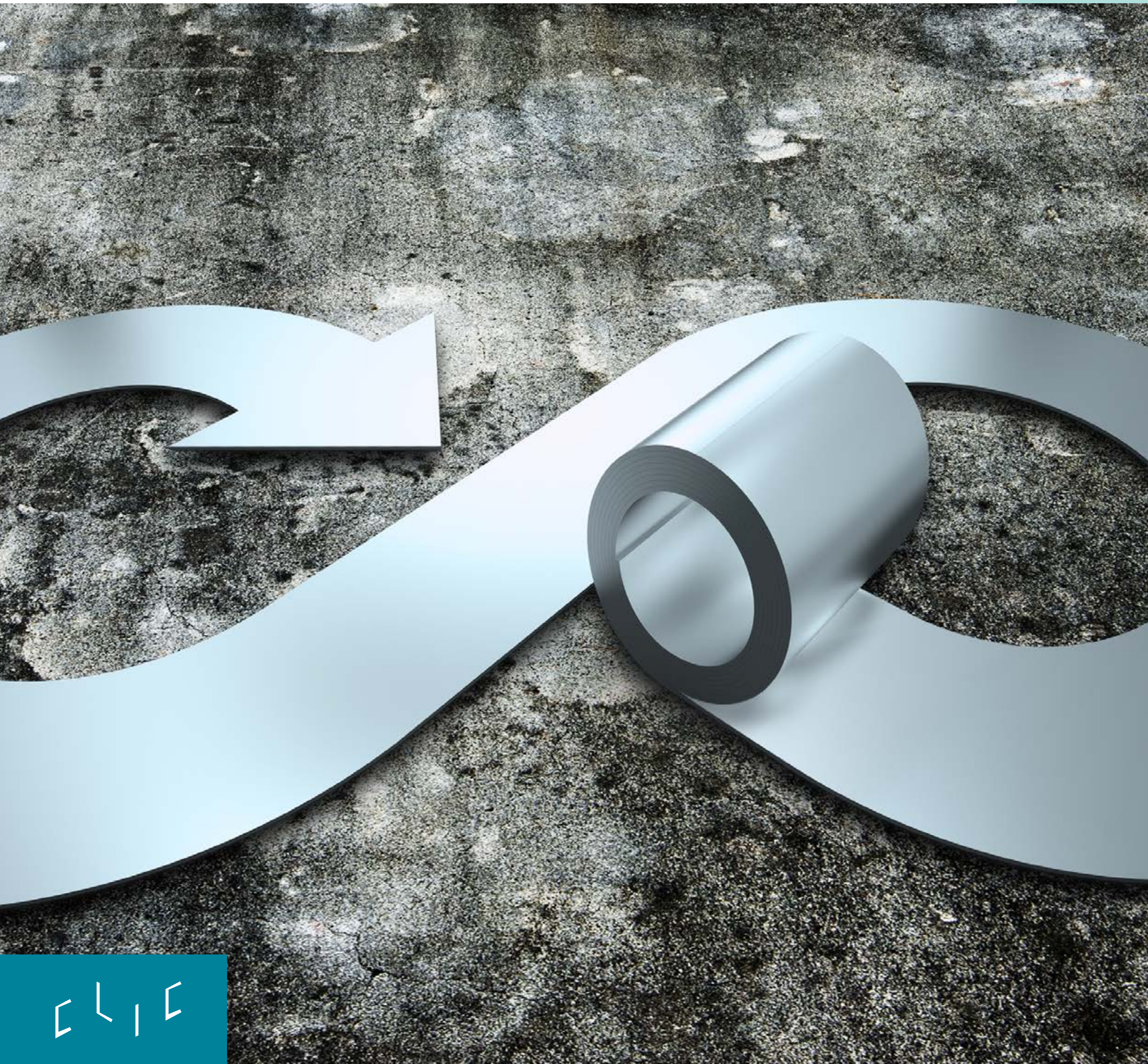
SYMMET

FINAL REPORT 2020

2020

Symbiosis of metals production and nature



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SYMBIOSIS OF METALS PRODUCTION AND NATURE

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SYMMET PREFACE

Juho Talonen & Timo Fabritius

The metallurgical industry in Finland is inherently driven toward metal recycling. For example, our steel and stainless steel production is largely based on secondary raw materials, so that it has one of the lowest specific CO_2 emission levels in the world.

The main requirements for competitiveness in the future are the capability to response flexibly to changing demands and the ability to produce metals at a high cost-efficiency with a remarkably reduced environmental impact. Along with other industries, the Finnish metal producers are striving for long-term national and EU level targets in terms of carbon neutrality. In reaching the long-term targets, a circular economy is an important pathway.

SYMMET – Symbiosis of metals production and nature – was aimed at finding ways to minimize waste materials or residues formation in metallurgical processes, and wanted to establish how to best utilize secondary raw materials in existing metallurgical processes. It also wanted to promote the creation of research-based innovations and new business, for instance through the development of added value products from the side streams of the metal industry. The SYMMET project supported the Finnish metal producers' leap towards a circular economy, which aims for zero waste, reduced use of primary raw materials, and a high degree of reuse and recycling of materials. Industrial benefits have been achieved in several unit processes regarding improved internal recycling and decreased landfilling. For instance, new potential cementitious binders and novel Ca based products have been developed in the project using metallurgical slags as raw material. It was also concluded that different wood-based side streams could be utilized as a reducing agent in new advanced non-ferrous slag treatment processes.

Integrating and utilizing new models as well as implementing novel secondary materials treatment methods in an industrial environment is not an easy task. For instance, extensive long-term research may be required to characterize and enable the use of new material streams. In many cases, completely new breakthrough technologies are needed to make treatment and utilization of material streams technically and economically feasible. Thus, integrated and successful collaborative approach between the industry, academy and SME's is needed. The short duration of the SYMMET project caused some challenges in realizing all the potential benefits in full-scale processes. However, the results indicate that the continuous research work that the Metals Producers Ecosystem has been actively doing can also benefit from such short-term investments, provided that there is continuity in the form of consequent programs, in the short or longer term.

An important impact of the SYMMET project has been its support for fundamental and academic research in the many fields of metal producing. Not only has this been crucial in several niche topics, such as reduction metallurgy, hydrometallurgy, phase equilibria, and thermodynamic simulations, but equally in other simulation and modeling techniques and novel treatment methods, as well as their implementation in the industrial processes. The close linkage provided by SYMMET has enabled the metallurgy research groups in Finnish universities to profile their activities and avoid overlaps, thus maximizing their skills coverage at the national level.

One of the most important enablers of this successful collaboration between the industry, SME's and academia has been the public funding from Business Finland. This funding has been key to achieving the challenging targets of the SYMMET project. We want to direct our gratitude to Business Finland, and we look forward to continuing the co-operation with Business Finland in future programs.

Dr. **Juho Talonen**
Chairman of SYMMET steering group
Senior Manager – Head of Program Management and Intellectual Property
Technology and Group Sustainability
Outokumpu Oyj

Professor **Timo Fabritius**
Principal investigator of SYMMET
Head of Process Metallurgy Research Unit
University of Oulu

SYMMET Program in a Nutshell

SYMMET in numbers

Duration	1.11.2018 – 31.10.2020
Budget	6.9 M€
Company budget	3.6 M€
Research institution budget	3.3 €
People involved	85
Publications	77

Consortium

The SYMMET project was designed based on a systemic view of the metals production ecosystem and its stakeholders. This view is manifested in the project organization, which involves partners from all process steps of metals production from raw material handling via metals production to recycling and the reuse of materials. The project covered a broad range of topics related to circular economy, ranging from low technology readiness level (TRL) experimentation at research institutes to higher TRL implementation at metal producing companies and SMEs.

Figure 1. **SYMMET Consortium**

SYMMET consortium 2020

The total program budget was EUR 6.9 million. The final project consortium consisted of eight companies and four research institutes:

1. Boliden Harjavalta Oy
2. Boliden Kokkola Oy
3. Outokumpu Stainless Oy
4. Outotec (Finland) Oy
5. Owatec Group Oy
6. SSAB Europe Oy
7. Tapojärvi Oy
8. Timegate Instruments Oy
9. Aalto University
10. LUT University
11. University of Oulu
12. VTT Technical Research Centre of Finland

Program structure and management

The research activities were organized along two cross-sectorial technology teams (TT) that spanned across the whole ecosystem: secondary raw materials and refractories (TT1), closing the material and energy loops (TT2), renewable energy sources and non-fossil reductants (TT3), and the treatment of rejects (TT4).

