based on industrial partners' point of view

outokumpu

Outokumpu's goal was to identify and reduce upstream CO_2 emissions (scope 3) by focusing on the selection of alternative raw materials, raw material sources, and consumables in the stainless steel smelting and refining process. Another interest was to scope and pilot potential technologies to replace hydrofluoric acid with less hazardous alternatives and improve overall pickling performance in the mixed acid pickling process at continuous strip annealing and pickling lines. Additionally, the aim was to identify ways to imeriup electrolytic pickling efficiency in stainless steel production. Finally, Outokumpu wanted to develop monitoring technology to gain a deeper understanding of refractory wear mechanisms of industrial-scale furnaces and utilize developed technology in a full-scale stainless steel production environment to validate the wear model created to predict refractory wear.

NEW BOLIDEN

Boliden Kokkola
Boliden Kokkola participated actively in TOCANEM WP3 - Circular economy.
Special attention was paid to the following tasks:
Task 3.6 Fayalitic slags in geopolymers and
Task 3.7 Production of CSAB cement.

Boliden provided fayalite-type slag for test work carried out at the University of Oulu. The slag had been processed in a pilot furnace in a continuous process to remove valuable and heavy metals. This highly iron-containing slag had been obtained in near carbon neutral pyrometallurgical processing and water cooled to obtain high strength and amorphous structure. It is well known that slag can be used to replace calcium carbonate in the cement process and can lower very high carbon dioxide emissions.

KIVISAMPO

KIVISAMPO OY aimed to expand and deepen its understanding of the metallurgical properties of briquettes derived from by-products of metallurgical processes. The overarching objective was to expand market opportunities for these products within Finland, the European Union (EU), and beyond.

The goals were achieved by:
- A comprehensive testing campaign: a broad campaign was conducted to test various waste materials, including dust from metallurgical processes, slag, and more.
- The production of auger pressed briquettes: a series of briquettes were produced using auger pressing technology, and these briquettes underwent testing in collaboration with AMCOM GROUP and the University of Oulu.
- An experimental industrial auger press was developed and used.

In 2021-2022, on an auger pressing industrial line developed by AMCOM, briquettes from slag were produced and used in the blast furnace process. Samples of these briquettes were sent to the University of Oulu for testing.

Jervois FINLAND

Recycling and the circular economy are increasingly important parts of the cobalt business. Recycling of cobalt raw materials is the most important factor as such, but recycling needs to be viewed in a broader way including recycling of used supplies and internal material flows. From a cobalt raw material point of view, Jervois Finland's utilization of recycled cobalt is currently between 10-15%. Recycling materials are mostly coming from the catalyst industry as spent catalysts or from the hard metal industry as impure cobalt residue where tungsten carbide (WC) has already been separated from hard metal scarp by a WC producer. The goal of Jervois Finland is to increase the level of utilization of recycling raw materials and one goal of this project has been to identify and develop processes that enable the usage of such materials, this means effective leaching processes, purification, and separation methods as well as precipitation of cobalt precursors with a lower CO_2-footprint. The other goals have been to find a way to effectively separate cobalt from side streams as well as to separate other valuable secondary metals from processed recycling materials. One of the important aspects of recycling is to evaluate the impact of recycling on the environment and therefore an LCA of recycling compared to virgin materials is needed. It is good not only to understand the impact of recycling of major metals but also to identify how recycling of minor metals affects the environment, i.e. which metals are good to be recycled and which not.

Jervois Finland is using hydrogen gas to reduce cobalt powders that are mainly used in the hard metal industry and diamond tooling. Excess hydrogen is required to complete the reduction of cobalt precursors, but on the other hand, the use of too much hydrogen is a cost factor, and it increases the CO_2 footprint. One of the goals of this project has been to examine the hydrogen reduction of cobalt salts to understand more fundamentally reduction kinetics and thus help Jervois Finland to optimize the usage of hydrogen.

fortum

Critical metals are of paramount importance for the development of a sustainable, technologically advanced, and environmentally responsible future. To ensure their availability, responsible mining practices and exploration of alternative materials will be essential to meet the growing demands of our modern world. The knowledge achieved in these studies will be utilized in future studies of end streams of IBA handling.

owatec

The Owatec Group, is a visionary in the circular economy, leading the way toward a sustainable future. By harnessing our expertise in environmental cleantech, specifically in industrial wastewater and sludge management, we strive to revolutionize the way resources are utilized. Our mission is to ensure clean water and sufficient raw materials everywhere while embracing the principles of the circular economy. We offer adaptable solutions to diverse water and sludge management challenges through our innovative technologies in sea containers. By seamlessly combining different units with distinct purposes, we provide a comprehensive approach that maximizes efficiency and minimizes waste.

SAPOTECH

The TOCANEM project was a great opportunity for Sapotech to develop its solutions in co-operation with research institutes, other SMEs, and steel industry experts. Contributing mainly to WP1 and WP3, Sapotech's main motivation was to push for solutions that allow carbon direct avoidance and increase circular economy through increased process efficiency. Several machine-vision solutions were researched and developed, based on different types of approaches, including 3D laser triangulation, LED-based dark-field illumination, and LIDAR (Light Detection and Ranging) technologies.

KEY RESULTS AND IMPACTS

Summary of the key results and impacts based on industrial partners' point of view

outokumpu

Potential alternatives to reduce raw material-related CO_2 emissions (scope 3) in stainless steel production were evaluated. For example, purchasing scrap with a 1% higher chromium content would reduce CO_2 emissions by 30%, and usage of nickel instead of FeNi would reduce CO_2 emissions by 40%. Outokumpu Stainless has realized these findings with its Circle Green® product with the lowest carbon footprint in the stainless steel industry.

Extensive review and compilation of various state-of-the-art descaling and pre-pickling techniques was done to reduce HF (hydrofluoric acid) consumption during the pickling of stainless steels. Additionally, prior findings on the utilization of lower neolyte concentration from the SYMMET project were piloted in a full-scale stainless steel pickling process by Outokumpu. The possibility to save up to 60% in neutral electrolyte pickling chemicals was noted as well as evidence on the possibility to reduce electric current applied due to increased efficiency in current distribution.

A method to monitor the refractory lifetime at ferrochrome converter was developed by prototyping and piloting a tuyere camera system in co-operation between Outokumpu & Sapotech. The new technology provides crucial information about the refractory wear status and enables further process optimization to reduce the wear and improve possibilities for preventive maintenance.

NEW BOLIDEN

Boliden Kokkola

Several peer-reviewed articles were made by the University of Oulu. The collaboration with UO was very good and we kept regular research meetings within these tasks. The results showed good cement properties and the high potential for using slag processed from landfilled zinc residues closing the circular economy. It was concluded that over 90% of the current landfilled waste, iron-rich sludges could be turned into metals and usable slag for cement making.

Jervois FINLAND

There are several key results from the public tasks of the TOCANEM project that are important to Jervois Finland. Understanding the fundamental kinetics of the reduction of cobalt salts helps to optimize the reduction conditions in actual processes. Additionally, understanding the leaching behavior of different raw materials in different conditions is important to plan suitable leaching and purification processes for such materials. The LCA of recycling vs. virgin materials has provided important information on how recycling major and minor metals affects the environment. This has been good information not only for Jervois Finland but also for our customers and partners. With the better understanding of the reduction kinetics of cobalt precursors Jervois Finland proceeded with its own trials and was able to optimize reduction conditions and reduce the level of used hydrogen gas. Research of leaching and purification techniques has helped Jervois Finland with its own company projects to develop suitable processes for several recycling materials. Some of these projects are still ongoing.

The LCA analysis of recycling vs. virgin materials is one of the key elements together with economics and metal price fluctuation to promote recycling in the future. Such an analysis has an important role when discussing recycling options with customers and partners now and in the future.

KIVISAMPO

How the results were utilized in practice:
- Technical Parameters: The research provided essential technical parameters that enable the design of more advanced briquetting setups using auger pressing technology. These improved setups offer enhanced operational characteristics.
- Product Diversification: The company has expanded its product range based on the knowledge gained from the research. This diversification is likely to lead to increased market competitiveness and a broader customer base.

As for KIVISAMPO'S academic contributions, based on the data obtained, two master's theses have been defended at the university, and preparations are underway for a doctoral thesis. Additionally, one article has been published in a peer-reviewed journal, and another is in progress.

In conclusion, KIVISAMPO's efforts in exploring the metallurgical properties of briquettes derived from metallurgical by-products have yielded significant results. Through comprehensive testing, collaboration with research institutions and partners, and the development of experimental industrial equipment, valuable insights have been obtained. These insights not only contribute to the advancement of briquetting technology but also expand the company's product offerings, aligning with its broader goals of market expansion and product diversification.

fortum

Fortum supports research of novel and low CO_2 technologies to recover critical battery metals sustainably from industrial side streams. The work in TOCANEM WP 3.16 provided Fortum with a better understanding of feasible recovery routes to recover, e.g. REEs with IX materials, and yielded valuable insights into novel material development, In WP 3.15 potential utilization routes for iron residue conversion routes were identified for further development.

OWATec

Owatec participated in task 3.18 CO_2 recovery and utilization in carbonate precipitation. Unfortunately, the wastewater stream intended for study did not meet the qualifications for the testing, so the tests were made with a different industrial wastewater. The results from the selective co-precipitation and parameters will be utilized in the development work of Owatec's equipment. Because of the unexpected challenges with sample quality, there were major changes to Owatec's own project plan. The original project plan was changed with the authorization of Business Finland to study the utilization of the pickling acid residue.

Metso

The integrity of metallurgical furnaces is of foremost importance in pyrometallurgical processing. The knowledge of the refractory degradation mechanisms provides tools to ensure safe operation and long campaign times of furnaces. The new data and results obtained can be utilized and lining design to guarantee excellent process performance.

SAPOTECH

Several innovative solutions were developed, tested, and piloted in the TOCANEM project. The key results that should be brought up here are: 1) the bulging/profile measurement of the slab narrow faces with 3D technology. The solution has already been commercialized with lots of new potential customers in the steel industry. By knowing the narrow face profile, customers can evaluate if a continuous casting machine mold is in the appropriate condition (taper). Additionally, based on the profile measurement, customers can flag slabs that could cause problems in the hot rolling stage. This information reduces the need for re-processing of semi-products resulting in better environmental performance. 2) Totally new inspection technology for the converter tuyere area by utilizing high resolution imaging and artificial intelligence-based methods. The system estimates the refractory wear around the tuyere area nozzles, making it possible for customers to evaluate and control the converter process more efficiently. An extended converter lifetime means monetary savings and reduced environmental burden. Thanks to the TOCANEM project, Sapotech has been able to add several technologies to its solution portfolio to make metal production more sustainable. Many of the developed solutions have already been offered to the end customers.

UNIVERSITY OF OULU

The TOCANEM project and Circular Economy at the University of Oulu
The TOCANEM project is an excellent opportunity to enhance the circular economy in the steel and metal industry. Large collaborative projects such as TOCANEM and FFS are key contributors to research in the field of circular economy at the University of Oulu's Process Metallurgy Research Unit. In the TOCANEM project, examples of research related to circular economy are apparent in WPs 2 and 3, which include a focus on biochar and cement research.

Producing cement accounts for about 8% of global manmade CO_2 emissions, thus there is a need for the utilization of alternative materials for cleaner cement production. In cement research, the aim is to reduce the amount of limestone as a raw material with iron-rich materials to avoid CO_2 emissions. Possibilities for reducing CO_2 emissions in cement research include replacing the Portland clinker with low-carbon supplementary cementitious materials, using alternative raw materials for Portland cement manufacturing, developing new binders not based on Portland clinkers, and capturing and sequestrating the CO_2 emitted by cement manufacturing plants. This topic has challenges related to making sure these new kinds of cement meet standards and health regulations and this area is the focus of research at the University of Oulu.

Another topic related to the circular economy in the TOCANEM project is biocarbon. Metallurgical biocarbon, meaning biogenic carbon that can be used in metallurgical processes, is an alternative to replace fossil-based carbon in the metallurgical industry. This area also poses challenges to ensure that the properties of metallurgical biocarbon are suited to requirements in metallurgical processes as biocarbon has a high surface area, high porosity and has its own mineralogical composition along with other key characteristics that need to be accounted for in various applications in metallurgical processes. Currently, the biocarbon is evaluated based on a comparison of key properties related to the fossil-based reference material and is being researched at the University of Oulu.

In summary, our research related to the circular economy is conducted in close collaboration with other research units and companies, and our focus is on material characterization and manipulation of properties, targeting towards best possible suitability for the best possible application.

TASK
3.1 SLAG COOLING

INTRODUCTION

The simplest method for slag cooling is cooling in an ambient atmosphere in a cooling yard. The cooling of stainless steel slag in an ambient atmosphere and the water cooling of slag have been simulated by e.g. Kärnä et al. Flash smelting technology has been widely applied in the smelting of copper and nickel sulfide concentrates. However, some matte is dispersed and entrained mechanically in slag and lost during tapping. Additionally, some copper and other valuable metals dissolve in the molten slag as oxides, resulting in a waste of resources. As a result, it is necessary to recover the metals in the slag using suitable methods. At present, the most common way is slow, controlled cooling in a transfer ladle and subsequent processing of the slag.

MATERIALS AND METHODS

The goal of this task was to see what factors affect slag cooling using industrial measurements and computer modeling. Another goal is to see if computer modeling is an effective tool for predicting slag cooling. In the measurements, the temperature of the slag was measured from three points in the slag pot. Measurements were made with both air- and water-cooled pots. In modeling, a 2d axially symmetrical model was used. The heat transfer between the slag and cooling water and between the pot and air were calculated using published correlations.

RESULTS AND DISCUSSION

During the measurements, water-cooled slag cooled slowly at first but then the temperature dropped rapidly to a low level. For air-cooled slag the cooling was slower and smoother. In the modeling a similar drop in temperature could not be achieved. The closest results were achieved by increasing the thermal conductivity of the solid slag and using a heat sink representing water boiling inside the cracks in the slag. A working model was not made within this thesis, but it requires further research.

PUBLICATIONS

Jokilaakso, A., Jylhä J.-P., Song, K., (2021), Submerged gas blowing and droplet settling modelling in copper matte smelting processes, EUROMAT 2021 (oral presentation).

Saarnisaari, A., (2021), Kuparikuonan jäähtymisen mittaus ja mallintaminen, master's thesis, Aalto University.

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TASK
3.2   ELECTROLYTIC PICKLING

declared by the producer is Cr 18.1, Ni 8.1, Mn 2, C 0.04, Si 1. In the cell seven electrodes were used (Fig. 30a), four saturated silver/silver chloride electrodes (SCE), Ref1 to Ref4, were used as reference electrodes and distributed equally through the cell, two carbon steel electrodes as cathodes (10x10x3cm) and a lead electrode as an anode (10x10x4cm), Fig. 30b.
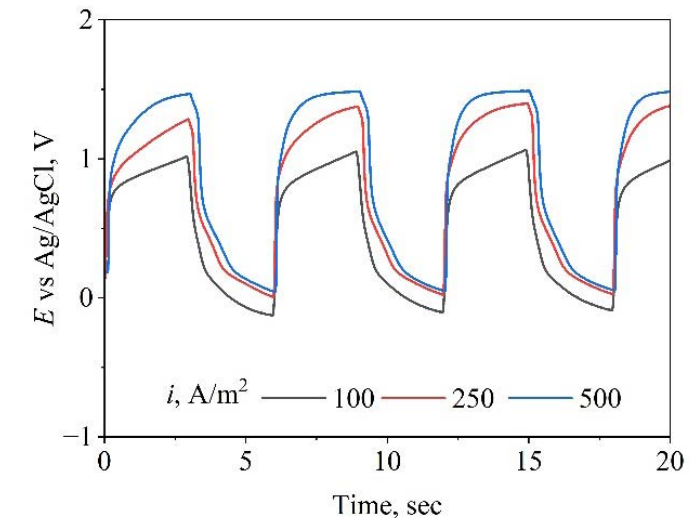
Figure 31. Potential distribution at stainless steel strip under cathode (Position 3, Fig. 30a) cathode measured by sensor (pulse 3 sec, pause 3 sec).

RESULTS AND DISCUSSION

In-situ measurements of the potentials of stainless steel strips on a large scale have been done. The effect of the geometry and time of pulses on the potentials of cathodes and anodes as well as 304 strips at 11 points of the cell were identified. The distribution of potentials were identified under the anode and cathode, and between the cathode and anode on the surface of stainless steel strips at current densities below and over industrial levels. The stainless steel strips behaved as a bipolar system in a dilute Na_2SO_4 solution and the concentrated potential under the anode does not reach the values necessary for removal of the oxide layer. The transient time in a three-electrode cell for austenitic 316L and duplex steel for oxidized and non-oxidized steel with different current densities and time of pulses to simulate the strip polarization in the industrial cell were tested and the time to reach a steady potential was found. EDS analyses of stainless steel strips before and after electrolytic pickling showed changes in the oxygen content of the stainless steel surface. Electrochemical impedance spectroscopy was offered for analysis of the efficiency of pickling.

PUBLICATIONS

Aji, A.T., Aromaa, J., Tuovinen, T., Riekki, R., Lundström, M., (2023), Finite Modeling and Simulation of the Effects of Neutral Electrolytic Pickling Process Parameters on EN 1.4404 Steel Strips, Metals, 13(12), 2001.
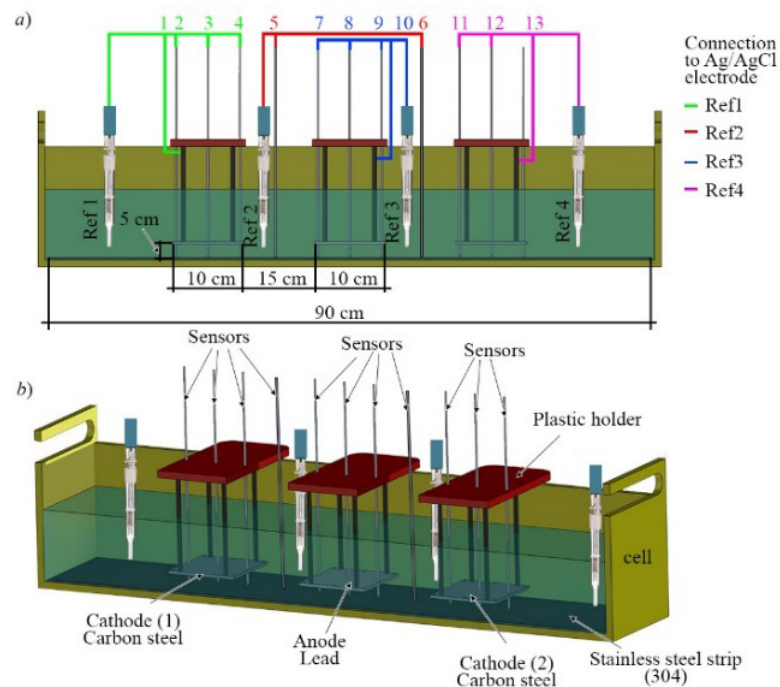
Figure 30. Cell for electrochemical neutral pickling (a) Electric connections of sensors and electrodes to reference electrodes and distances between components of the cell, (b) Description of components of the cell.

INTRODUCTION

The process of stainless steel production includes various heat treatments that lead to the formation of an oxide layer (50 to 500 μm). To restore the corrosion resistance properties of the stainless steel oxide layer must be removed. Importantly the material losses should be minimized during pickling while ascertaining a good surface removal of oxides. This improvement can be achieved by precisely controlling the potential on the surface of the strip.

MATERIALS AND METHODS

All electrolysis was carried out at a temperature of 70 ± 1 °C in a rectangular electrolyzer in a Na_2SO_4 solution (Fig. 30) with dimensions 90x15x50 (20 L of solution) in galvanostatic mode with a power supply EA-PS 3040-20 C. The stainless strip (304) area was 1350 cm^2(90x15 cm). The weight percent elemental composition of ASTM304 stainless steel as

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TASK
3.3 PREDICTION OF REFRACTORY WEAR

INTRODUCTION

Refractories interacting with molten slag and gaseous process environments can be unexpectedly compromised concerning their durability and can display complex failure modes. In flash smelting furnaces, the resistance of refractories to high temperatures, thermal gradients, molten slag, and interactions with sulfur-containing atmospheres is essential. Magnesia-chromite refractories fulfill most of these requirements, however, their possible interactions with the SO_2-rich smelter atmosphere are yet not known. This task was designed to bridge this knowledge gap.

MATERIALS AND METHODS

Unused magnesia-chromite refractories and spent refractories sampled from a nickel flash-smelting furnace were analyzed and compared to shed more light on the interactions between the gas phase and the refractory material. The brick was a magnesia-chromite product of type MCr50, ISO 10081-2, by RHI Magnesita. The composition of the brick was (in wt.%): 59.5 MgO, 19.0 Cr_2O_3, 13.5 Fe_2O_3, 6.0 Al_2O_3, 1.3 CaO, and 0.5 SiO_2, with an apparent porosity of 17.0 vol.%. The bricks were examined using X-ray Fluorescence (XRF) measurements. The cut specimens were subjected to mercury porosimetry and μ-computed tomography (μ-CT) without further sample preparation procedures. X-ray diffraction (XRD) measurements were conducted for gently ground specimens. The overall microstructure of the refractory bricks, both unused and spent, was investigated using light microscopy and scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS) for compositional analyses and electron backscattered diffraction (EBSD) for crystallographic investigations. Thermodynamic modeling was used to examine how impurities originating from side streams transfer to the gas phase and further how these vaporized components affect refractory wear. So far, the advantages and disadvantages of different approaches in computational fluid dynamics (CFD) modeling have been examined. A Laser Flash Apparatus (LFA) was used at Aalto University to measure the thermal diffusivity of unused MgO-Cr_2O_3, Al_2O_3-Cr_2O_3, and SiC refractories up to 1400 °C under an N2 atmosphere. A contact angle measurement was conducted at Aalto University to observe the wetting behavior of Cu/Ni slag and Cu/Nimatte on MgO-Cr_2O_3, Al_2O_3-Cr_2O_3, and SiC refractories (~25mm x ~25mm x 5mmH, roughness: 1um). Each sample was subjected up to 1500 °C under an Ar or SO_2-CO-CO_2 atmosphere.

RESULTS AND DISCUSSION

The results revealed the presence of two phases in the as-received refractory material: magnesia, MgO, and magnesia-chromia spinel, $MgCr_2O_4$. The MgO phase, seen in darker grey contrast in SEM images (Figure 32 a-b), was the aggregate, while the spinel phase $MgCr_2O_4$, seen in the lighter grey contrast, was the matrix phase and glued the aggregates together. Additionally, pores were detected in the specimens (seen as black contrast in SEM images). EDS analyses for the two phases revealed that the MgO phase was essen-

tially rich in magnesium (43.8 wt.%) and oxygen (35.0%) but also involved iron (9.2%), chromium (9.0%), and aluminum (3.0%). The $MgCr_2O_4$ spinel phase contained, on average, plenty of chromium (31.9%) and oxygen (34.1%), with also magnesium (15.3%), iron (9.8%), aluminum (8.3%), and minor amounts of titanium (0.5%) were detected. Image analyses gave the following areal fractions: pores 11.5%, MgO 46.3% and $MgCr_2O_4$ 42.2%. μ-CT investigations (Figure 32 c) revealed that microstructure was composed of areas falling within three density categories. The low-density areas (red) represented MgO, medium-density areas contained the precipitates of $MgCr_2O_4$ embedded in MgO, and high-density areas corresponded to individual grains of $MgCr_2O_4$.
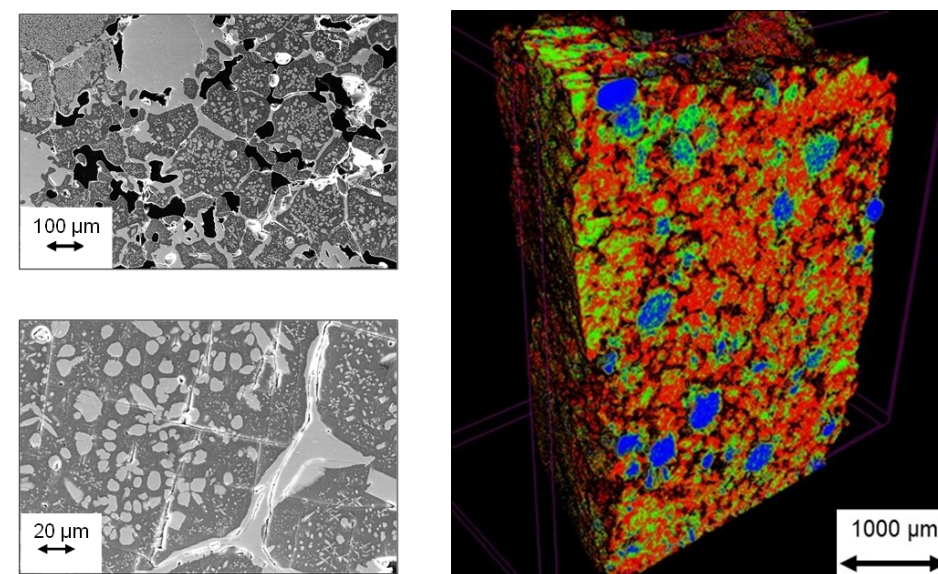

Figure 32. Microstructure of the unused magnesia-chromite refractory. A and b) SEM back-scattered electron (BSE) images, c) μ-CT image, showing the 3-dimensional density structure. The colors correspond to low density (red), medium density (green), and high density (blue). The black regions are pores.

In the spent refractories, three reaction zones could be identified (Figure 33). Zone 1 was located towards the hot gas space of the furnace interior and was characterized by a blueish-greenish color. Underneath this zone, often separated by visible macrocracks, was the brownish Zone 2. Towards the cooled external wall was Zone 3, characterized by white and light grey shades. The blueish-greenish color of the refractory within the hot zone was essentially due to interactions with the molten slag, with metal residues. The middlemost zone was structurally closest to the original unused material, yet it contained some additional $CaSO_4$. In the cool zone, enabled by the travel of chemical species, such as SO_2 and SO_3, and driven by thermal gradient, both $MgSO_4$ and $CaSO_4$ (Figure 34) were evidenced.
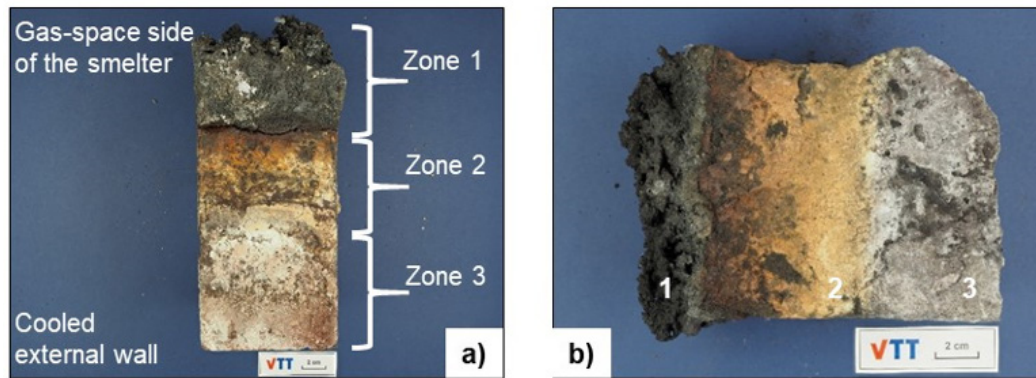
Figure 33.

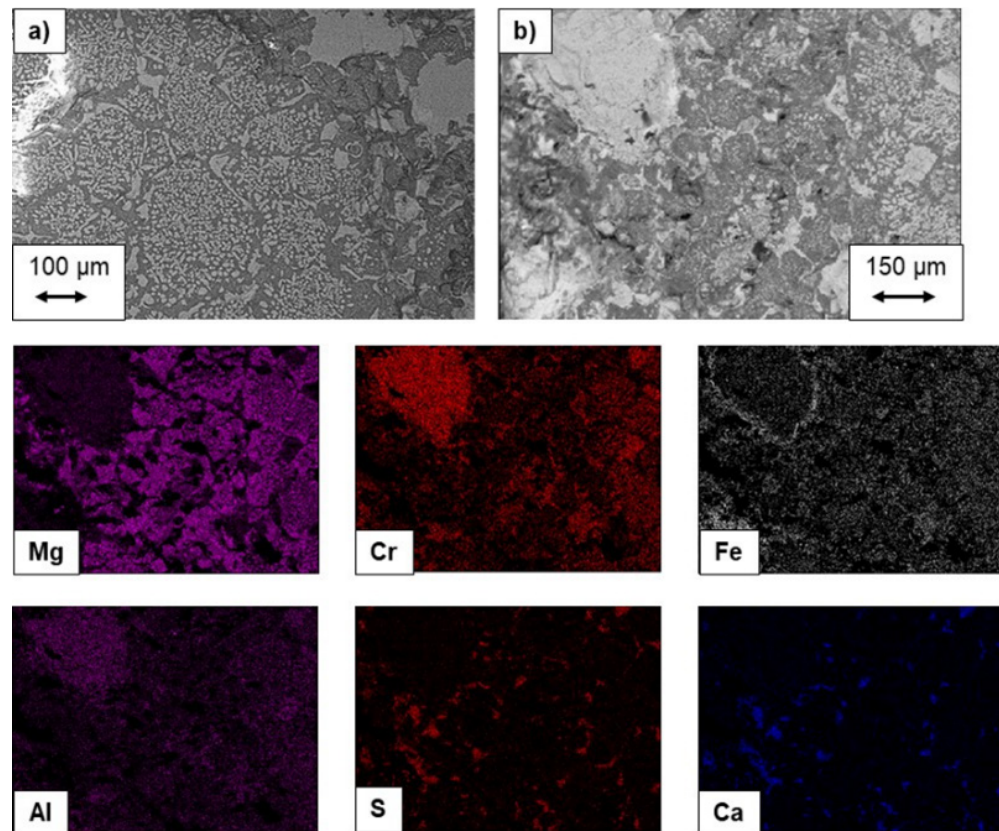*Figure 34.*

Based on the IC analyses, none of the refractory materials convert SO_2 to SO_3, so the SO_3 formation is most likely catalyzed by the process of dust and deposit on the refractory surface. The experiments addressing the reactions between SO_2 and the as-received materials are still partly ongoing, but the results suggest that SO_2 is not responsible for material degradation. Similar tests with SO_3 are currently in progress in collaboration with BAM, and the results will be available before the end of the project. Regarding the slag immersion tests, interactions between the slag and the refractory contribute to the dissolution of elements from the slag to the refractory and vice versa, yet this is foreseen to play only a minor role concerning interactions with the gas phase. In thermodynamic modeling, the initial gas-phase composition for calculations was optimized to examine the behavior of foreign substances in a flash smelting furnace. So far, the behavior of Zn and Cu in the gas phase as functions of chlorine and oxygen content have been addressed, and the preliminary calculations show that the presence of different Zn/Cu compounds in the gas phase and their condensation/solidification depended on the gas phase composition in addition to temperature. Next, similar calculations will be carried out for iron, lead, arsenic, and cadmium compounds. The modeling activity has focused particularly on degradation mechanisms resulting in catastrophic refractory brick failure due to the brick reacting with the process environment and chemical reactions taking place within its respective microstructure. To address these complex micro-mechanisms, a multiscale modeling approach was developed which accounts for the various mechanistic couplings between the material and the operating environment at the scale of the material microstructure. A schematic of the toolset is presented in Figure 35. Within the task, the developed tools were validated against field and laboratory-scale experiments, and sensitivity analyses were performed to investigate how improvements in refractory durability and lifetime can be obtained. The developed capabilities provide systematic means for refractory selection and assessment of lifetime for novel processes or otherwise challenging operating environments.
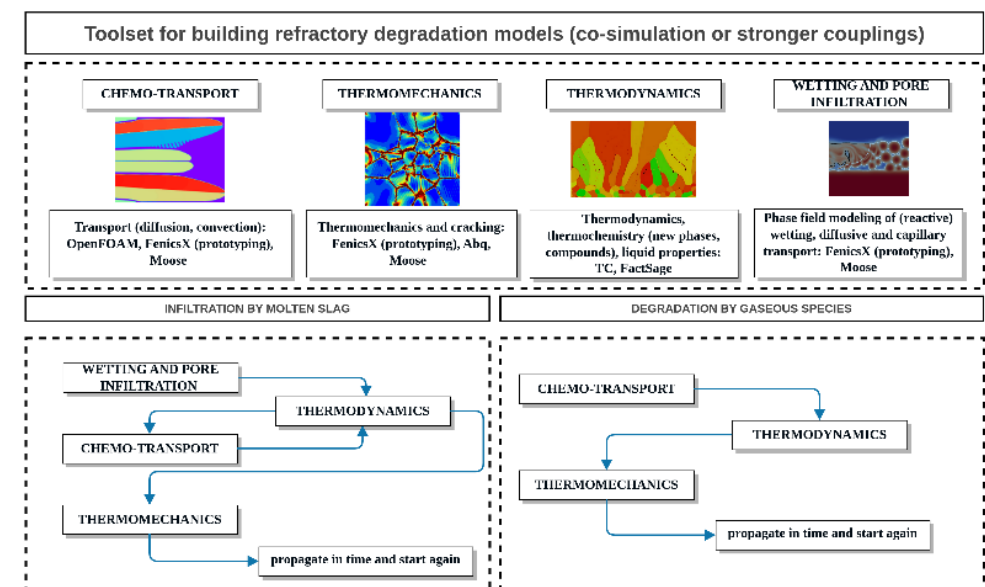

Figure 35. Toolset for modeling infiltration-related degradation mechanisms.

For LFA, the results showed SiC (6~14mm2/s)>Al_2O_3-Cr_2O_3» MgO-Cr_2O_3 (1~3mm2/s). For used MgO-Cr_2O_3, its thermal diffusivities have similar values to the unused one, regardless of depth from the hot surface. The thermal diffusivity and thermal conductivity were also modeled using the Factsage software and results for the MgO-Cr_2O_3 refractory showed good agreement with the experimental data, whereas the Al_2O_3-Cr_2O_3 showed larger differences, due to the formation of solid solutions that were not incorporated in the model. For contact angle measurement, the results showed that MgO-Cr_2O_3 tends to have better corrosion resistance against Cu/Ni slag and matte than Al_2O_3-Cr_2O_3 and SiC.

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Ville-Valtteri Visuri, University of Oulu

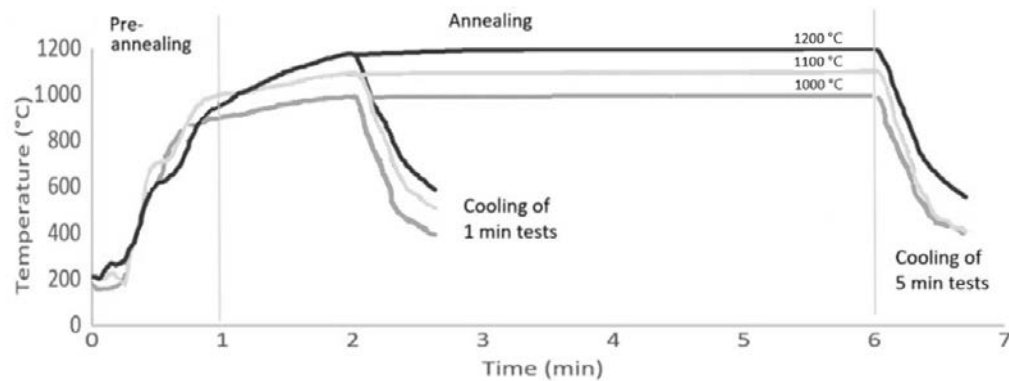| TASK 3.4	OPTIMIZATION OF SCALE FORMATION RELATIVE TO ANNEALING CONDITIONS AND ELECTROLYTIC PICKLING

Figure 36. Annealing heating profiles.

INTRODUCTION

After cold rolling, annealing produces an oxide scale layer on the surface of the stainless steel strip. The oxide scale layer must be removed by the pickling process including electrolytic and mixed acid pickling to produce a clean surface for the product material. The temperature, time, and atmosphere as annealing conditions, and microstructure and chemical composition of the steel grade affect oxide scale formation, and thus, the efficiency of the pickling process. The development of heating methods towards CO_2-free heating in the annealing furnace by utilizing enriched air, oxyfuel, or hydrogen fuel combustion changes the composition of the furnace gas atmosphere, which affects the surface oxidation and removal of oxide scale.

MATERIALS AND METHODS

Annealing of cold rolled stainless steel was performed in the laboratory using a vertical tube furnace with a vertical adjustment of the sample's position concerning the furnace's hot spot. The studied steel grades included austenitic AISI 304 and AISI 309, and ferritic AISI 441 and EN 1.4622. Simulated heating curves at high temperatures were used in annealing tests. A simulated oxyfuel method and hydrogen combustion were compared to current natural gas combustion with an air-based furnace gas atmosphere. Oxide scales were characterized by FESEM-EDS and GDOES. Electrolytic pickling was performed for steel grades EN 1.4622 and AISI 309 to reveal pickling differences compared with different oxide scales.