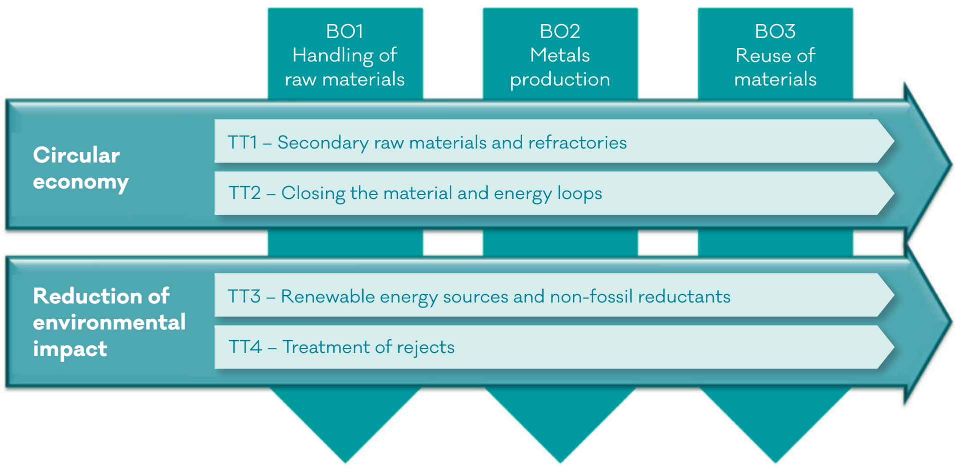

Figure 2. **Schematic illustration of the project structure.**

The coordination of the research activities was organized by a steering group and two management groups (TT1 + TT2 and TT3 + TT4). The steering group consisted of the project partners' representatives and expert members. Its main function was to oversee the overall management of the project, including shaping of the consortium agreement and outsourcing the project coordination. After reviewing several offers, the project coordination was contracted to CLIC Innovation Oy and Pirjo Kaivos was appointed as the project coordinator.

The management group TT1 + TT2 focused on topics related to circular economy, while the management group TT3 + TT4 covered topics related to the reduction of the environmental impact. The management groups were led by rotating chairs from the industry together by secretaries from the research institutes.

	Chair	Secretary
TT1+TT2	Project year 1 Timo Paananen SSAB Europe Oy Project year 2 Esa Puukko Outokumpu Stainless Oy	Ville-Valtteri Visuri University of Oulu Substitute: Aleksi Laukka
TT3+TT4	Project year 1 Matti Luomala Outotec (Finland) Oy Project year 2 Petri Latostenmaa Boliden Harjavalta Oy	Minna Rämä Aalto University Substitute: Ari Jokilaakso

Impact

Several new concepts for reusing and recycling the by-products of metals production were investigated. As for ironmaking, the systematic study of the possibilities to recycle slags and dusts in hot metal desulfurization revealed an economic potential of recycling ladle slag.

An extensive infrastructure for the physical simulation of scale formation during annealing as well as the subsequent electrolytic picking of the same workpiece was set up at the University of Oulu. The equipment can be used, for example, for optimizing the furnace atmosphere. The project has received industry interest, which has sparked many new contacts and ideas for further research. One excellent example of valuable collaboration between the consortium partners is a novel technology for cyanide removal from process waters developed by Owatec Group Oy.

To foster dissemination of the result in the scientific community, research institutes together with partner companies engaged actively in publishing, producing a total of 32 journal papers. and 13 conference papers. This represents a significant scientific contribution to the study of circular economy in metal production. The publications form valuable references for application of supporting funding from Academy of Finland, European Union and various foundations. Extensive international collaboration was realized through research visits to RWTH Aachen University (Ville-Valtteri Visuri, 2019), Shanghai University (Mamdouh Omran, 2019), Montanuniversität Leoben (Anne Hietava, 2020) and Murdoch University (Tuomas Vielma, 2020).

Through publishing, SYMMET also provided a platform for training professional researchers with a doctoral qualification. A total of 3 doctoral students finished their thesis during SYMMET, while several others have gotten a flying start for their doctoral theses. Furthermore, the SYMMET enabled 19 students to finish their master´s theses in close-knit collaboration between research institutes and industry. These new talented researchers and engineers trained during the SYMMET project will provide an important stimulus for strategic renewal long after the project has ended.

Docent **Ville-Valtteri Visuri**
R&D Manager
Outokumpu Stainless Oy

I would like to warmly thank all the participants for an excellent job. The good collaboration and results achieved in the SYMMET project will certainly lead the Metals Producers Ecosystem towards a circular economy. It has been a great pleasure to be part of such a professional and committed consortium.

Pirjo Kaivos
Project Coordinator
Head of Circular Economy
CLIC Innovation Ltd

SYMMET Steering Group

Dr. Juho Talonen	Outukumpu Oyj, chairman
Petri Latostenmaa	Boliden Harjavalta Oy
Dr. Justin Salminen	Boliden Kokkola Oy
Dr. Mikko Ylitalo	Outokumpu Stainless Oy
Jouni Pihlasalo	Outotec (Finland) Oy
Jaakko Pellinen	Owatec Group Oy
Jarmo Lilja	SSAB Europe Oy
Seppo Ahola	Tapojärvi Oy
Mari Tenhunen	TimeGate Instruments Oy
Prof. Ari Jokilaakso	Aalto University
Prof. Tuomo Sainio	LUT
Prof. Timo Fabritius	University of Oulu
Dr. Lotta Rintala	VTT
Prof. Pertti Koukkari	VTT
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Ritva Heikkinen	Business Finland
Dr. Kimmo Järvinen	Association of Finnish Steel and Metal Producers
Pirjo Kaivos	CLIC Innovation, secretary
Kari Keskinen	Business Finland
Dr. Aleksi Laukka	University of Oulu
Sisko Sipilä	Business Finland
Docent Ville-Valtteri Visuri	Outokumpu Stainless Oy

International collaboration and networking

The SYMMET consortium fostered national and international co-operation with research parties' existing and new contacts with international experts and universities, and almost 20 scientific papers were written with network university representatives.

Aalto University, CMET research groups have continued comprehensive collaboration especially with Central South University of China (P.R. China), CSU, in the form of joint doctoral student supervision, publications, and seminars. In 2018 Aalto University professors Mari Lundström and Ari Jokilaakso were granted with the title of Guest Professor in the CSU, see Figure 3. Additionally, cooperation with Bandung Institute of Technology, Seoul National University, and University of the Witwaterstrand, to name a few, continued actively. One highlight in networking and international collaboration was the 3rd International Process Metallurgy Symposium in November 2019, from which the opening session in Dipoli, Otaniemi is shown in Figure 4. The symposium hosted dedicated sessions to SYMMET and BAT-Circle projects, financed by **Business Finland** and two large ecosystems in Finland: **Metals Producers** and **Battery Materials ecosystem**. Additionally, the **MSCA-ETN Socrates** (EU Framework Program for Research and Innovation Horizon 2020) students from different European countries had a major input with their presentations, with metallurgy students from Finnish universities.

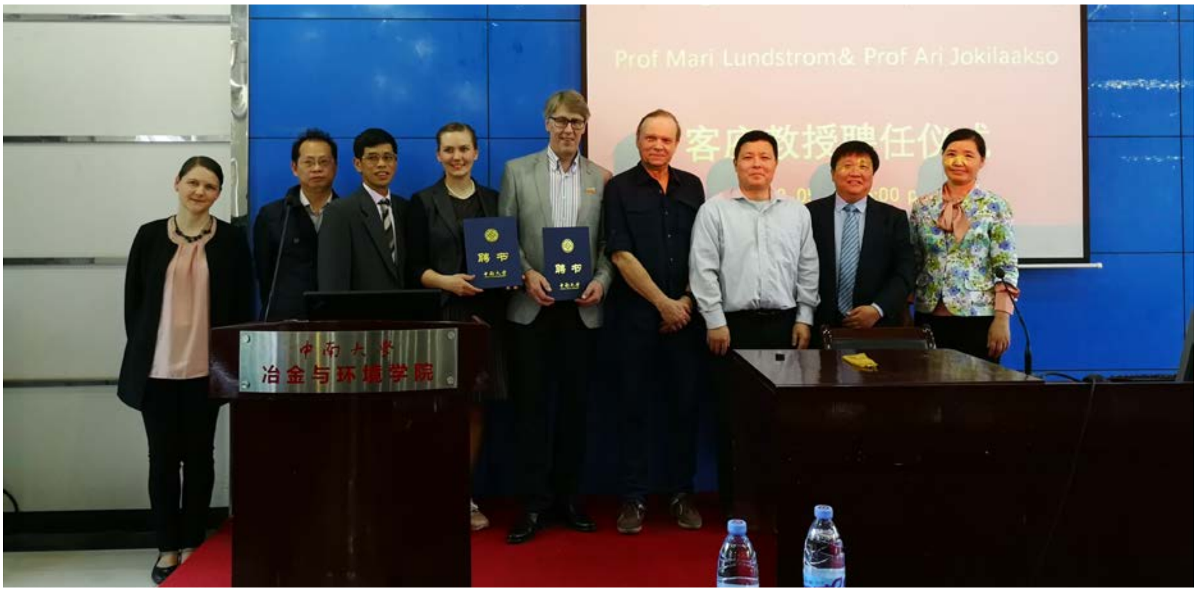

Figure 3. **Visiting Professorship honoring in CSU in 2018. Professors Mari Lundström and Ari Jokilaakso in the middle. Also, professor emeritus Pekka Taskinen shown in the picture – he was the guest professor in CSU during 2012-2017.**

Figure 4. **Opening session of the 3rd International Process Metallurgy Symposium in Dipoli, Otaniemi.**

University of Oulu has been engaged in several supporting projects in the Horizon 2020 (H2020) and Research Fund for Coal and Steel (RFCS) programs. In addition, University of Oulu has an on-going EIT Raw materials project (MINPET, CIRRUS) and ERA-MIN project (FLOW). Moreover, several H2020 and RFCS applications in supporting topics are currently in progress. During the project University of Oulu has had on-going research collaboration with 10 foreign universities related to circular economy topics. The most important international collaborators in a form of joint publications and research exchanges have been RWTH Aachen, Mountain University of Leoben, Shangai University and Politechnico Milano.