RESULTS AND DISCUSSION

Short-term annealing for cold-rolled stainless steel produced different oxide scales depending on the annealing conditions and steel grades. The development of the oxide scale structure varied from a thin chromium oxide layer to a thick layered iron oxide-containing structure. The oxidation of steel grades AISI 309 and EN 1.4622 was less compared to grades AISI 304 and AISI 441, and the oxyfuel method for natural gas caused more oxidation for the latter steel grades. In addition, by changing the fuel gas of furnace heating from natural gas to hydrogen, the progress of oxidation can proceed even further. The formation of silicon-enriched oxide decreased the efficiency of electrolytic pickling for the removal of the oxide scale layer from the surface, and the efficiency was better using a shorter annealing time.
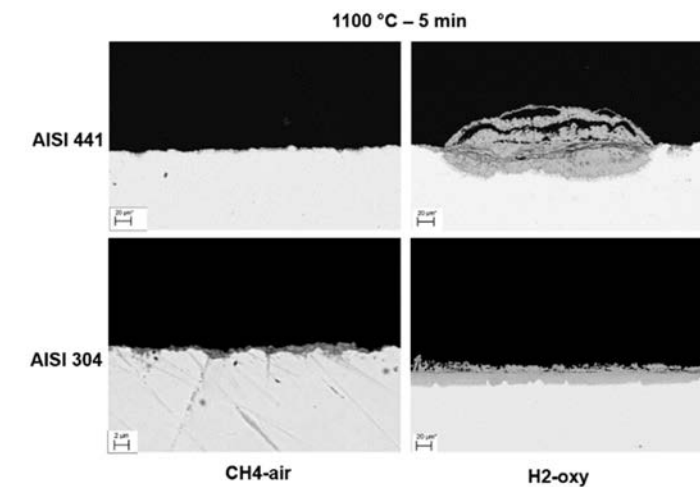
Figure 37. Atmosphere effect on oxide scale formation.

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TASK
3.5
BIPOLAR NEUTRAL ELECTROLYTE PICKLING OPTIMIZATION

INTRODUCTION

In this task, the bipolar neutral electrolytic pickling of stainless steel was studied. Efficient neutral electrolyte pickling reduces the pickling time for mixed acid pickling and therefore nitrous side reactions. This most likely holds for HF-free pickling, reducing the technical requirements for environmentally friendlier pickling. In this task, a stabile anode material selection for a bipolar pickling device was studied (Mörttinen 2022a). The reaction mechanisms of cathodic polarization in neutral electrolytic pickling were studied (Mörttinen 2022b). A factorial analysis of the impurities, pH, and temperature in a neutral electrolyte solution (Ni(II), Fe(II/III), Cr (III), and chromate (VI) were done (Tuovinen et al. 2023). Further, ultrasound-assisted bipolar neutral electrolytic pickling was studied (Igbon 2023).

MATERIALS AND METHODS

The neutral electrolyte pickling was studied using cold-rolled and annealed AISI304. The effects of the cathodic current density, polarization time, and pH on the oxide layer were studied gravimetrically and with X-ray photoelectron spectroscopy (Mörttinen 2022b). The effect of ultrasound on the pickling efficiency was examined by measuring gravimetric changes, the current efficiency of bipolar cells and with a scanning electron microscope (Igbon 2023). In the study by Tuovinen et al. (2023), the effect of the most prominent species dissolved during pickling, (iron, chromium, nickel) were measured using a bipolar neutral electrochemical system. The solutions were standardized in both temperature at 70 °C and conductivities, at 88.8 mS $\cdot$ cm^{-1} at 22 °C. Both the cell efficiency and reaction efficiency were determined by measuring the part of the total current passing through the sample and by comparing the theoretical mass change caused by the dissolution to the gravimetric mass change.

RESULTS AND DISCUSSION

Based on the results (Mörttinen 2022b), the best results for scale removal from AISI 304 during unipolar pickling were achieved using a high cathodic current density of 480 mA/cm² and short polarization time of 15 seconds (5-second pulses). The worst results for scale removal were achieved using a high cathodic current density of 480 mA/cm² and a high polarization time of 90 seconds (30-second pulses). The effect of ultrasound on the pickling efficiency was studied (Igbon 2023). Based on a factorial analysis, by applying high amplitude ultrasound the current distribution efficiency increased on average by 3%. At the same time, the mass loss rate increased by 50%. Low amplitude ultrasound reduced the current efficiency and only slightly increased the mass loss rate.

$i_{cathodic}$, [mA/cm²]	$t_{cathodic}$, [s]	$R_{eff.}$ [%]	Reduction in atomic-%, (chromium oxide), [%]
9	15 (5 second pulses)	66,14	49,25
454	15 (5 second pulses)	53,67	47,38
480	15 (5 second pulses)	63,02	56,31
480	90 (30 second pulses)	41,55	13,94

pH	R_{eff} [%]	Reduction in atomic-% (chromium oxides), [%]
3.5	71,85	48,5
6	66,22	63,5

Figure 38. Effect of the current density, polarization time, and pH on the scale removal efficiency (Mörttinen, 2022b).

Table 3. Measured and calculated results for the total efficiency of varied metal sulfate concentrations. The theoretical Δm assumes a current efficiency of 10%. (Tuovinen et al. 2023.)

Salt	Metal concentration (g $\cdot$ kg^{-1})	Theoretical Δm (mg)*	Measured Δm (mg)	Reaction efficiency (%)	Cell efficiency (%)	Total efficiency (%)	Residual scale (A-%)
Na$_2$SO4	-	0.87	0.88	10.1	36.9	3.7	20 ± 4
H$_2$SO$_4$	pH 3	0.88	1.35	15.3	37.3	5.7	23 ± 3
K$_2$CrO$_4$	2	0.81	0.71	8.8	34.1	3	19 ± 4
K$_2$CrO$_4$	3.99	0.62	0.69	11.1	26.3	2.9	32 ± 7
K$_2$CrO$_4$	8	0.66	0.53	8	28	2.2	36 ± 3
Cr$_2$(SO$_4$)$_3$	7.87	0.73	0.78	10.7	31	3.3	30 ± 20
NiSO$_4$	1.00	0.84	1.13	13.5	35.4	4.8	19 ± 3
Fe$_2$(SO$_4$)$_3$	0.96	1.09	1.21	11.1	46.1	5.1	25 ± 13
FeSO$_4$	1	0.78	0.47	6	32.9	2	28 ± 8

The effect of dissolved species on pickling efficiency was studied (Tuovinen et al. 2023) (see Table 3). The key findings of this study were as follows. During neutral electrolyte pickling, the metal oxide layer scale dissolves. The main mechanism is the anodic dissolution of chromium (III) oxide as soluble chromate (VI). As expected, the lower pH increased the pickling efficiency, mostly by increasing the apparent reaction efficiency while maintaining a similar cell efficiency to sodium sulfate. Nickel (II) and iron (III) -ions increased the pickling efficiency. In the case of iron (III), the effect is likely contributed to the $Fe^0/Fe^{2+}/Fe^{3+}$ -system utilized in the nitric acid-free acid pickling of stainless steels, although sludge accumulation was significant during pickling. The mechanism that nickel-ions have for increasing pickling power was not clear, although a similar effect was observed in our previous research (Tuovinen et al. 2021). The worst results were gained with an Fe(II) solution, suggesting some merit for controlling the redox potential of operating neutral electrolyte pickling tanks. The results emphasize the need for metal removal during neutral electrolyte pickling, rather than relying on the self-regenerating properties of neolyte pickling and the precipitation of dissolved species.

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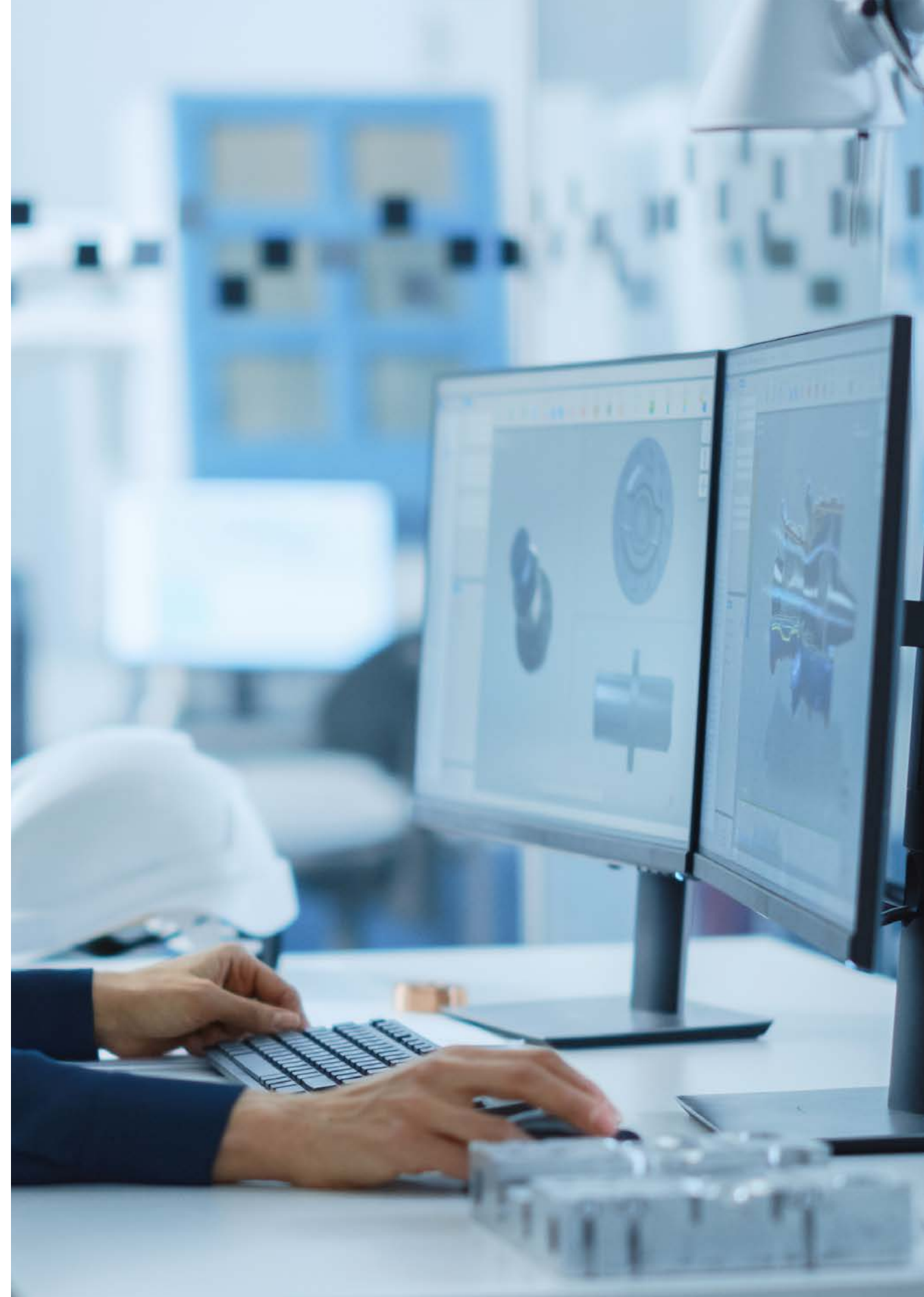
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TASK
3.6
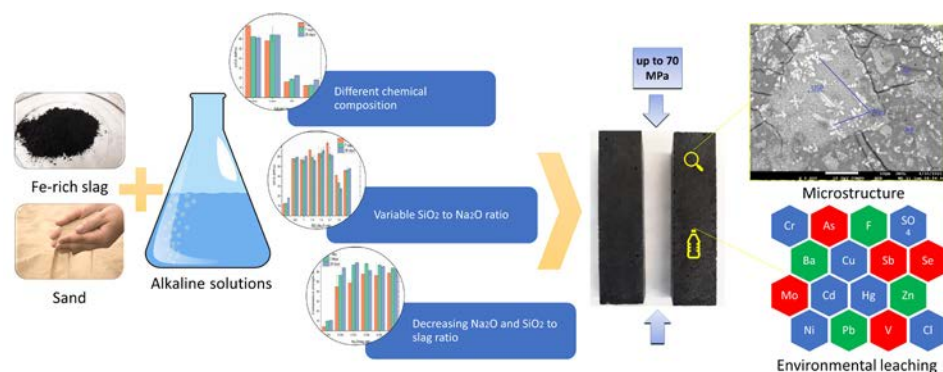FAYALITIC SLAGS IN GEOPOLYMERS

Figure 39. The overall scheme of the experimental procedure used to obtain Fe-rich AAMs.

INTRODUCTION

One promising avenue of research is the recycling of metallurgical and mining waste into construction materials, as the volume of waste often matches the needs of construction applications. To reduce carbon emissions and to find alternative binders, alkali-activated materials (AAMs) and geopolymers have drawn attention. Fe-rich binders have the potential to replace a significant portion of the demand for conventional cement. This project aims to understand the reactivity of Fe-rich precursors during alkali activation, enhance the dissolution rates of Fe compounds, and explore the behavior of Fe-rich waste aggregates in various binder compositions. Additionally, it assesses the durability, environmental impact, and recyclability of the resulting construction material. Further, different co-binders were studied to improve the properties of slag with a lower reactivity. Ultimately, this project seeks to transform underutilized residues into sustainable, low-CO_2 raw materials for the construction sector, contributing to a more environmentally friendly approach (Fig. 39).

MATERIALS AND METHODS

The project's *starting materials* consist of non-ferrous metallurgical slag, specifically industrial fayalite, and wüstite slag sourced from Boliden Harjavalta and Boliden Kokkola in Finland. A comprehensive characterization of the slag includes chemical, physical, and mineralogical analyses, along with microstructural examination. A chemical composition analysis was performed using X-ray fluorescence analysis (XRF) or inductively coupled plasma mass spectrometry (ICP-MS), mineral composition determined through X-ray diffraction analysis (XRD), and energy- and wave-dispersion spectrometry (EDS-WDS). T*he hydraulic reactivity* of the clinkers was assessed using isothermal calorimetric measurements. To gain deeper insights into the reactivity, dissolution tests were conducted, comprising batch dissolution and batch titration experiments. Evaluating *cementitious properties* was done by using mortars and pastes prepared by mixing slag powder with different activators. Determination of the paste nanostructure involved a range of techniques, including XRD, thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX), and STEM-EDX. *The performance and durability* stage encompassed the assessment of the hardened properties and durability of the hydrated materials. The hardened properties included the measurement of compressive and flexural strengths (in accordance with EN 196-1), porosity, and density. Durability studies included multiple tests such as drying shrinkage (as per ASTM C157), a freeze-thaw resistance test (according to EN 12390-9) and leaching tests following EN 12457-1 standards.

RESULTS AND DISCUSSION

In this study, iron-rich alkali-activated material (AAM) was produced using Fe-rich slag. The main findings are described in the following. Compressive strength testing revealed comparable results for mortar activated with potassium and sodium hydroxide solutions, reaching 22.4 and 18.1 MPa at 28 days, respectively. Silicate solution activation resulted in significantly higher strengths, up to 70 MPa, achieved within just 1 day. XRD analysis indicated the formation of Fe-rich C-S-H structure of tobermorite type for all solutions, with minor strätlingite in hydroxide-based solutions. SEM-WDS analysis showed uniform enrichment of Fe along with Ca, Al, and Si, approximating a cement formula of C0.5A0.5F1.5S1H0.1, with limited involvement of Na and Mg. To reduce the environmental and economic impact of the activating solution, dilution and a minimal addition of liquid silica improved the compressive strength up to 60 MPa. Replacing a portion of the solution with water (up to 28.8%) reduced the Na_2O and SiO_2 contents without a significant strength loss, but a very low solution content (8 wt.%) hindered effective mixing and molding, resulting in reduced 1-day compressive strength (10 MPa). Environmental leaching increased for certain metal(loid)s and SO_4 due to oxyanion formation during the Zn slag alkaline activation, with further increases with silicate-based solutions. Conversely, Ba, Pb, and Zn showed immobilization, which was likely due to inclusion in the C-S-H matrix or the formation of additional silicate phases. Fe-rich AAMs from wüstite- and fayalite-bearing slags were evaluated for high-temperature applications up to 1000ºC. Compressive strength exhibited fluctuations up to 400ºC due to water evaporation, followed by a drop to 25 MPa at 600ºC due to gel structure collapse and subsequent strengthening to 50 MPa above 600ºC, accompanied by ceramic formation. Tests were conducted to assess the effect of incorporating ladle slag (LS) and blast furnace slag (BFS) as co-binders on the fresh and hardened state properties of geopolymer mortars. The addition of LS or BFS increased its reactivity and consequently increased the compressive strength. The addition of LS or BFS increased the mechanical properties and thermal stability of the samples. Blended mortars exhibited superior thermal stability, higher residual mechanical properties, fewer voids and cracks, and a denser microstructure than solely FS-based mortars.

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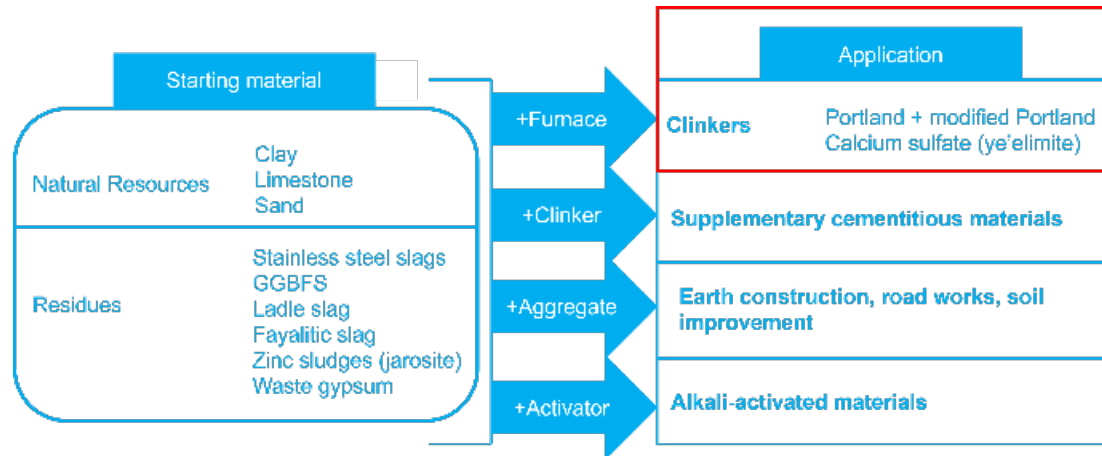
TASK
3.7
PRODUCTION OF CSAB CEMENT

Figure 40. Schema of the production of calcium sulfoaluminate (CSA) and OPC clinkers from industrial by-products.

INTRODUCTION

The bulk of the traditional Portland cement (OPC) industry's environmental burden is from the calcareous source. Calcium is mostly available naturally as limestone ($CaCO_3$), where almost half of the mass is eventually released as CO_2 during clinker manufacture. Iron (Fe) rich materials are potential raw materials for alternative types of cement to replace OPC. Future studies to improve the knowledge of how to utilize high iron-containing slag (such as steelmaking slag) in cement manufacture and how to improve the reactivity of iron-bearing cement phases are suggested. The possible utilization of steelmaking slag and other byproducts can include altered PC (Portland cement), ye'elimite, and belite cements with increasing ferrite (C4AF) content. When industrial byproducts are utilized as raw materials, the raw materials must be available locally to avoid long and expensive logistics, valuable compounds (V, Fe, Cr etc.) should be removed from the byproducts before use, and the environmental risks need to be assessed. The utilization of iron-rich by-products from metallurgical industries was studied as raw materials to replace virgin raw materials in cement production. The status of the research and most effective way to utilize industrial by-products were studied in a review publication titled "Sustainable iron-rich cements: Raw material sources and binder types" that was published in cement and concrete research. To be feasible to produced commercially CSA type of cements require alumina containing locally available raw materials. During the early stages of research, it was found that in Finland there existed some potential alumina sources such as alumina dregs/dross, ladle slag and natural clay. However, the availability, impurities and nature for example water content were challenging for CSA cement production. The goal of the study was to increase the amount

of iron in the clinker recipe so that more iron-rich slag can be utilized. It was decided that it would be more convenient to first increase the amount of iron in conventional OPC types of clinkers instead of CSA clinker systems. The main objective was then to enhance the hydration properties of brownmillerite in these already-known systems. The clinker phase composition was adjusted to contain more iron-rich phases, among which the most common is brownmillerite (C4AF), also commonly known as the ferrite phase in cement. Brownmillerite is less reactive in the presence of gypsum than tricalcium aluminate and alite phases, and cements with a high ferrite content generally show a slower early-age strength gain. Additives such as tertiary alkanolamines can catalyze the ferrite hydration after the sulfate depletion point. Another potential way to accelerate the ferrite reactivity is to use a gypsum-less system, where a mix of hydrolyzable alkali metal salt and a superplasticizer with a hydroxyl group is used. Sodium carbonate or soda ash is such a hydrolyzable alkali metal salt that can react with calcium ions dissolving from ferrite to form calcium carbonate, which reduces the calcium ion concentration in the solution and on the surface of the ferrite, increasing the dissolution rate and reactivity. Sodium carbonate addition precipitates calcium carbonate with directional crystalline growth with a large number of interspaces, which does not restrict ion and water transport, and continues the hydration reaction. As the addition of soda ash has already been proven to accelerate the hydration of ferrite, using soda ash to accelerate the hydration of ferrite-rich clinker is promising. Another way to improve the hydration of the C4AF phase in OPC cement systems is to carbonate it during the fresh state. The mechanism is the same as with soda ash addition since the CO_2 gas atmosphere improves $CaCO_3$ formation at the early age of hydration.

MATERIALS AND METHODS

Study 1) Two pure ferrite phases with formula C4(AxF2-x), where x= 1 and x=0.5, were produced in a muffle furnace and their mineralogy was analyzed with XRD. Hydration products of C4AF and C4A0.5F1.5 with and without gypsum additions were studied after 7 days of curing and the crystalline phases were analyzed with XRD-analysis. Study 2) EAF and slag were used as an ideal alternative feedstock for modified OPC clinker. First, the effect of gypsum and limestone additions on hydration and strength properties was tested and then in the next steps the effect of dissolved Na_2CO_3 and CO_2 atmosphere on hydration was studied. The raw materials and produced clinkers were studied using optical microscopy, XRD, XRF, and FESEM-EDS analysis. The clinkers were produced in a muffle furnace. The hydrated cement/concrete was studied using TGA/DTG, isothermal calorimetry, XRD and FESEM-EDS.

RESULTS AND DISCUSSION

It was found that according to a Rietveld analysis, the C4AF sample produced had a brownmillerite content of 96.4 wt.%. The Rietveld analysis for C4A0.5F1.5 showed that when the iron content in the raw mix increased, brownmillerite was present as two polymorphs: idealic ferrite (C4AF) and iron-rich brownmillerite. Additionally, some calcium iron oxide (CF) was detected. It was found from the hydrated samples that the major hydration product was katoite which was in line with previous studies. With a gypsum addition the main hydration product was kuzelite (AFm) and ettringite was only present in sample C4A0.5F1.5 + CW + C\$H2. High iron-rich ferrite C4A0.5F1.5 had lower hydration rates with gypsum additions than C4AF. The findings for pure ferrite can be applied to both modified OPC and CSA systems. Alite-ferrite clinker was produced from EAF and BOF slag and pure natural materials at 1400–1450ºC. Slag is an ideal alternative feedstock for cement clinker preparation as the expected mineralogy of alite and ferrite was achieved. In hydration studies, firstly it was found that gypsum was a better additive for accelerating the hardening of the mix than limestone during the time analyzed; with better strength and early hours hardening. The hydra-

tion products observed using DTG were ettringite, calcium silicate hydrate, portlandite and carbonated phases. likely calcium carbonate, which was predominant in samples where $CaCO_3$ was used as an additive. The results show the potential of using these steelmaking residues as raw materials for cement and thus promoting a circular economy. In the second stage, hydration was studied in the presence of dissolved Na_2CO_3. We found that there is an optimum soda ash dosage (2.5% by mass of clinker for w/b = 0.35, and 5% by mass of clinker for w/b = 0.45) to accelerate the major alite hydration peak, as confirmed from the calorimetry data and the portlandite content indirectly observed from the XRD and TGA data. In the third stage, atmospheric carbonization was successfully used to enhance the strength of iron-rich modified OPC cement. If a suitable alumina-rich raw material for CSA cement production could be found, the findings of this study could be applied to enhance the ferrite hydration also in the case of CSA cements.

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TASK
3.8   HYDROGEN REDUCTION OF COBALT SAMPLES

INTRODUCTION

Hydrogen can be utilized as a reducing agent when high-purity metals are produced from their different compounds. The advantages of this process are low operating temperatures and the recovery of pure metal products without harmful by-products because the only liberated side product is water vapor. In this task, the aim was to investigate the kinetics of hydrogen reduction for different cobalt samples through laboratory-scale thermogravimetric experiments (TGA) and gain information about the mechanism occurring during reduction and the process parameters affecting the reduction phenomena. The derived data was fitted to different solid-state kinetic models to determine the most suitable model describing the reaction and kinetic parameters were calculated using the models found in the literature.
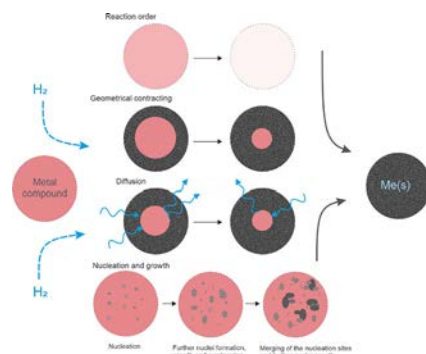
MATERIALS AND METHODS

The materials consisted of commercially available Co samples $CoCO_3$, $Co(OH)_2$, and $Co-C_2O_4$ (Alfa Aesar) and a selection of Co samples provided by Jervois Oy. The reduction test was carried out with a Netzsch STA 449 F3 coupled with a mass spectrometer and heating was done in an inert gas (Ar). In the first stage, the samples (100 mg) were reduced non-isothermally with 5% H_2 from room temperature to 900 °C (40 °C/min). In the second stage, isothermal 10% H_2 reduction experiments were carried out at three constant temperatures 300, 400, and 500 °C. Isothermal data was used to determine the kinetic parameters (Ea, k) and for the analysis of suitable kinetic models. The metallic cobalt products were analyzed using FESEM (Zeiss Sigma). Thermodynamic modeling of the different Co compounds was carried out using HSC Chemistry software.

Table V. Experimental values

Temperature °C	Holding time (h)	Gas composition	Heating rate	Heating gas	Cooling rate	Cooling gas
300	1	10 % H_2 + Ar	20 °C/min	Ar	40 °C/min	Ar
400	1	10 % H_2 + Ar	20 °C/min	Ar	40 °C/min	Ar
500	1	10 % H_2 + Ar	20 °C/min	Ar	40 °C/min	Ar

## RESULTS AND DISCUSSION

The non-isothermal experiments revealed that there are at least two stages in the reduction cycle of $CoCO_3$ and $Co(OH)_2$. In the first state, the compound decomposes to cobalt oxide (CO_3O_4 or CoO) when the temperature is raised above 200 °C. This occurs before the actual reduction and reaction with H_2. The reduction starts around 300 °C and at lower operating temperatures the reduction overlaps with decomposition reactions. All the samples were reduced to metallic cobalt even at the lowest temperature within the 1-hour reduction period. When the temperature was raised to 400 and 500 °C, the conversion rate of all Co compounds to metallic Co increased significantly. The best fit from the solid-state kinetic models was concluded to be geometrical contracting models R2 and R3 and nucleation (Avrami-Erofe'ev) models AE1 and AE2 although the fit of the expected conversion to the experimental data was only satisfactory. Especially in the lower temperature range (300 °C), none of the models fit the experimental data well. The calculated activation energy values for H_2 reduction of $CoCO_2$, $Co(OH)_2$, and Co_3O_4 were between 5–70 kJ/mol, 15–32 k/mol, and 35–45 kJ/mol, respectively. The variation between Ea-values is due to different Co-contents of the sample so that lower content value gives lower E_a-values.

More investigation about the mechanisms and effects of different process parameters (temperature, H_2 flow, heating rate) and sample characteristics (particle size and morphology) is required to fully understand the mechanisms behind the reaction. These results gave good insight into the matter and the research will be continuing in the future.
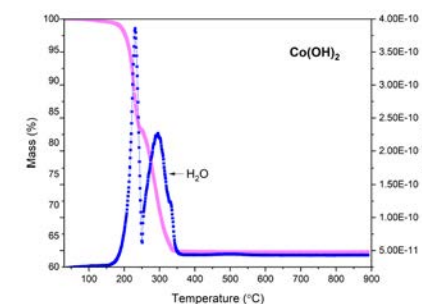
Non-isothermal conversion curve for $Co(OH)_2$
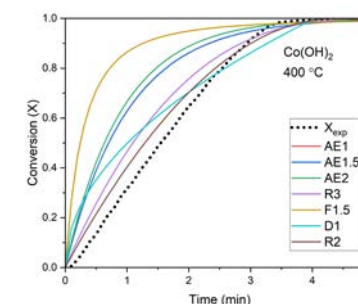
Model predictions for H_2 reduction of $Co(OH)_2$ at 400 °C
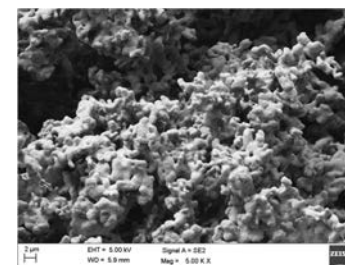
FESEM image of Co product reduced non-isothermally from $CoCO_3$
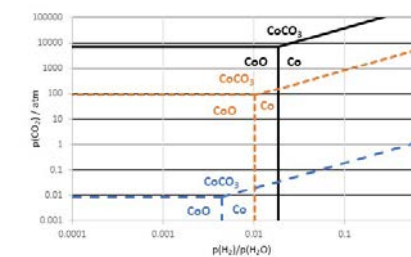
Phase diagram for Co-C-O-H system in temperatures 100, 300 and 500 °C

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TOCANEM

FINAL REPORT 01/2024

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TASK
3.9

CIRCULAR ECONOMY RELATED TO METAL-CONTAINING MATERIAL FLOWS

INTRODUCTION

In this task, metal recovery from secondary material flows is studied. These included spent catalysts, hard metal waste fractions, and cathode materials. Selective leaching was done, and the leaching conditions (e.g. leaching agent, temperature) were optimized with the aim of achieving a high yield of valuable metals. The kinetics and thermodynamics of the leaching were studied. Analytics were developed for the challenging sample matrix (Karppinen 2023).

MATERIALS AND METHODS

Analytical methods were developed for recycled materials based on melting receipts, and the challenge was the lack of a suitable reference method. The obtained melts were measured by X-ray fluorescence (XRF) and after leaching using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and the results were compared. A leaching column (Fig. 41) was used in the leaching experiments. The challenge was the heterogenous nature of materials containing metallic, sulfidic, and oxide phases (see Fig. 41).
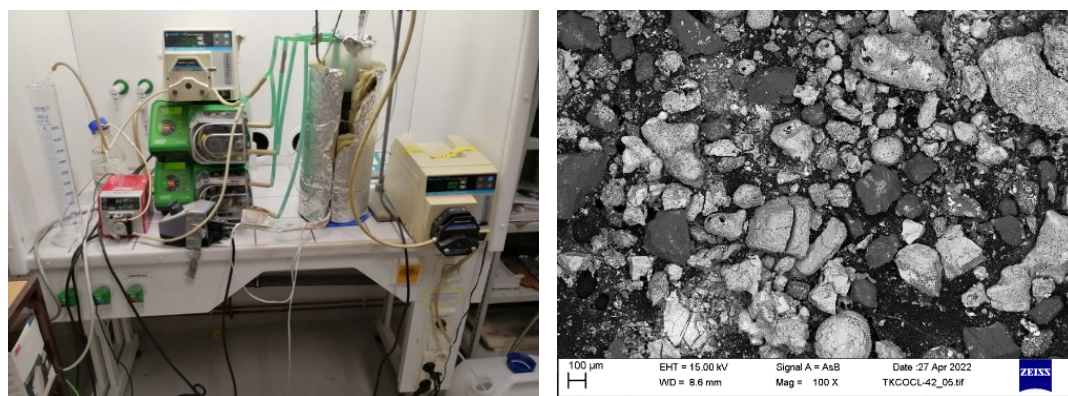

Figure 41. Leaching column (left) and SEM image of heterogenous Co-containing recycled material (right).

Column leaching was done under acidic leaching conditions in the presence/absence of an oxidizing agent. The acid and oxidant concentrations were optimized. Temperature, pH, flow rates, and redox potential were followed during the leaching experiments (Tynjälä et al. 2023). The total leaching time was dependent on the sample but was typically a few hours.

RESULTS AND DISCUSSION

The development of analytical method(s) was successful, but challenging, for these samples. The mass balance was not correct at the beginning of experiments due to the unleached material for chemical analysis. Sample processing was done using three different approaches. Phase identification was done by XRD, and based on that, the leaching receipt was developed. Parallel melts were done in nickel and zirconium cups which were used for XRF, and microwave digested samples were analyzed by ICP-OES. The combination of these three approaches gave accurate enough elemental analysis of samples (Karppinen 2023). The method developed was further used in the project. During the leaching high recoveries for Co were obtained. In most cases, leaching was also selective. For metallic phases, the role of oxidizing agent (e.g., oxygen gas) and acid concentration (1–1.5 mol/L) was important. It also enabled the use of lower leaching temperatures. Leaching was possible when the redox potential was high enough (>400 mV) confirming the presence of oxidizing conditions. If this was not valid, leaching stopped and the surface of the material passivated. Thus, without a leaching agent the leaching of metallic phases was not possible, or the leaching rates were very low.
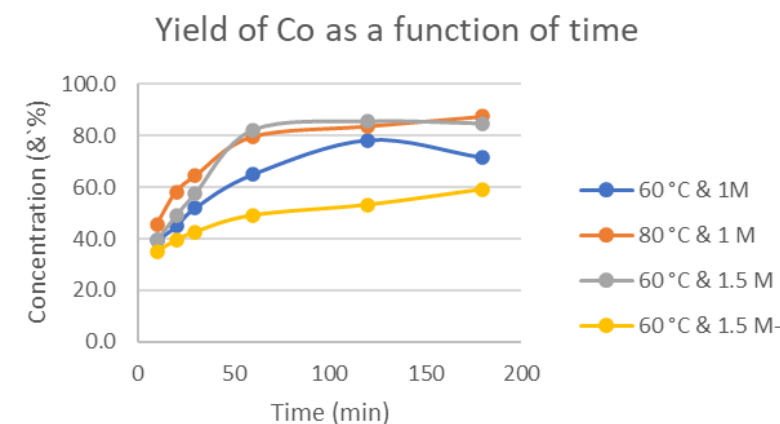

Figure 42. Yield of cobalt in the acidic leaching experiments from Co-containing recycled material (1.5 M- is done without oxidant).

PUBLICATIONS

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TASK
3.10 CHEMICAL PRECIPITATION

INTRODUCTION

Concentrated recycled metal solutions were used for batch, semi-batch, and continuous flow chemical (co)precipitation experiments. Precipitation parameters (pH, T, time, concentrations, additives for precipitation, agitation rate) are studied. Depending on the quality requirements of the final precipitate, some additives and doping agents can be used in the precipitation. Physical and chemical properties of cobalt precipitates are characterized using e.g. specific surface area, apparent density, residue metal concentration, particle size, XRD, FIB-FESEM, EFTEM, Raman, and EPMA. Further, mass balances are considered.

MATERIALS AND METHODS

Metal solutions from leaching experiments were used for precipitation. These metals were precipitated as carbonates or as hydroxides from concentrated, typically sulfate solutions. In these experiments, the aim was not only to recover metals but also to produce the precipitate, e.g. the battery precursor following the physical and chemical properties of the precipitate carefully. This decreases the steps for further processing.

Figure 43. Precipitation reactor. Also autoclave precipitations were done.

RESULTS AND DISCUSSION

Recycled solutions worked well in the precipitation reactions. The most important aspect is to keep solutions concentrated. The growth of the particle size was followed during the precipitation. In these experiments the growth of secondary particles especially determines the quality of the precipitate. Most of the impurities (except alkaline metals) from the recycled solutions precipitated to a large extent. These impurities had a minor effect during the precipitation reactions, but affected the further use of precipitate. Impurities were determined by ICP-OES and by elemental mapping (EPMA).
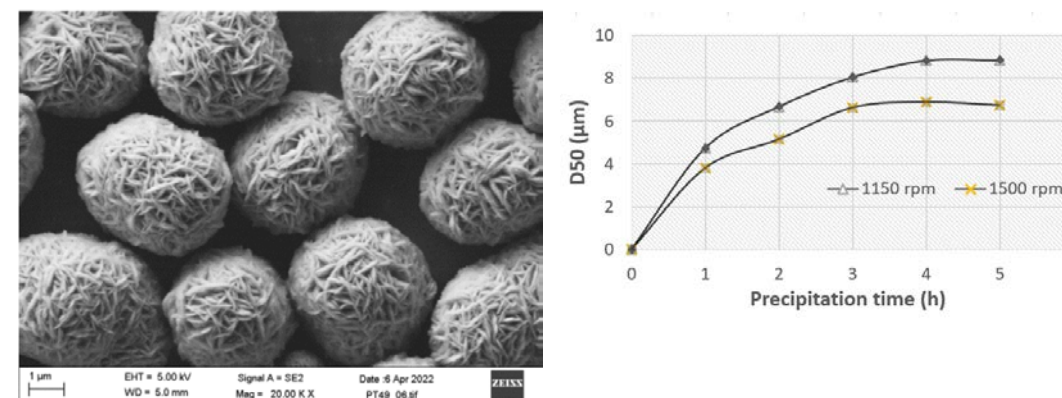
Figure 44. Precipitated hydroxides from recycled solutions and the growth of particle as a function of precipitation time (Tynjälä et al. 2022).

To conclude, when recycled materials are used, the most important thing is to recover elements directly in the form they can be utilized in. In this research, metal sulfate solutions were not crystallized because it is an energy-intensive approach and makes one extra step for the recovery value chain.