Lappeenranta University of Technology (LUT) collaborated with Universidade Federal do Rio de Janeiro (UFRJ; Rio de Janeiro, Brazil) in liquid-liquid extraction in columns, especially hydrodynamics and transfer phenomena. This benefitted the extraction process development, which was the main topic of LUT in SYMMET. VTT Research Institute of Finland, in turn, co-operated with Mountain University of Leoben, Austria in developing the treatment of coupled ferrous and non-ferrous waste for optimized recovery of their metal values and for gaining a waste-free recycling process with minimum CO_2-impact. The research combined the benefits of VTT's hydrometallurgical technology with the expertise of Mountain University of Leoben on pyrometallurgical treatments of steel and zinc manufacturing residues.

CIRCULAR ECONOMY

Summary, key results and impacts

The technology teams 1 and 2 focused on topics related to a circular economy resulting in new implementations, improved knowledge and possibilities to change processes toward more sustainable practices. The activities consisted of a literature review, laboratory-scale research, pilot tests, and full-scale industrial trials and measurement campaigns. The activities were conducted by research institutes (University of Oulu, Aalto University, VTT and SWERIM), SMEs and other domestic companies (FESCON, MASERCATA, Reijo Mehtälä Oy, Pöyry), and participants (SSAB, Outokumpu).

The potential to refine metal oxide materials in converter processes was thoroughly studied from thermodynamic (University of Oulu), economical and practical availability points of view. One new oxide material was identified that would improve competitiveness in special steel grade market if long-term industrial piloting in Outokumpu will be successful. The internal and external re-usage potential of refractory waste was also fully scoped by doing a literature review (University of Oulu), a chemical analysis of all available streams (University of Oulu) and workshops with experts. Most of the findings could not be realized immediately due to investment needs but the data gathered will be used when planning new strategies of refractory management of Outokumpu.

Potential intermediate products to replace externally produced and delivered additives were scoped. Usage of in-house chrome pellets at Outokumpu Tornio Works was industrially tested but the usage of fine concentrate as a replacement of casting sand requires asbestos-free chrome ore. A new testing method was developed and validated during the project to enable industrial testing in the near future. The possibility to replace primary coke with coke dust left from primary coke handling will be industrially validated. The internal recycling potential of dust and slags has been studied from many aspects in the process environment consisting of a submerged arc furnace (SAF), conventional electric arc furnaces (AC EAF), a converter (CRC) and a new type of electric arc furnace (DC 6-in-line). With developed thermodynamic simulators (University of Oulu, VTT), the effect of different recycling scenarios on productivity and product properties can be evaluated.

Recycling economy of challenging materials in and from SSAB Raahe (i.e. BF and BOF sludges) was studied because re-handling of these challenging materials is imperative to make recycling processes be economically feasible. Challenges arise from the material properties, as sludges are sticky, wet and contain contaminants. Processability of sticky sludge in laboratory scale was done with University of Oulu. The aim was to modify flowability and viscosity of the sludges to find out if it is possible to feed to agglomeration processes. For different sludges, drying was studied with Pöyry and FESCON. A plasma furnace was utilized to yield metals directly from sludge with Masercata. Each part was successfully field tested, and further development will be carried after the project has ended. Increasing the recycling rate of landfilled materials include multiple research aspects contributing to circular economy goals. The utilization of dust originating from desulphurization as a substitute in cement, and using iron oxide and zinc containing dusts as in desulfurization were performed with University of Oulu.

The critical process conditions of harmful agglomeration phenomena that could be exposed with a higher load of recycled feeding material into Outokumpu's submerged furnace (SAF) have been experimentally defined. Experimental work required big modifications to the laboratory furnace to simulate the harsh conditions in a SAF. The process trial to recycle metal oxides via a SAF in briquettes-form proved that more attention has to be paid to the conductivity of the secondary feeding material (University of Oulu). The usage of capsulation technology to internally refine metal dust in a chrome converter was planned but industrial testing has high risks. For SSAB Raahe, the agglomeration of mill-scale to briquettes was researched. Briquettes serve as a way to introduce fine, recycled materials to the BF process and mill-scale is a main ingredient in these briquettes. However, the capacity of the briquetting plant and BF charging of briquettes are limited. A pilot scale study with SWERIM was successfully conducted in making mill-scale briquettes and charging them directly to converter, liberating recycling capacity. Plant trials are now planned for autumn 2020.

Process efficiency increase translates well to CO_2 emission reductions, and in the SSAB Raahe desulphurization process stage emission reduction was gained by increasing the efficiency of the used lime-based reagent through modeling. A reliable model to predict individual injection and handling results, as well as a CFD model to optimize injection parameters in the process was developed. Fine coal used in coke making causes hard to detect and control dust emissions during coking oven charging.

The detection and control of this dust was implemented to on-line use in SSAB Raahe in co-operation with VTT and further optimization of the tool will be continued.

Ladle slag from SSAB Raahe was studied in two aspects: the effect the ladle slag has on the efficiency of desulfurization process, and the potential in utilizing it as a modifying agent in initial slag. A novel model was developed to predict sulfide capacity of the slag, aiding the operation of the desulfurization process. Industrial test on utilizing the ladle slag as an addition to the initial desulfurization slag showed another great potential in improving the process further.

Regarding the environmental impact, Outokumpu heavily focused on improving the process performance of the pickling of cold rolled stainless steel and the regeneration process of recycled chemicals. Fundamentals of scale formation in the annealing process that creates a need for pickling were experientially studied, and equipment to study electrolytic pickling efficiency for annealed samples was developed (University of Oulu). Having a scale formation module in the annealing simulator that was developed allows the definition of processing parameters that minimize scale formation and the need for pickling. Fundamental reactions in electrolytic pickling were modelled. Further development is still required to use the model for design and parameter optimization. A dynamic simulation model for a complex acid pickling system was developed and will be used later to optimize the dosing practices of mixed acids. A new on-line measurement technology to monitor sulfur content that is a key control variable in the regeneration process was demonstrated.

SYMMET

CIRCULAR ECONOMY TASK SUMMARIES

1

MODELLING OF AOD SLAG COOLING

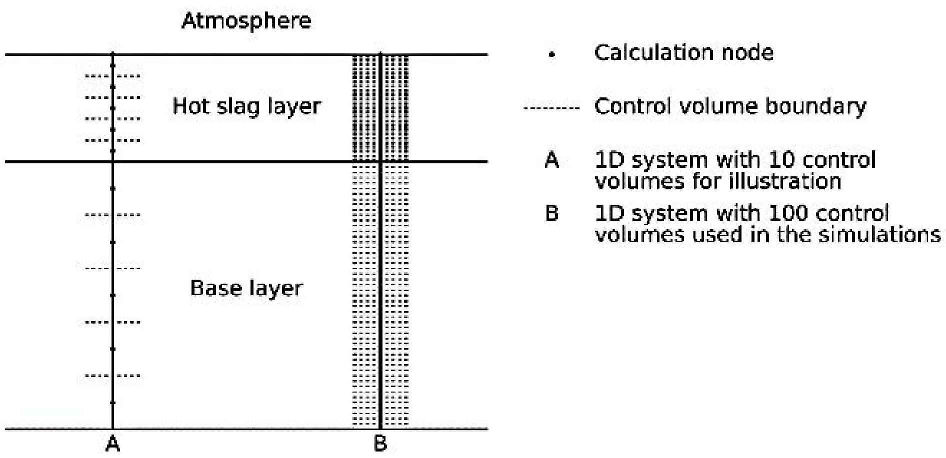

Figure 5. **A schematic illustration of the calculation domain.**

Description

The AOD process produces large amounts of slag, which need to be cooled down to room temperature before further processing. In contemporary practice, the slag is cooled in ambient air in the slag yard.

Application

A 1-dimensional mathematical model was developed to simulate slag cooling under conditions of ambient air cooling or water-cooling. In the model, the heat transfer in the slag and the ground below the slag is described using heat conduction equations, which are solved for 50 control volumes in both slag and ground. The ambient cooling and water cooling affect the highest slag control volume via heat transfer coeffcient.

Results

As expected, water cooling was found to enhance the rate of slag cooling in comparison to ambient cooling. The surface of the slag quickly reached the temperature of water, while a large temperature gradient formed within the slag. Consequently, the spraying rate of water-cooling was had only a little effect in the studied interval of water spraying rates.