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Tynjälä. P., Laine P, Välikangas. J., Kauppinen T., Lassi U., (2022), Effect of process conditions on the co-precipitation of Ni(OH)$_2$ for LNO battery chemical, In: Ila, Mitra; Louhi-Kultanen, Marjatta , BIWIC 2022 : 27th International workshop on industrial crystallization : 31 August – 2 September, 2022, pp. 59-63.

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TASK
3.11 KINETICS AND THERMODYNAMICS OF CONCENTRATED METAL SULFATE SOLUTIONS

INTRODUCTION

Various thermodynamic properties of industrially relevant aqueous metal sulfate systems were determined experimentally, using both commercial and custom-built apparatuses available at the University of Oulu and our collaborators, namely Aalto University and Murdoch University (Fig. 45). These data were combined with the various literature data to yield a comprehensive model for the thermodynamic properties of complex solutions containing different metal sulfates and sulfuric acid.

MATERIALS AND METHODS

Stock solutions of the desired metal sulfate were always prepared from a commercial sample, crystallized from pure water, and slightly acidified with sulfuric acid. Concentrations of the stock solutions were typically determined by two independent methods, e.g. evaporative gravimetry and complexometric titrations with a typical agreement of 0.1%. Density determinations were performed with both commercial (DMA 5000M, Anton Paar, Graz, Austria) and custom-built devices. Solubility determinations were performed with the purpose-built apparatus "Hedgehog 1" (Fig. 45a). Calorimetric determinations were performed with a commercial differential microcalorimeter (Model C80, Setaram, Lyon, France) (Fig. 45b).
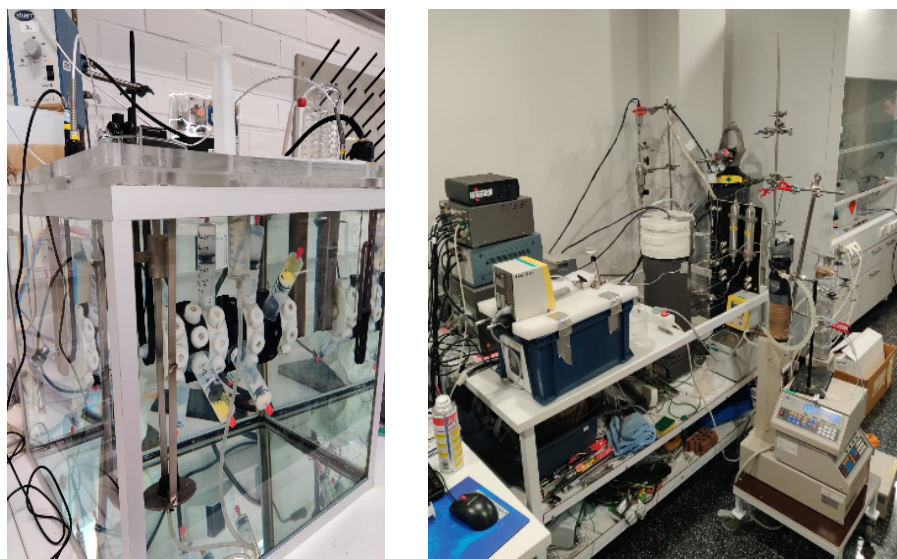
Figure 45. a) "Hedgehog 1", a purpose-built device for the accurate determination of solubilities.
b) C80 differential microcalorimeter set up for heat of dilution measurements.

RESULTS AND DISCUSSION

The newly determined experimental data and analysis of the various literature data highlight fundamental similarities between the different metal sulfates and suggest simple interactions between them in mixed solutions. For example, the molar volumes of the metal sulfates, calculated from the density determinations, show that apparent molar volumes of the mixed solutions can be linearly interpolated from the values for pure metal sulfate solutions. This kind of linear mixing is known as Young's rule. Similar behavior were observed also for the heat capacities of the metal sulfate solutions. These observations significantly simplify estimating the behavior of arbitrarily complex metal sulfate solutions at industrially relevant concentrations and conditions (e.g., Fig. 46).
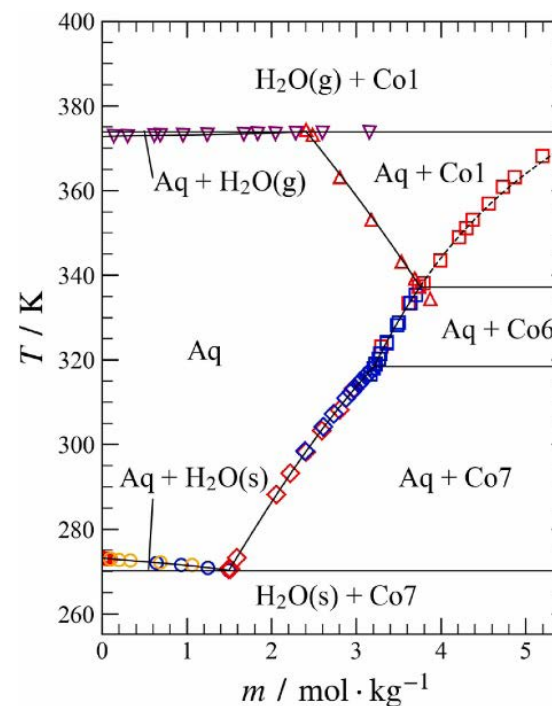
Figure 46. Isobaric phase diagram for the binary $CoSO_4 - H_2O$ system (Vielma 2021).

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Vielma, T., Hefter G., (2023), A critical review of the thermodynamic properties of industrially relevant aqueous metal sulfate solutions, manuscript.

TASK
3.12 LIFECYCLE ANALYSIS OF COBALT PROCESSING

Figure 47. The systems studied for hard metal chemical recycling. SX stands for solvent extraction and APT for ammonium paratungstate.

INTRODUCTION

Cobalt is a critical metal, and its demand is projected to increase substantially due to the move towards electric mobility. Although the production o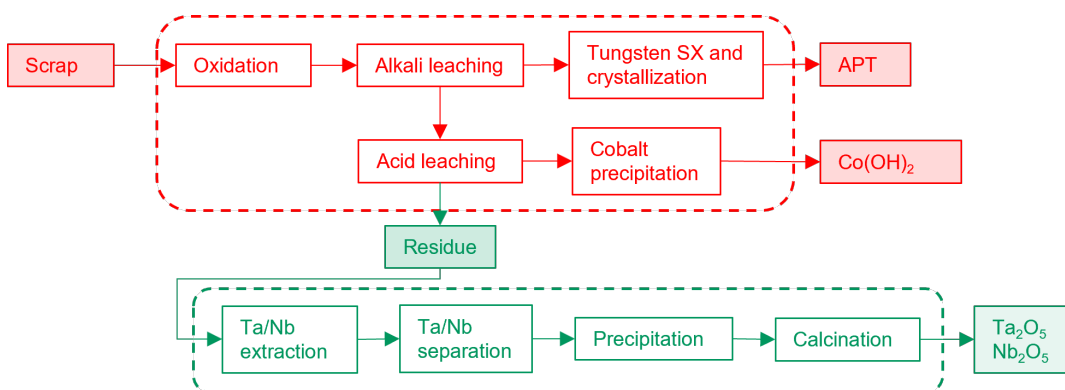f cobalt is geographically very concentrated and the EU is reliant on importation to supply the demand, the EU does have some stocks of cobalt in the form of secondary raw materials. These include materials such as post-consumer batteries, hard metal scrap, superalloy scrap, and spent catalysts. Secondary materials vary in composition but often contain valuable metals in higher concentrations than their ores. However, they also typically contain many valuable metals which can be recovered in recycling processes. When studying the environmental impacts of just one of these metals, the environmental load produced must be shared between all the produced products. Cobalt, due to the previously mentioned factors, makes for a useful and interesting case study to develop information on sharing the environmental load between co-products in life cycle assessments (LCAs) of metal refining processes.

MATERIALS AND METHODS

Three LCAs were performed for two cobalt-containing raw materials, hard metal scrap, and a spent cobalt catalyst. The life cycle inventory (LCI) data that formed the basis of the life cycle impact assessment (LCIA) was gathered using process simulation. Simulations of the recycling processes were done in the Sim-module of HSC Chemistry 10 and the LCI was calculated based on mass and energy balances. The LCIA was performed in GaBi LCA software and using the ReCiPe 2016 (H) impact assessment method. The largest contributors were identified from the different unit processes and/or the chemicals and utilities consumed in the processes. The results on the environmental impacts of the recycling processes were compared to the environmental impacts of producing equivalent products from primary raw materials.

RESULTS AND DISCUSSION

The results showed that for the most part, the environmental impacts of the hydrometallurgical recycling processes originated from the background processes, i.e. the chemicals and utilities consumed in the processes. Often a limited number of the consumed materials were responsible for a large share of the total environmental impacts, providing information on where process development may be most beneficial for reducing the potential impacts. In comparison to production from primary raw materials, recycling performed better environmentally. The benefit was partly dependent on the composition of the raw material with increasing shares of valuable metals reducing the impacts. The impacts of recycling tungsten and cobalt from hard metal were below 50% of primary production values in all the investigated impact categories. For tantalum and niobium environmental benefits were only evident for relatively high concentrations in the raw material. Using different allocation schemes for the results showed that the allocation key and method chosen can have a clear impact on how the environmental load is shared between co-products. Economic allocation should only be used if the price difference of the products is substantial. Subdivision of the process as far as possible (e.g. through process simulation) to achieve monofunctional unit processes is necessary to achieve an accurate result.
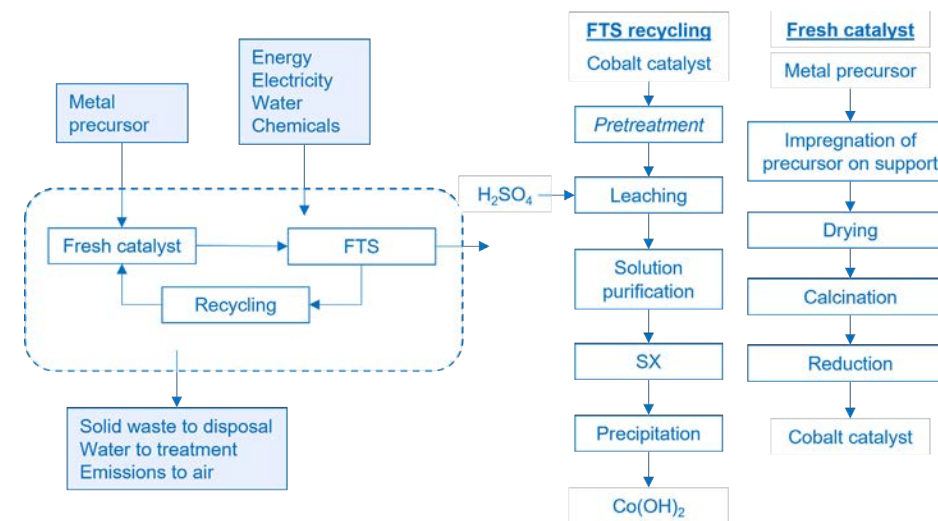
Figure 48. The systems studied for spent cobalt catalyst recycling. FTS stands for Fischer-Tropsch synthesis and SX for solvent extraction.

PUBLICATIONS

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TASK
3.13 RECOVERY OF VALUABLE METALS FROM INDUSTRIAL SIDE STREAMS AND SECONDARY RAW MATERIALS IN COBALT PLANT

INTRODUCTION

A large volume of waste solutions, called side streams, are generated during the hydrometallurgical processes, which contain valuable metals and acids. Valorization of industrial side-streams maximizes resource recovery, reduces costs, and minimizes negative environmental effects. In this study, cobalt and oxalic acid were considered to have high potential for recovery with the solvent extraction method.

MATERIALS AND METHODS

A synthetic aqueous solution containing 10.2 g l–1 oxalic acid, 37.5 g l–1 hydrochloric acid, and 1.1 g l–1 cobalt, and tri-butyl phosphate (TBP), a commercial mixture of trialkyl phosphine oxides with n-octyl and n-hexyl groups (CYANEX 923), trioctylmethylammonium chloride (Aliquat 336), and trioctylamine (TOA) as organic reagents diluted with Exxsol D80 were used in solvent extraction experiments. Additionally, screening experiments for cobalt extraction were conducted with saponified D2EHPA and CYANEX 272 as acidic reagents and the same abovementioned low chloride solution. Moreover, Aliquat 336, TOA, and Alamine 304 were used as amine reagents from high chloride solution. TBP, 1-decanol, and m-xylene were used as modifiers for amine reagents to eliminate the third phase. All extraction experiments were conducted in separatory funnels using a laboratory shaker. Subsequently the raffinates were analyzed with ion chromatography (Schimadzu, Shodex IC SI-50 4E) and an atomic adsorption spectrometer (AAS, Thermo Scientific, iCE 3000) for determining the concentration of acids and cobalt, respectively.

RESULTS AND DISCUSSION

The screening solvent extraction experiments were conducted at a temperature of 20 ± 1 °C, with an equilibration time of 30 minutes and an organic-to-aqueous (O/A) ratio of 1:1. The results indicated that TBP, CYANEX 923, and Aliquat 336 exhibited promising affinity for the extraction of oxalic acid, with separation factors of 46.40, 204.70, and 30.71, respectively. TBP and CYANEX 923 achieved rapid extraction, reaching equilibrium within 1 minute, while Aliquat 336 had a slower reaction rate, requiring 30 minutes to reach equilibrium. Furthermore, the findings revealed that increasing the temperature led to enhanced oxalic acid extraction with CYANEX 923 and Aliquat 336 but reduced the extraction efficiency with TBP. Increasing the solvent concentration improved the effectiveness of extracting oxalic acid in all three solvent systems. Considering the co-extraction of hydrochloric acid and the required phase disengagement time, the optimum organic system for loading and stripping isotherm studies (Figure 49) consisted of 1.83 M TBP, 0.25 M CYANEX 923, and 1.09 M Aliquat 336. McCabe-Thiele diagrams demonstrated that the extraction efficiencies of oxalic acid after three counter-current stages using these solvents were 96.2%, 93.4%, and 88.2%, respectively. Additionally, the stripping isotherm results indicated that after four counter-current stripping stages, 95.5%, 88.4%, and 89.1% of the oxalic acid could be stripped from TBP, CYANEX 923, and Aliquat 336, respectively. Overall, the equilibrium experiments determined that 1.83 M TBP was the most effective solvent reagent for oxalic acid recovery. The results showed that over 99% of oxalic acid could be extracted through

four stages from the feed solution at a temperature of 20 ± 1 °C, 1 minute of residence time in the mixer, and an O/A ratio of 1:1. Under these conditions, the co-extraction of hydrochloric acid and cobalt was 14.7% and 5.1%, respectively. Additionally, 94.0% of the loaded oxalic acid could be stripped from TBP using pure water through four counter-current stages at a temperature of 20 ± 1 °C, an O/A ratio of 1:2, and 1 minute of residence time in the mixer. The developed process in this study achieved an overall recovery of oxalic acid of 93.35% with a purity of 98.55% from the feed solution containing hydrochloric acid. Besides oxalic acid recovery, screening experiments for the solvent extraction of cobalt with acidic and amine extractants were performed. The result showed that the extraction efficiency of cobalt was 98% (pHeq = 5) and 100% (pHeq = 7.5) from the aqueous solution ([HCl] = 1M) with 0.8 M D2EHPA and 0.8 M CYANEX 272 (saponified with NaOH), respectively. By increasing the chloride concentration up to 7M, amine extractants such as TOA, Aliquat 336, and Alamine 304 diluted in Exxsol D80 were used as reagents. Further, TBP, 1-decanol, and m-xylene were used as modifiers. The results showed that these amine reagents had a high affinity for cobalt extraction. The findings of screening experiments showed that 5 minutes was enough to reach equilibrium with all amine extractants. In addition, increasing the temperature did not affect the cobalt extraction efficiency with amine extractants.
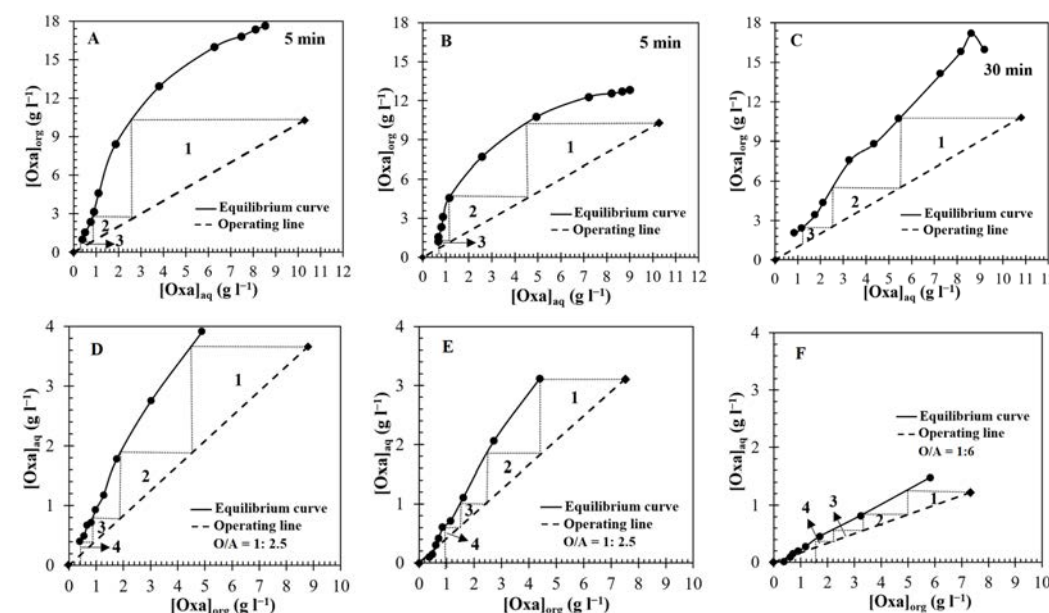
Figure 49. Oxalic acid loading (A, B, C) and stripping (D, E, F) isotherm experiments of A, D) 1.83M TBP, B, E), 0.25 M CYANEX 923 and C, F) 1.09 M Aliquat 336 at T = 20 ± 1 °C, O/A = 1:1, and 250 rpm shaking.

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Illia Tkalenko, AMCOM GROUP LLC

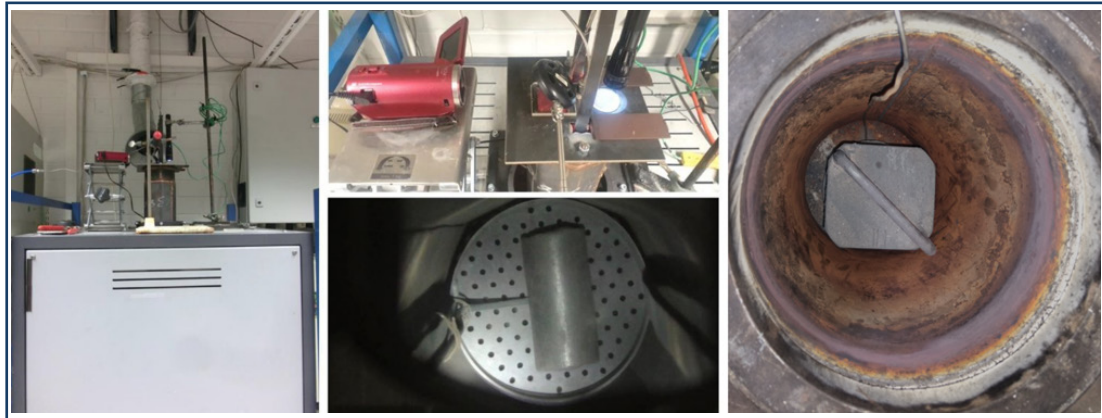| TASK 3.14 | METALLURGICAL PROPERTIES OF THE BRIQUETTES |

Figure 50. BFS and RUL setup. Left: view from front of the BFS; top middle: view from above the BFS; bottom middle: the BFS video camera image on tablet; right: RUL cylinder with a weight.

INTRODUCTION

The general task in this study was to evaluate the suitability of self-reducing auger pressing briquettes (APB), which are agglomerates manufactured using an extrusion-based briquetting technique, for blast furnace (BF) and electric arc furnace (EAF) use by considering the main metallurgical properties: reducibility, swelling and cracking. There are no standardized tests for briquettes.

MATERIALS AND METHODS

BF sludge, mill scale, and EAF dust, metallurgical by-products, were the main raw materials of the briquettes in addition to slaked lime, bentonite, and binders. Charcoal was added to some of the recipes as a reducing agent. Two non-standardized methods pictured in Figure 50 were used: blast furnace simulator (BFS) able to simulate the temperatures and gas atmospheres of the actual BF process, and reduction under load (RUL) able to simulate physical load at the same time giving information about sample plasticity. Iron ore pellets and industrial briquettes were used as reference samples. BFS was capable of simulating temperatures up to 1100 °C and RUL up to 1000 °C. A separate program with BFS was used to simulate EAF conditions. Mineralogical characterization was utilized to study phase transformations during the reduction experiments.

RESULTS AND DISCUSSION

Based on the results, auger pressing briquettes are a promising raw material for BF use from the perspective of metallurgical properties. No problems were found during the indus-

trial-scale BF trials. Adding biocarbon to the briquettes is a compromise between reducibility and strength properties because the briquette structure becomes plastic already with the addition of 4% biocarbon. Suitability for the EAF process requires further research.
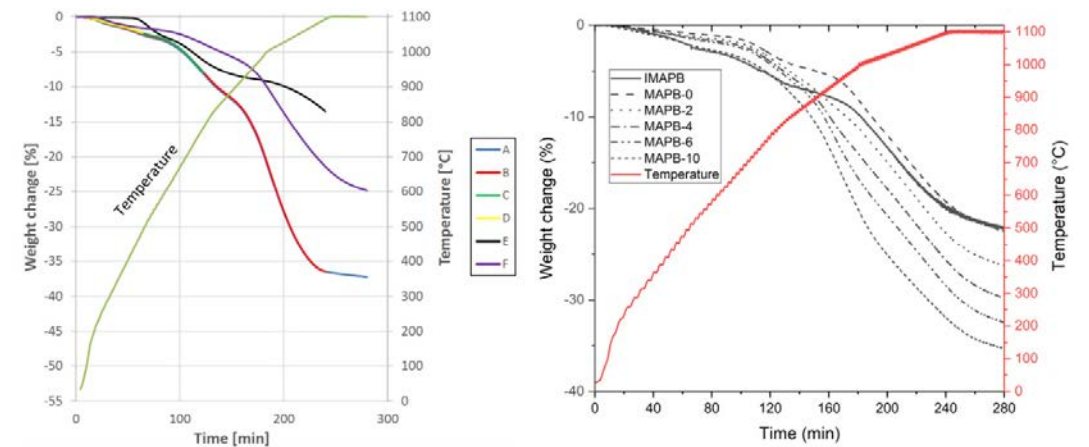

Figure 51. Results from BFS experiments. Left: weight loss results for APB (A-D) in different reduction experiments, where the aim was to reduce oxidic iron to either magnetite, wüstite or metallic iron, as well as tests for iron ore pellets and reference briquette (E and F); Right: weight loss results for industrial briquettes (IMAPB) and briquettes with biocarbon addition (MAPB-X).

PUBLICATIONS

Saroukhani, S., (2022), Analyzing mechanical strength and reducibility of auger pressing briquettes from steel plant by-products, master's thesis, University of Oulu.

Vitikka, O., Iljana, M., Heikkilä, A., Tkalenko, I., Koriuchev, N., Malkki, A. and Fabritius, T., (2022), Evaluation of the Suitability of Auger Pressing Briquettes for blast furnace use, presented on Sep 1st, 2022, at 8th ECIC & 9th ICSTI 2022 Congress.

Vitikka, O., (2021), High-temperature properties of auger pressing briquettes under simulated blast furnace conditions, master's thesis, University of Oulu.

Vitikka, O., Iljana, M., Heikkilä, A., Tkalenko, I., Koriuchev, N. Shehovsov, D., Malkki, A. and Fabritius, T., (2022), Suitability of Auger Pressing Briquettes for Blast Furnace Use Based on Laboratory Tests, Minerals, 12(7), 868.

Vitikka, O., Iljana, M., Heikkilä, A., Tkalenko, I., Malkki, A. and Fabritius, T., Effect of Biocarbon Addition on Metallurgical Properties of Mill Scale-Based Auger Pressing Briquettes, manuscript.

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TASK
3.15

METALLURGICAL TREATMENT OF IRON-CONTAINING SLAGS AND SLUDGES

INTRODUCTION

In this task, metallurgical treatment and metal recovery from secondary material flows were studied. These material flows include ferrous slag and sludges from industry. There are also side streams with fossil and renewable-based carbon as sources for reduction purposes. Thermal treatments were also used to pyrolyze renewable carbon for reduction purposes together with pyrometallurgical processing of metal-containing side streams. High temperature oxidation and reduction treatments were studied to improve metal yields and make metal recovery possible from secondary material flows. Selective leaching of slag and sludges was done, and the leaching conditions (e.g. leaching agent, L/S ratio, temperature, pH) were optimized with the aim of high yield of valuable metals. Obtained metal solutions were purified and metals were recovered by chemical precipitation. The kinetics and thermodynamics of leaching and precipitation were studied.

MATERIALS AND METHODS

Manganese sludge was provided by Fortum Waste Solutions. It was rich in manganese (~60 wt%) but also contained a few wt% of Co and Ni. Sludge was treated by ammonium sulfite reduction using the following reaction parameters: L/S = 10:1–5:1, T = 60–110 °C, SO_3: Mn = 1–1.5, and pH = 7–10. Further, as an alternative, Co/Ni removal (by leaching) was studied by water extraction, ammonium extraction without reduction, and acid extraction instead of ammonium reduction. The yields of cobalt and nickel were determined by AAS. Further, the decomposition of ammonium manganese sulfate was studied by TG, and the formation of ammonium manganese sulfate was eliminated by appropriate reaction conditions.

RESULTS AND DISCUSSION

Dried manganese sludge (23% moisture) and the results of the reduction experiments are shown in Fig 52. Pyrometallurgical reduction for the obtained MnO_2 sludge was done in the temperature range of 100–1100 °C in steps of 100 °C. As expected, the full reduction of material from MnO_2 to MnO is minor at lower temperatures. Additionally, a high cobalt content was still present after the reduction. In parallel to the reduction, leaching experiments for the MnO_2 sludge were done. Ammonium sulfite (see reaction conditions above) was used to leach out the Co and Ni in the solution with simultaneous reduction of manganese from Mn(IV) to Mn(II). One option studied was acid leaching or the use of an NH_3-NH_4-solution without the reductant, as described above. Based on the experiments, we proposed a reaction scheme (see Figure 53) for MnO_2 conversion to $Mn(OH)_2$ which would be possible, but which also unfortunately $Mn(OH)_2$ easily oxidizes. Therefore, a new direct conversion route for MnO_2 conversion to $MnCO_3$ was proposed (Kauppinen et al. 2023). As shown in Fig. 53, Co and Ni can be recovered by CO_2 precipitation. CO_2 gas acts both as a chemical reducing the pH and as a precipitant. The residue is an ammonium sulfate solution and

optional precipitation by NaOH. The high pH reduces the solubility of ammonia and precipitates Ni and Co as hydroxides. In this case, it would be feasible to coprecipitate these from the solution directly in the form of NMC by adjusting the Ni:Co:Mn ratios. The disadvantage is the remaining sodium sulfate solution. In the case of partial reduction of manganese, pyrometallurgical reduction is one option. The potential ammonium manganese sulfate can be reduced at 350 °C, and MnO can be converted to $Mn(OH)_2$ at 150–200 °C in an H_2O-H_2 atmosphere.
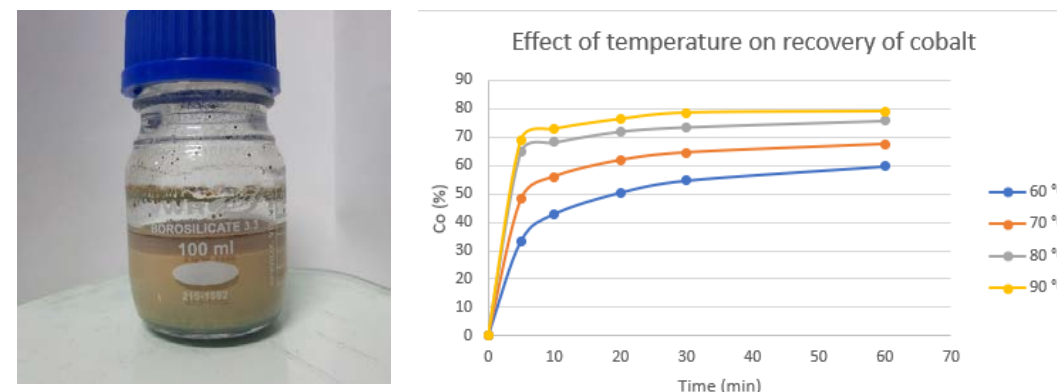

Figure 52. Dried MnO_2 sludge (moisture 23%) and effect of temperature for Co recovery at different temperatures.
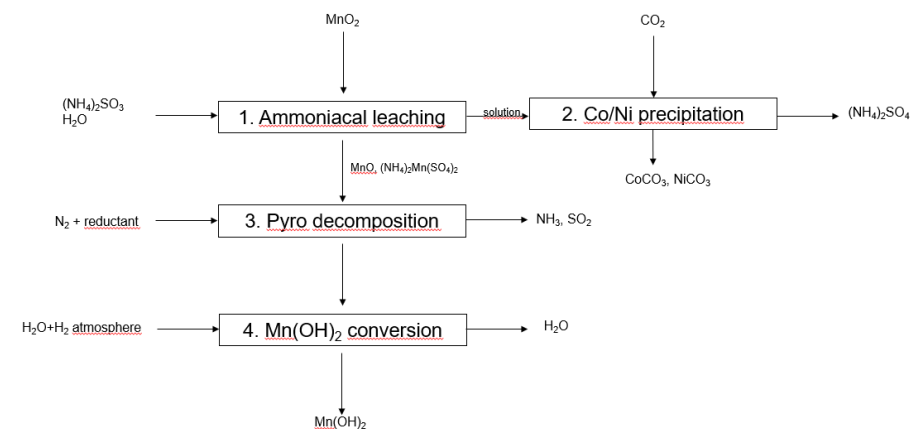

Figure 53. Proposed processing of MnO_2 to $Mn(OH)_2$.

PUBLICATIONS

Kauppinen, T., et al., (2023), Direct conversion of $Mn(OH)_2$ to $MnCO_3$, manuscript.

Contact persons
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Santeri Kurkinen, LUT University

TASK 3.16

ION EXCHANGE CHROMATOGRAPHY IN RECYCLING OF VALUABLE METALS
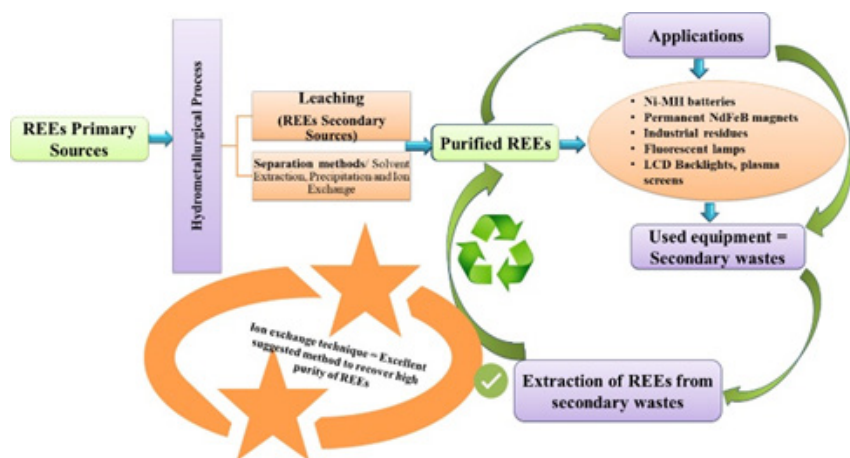

Figure 54. Ion exchange for the separation of rare earths from secondary resources.

INTRODUCTION

In this task, we undertook extensive research and experimentation on rare earth metals (REEs) and their recovery. This work is of paramount importance due to the near depletion of non-renewable primary sources of REEs from excessive global demand. Our focus shifted toward recycling secondary sources and developing effective separation materials. This report summarizes our significant progress in composite material development, selective REE recovery, and REE separation solutions.

MATERIALS AND METHODS

Our research encompassed several key steps and methodologies, including the synthesis of the innovative Gle@Na_Bex:y composite material via an in-situ hydrothermal route followed by freeze-drying, as well as the creation of the CoFeM@Be_IIM nanocomposite material, which combined adsorption capacity, magnetic separation performance ($CoFe_2O_4$), and ion-imprinted material separation selectivity. We further conducted a comprehensive characterization of the composite materials, utilizing various techniques. Additionally, the separation of REEs from an aqueous solution was used as a model system to demonstrate the material's ability for selective metal recovery. The best conditions (T, pH, time) for REE sorption were assessed using equilibrium batch adsorption experiments. Furthermore, molecular modeling techniques were employed to elucidate the sorption mechanism of rare earth element ions, significantly enhancing our understanding of the materials' performance and their potential applications in selective adsorption. Extraction of REEs from phosphogypsum matrix was achieved with commercially available chelating IX resins. The method used for extraction was the resin-in-leach (RIL) method, which allows selective and efficient recovery of REEs over impurities (excl. Iron). REE leachate was processed with conventional strong base anion (SBA) IX resins to separate elements from each other.
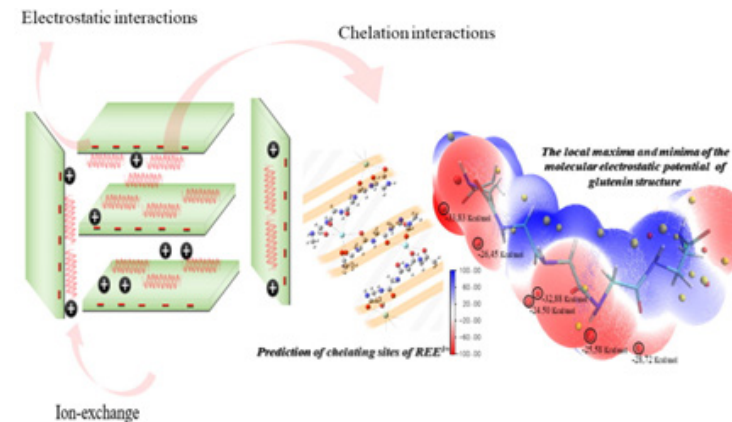

Figure 55. The arrangement of glutenin extracted and Na-bentonite in the Gle@Na_Be composite.

RESULTS AND DISCUSSION

In this task, we conducted extensive research and experimentation on rare earth metals (REEs) and their recovery due to their critical importance in modern industries and technological development. Consequently, our focus shifted toward the recycling of secondary sources and the development of effective separation materials. In this task, we achieved significant progress in composite material development by successfully synthesizing an innovative Gle@Na_Bex:y composite via an in-situ hydrothermal route followed by a freeze-drying process. A thorough characterization of the Gle@Na_Bex:y composites was carried out using a range of techniques, including FTIR, XRD, SEM-EDS, TGA, BET surface area analysis, and zeta potential measurements, all of which confirmed the successful integration of glutenin into the Na-bentonite clay matrix. This composite material exhibited remarkable potential for selective recovery of REEs, as exemplified by its efficient adsorption capacities, with a maximum of 76.87 mg/g for Y^{3+}, 56.71 mg/g for La^{3+}, and 74.61 mg/g for Nd^{3+}. Additionally, molecular modeling techniques were employed to elucidate the sorption mechanism of REE ions, enhancing our understanding of the material's performance and its promising prospects for REE removal. Additionally, in parallel with the above research, we conducted a separate study that yielded concrete results. We successfully obtained an REE leachate as a product from RIL extraction, boasting a purity level surpassing 98% and a concentration of 3.2 g/L. After separation steps with SBA resins, a Pr+Nd mixture with a purity of 96% was achieved.

PUBLICATIONS

El Ouardi, Y., Virolainen, S., Mouele, E.S.M., Laatikainen, M., Repo, E. and Laatikainen, K., (2023), The recent progress of ion exchange for the separation of rare earths from secondary resources–A review, Hydrometallurgy, 218, 106047.

El Ouardi, Y., Lamsayah, M., Butylina, S., Geng, S., Esmaeili, M., Giove, A., Mouele, E.S.M., Virolainen, S., El Barkany, S., Ouammou, A. and Repo, E., (2022), Sustainable composite material based on glutenin biopolymeric-clay for efficient separation of rare earth elements, Chemical Engineering Journal, 440, 135959.

El Ouardi, Y., A Sustainable Solution for Rare Earth Element Separation, 16th Annual International Conference on the Challenges in Environmental Science & Engineering CESE-2023 Conference (Perth, Australia), submitted.

Kurkinen, S., (2023), Chromatographic Separation of Rare Earth Elements as Anionic Complexes by Ion Exchange, ALTA 2023 Conference, oral presentation.

TASK
3.17

DEVELOPMENT OF A MATHEMATICAL MODEL FOR PREDICTING
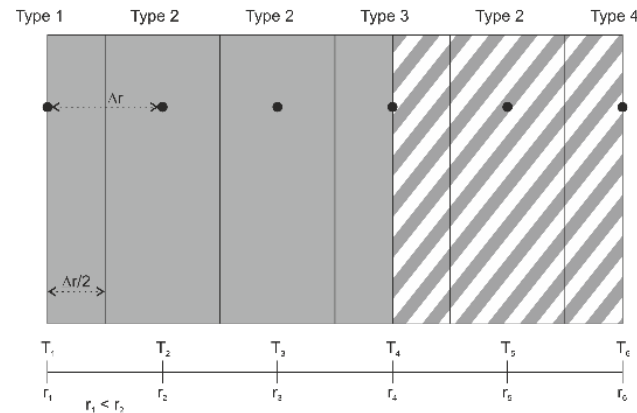THE THERMAL CONDITION AND HEAT CONTENT OF THE LADLES IN
STAINLESS STEELMAKING

Figure 56. Schematic example of the nodal structure of the model.