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Publications

Kärnä, A., Visuri, V.-V., Heikkinen, E.-P. , Sulasalmi, P., Torvinen, P., Koskinen, J., Fabritius, T. 2020. Numerical modeling of Argon-Oxygen Decarburization slag cooling. Steel Research International. Article 2000054.

Kärnä, A., Sulasalmi, P., Visuri, V.-V., Fabritius, T. 2019. Numerical modelling of slag cooling. Proceedings of the 4th European Steel Technology and Application Days. Stahlinstitut VDEh, Düsseldorf, Germany.

Visuri, V.-V., Heikkinen, E.-P., Kärnä, A., Sulasalmi, P., Fabritius, T. Numerical modelling of AOD slag structure during cooling. Proceedings of the 11th International Conference on Molten Slags, Fluxes and Salts. Seoul. Forthcoming.

2 THE DEVELOPMENT OF A LABORATORY METHOD FOR CASTING SAND CHARACTERIZATION

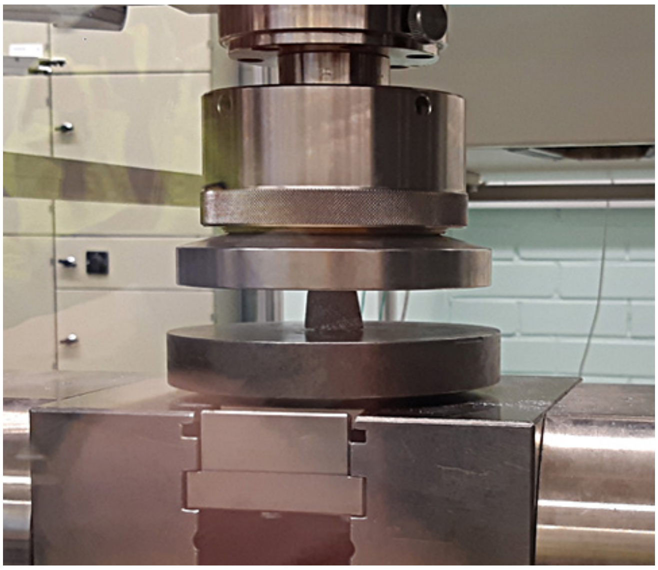

Figure 6. **Sintered casting sand being pressure tested.**

Description

Casting sand is used in the steel melt shop to protect the ladle emptying mechanism from molten steel. The casting sand must not sinter too much since that will limit the opening mechanism at the casting station. Instead, the casting sand should sinter at a high enough temperature, a long enough time. In order to test alternative materials for sand casting, such as a fine concentrate from Kemi's mine, a new laboratory method for casting sand characterization had to be developed.

Application

Different mixtures were heated up to 1550 °C and kept in the furnace for 20 or 60 minutes. After the sample was heated, special pressure testing was executed to obtain objective hardness numbers. The results were compared to known references and the hypothesis.

Results

By using this method, the following hypothesis could be confirmed:

- Higher SiO_2 and C-contents added separately, decelerate sintering
- An added combination of SiO_2 with added Carbon increases strength.
- A higher temperature, a longer time and a larger surface area all accelerate sintering.

Therefore, by adding >50 % SiO_2 to the fine concentrate, it is possible to reduce the sintering amount to simulate the current casting sand. The methods used make it possible to compare casting sand from different casting sand suppliers and different varieties of casting sands.

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3 THE POTENTIAL OF OXIDE MATERIAL REDUCTIONS IN CONVERTER PROCESSES

Figure 7. **Chromite pellets.**

Description

The utilization of chromite pellets from intermediate processing in converters to get rid of excess silicon, e.g. after the chromium converter process, AOD pre-melt treatment, and in the case of carbon blow after the reduction, desiliconization is always needed before the blow. In that way the operation is faster and temperature control is much easier.

Application

The first step to introduce new oxide material in the process was to make thermodynamic simulations. Based on those simulations, reactions should happen very efficiently. Behavior of the material during feeding has to be normally tested by production trials. Therefore the second step was to make instructions for the validation trials. The final step was the execution of supervised trials.

Results

Preliminary tests have been done. Technical issues related to charging have been solved and the material performs well in a silo system. No problems were observed in feeding into the process. Reduction chemistry and thus material balance calculations require additional full-scale tests.

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4 A SIMULATION TOOL FOR INTERNAL SIDE STREAM UTILIZATION

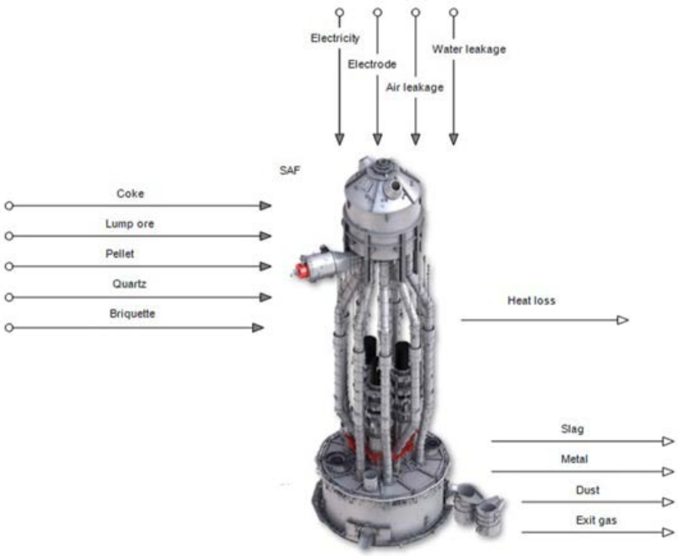

Figure 8. **Schematic illustration of the SAF process and related heat and material flows in HSC Sim.**

Description

There is an increased demand to improve the utilization of by-products of ferrochrome production. The main reduction process in ferrochrome production is the submerged arc furnace (SAF). As the first step, a mass and energy balance based simulation model for SAF was developed in the HSC Sim environment of the HSC Chemistry 9 software. The model represents a starting point for evaluating the ways to change the process energy and mass flows, e.g. introducing new material streams and the recycling of existing side streams. Furthermore, electrical conductivity measurements for industrial test briquettes were made to further understand their effect on the behavior of the SAF.

Application

A simulation model can be applied for studying the downstream effect of utilizing side streams within the process or changing some of the material streams in the process. The model is tailored for the studied SAF furnace. The model can be easily coupled with other modular unit process models executed in the HSC Sim environment, thereby enabling the simulation of the down-stream effect of process modifications.

Results

The HSC Sim model developed represents steady-state operation and can be used as a tool when estimating the effects of input material flows on the output of SAF. The electrical conductivity of briquettes was compared to pellets and the findings show that briquettes have a higher conductivity in all studied temperatures.

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Publications

Heikkinen, E.-P., Vallo, K., Ikäheimonen, T., Fabritius, T. A computational study on the mixing and reduction of slags from ferrochrome and stainless steel production. Proceedings of the 11th International Conference on Molten Slags, Fluxes and Salts. Forthcoming.

5 THE AGGLOMERATION OF MATERIAL IN A SUBMERGED ARC FURNACE

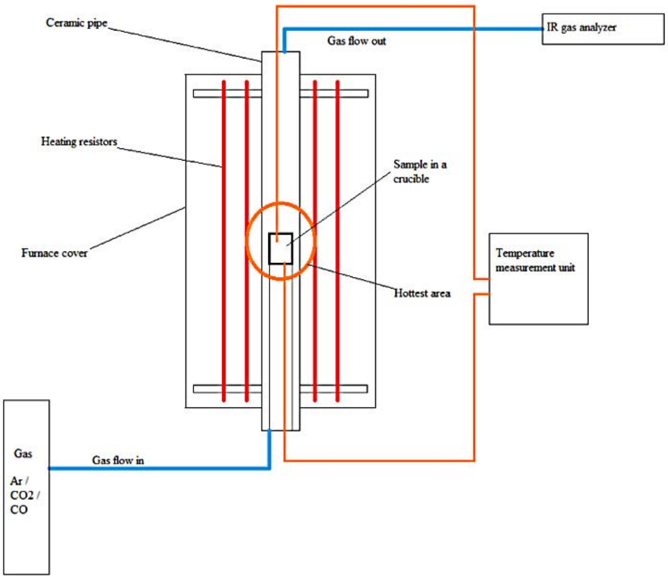

Figure 9**. A schematic illustration of the SAF simulator.**

Description

The main motivation was to study mechanisms for the agglomeration of feed material in a submerged arc furnace (SAF). Agglomeration is known to cause problems to material and gas flow and electrical conductivity, leading to production losses over a long period of time. The aim of this work was to simulate process conditions in a laboratory, and to study when agglomeration occurs.

Application

A SAF simulator is made by modifying a thermogravimetry furnace. The furnace can be used in temperatures of up to 1590 °C with adjustable heating rates and holding times. Tests were run with both Ar and CO atmospheres. A pipe is set on the bottom of the furnace, and above that, a crucible is placed upside down. This creates a stand for the crucible which contains test material. It is important that the test material is in the middle of furnace because it is the hottest place in the furnace.