INTRODUCTION

The ladle thermal state significantly affects the temperature of tapped steel, in turn affecting the quality of the product, and possibly causing process disturbances, if not controlled properly. Understanding and controlling the ladle thermal state enables better control of the melt temperature during secondary steelmaking and the casting process. The aim of this task was to develop a fast one-dimensional mathematical model for the thermal state of a steelmaking ladle. The calculation domain was discretized using the finite difference method, and two time integration methods were implemented and compared. The model was implemented in the Python programming language for fast model development.

MATERIALS AND METHODS

In its calculations, the model considers the molten steel in the ladle as a single lumped capacitance while the ladle wall and top slag are divided into smaller nodes. The ladle bottom has not been considered in the current model. The nodal structure of the model is built using four different types of nodes, illustrated in the figure above. These nodes correspond to different parts of the ladle refractory wall, or the top slag. Type 1 nodes are the innermost nodes in contact with the melt, type 2 nodes are the bulk nodes consisting of a singular material, type 3 nodes are the boundary nodes where the refractory material changes, and type 4 nodes are the outermost nodes in contact with the outside air. Different nodes use different heat transfer and conservation equations.

The considered heat transfer mechanisms differ based on the location, and current processing step. While the ladle is empty, thermal radiation and convective heat transfer occurs on the inside and outside surfaces of the ladle wall, and during the filled period radiative and convective heat transfer occurs on the outside surface of the ladle wall and from the top of the slag.

The conductive heat transfer within the ladle wall and the slag differ slightly from each other, as due to its shape, the wall, uses equations derived for radial thermal conduction, and the slag uses equations derived for flat surfaces.

The one-dimensional temperature profile at the new time was solved using the Newton-Raphson method. For time integration, the implicit Euler and Crank-Nicolson methods were both implemented and compared.

RESULTS AND DISCUSSION

The two time integration methods were compared, and it was concluded that while the results of the Crank-Nicolson method were less affected by the used time-step size, the implicit Euler method, with small time-step sizes, produced practically identical results, was more stable and still fast enough for online-applications, and therefore the better of the two methods.

The model performance was validated using thermal imaging data collected by Sapotech at Outokumpu Stainless Oy, and by comparing the model with a previous model developed by Fredman & Saxén. Based on the thermal imaging data, it was concluded that while the model was unable to accurately predict the short-term temperature changes at the mantle, it could reproduce the main trends of the temperature evolution. When comparing the model with the one developed by Fredman & Saxén, the results suggested that the model generally reproduces the temperature profile of the wall well but slightly overestimates the refractory temperature at the outer layers, and during cooling underestimates the temperature at the inner layers. The first version of the model was presented in the master's thesis of Mäkelä (2022). The model and its validation were improved and adapted into a peer reviewed journal publication Mäkelä et. al. (2023).
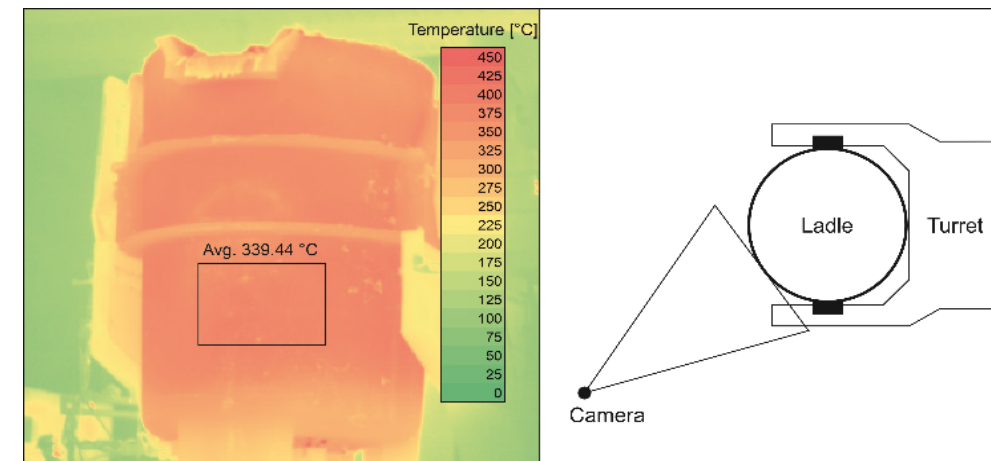

Figure 57. Thermal image of the ladle for qualitative validation of the mode.

PUBLICATIONS

Mäkelä, I., (2022), A mathematical model for the thermal state of a steel ladle, master's thesis, University of Oulu.

Mäkelä, I., Visuri, V.-V., Fabritius, T., 2023, A mathematical model for the thermal state of a steel ladle, Ironmaking & Steelmaking, 50(7): 867-877.

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Ulla Lassi, University of Oulu

TASK
3.18 CO_2 RECOVERY AND UTILIZATION IN CARBONATE PRECIPITATION

INTRODUCTION

In this task, CO_2 recovery from effluent gases in the steel industry was studied. The solubility of gas in selected wastewater fraction was first evaluated, and parameters (temperature, gas concentration, etc.) affecting the gas solubility were studied. Selective co-precipitation was done to recover metal carbonates from the wastewater solution. The precipitation conditions (e.g. precipitant, temperature) were optimized with the aim of obtaining a high yield of valuable metal carbonates. The kinetics and thermodynamics of the precipitation were studied. Overall, the total aim is to reduce CO_2 emissions in the steel industry.

MATERIALS AND METHODS

Industrial wastewater(s) were used (from the mining industry), containing Mg and Ca ions. Carbonates were first precipitated under pressurized conditions (which is not feasible for wastewater on an industrial scale) and then using a self-made system for atmospheric pressure precipitations (see Figure 58). In this, CO_2 gas was used as precipitant. It was introduced to the reactor through a 0.5-micron carbonation stone to confirm the uniform distribution of gas bubbles. The effects of the temperature, pH, gas flow rate, and initial concentration (~1400 ppm and ~500 ppm for Mg and Ca, respectively) were studied. The yield and purity of the metal carbonate and residue metal concentration were monitored.

Figure 58. Reactor for CO_2 precipitation experiments.

RESULTS AND DISCUSSION

Based on the results, all parameters have some effect on the precipitation. The temperature was optimized to maximize the yields. At pH 12, the residual metal concentration in the solution was < 10 ppm indicating high yields of carbonates. The purity was measured by X-ray diffraction, and this indicated the presence of several phases, i.e. the purity of precipitates was not as high as possible. The precipitation of mixed phases of Ca and Mg carbonates and hydroxides was observed. The precipitation time was also optimized to prevent back-leaching of magnesium. The gas flow rate was 1 L/min, which was found to be suitable for efficient precipitation.
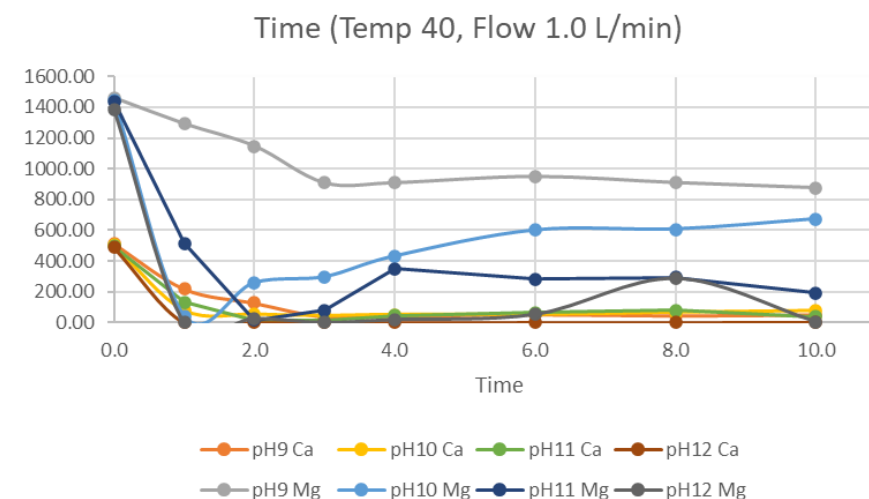

Figure 59. Effect of pH and precipitation time on the formation of Mg and Ca carbonates (Harju 2023).

PUBLICATIONS

Alm, E.-S., (2023), Hiilidioksidin liukoisuus ja metallikarbonaattien saostaminen, master's thesis, University of Oulu.

Harju, A., (2023), research project report.

INTERNATIONALIZATION

The TOCANEM research community has been well connected in the international scientific network with leading research institutes. As result of active international collaboration research exchanges, organized data transfer and joint publications have been arranged during the TOCANEM project despite the COVID pandemic. Additionally, funding has actively been applied regarding the research related to the TOCANEM project. Examples of projects that have already received funding include the HELIOS and H2PlasmaRed projects.

International collaboration in WP1

Collaboration	Type	TOCANEM RI(s)	Contact(s)	More information
KU Leuven	Research	University of Oulu, Outokumpu	Timo Fabritius, Ville-Valtteri Visuri	HELIOS; MSCA Doctoral Networks 2022 (HORIZON-MS-CA-2022-DN-01): European Training Network for the adoption of hydrogen metallurgy in the climateneutral production of steel with the following partners: KU Leuven, MUL, ArcelorMittal, Aperam, SSAB, Outokumpu, Voest-Alpine.
Max Planck Institute	Research/ Joint application	University of Oulu	Timo Fabritius, Henri Pauna, Ville-Valtteri Visuri	H2PlasmaRed, Horizon Europe proposal preparation, consortium members include MUL and RWTH Aachen.
Murdoch university, Australia	Exchange	LUT University	Sami Virolainen/NN	20220530: Now the visit is possible according to the current Covid situation. Looking for the visitor researcher.

International collaboration in WP2

Collaboration	Type	TOCANEM RI(s)	Contact(s)	More information
Witwaterstrand University, South Africa	Exchange	Aalto University, Boliden Kokkola	Mari Lundström	Exchange researcher from Wits university to Aalto; Samaneh Teimouri arrived in Finland (4-6/2022).
Jernkontoret	Seminar	University of Oulu	Timo Fabritius	SWE-FIN Biochar seminar 28.–29.9.2022
Nordic biochar network	Research	VTT	Esko Salo	Network building between the biochar network and RIs.
Biocarbon Task Group	Research	VTT, University of Oulu	Esko Salo, Aki Koskela	Standardization of biochar properties: international task group to define standards from different aspects of biochar usage and manufacture. Information sharing inside the consortium: common goals regarding the standardization of biochar (e.g., reductivity requirements) in, e.g., the metallurgical industry.
Orta Doğu Teknik Üniversitesi	Internship	University of Oulu	Tiina Laitinen/ Esa Muurinen	Intern Negar Sharifi.

International collaboration in WP3

Collaboration	Type	TOCANEM RI(s)	Contact(s)	More information
USTB, China	Exchange	University of Oulu	Yong Lin, Timo Fabritius	Exchange researcher Yong Lin from the University of Science and Technology of Beijing; a topic on pretreatments for slag in improving its recyclability, 10 months in the project. Funded by CSC.
EIT-raw materials	Research/education	Aalto University, Metso Outotec	Daniel Lindberg	Funding accepted! Course in LCA and thermodynamic calculations in battery chemical production.
Norwegian Research Council	Research/ Joint application	Aalto University	Daniel Lindberg	Research application regarding biochar usage in metals production, partners from Finland, Norway, and Austria.
Central South University (China)	Exchange	Aalto University	Riina Aromaa	Exchange researcher from Central South University, China; Tianxiang Nan.
Murdoch university, Australia	Research	University of Oulu	Tuomas Vielma/ Ulla Lassi	Exchange starting in fall 2022.
AMCOM Group LLC, USA	Research	University of Oulu, Kivisampo Oy	Mikko Iljana/ Timo Fabritius	AMCOM performs crushing strength tests for briquettes. Joint publication and HE application planned.
Nelson Mandela University	Research and Exchange	LUT University	Sami Virolainen, Katri Laatikainen, Youssef El Ouardi	Research collaboration in 2021-2022: joint publications, 1-2 mo research exchange by Dr. Youssef El Ouardi. 20220530: On hold due to geopolitical reasons.
University of Toulon	Research and Exchange	LUT University	Sami Virolainen, Katri Laatikainen, Youssef El Ouardi	Research collaboration ongoing in 2021-2022: joint publications, short visit in 2022 by Katri Laatikainen and Y. El Ouardi. 20220530: Dr. Laatikainen is no longer a fulltime employee at LUT and therefore the visit has not been done yet. Joint publication done.
Fez University (Morocco)	Research and Exchange	LUT University	Sami Virolainen, Katri Laatikainen, Youssef El Ouardi	Research collaboration in 2021-2022: joint publications, a short visit in 2022 by Katri Laatikainen and Y. El Ouardi. 20220530: Dr. Laatikainen is no longer a fulltime employee at LUT and therefore the visit has not been done yet.
University of Mohammed First (Morocco)	Research and Exchange	LUT University	Sami Virolainen, Katri Laatikainen, Youssef El Ouardi	Research collaboration in 2021-2022: joint publications, short visit in 2022 by Katri Laatikainen and Y. El Ouardi. 20220530: Dr. Laatikainen is no longer full-time employee at LUT and therefore the visit has not been done yet. Joint publication done.

Collaboration	Type	TOCANEM RI(s)	Contact(s)	More information
Luleå University of Technology	Research and Exchange	LUT University	Sami Virolainen, Katri Laatikainen, Youssef El Ouardi	Research collaboration ongoing in 2021-2022: joint publications. 20220530: Done.
Sidi Mohamed Ben Abdellah University (Morocco)	Research and Exchange	LUT University	Sami Virolainen, Katri Laatikainen, Youssef El Ouardi	Research collaboration in 2021-2022: joint publications, a short visit in 2022 by Katri Laatikainen and Y. El Ouardi. 20220530: Dr. Laatikainen is no longer a fulltime employee at LUT and therefore the visit has not been done yet. Joint publication done.
Ecole Polytechnique de Montreal	Exchange	Aalto University	Daniel Lindberg	
Lawrence Livermore National Laboratory	Research and Exchange	VTT, M:O	Anssi Laukkanen	
Collaboration	Type	TOCANEM RI(s)	Contact(s)	More information
Bundesanstalt für Materialforschung und -prüfung	Research and Exchange	Åbo Akad-emi	Leena Hupa	Short visits and longer visits for performing experiments.
ITB Bandung, Indonesia	Exchange	Aalto University	Ari Jokilaakso	Exchange researcher from ITB, Indonesia, Fauzy Risky.
Sustainable Materials Management, VITO, Belgium	Research	University of Oulu	Visa Isteri/ Katja Ohenoja	Joint publications during the project.
Department of Materials Science and Engineering, The University of Sheffield, UK	Exchange	University of Oulu	Visa Isteri/ Katja Ohenoja	
Department of Materials and Chemistry, Vrije Universiteit Brussel, Brussels, Belgium	Research	University of Oulu	Visa Isteri/ Katja Ohenoja	Joint publications during the project.
LTU Sweden	Research/Joint application	University of Oulu	Toni Kauppinen/ Ulla Lassi	ERA-NET Joint application: Co-recovery from recyclable materials, rejected on a technicality, resubmitted in 2022.

EU MATTERS REGARDING TOCANEM

The TOCANEM project has a multitude of different types of collaboration in Europe. The university of Oulu has collaboration with VTT to determine standardization for biocarbon manufacture and usage, the first milestone being on metallurgical use. Collaboration between the partners forms the biocarbon task group. There will also be a course held at Aalto University about LCA and thermodynamic calculations in battery chemical production, which is a collaboration between Aalto University and EIT RawMaterials.

There are numerous project applications from universities. Examples of these include an application regarding biochar usage in metals production from the Norwegian research council and the ERA-NET joint application between the University of Oulu and LTU Sweden on the topic Co recovery from recyclable materials. Joint research is done also with VITO Belgium, Vrije Universiteit Brussel, and the University of Oulu on Geopolymer and CSAB cement research. The University of Oulu has also submitted research applications to Opti-MCE (EU RFCS): RWTH Aachen, DEW, Celsa.

There are numerous different big international projects that have already begun or are planned to start during the year 2024. As an example, four projects (Sus4Planet, TWIN-GHY, Helios and H2PlasmaRed) mainly focusing on hydrogen metallurgy are described in the following tables.

Digital TWINs for Green Hydrogen transition in steel industry

Acronym	TWINGHY	Partners	CELSA, Barna Steel, Fives Steel, Nippon Gases, Barcelona Supercomputing Center, RWTH Aachen University, University of Oulu, Calderys, Swerim Ab, and SSAB EMEA.
Budget (University of Oulu)	296,270 €	Funder	European Union; Research Fund for Coal and Steel
Budget (total)	9,040,000 €	Timeframe	01.01.2023–30.06.2027

Description

TWINGHY will demonstrate an optimized heat transfer process based on hybrid burners in reheating furnaces, progressively decarbonizing the reheating process through the increase of H_2 in combination with O_2 and by monitoring and controlling it through a digital twin. Two types of hybrid natural gas–hydrogen burners will be developed: one based on air and the other one on oxy-combustion. They will be integrated into an operational industrial-scale reheating furnace demonstrator. To support that transition to hydrogen, a digital twin methodology will be developed and applied to the demonstrator and a replication site. In parallel, a physics-based model will be created and validated on both sites too. The performances of both digital approaches will be compared. From the successful implementation of these actions, TWINGHY will contribute to the synergetic green and digital transitions of the steel industry. It will help bring about significant CO_2 emission reductions while also saving energy and maintaining low NO_x emissions. The TWINGHY solution is designed to be adapted to existing steel industry furnaces that still have a long lifespan ahead, avoiding the need to replace the whole furnace, therefore saving resources. Moreover, the predictions from the advanced digital tools will facilitate the smoothness of the transition, thus allowing for it to be done without disturbing production.

The activities at the University of Oulu focus on studying differences in oxide formation amounts/rates and morphologies between current heating practices for select steels and proposed improvements incorporating hydrogen as a fuel and oxy-combustion. A reference oxide formation database for selected steels will be formed based on the current practice of natural gas burning with air. Using different burner practices with the aim of GHG reductions from the reheating process, a comparative dataset in relation to the oxide scale formation amounts will be formed and compared to the reference case. Based on the results, information on which steel types are most prone to high changes to oxide formation during the switch to greener heating practices will be formed. The results will also allow us to gauge whether the current descaling processes are adequate to remove the oxide scale before rolling in the case of a furnace fueled by hydrogen.

Hydrogen plasma reduction for steelmaking and circular economy

Acronym	H2PlasmaRed	Partners	MUL and RWTH Aachen
Budget (University of Oulu)	969,675 €	Funder	Horizon Europe - IA
Budget (total)	N/A	Timeframe	01.01.2024–31.12.2028

Description

Our ambition is to introduce a near CO_2-free reduction process to support the goal of the Paris Agreement—a 90% reduction in the carbon intensity of steel production by 2050. To achieve this, H2PlasmaRed will develop HPSR from TRL5 to TRL7 by demonstrating the HPSR in a pilot-HPSR reactor (hundred-kilogram-scale) that is an integrated part of a steel plant, and in a pilot-scale DC electric arc furnace (5-ton scale) by retrofitting the existing furnace. The project's end goal is to establish a way to upscale the process from the pilot-scale to industrial practice. To support this goal, the novel sensors and models developed and implemented in the project are used for HPSR process optimization from a reduction, resource, and energy efficiency standpoint.

Doctoral Network on the adoption of Hydrogen Metallurgy In the climate-neutral production Of Steel – HELIOS

Acronym	HELIOS	Partners	KU Leuven, MUL, ArcelorMittal, Aperam, SSAB, Outokumpu, Voest-Alpine
Budget (University of Oulu)	N/A	Funder	The European Union
Budget (total)	N/A	Timeframe	N/A

Description

The HELIOS doctoral network will train 10 motivated and talented doctoral candidates (DCs) in breakthrough technologies for the hydrogen-based production of green steel, including both carbon steel and stainless steel. These DCs will be equipped with the necessary science capital and diverse transferable skills to pursue their careers in Europe and become the experts that our society needs to achieve the climate-neutral production of steel by 2050.The intersectoral training program (HELIOS has 4 academic and 1 non-academic beneficiary) is dedicated to the technical and economic challenges and innovative developments associated with the transition to hydrogen-based green-steel production. It covers a wide area, ranging from process development, monitoring, engineering and modelling to safety engineering and lifecycle and economic analysis. The combination of state-of-the-art doctoral research projects, intersectoral secondments and supervision by leading companies and universities will be the foundations of HELIOS's success.
The research objectives of the HELIOS project are to:

- engineer processes and develop models to leverage the H-DR route to the same state-of-the art level as the BF-BOF route in Europe with respect to process, energy, and resource efficiency as well as product quality.
- develop first-of-a-kind hydrogen plasma-based reduction processes for stainless-steel producers and their raw-material producers.
- develop metal-recovery processes for residues from steel production based on hydrogen and/or hydrogen plasma-based reduction.
- develop measuring and analysis tools and models to support the application of hydrogen-based processes in the carbon and stainless-steel production routes.

PUBLICATIONS

K1-MET Competence Center of Sustainable Digitalized Metallurgy for a Climate Neutral and Resource Efficient Planet

Acronym	K1-MET Sus-Met4Planet	Partners	42 national and international company and scientific partners
Budget (University of Oulu)	N/A	Funder	N/A
Budget (total)	N/A	Timeframe	01.07.2023–30.06.2027

Description

The metal-producing industry is crucial for both Austria and the European Union, providing jobs and vital resources to various industrial ecosystems. However, it faces challenges due to its significant CO_2 emissions. The K1-MET SusMet4Planet project aims to address these challenges by focusing on three main areas:

1. **Metallurgical process efficiency and circularity,**
2. **Decarbonisation and sector coupling,**
3. **Simulation and data analyses.**

The project is coordinated by K1-MET GmbH and will involve research, experiments, modeling, and demonstrations of specific technologies to achieve these objectives. With a large consortium consisting of many different companies, universities, and scientific experts, K1-MET SusMet-4Planet seeks to advance sustainable metallurgy, reach climate goals, and strengthen its position as a leading research organization in sustainable metallurgy both in Austria and at the international level.

University of Oulu's contribution to the project will involve research of hydrogen plasma smelting reduction (HPSR). Collaborative work on the subject will be done during the following years.

Articles in scientific journals

1. Adediran, A., Yliniemi, J., Carvelli, V., Adesanya, E., Illikainen, M., (2022), Durability of alkali-activated Fe-rich fayalite slag-based mortars subjected to different environmental conditions, Cement and Concrete Research, 162, 106984.
2. Adediran, A., Yliniemi, J., Lemougna, P.N., Perumal, P., Illikainen, M., (2023), Recycling high volume Fe-rich fayalite slag in blended alkali-activated materials: Effect of ladle and blast furnace slags on the fresh and hardened state properties, Journal of Building Engineering, 63, 105436.
3. Adediran, A., Yliniemi, J., Moukannaa, S., Ramteke, D.D., Perumal, P., Illikainen, M., (2023), Enhancing the thermal stability of alkali-activated Fe-rich fayalite slag-based mortars by incorporating ladle and blast furnace slags: Physical, mechanical and structural changes, Cement and Concrete Research, 166, 107098.
4. Airaksinen, S., Haapakangas, J., Laukka, A., Heikkinen, E.-P., Fabritius, T., (2023), Oxide scale formation of stainless steels with different heating methods – Effect of hydrogen as fuel, Steel Research International, 2300334.
5. Airaksinen, S., Laukka, A., Heikkinen, E.-P., Riekki, E., Fabritius T., (2022), From Fossil fueled to hydrogen fueled annealing furnaces: Effects on oxidation of stainless steels, Steel Research International, 94(5), 2200305.
6. Airaksinen, S., Tuovinen, T., Vuolio, T., Laukka, A., Heikkinen, E.-P., Riekki, E., Fabritius, T., (2021), Oxide scale formation of EN 1.4622 and EN 1.4828 stainless steels during annealing and descaling behavior in neutral electrolytic pickling, Steel Research International, 93(1), 2100366.
7. Aji, A.T., Aromaa, J., Tuovinen, T., Riekki, R., Lundström, M., (2023), Finite Modeling and Simulation of the Effects of Neutral Electrolytic Pickling Process Parameters on EN 1.4404 Steel Strips, Metals, 13(12), 2001.
8. Aromaa, R., Rinne, M., Lundström, M., (2023), Life Cycle Assessment of Tantalum and Niobium Recycling from Hard Metal Scrap, ACS Sustainable Chemistry & Engineering, 11(41): 14997–15005.
9. Aromaa, R., Rinne, M., Lundström, M., (2022), Comparative life cycle assessment of hard metal chemical recycling routes, ACS Sustainable Chemistry & Engineering, 10(31): 10234–10242.
10. Attah-Kyei, D., Klemettinen, L., Taskinen, P., Jokilaakso, A., Lindberg, D., Michalik, R., (2022), Hydrogen as carbon free reducing agent in non-ferrous slag fuming, Metallurgical and Materials Transactions B, 53(6): 3775–3792.
11. Attah-Kyei, D., Sukhomlinov, D., Tiljander, M., Klemettinen, L., Taskinen, P., Jokilaakso, A., Lindberg, D., (2023), A Crucial Step Towards Carbon Neutrality in Pyrometallurgical Reduction of Nickel Slag, Journal of Sustainable Metallurgy, 9: 1759–1776.
12. Chen, M., Sukhomlinov, D., Taskinen, P., Tiljander, M., Lindberg, D., Jokilaakso, A., (2023), Phase relations of the MgO-SiO2-CrOx system at 1600 °C in air and reducing atmospheres, Journal of the American ceramic society, 106(10): 6230–6243.
13. Chen, M., Sukhomlinov, D., Taskinen, P., Tiljander, M., Lindberg, D., Jokilaakso, A., (2023), Phase equilibria of the Al2O3-SiO2-CrOx system at 1600 °C in air and reducing atmospheres, Journal of European Ceramic Society, 43(14): 6527–6535.

14. Chen, M., Sukhomlinov, D., Taskinen, P., Lindberg, D., Michalik, R., Jokilaakso, A., (2023), Phase equilibrium study of the CaO-SiO2-CrOx system at 1600 °C in reducing atmospheres, Journal of the American Ceramic Society, accepted.

15. El Ouardi, Y., Lamsayah, M., Butylina, S., Geng, S., Esmaeili, M., Giove, A., Massima Mouele, E.S., Virolainen, S., El Barkany, S., Ouammou A., Repo, E., Laatikainen, K., (2022), Sustainable composite material based on glutenin biopolymeric-clay for efficient separation of rare earth elements, Chemical Engineering Journal, 440, 135959.

16. El Ouardi, Y., Virolainen S., Massima Mouele, E.S., Laatikainen, M., Repo E., Laatikainen, K., (2022), Recent Progress On Advanced Ion Exchange For Separation of Rare Earth Elements From Secondary Resources – A review, Hydrometallurgy, 218, 106047.

17. Jylhä, J.-P., Jokilaakso, A., (2023), CFD-DEM models for matte droplet settling in a flash smelting settler, Heliyon, 9(11), e21570.

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19. Laukka, A., Heikkinen, E.-P., Fabritius, T., (2021), The Atmosphere's Effect on Stainless Steel Slabs' Oxide Formation in a CH4-Fuelled Reheating Furnace, Metals, 11(4), 621.

20. Mäkelä, I., Visuri, V.-V., Fabritius, T., (2023), A Mathematical Model for the Thermal State of a Steel Ladle, Ironmaking & Steelmaking, 50(7): 867–877.

21. Pankka, I., Taskinen, P., Salminen, J., Lindberg, D., (2022), Elemental distributions of trace elements in non-ferrous iron residue hydrogen reduction, JOM, 75(6): 2026–2033.

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23. Ponomar, V., Adesanya, E., Ohenoja, K., Illikainen, M., (2022), High-temperature performance of slag-based Fe-rich alkali-activated materials, Cement and Concrete Research 161, 106960.

24. Ponomar, V., Ohenoja, K., Illikainen, M., (2023), Optimizing activating solution and environmental leaching characteristics of Fe-rich alkali-activated Zn slag, Journal of Hazardous Materials, 445, 130575.

25. Pöyhtäri, S., Ruokoja, J., Heikkinen, E.-P., Heikkilä, A., Kokkonen, T., Tynjälä P., (2023), Kinetic Analysis of Hydrogen Reduction of Nickel Compounds, Metallurgical and Materials Transactions B, https://doi.org/10.1007/s11663-023-02955-6

26. Rinne, M., Halli, P., Aromaa, J., Lundström, M., (2022), Alternative Method for Treating Electric Arc Furnace Dust: Simulation and Life Cycle Assessment, Journal of Sustainable Metallurgy, 8(2): 913–926.

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28. Teimouri, S., Potgieter, J. H., Lundström, M., Billing, C., Wilson, B. P., (2022), A New Hydrometallurgical Process for Metal Extraction from Electric Arc Furnace Dust Using Ionic Liquids, Materials, 15(23), 8648.

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31. Vitikka, O., Iljana, M., Heikkilä, A., Tkalenko, I., Koriuchev, N., Shehovsov, D., Malkki, A., Fabritius, T., (2022), Suitability of auger pressing briquettes for blast furnace use based on laboratory tests, Minerals 12(7), 868.

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2. Aromaa R., Rinne, M., Lundström, M., (2021), The environmental impacts of hydrometallurgical cobalt sulfate production from Finnish ores, Sustainable Minerals '21.

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4. Baral E., Isteri, V., Adesanya, A., Hanein, T., Fabritius, T., (2023), Early-Age Hydration of an EAF Slag Based Alite–Ferrite Cement Clinker in the Presence of Na2CO3, SynerCrete'23.

5. Isteri, V., Ohenoja, K., Hanein, T., Fabritius, T., (2022), Iron containing phases in cement clinker, 41st Cement and Concrete Science Conference, Leeds 12-13.9.2022.

6. Jokilaakso, A., Jylhä J.-P., Song, K., (2021), Submerged gas blowing and droplet settling modelling in copper matte smelting processes, EUROMAT 2021 (oral presentation).

7. Jyrkönen, S., Björklund P., Lindgren, M. Pesonen, L., Hamuyuni J., (2022), CO2 emission reduction by optimized process control, Copper 2022.

8. Kallio, R., Heikkinen, E.-P., (2023), Overview of recent research activities on circular economy in the iron & steel industry at the Process Metallurgy Research Unit, University of Oulu, 2023 ESTEP Annual event.

9. Kurkinen, S., Sainio, T., Virolainen, S., (2023), Chromatographic Separation of Rare Earth Elements as Anionic Complexes by Ion Exchange, ALTA 2023.

10. Lassi, U., Vielma, T., (2021), Improving inorganic circular economy – Case studies from the University of Oulu, IPMS 2021, Espoo (oral presentation).

11. Laukkanen, A., Pinomaa, T., Lindroos, M., Ren, S., Kaipainen, J., Andersson, T., Huttunen-Saarivirta E., (2021), Multiscale and multi-physical modeling of refractory degradation – case "Tocanem", IPMS 2021, Espoo (oral presentation).

12. Lehmusto, J., Hupa, L., Söyrinki, S., Lagerbom, J., Jokiaho, T., Que, Z., Huttunen-Saarivirta, E., Määttä, J., Lindgren M., (2023), Interactions between the gas phase in a nickel flash smelting furnace and the refractory lining, UNITECR2023.

13. Lehmusto, J., Söyrinki, S., Lagerbom J., Huttunen-Saarivirta E., Lindgren, M., Hupa, L., (2022), Gas-phase-induced refractory degradation, EUROCORR 2022.

14. Lehmusto, J., Söyrinki, S., Lagerbom, J., Jokiaho, T., Que, Z., Määttä, J., Hupa, L., Huttunen-Saarivirta, E., Lindgren, M., (2024), Characterization of a nickel flash smelter refractory material – The effect of thermal gradient, in the proceedings of the 2024 TMS Annual Meeting & Exhibition.

15. Ponomar, V., (2023), High-temperature performance of Fe-rich alkali-activated materials based on jarosite residue slag, 6th Annual International Conference on "Eco-Sustainable Construction Materials", Paris, France.
16. Tuovinen, T., et al., (2021), The effect of current density during bipolar neutral electrolyte pre-pickling to hydrochloric acid–hydrogen peroxide final pickling, European Steel Technology and Application Days 2021.
17. Vitikka, O., Iljana, M., Hietava, A., Fabritius, T., Koriuchev, N., Tkalenko, I. and Malkki, A., (2022), Evaluation of the Suitability of Auger Pressing Briquettes for Blast Furnace Use, Conference, ECIC-ICSTI 2022.
18. Wan, X., Sukhomlinov, D., Taskinen, P., Lindgren, M., Jokilaakso, A., (2022), Condensation of arsenic in FSF atmospheres in typical WHP and ESP conditions, Copper 2022.

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1. Visuri, V.-V., Holappa, L., "Converter Steelmaking," Treatise on Process Metallurgy – Volume 3: Industrial Processes (Seetharaman, S., Guthrie R., McLean, A., Seetharaman, S., Sohn, H., eds.), Elsevier, 2024.

Doctoral theses
1. Abdelrahim, A., (2023), Towards lower CO_2 emissions in iron and steelmaking – Hydrogen-assisted reduction and cement-free briquettes, doctoral thesis, University of Oulu.
2. Jantunen, N., (2023), Development of liquid–liquid extraction processes for concentrated hydrometallurgical solutions, doctoral thesis, LUT University.
3. Koskela, A., (2023), Utilization of lignin-based biocarbon in pyrometallurgical applications, doctoral thesis, University of Oulu.

Master's theses
1. Alaviitala, T., (2022), Liekkisulatusuunin näytteenottimen kehittäminen, master's thesis, University of Oulu.
2. Alm, E.-S., (2023), Hiilidioksidin liukoisuus ja metallikarbonaattien saostaminen, master's thesis, University of Oulu.
3. Grönqvist, N., (2023), Catalytically graphitized carbon for Li-ion batteries and other energy storage applications, master's thesis, University of Oulu.
4. Harju, A., (2021), Chromium converter process slag line wear now and in acidic practice, master's thesis, University of Oulu.
5. Igbon, C., (2023), Ultrasound-assisted neutral electrolytic pickling of stainless-steel surfaces, master's thesis, University of Oulu.
6. Karppinen, A., (2022), Characterization of challenging Co-containing samples for circular economy, master's thesis, University of Oulu.
7. Kinnunen, O., (2023), Optimization of solution parameters affecting current efficiency, specific energy consumption and zinc growth, master's thesis, University of Oulu.
8. Kuurre, S., (2021), Physico-chemical Properties of Slag in the SAF Process, master's thesis, University of Oulu.

9. Kähkönen, R., (2022), Mikrorakenteen ja hehkutuksen vaikutukset kuumavalssattujen ruostumattomien terästen peittauksessa, master's thesis, University of Oulu.
10. Kälkäjä, K., (2022), The effect of admixtures on the mechanical properties and durability of Fe-rich alkali-activated materials, master's thesis, University of Oulu.
11. Lassila, E., (2023), Effect of scale formation on the emissivity of austenitic stainless steels in an annealing furnace, master's thesis, University of Oulu.
12. Mäkelä, I., (2021), Mathematical model for the thermal state of a steel ladle, master's thesis, University of Oulu.
13. Mörttinen, J., (2023), Stabile anode materials for bipolar electrolytic pickling, master's thesis, University of Oulu.
14. Pankka, I., (2021), Thermodynamic modeling of thermal treatment of zinc leaching residue, master's thesis, Aalto University.
15. Ruokoja, J., (2021), Metalliyhdisteiden vetypelkistyksen kinetiikka, master's thesis, University of Oulu.
16. Rytky, S., (2023), Direct reduction of chromite using the FFC Cambridge method, master's thesis, University of Oulu.
17. Saarnisaari, A., (2021), Thermal conductivity of copper smelting slags, master's thesis, Aalto University.
18. Saroukhani, S., (2022), Manufacture and properties of self-reducing briquettes, master's thesis, University of Oulu.
19. Sipilä, V., (2022), Measuring and modelling of residence time distributions in mixer-settler reactors, master's thesis, LUT University.
20. Tarkka, A., (2021), Kinetics of gasification of biochar made of Kraft lignin, master's thesis, University of Oulu.
21. Vaarala, K., (2021), The Optimization Of The Scale Growth Model For Line Annealing In Stainless Steel Production, master's thesis, University of Oulu.
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Bachelor's theses
1. Riippi, N., (2023), Arvokkaiden metallien talteenotto käytetyistä katalyyteistä, bachelor's thesis, University of Oulu.
2. Salo, E., (2023), Faasirakenteen määrittäminen FeCr- ja AOD-kuonia sekoitettaessa muodostuvalle sekakuonalle, bachelor's thesis, University of Oulu.
3. Sassi, E.-M., (2023), Valokaariuunin elektrodien kuluminen, bachelor's thesis, University of Oulu.
4. Simonen, S., (2022), Terästen hapettumiskoejärjestelyn herkkyysanalyysi – Lämpötilan vaikutuksen arviointi, bachelor's thesis, University of Oulu.
5. Tikkanen, A., (2022), Terästen hapettumiskokeiden herkkyysanalyysi – kaasujen virtausnopeuden vaikutuksen arviointi, bachelor's thesis, University of Oulu.
6. Ylitalo, L., (2023), Microalloying in the manufacturing of stainless steel, bachelor's thesis, University of Oulu.