Results

A total of 15 tests have been conducted and some agglomeration has occurred. More research work is needed to find the area where agglomeration occurs. In an inert atmosphere, agglomeration was very weak and only occurs in high temperatures of over 1500 °C. The agglomeration was found to be more pronounced in the CO atmosphere, where agglomeration occurred at about 1500 °C, forming a strong agglomerate. Further tests are planned to be conducted at a lower temperature to find a temperature limit for agglomeration and to study the effects of temperature and time in more detail. The results suggest that agglomeration happens by sintering in reducing conditions.

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6 THE DEVELOPMENT OF AN ANNEALING LINE SIMULATOR

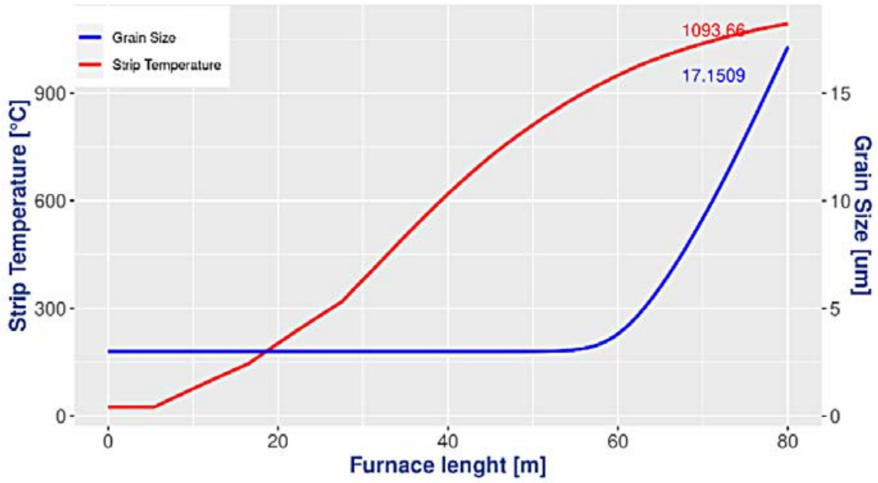

Figure 10. **Temperature and grain size in the strip passing through the line annealing furnace calculated by the simulator.**

Description

The annealing line is a process step in which strips are continuously passed through the annealing furnace. Accurate control of heating and cooling is needed to produce steel with the desired micro-structure and properties. The aim of this work was to develop an offline tool for predicting the evolution of temperature, the oxide scale thickness, and the grain size in the annealing line process. The simulator enables the determination of optimal process parameters such as line speed and furnace temperature profile for different cases. Improved process control is expected to yield 5 % savings in energy and the same reduction in the CO_2 emissions.

Application

The annealing line simulator was implemented on the Elmer open source finite element software. A new module, MarchingOdeSolver, was developed by CSC for integrating the models describing the growth of oxide scale and grain growth in the moving strip. This module is coupled with a fully featured heat transfer module. The coupled solution is extremely efficient – the solution only takes 2 – 3 minutes on a laptop computer.

Results

The annealing line simulator is parametrized and capable of modelling any continuous annealing line. As a pilot case, annealing of cold-rolled grade 1.4307 austenitic stainless steel in the annealing and pickling line two in Outokumpu Tornio Works was modelled. The kinetics of oxidation was modelled based on a laboratory test carried out in the University of Oulu. The results were validated using temperature and grain size measurements made in industrial production.

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7 ACID ANALYTICS FOR METAL RECOVERY PROCESSING

Figure 11. **Studying conductivity behavior in different temperatures.**

Description

In the Tornio cold rolling mill, the used mixed acids from the annealing and pickling processes are regenerated by evaporation and the metals in the solution are crystallized. Sulfuric acid plays a vital role in the regeneration process, especially in the recovery of metals. Online monitoring of sulfuric acid concentration would enhance metal recovery and process efficiency. And so, a research was conducted to investigate the idea of measuring sulfuric acid content by conductivity in a mixed acid solution. Also, the goal was to gain a better understanding of how sulfuric acid could be used as the driving online parameter in the crystallization of metal sulfates from a mixed acid solution.

Application

During the full-scale production trials held in regeneration plant 2, a Valmet 4-electrode conductivity sensor (4300-series) was used. The sensor faced harsh acidic conditions as well as a mix of different ions and solids. When considering the measurement itself, conductivity is affected by all the ionic components in the mixed acid solution. It can vary from different metal ions to residual hydrofluoric and nitric acid.

Results

Regarding mechanical resistance, the sensor proved to be resilient in an extreme production environment. Considering the results, the method showed promise for analyzing the sulfuric acid content in the mixed acid solution. Further studies should be conducted for the sensor recipe as well as connecting information from the sensor to the feed pump of sulfuric acid.

Contact persons

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8 MEASURING DUST EMISSIONS DURING CHARGING IN A COKE OVEN PLANT

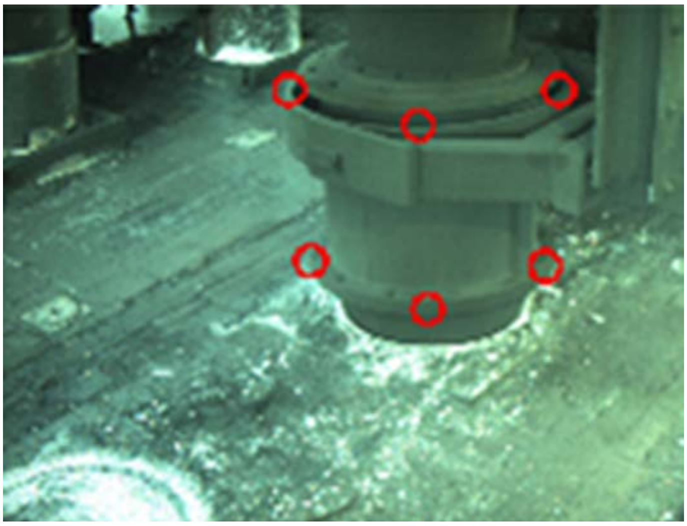

Figure 12. **Coking oven charging equipment with machine vision focus areas (marked in red).**

Description

Metallurgical coke is the main fuel and reducing material of iron ore in a blast furnace process which is the most commonly used process for ironmaking. Coke is produced in coking ovens at a coking plant. In the coke production, the coking ovens are charged with fine coal and the oven is then heated up under a nitrogen atmosphere for a certain period of time. Charging the coking ovens with fine coal occasionally causes dust emissions which are difficult to measure and control. The aim of this work was to create an online camera-based dust detection system for coking ovens during charging to improve dust emission detection and control.

Application

The camera systems and software were installed and set up in co-operation with VTT in the coking ovens at the coking plant of SSAB Europe, Raahe Steel Works. The online camera-based dust detection system was created and test trials were conducted in the industrial environment of the coking plant in co-operation with VTT.

Results

The online camera-based dust measurement system created during the SYMMET project showed good results on the detection of dust emissions during the charging of coking ovens. Further optimization of the tool will be continued.

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9 THE UTILIZATION OF A LADLE SLAG IN THE HOT METAL

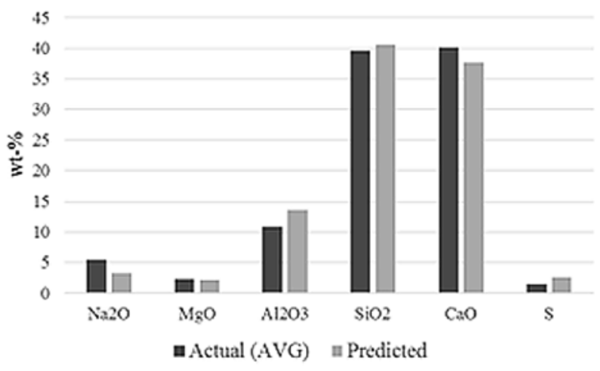

Figure 13. **The average of the normalized measured compositions of the initial slag in the case of ladle slag addition, combined with the predicted composition (m_O = 185.4 kg).**

Description

The primary desulfurization process is used for sulfur removal from hot metal at SSAB Europe Oy, Raahe Steel Works. The primary desulfurization process has variance in its efficiency which is presumably partly due to the fact that the amount and composition of initial slag in primary desulfurization exhibit large variances. The main goal of the work was to study the composition and amount of initial slag, and to identify the effect of initial slag on the efficiency of the desulfurization process. Another aim of the work was to test the utilization potential of ladle slag as a modifying agent to the initial slag.

Application

In order to study the composition and amount of initial slag, a measurement campaign was organized at SSAB Raahe. Additionally, an industrial test-run was conducted, during which the utilization potential of ladle slag was tested in initial slag modification by standardizing initial slag composition with a ladle slag addition. The effects of the ladle slag addition on the liquid fraction, dynamic viscosity and the sulfide capacity of the slag were estimated beforehand.

Results

A data set of the initial amount and composition of the slag was established in the work. Sulfide capacities of the slags were calculated and compared to those estimated utilizing a model found in the literature. A novel model for predicting the sulfide capacity of the slag was constructed. The test-run showed promising results for the utilization of the ladle slag as an addition to the initial slag with respect to the hot metal desulfurization process.

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Publications

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10 THE CAPACITY MANAGEMENT OF COPPER ELECTROREFINING ANODE SLIME TREATMENT

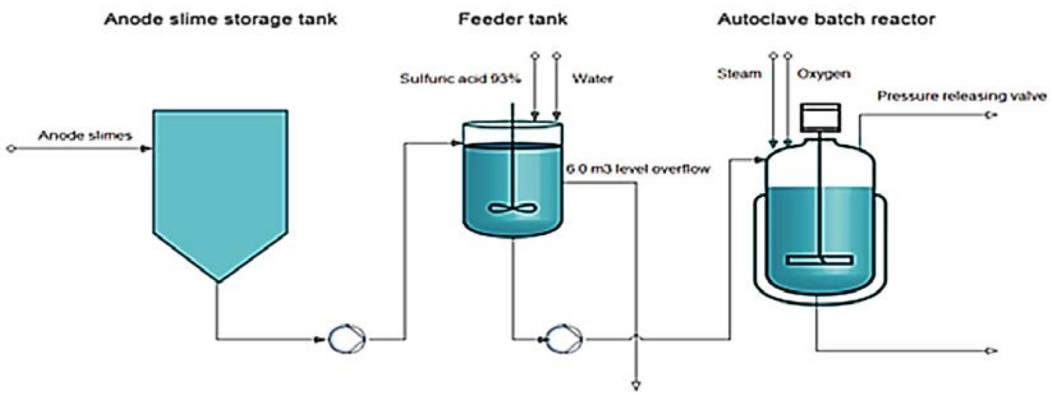

Figure 14. **General flowsheet of anode slime leaching.**

Description

Anode slimes generated during the electrorefining of copper are treated in order to extract valuable metals like gold, silver and palladium. The aim of this study was to investigate innovative options to increase the processing capacity of the leaching stage of anode slimes.

Application

Two research hypotheses were set up: The capacity can be increased by (1) increasing the batch size or by (2) introducing a supporting leaching stage in atmospheric conditions. Testing of the hypothesis was initially done on laboratory-scale and then on full production scale in Boliden Harjavalta's Copper refinery in Pori.

Leaching experiments on laboratory-scale were carried out at sulfuric acid concentrations of 100 – 300 g/l and temperatures of 40 – 80 °C. The industrial-scale experiments were carried out in an industrial autoclave and in an atmospheric reactor.

Results

The atmospheric leaching showed slow leaching kinetics for copper leaching, but a low leaching degree of selenium and tellurium might open new possibilities for circulating the leaching solution in the refinery process. Based on industrial-scale tests, increasing the batch size was found to be the most practical alternative for increasing the production output.

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Publications

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11 CRITICAL AND PRECIOUS METALS RECOVERY FROM WEEE AND ENERGY STORAGE MATERIALS IN COPPER PRODUCTION

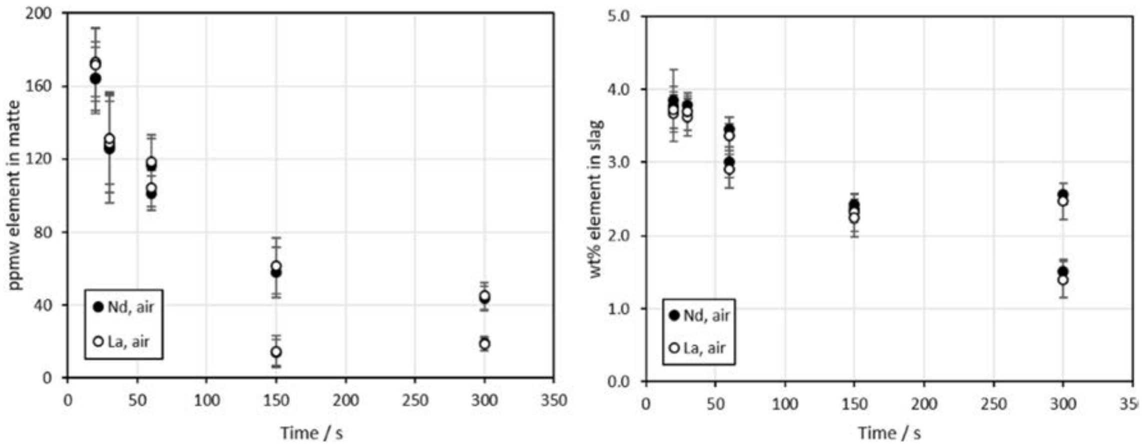

Figure 15. **The concentration of La and Nd in matte and slag as a function of time.**

Description

Electronic devices can contain precious metals more than their respective primary ores, which in many cases are depleting. Pyrometallurgical methods of WEEE recycling are advantageous, because the processes can accept many forms of scrap and there are existing facilities for WEEE smelting. With an increasing amount of electronic devices and electric vehicles, the amount of lithium ion batteries will also increase in the future. Recycling those critical and precious metals is increasingly important. The goal of our study was to investigate the possibility of integrating the existing primary copper smelting with the recycling of WEEE and EoL Energy Storage Scrap. The behavior of rare and critical metals in high temperature processes was investigated as a function of time. The employed experimental technique included high-temperature heating of the sample at a controlled temperature and a gas atmosphere, followed by rapid quenching into an ice-water mixture to capture the time dependent change in the sample.

Application

The studies provided fundamental kinetic distribution behavior of precious metals and critical metals, which can be used for process development, evaluation, and optimization. The aim in the future is to formulate kinetic rate equations describing the behavior of trace elements in copper smelting conditions based on the experimental results of this research. These rate equations will be used for optimizing the processes so that they are utilizing the WEEE and EoL energy storages feed as efficiently as possible, and for improving the modelling of time-dependent high-temperature processes.

Results

The time-dependent behavior of precious metals, Rare Earth Elements (REEs), and critical battery materials in a copper matte-slag system in simulated copper flash smelting conditions was studied. Precious metals favor the copper and iron-bearing phases over the slag phase and the formation of precious metal droplets and the migration to the matte phase begins almost instantly, when the system reaches a high enough temperature. Cobalt distributes quite evenly between the slag and the matte whereas lithium, manganese, and REEs deport predominantly in the slag at all investigated oxygen partial pressures.

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12 APPLIED MICROWAVE IN THE PROCESSING AND RECYCLING OF BLAST FURNACE (BF) AND BASIC OXYGEN FURNACE (BOF) SLUDGES (SSAB)

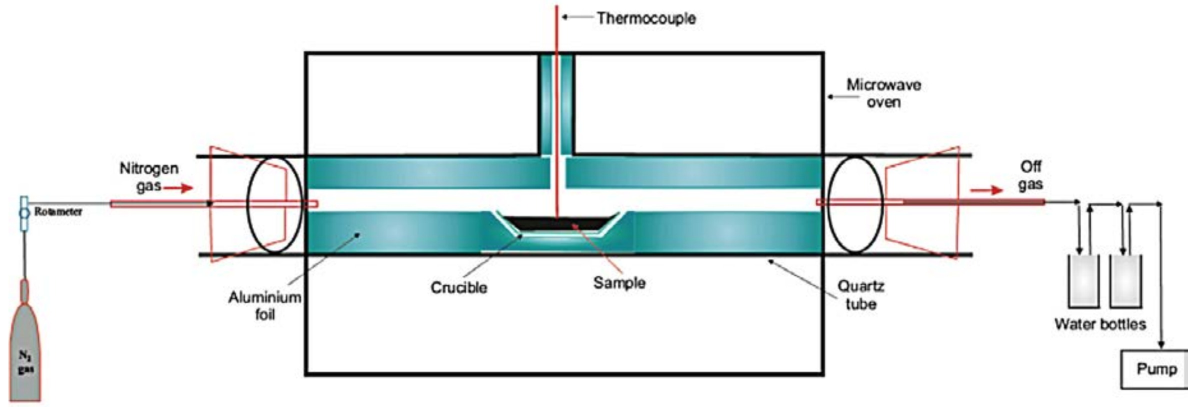

Figure 16. **Schematic diagram of the microwave experimental set-up.**

Description

Blast furnace (BF) and basic oxygen furnace (BOF) sludge are fine wastes generated during the purification of the flue gases emitted by the furnace. The sludges contain metals in the form of oxides, which can be reduced and re-used in the steelmaking cycle. The recycling of wastes back to steel production is hindered owing to the presence of zinc, which causes operational difficulties in the steelmaking processes.

Application

A new pre-treatment technology for the removal of zinc and volatile components in the fines based on microwave heating was proposed. The objectives of the proposed method was to utilize the advantages of microwave energy in the following simultaneous reactions:

1. Microwave drying of BF and BOF sludges.
2. Microwave removal of Zn from BF and BOF sludges.
3. Microwave reduction of iron oxide included in BF and BOF sludges.

Results

The microwave experiments have been carried out on a laboratory scale. The information obtained in the laboratory-scale microwave experiments such as the materials absorption of microwaves, and zinc removal rate and iron recovery, will be used later to design an industrial-scale microwave application. The results show that microwave was efficient for processing and recycling BF and BOF sludges.

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Publications

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13 LABORATORY ANNEALING OF COLD-ROLLED STAINLESS STEEL

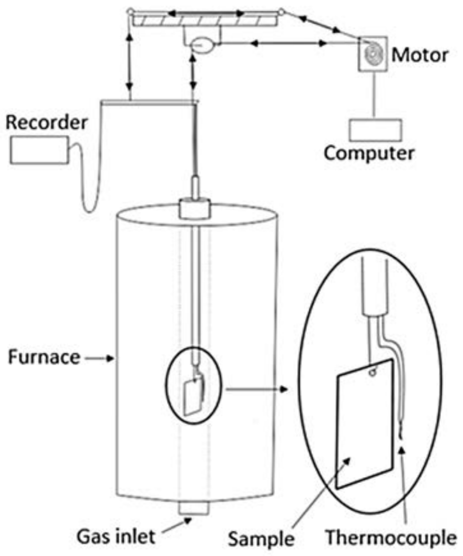

Figure 17. **Experiment setup for sample vertical adjustment in TG-furnace.**

Description

Annealing of cold-rolled stainless steel produces a thin oxide scale layer on the surface of the steel. The oxide scale is removed by pickling in the next step of the process. Annealing conditions affect the properties of the oxide scale, and the type of the scale influences the efficiency of the pickling process. The laboratory annealing allows the optimization of the annealing temperature, time and atmosphere for different steel grades regarding the oxide scale formation. The aim of the study was to simulate the final annealing of stainless steel in the laboratory, characterize the formed oxide scale and remove it with neutral electrolyte pickling.

Application

The annealing device was constructed in connection with a vertical tube furnace. The heating profile was produced in an isothermal furnace by adjusting the vertical position of the stainless steel sample in the furnace with a computer-controlled electric motor. The vertical temperature profile of the furnace was determined at different operating temperatures. These profiles were used in calculating the required vertical position for the sample in the furnace to be in a given time-step to simulate the industrial annealing furnace's heating profile.

Results

Annealing of cold-rolled AISI 304 stainless steel in water vapor containing atmosphere with different temperature and time was used to produce the oxide scales. The thickness, morphology and composition of the oxide scale were found to be annealing temperature and time dependent. The annealing conditions in which the oxide scales change significantly were determined. Under these conditions, a clear decrease in the efficiency of electrolytic pickling was also observed. In future work, the oxide scale formation of different steel grades in different conditions will be studied.

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Publications

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14 DATA-DRIVEN MODELLING OF HOT METAL DESULFURIZATION

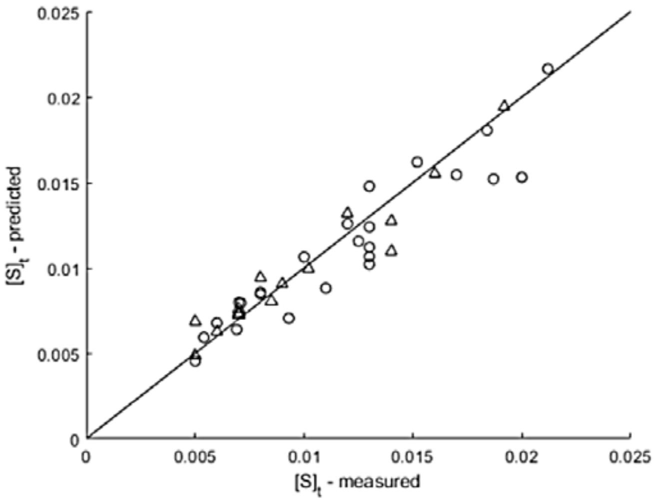

Figure 18. **Measured and predicted sulphur contents.**

Description

In this task, a data-driven modelling framework for hot metal desulfurization was developed. The developed tools can be used for systematic gray- and black-box model identification for the process. The main emphasis of the package was to quantitatively explain some key phenomena, but also to use the models for prediction.

Application

When implemented, the tools can be used for offline identification and due to low computational load, the pre-trained models are applicable in online use. More specifically, the use of models would allow more systematic control of the hot metal desulfurization process.

Results

The results of this study show that the data-driven models are well-suited for predicting the end content of sulfur in the process, as well as the sulfide capacity of the slag phase. In addition, the evolutionary search algorithms were found very efficient both in input variable selection and model parameter identification tasks.

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15 THE EVALUATION OF THE COMPOSITION OF LADLE FURNACE SLAG WITH OPTICAL EMISSION SPECTROSCOPY

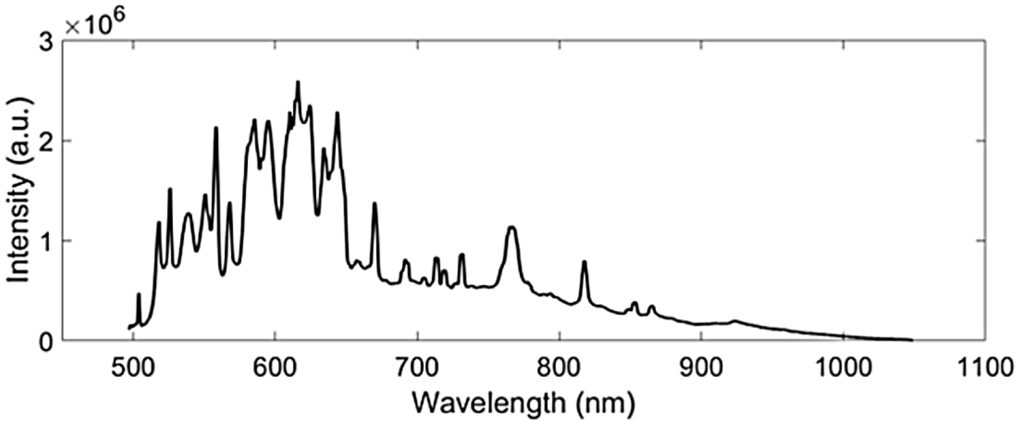

Figure 19. **The optical emission spectrum from an industrial LF.**

Description

A ladle furnace (LF) is an essential part of steel refinement in electric steelmaking. Since the chemical and physical properties of slag have a key role in the process, online data of slag composition would be of great value. Optical emission spectroscopy (OES) is a method that is capable of online data acquisition with equipment that withstands the extreme furnace environment. In high temperatures, such as the electric arc of LF, each atom and molecule radiate with element specific wavelengths. These optical emissions are measured with a spectrometer, resulting in the optical emission spectra that contain optical emission lines from each particle within the arc. With this element sensitive measurement method, the slag composition can be evaluated. Due to the high temperature of arcs, plasma diagnostics can be used as a data validation tool for the OES data.

Application

Three spectrometers were used to measure the optical emissions from the arc of a 140 t industrial LF at Deutsche Edelstahlwerke, Germany. Light from the arc was guided to the spectrometers with optical fibers that were attached to a measurement head. The measurement head was located 5 m away from the LF and looked into the furnace through the gap between the furnace roof and the ladle. The OES equipment was capable of online data acquisition and did not require any maintenance during the measurement campaign. Reference slag composition data was measured with X-ray fluorescence (XRF).

Results

Atomic optical emission lines of calcium, magnesium, and manganese were analyzed from the emission spectra. These lines were used to correlate the OES data with XRF results of CaF_2, MgO, and MnO. Promising correlations between these components were found, together with a correlation between calcium plasma temperature and XRF analyzed CaF_2 slag content. Equilibrium composition calculations were performed to study the composition of arc plasma, indicating that most of the molecular components are in their atomic counterparts in the plasma already at 5000 K. Furthermore, the amount of atomic magnesium in the plasma stays relatively constant despite changing plasma temperature, making it a suitable reference element for OES correlation.

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Publications

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SYMMET

16 ALKALI ACTIVATION OF ZINC RESIDUE SLAG

Description

Alkali activated materials are alternative solutions for using ordinary Portland cement in construction. Alkali activation is the generic term which is applied to the reaction of a solid aluminosilicate under alkaline conditions to produce a hardened binder. In this work, alkali activation of iron-rich slag from zinc production was studied.

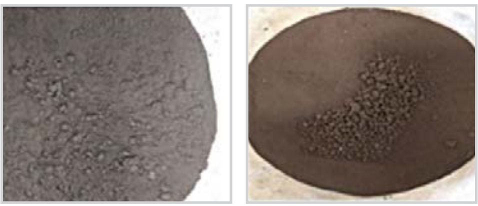
Application

Zinc residue slag was ground to fine powder, and then sieved through a 63 µm sieve. Then it was mixed with different co-binders and cast in 20 x 20 x 80 mm molds. Mechanical properties were studied after 28 days of curing. See figure below for different process steps:

Results

- Zinc residue slag is a promising raw material for alkali activation
- At least 30 MPa can be reached which is the strength of normal concrete
- Metakaolin is the best co-binder for zinc residue slag
- Also 100 % eco-mortar from the zinc residue slag can be produced -> one part needs to be ground into a fine powder and the second part can be used 'as is'

Milled zinc residue slag



Alkali-acivation of slag

Samples cased with 20x20x80 mm moulds.

Figure 20. **Ground zinc residue slag is a promising material for alkali activated materials**

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17 DISTRIBUTION OF RARE AND CRITICAL METALS IN PYROMETALLURGICAL PROCESSING OF WEEE AND EOL ENERGY STORAGE SCRAP

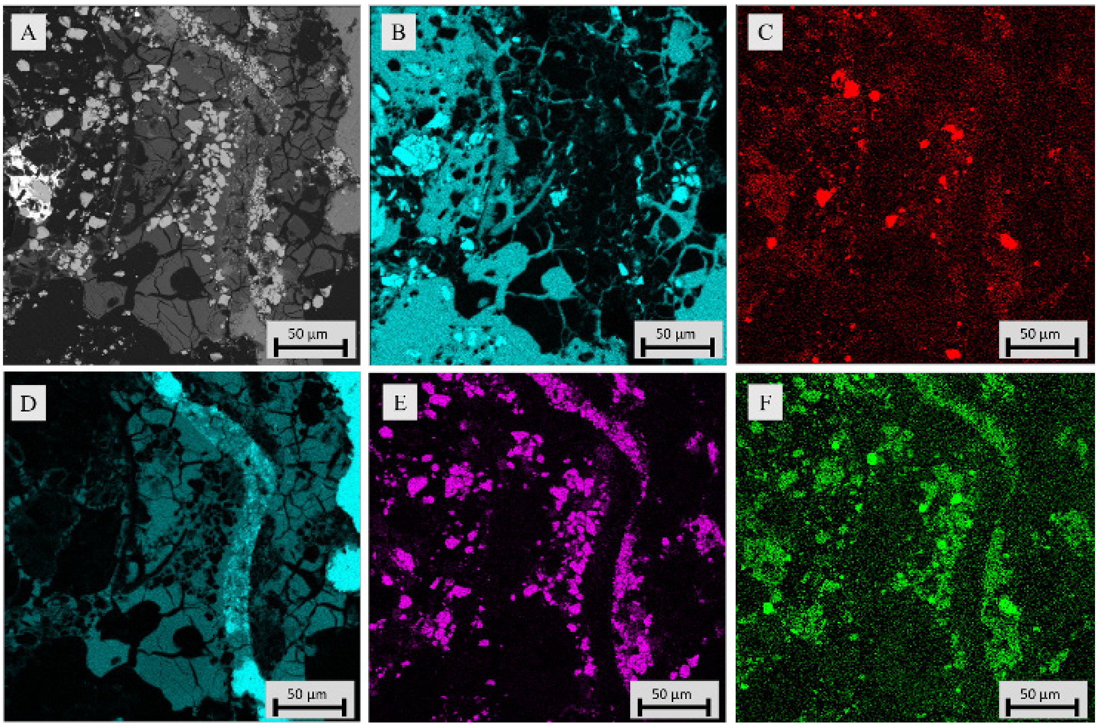

Figure 21. **Froth flotation fraction with battery scrap used as raw material for nickel slag cleaning. EDS-mapping of O – 1 min froth fraction, (A) overview, (B) carbon, (C) manganese, (D) aluminum, (E) cobalt and (F) nickel.**

Description

Recycling metals from different waste streams must be increased in the near future to secure the availability of metals that are critical for high-tech applications, such as batteries for e-mobility. The goal of our study was to investigate the possibility of integrating the existing pyrometallurgical processes, e.g. primary and secondary copper smelting and nickel-slag cleaning process with the recycling of WEEE and EoL Energy Storage Scrap. The behavior of different rare and critical metals in high temperature processes was investigated in equilibrium and as a function of time. The employed experimental technique included high-temperature heating of the sample at a controlled temperature and a gas atmosphere, followed by rapid quenching into an ice-water mixture.

Application

The studies provided fundamental thermodynamic data about the distribution behavior of battery metals, which can be used for process development, evaluation, and optimization. The aim in the future is to formulate kinetic rate equations describing the behavior of trace elements in copper smelting conditions based on the experimental results of this research. These rate equations will be used for optimizing the processes so that they are utilizing the WEEE and EoL energy storages feed as efficiently as possible, and for improving the modelling of time-dependent high-temperature processes.

Results

It was discovered that in simulated copper smelting most cobalt can be recovered into the copper alloy in extremely reducing process conditions, whereas lithium, manganese, and Rare Earth Elements deport predominantly in the slag at all investigated oxygen partial pressures.

The integration of battery scrap recycling and nickel slag cleaning by reduction with methane was experimentally researched for the first time. It was noted that a higher initial amount of cobalt in the feed mixture increased the recovery of cobalt to the metal alloy. This study confirmed the possibility of replacing coke with methane as a non-fossil reductant in nickel slag cleaning on a laboratory scale.

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Publications

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18

COMPUTER MODELLING THERMODYNAMIC AND KINETIC PHENOMENA IN NON-FERROUS METALS PRODUCTION

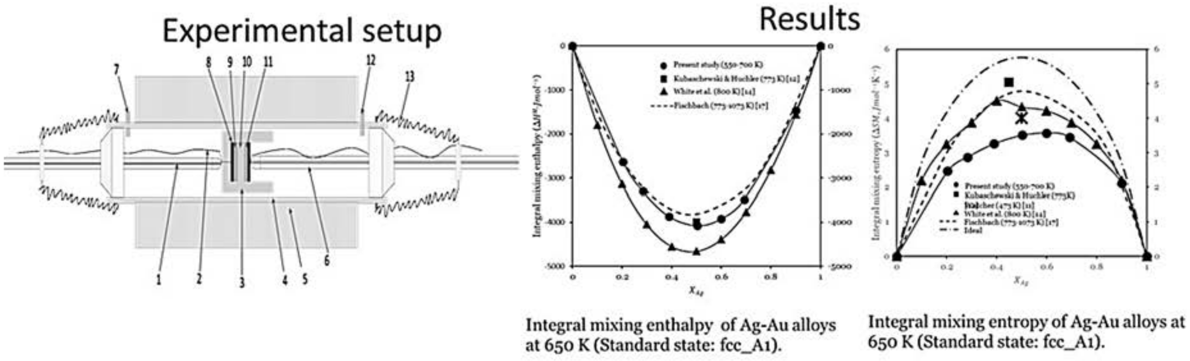

Figure 22. **EMF-measurements with Ag conducting electrolyte of Ag-Au alloy**

Description

Today's process control software is based on parameters derived from industrial practice and collected data, supported with thermodynamic data. Raw materials entering metallurgical processes, however, contain increasing amounts of trace elements and impurities whose impact in thermodynamic properties of melts in metallurgy (especially slags) is tremendous, but not known in detail. The digitalization of all data and fundamental rate equations, which are the exceptionally important outcomes, and combined with the internet of things will finally make it possible to start increasing yield and real time control of emissions and waste production or composition towards closed processes which can be controlled with predictive real-time algorithms.

Application

The studies provided new thermodynamic data that was used to optimize thermodynamic models for alloys and slags in nickel and copper smelting. In the future, kinetic rate equations will be formulated to describe the behavior of trace elements in copper smelting conditions based on the experimental results of this research. In the present work, the solubility of carbon in molten iron-nickel-cobalt alloys was measured and modeled, as well as the thermodynamic properties of Ag-Au alloys.

Results

It was shown that a new approach to modeling the carbon solubility in Fe-Ni and Ni-Co molten alloys with the quasi-chemical model gives better predictions in multicom xponent systems, and can give better predictions on the slag/alloy or slag/matte behavior in pyrometallurgical processes.

The thermodynamic behavior of Ag-Au was measured and modeled based on the experimental results, and the recovery of Ag and Au in smelting can be more accurately predicted in future processes.

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19 USING NON-FOSSIL REDUCTANTS IN NON-FERROUS AND DUSTS: INTERNAL RECYCLING, GEOPOLYMERS AND OTHER BINDER SYSTEMS

Description

Owing to their use in technological and strategic applications like semiconductors, infrared optics, optical fibers, medicine, and catalysis, Ga, Ge and In are becoming increasingly important for the global industry. Although Ga, Ge and In are often found together in nature, they generally only exist in trace amounts in many minerals, from which the extraction is not usually economically viable. Currently, gallium and germanium are mainly recovered from the metallurgical by-products of zinc, copper and aluminum. Therefore, the utilization of by-products and the recycling of valuable elements is of importance.

Application

Zinc refinery residues, which are the typical by-products of hydrometallurgical zinc processes, usually contain between 0.20 – 0.50 wt% Ge and 0.30 – 0.40 wt% Ga with Zn, SiO_2, Cu, Fe and Pb as the main components (Liu et al, 2016). Both Ga and Ge exist as their dissociative or combined oxides with iron and silica. As Ga and Ge are difficult to recover and to separate from such compounds, currently there is no mature industrial process for Ga, Ge and In recovery from these types of residue.

Results

A literature study was conducted in order to study In, Ga and Ge leaching, and specifically tannin precipitation. It was discovered that recovery of Ga and Ge from process residues has been investigated, e.g. by sulfuric acid leaching, pressure sulfuric acid leaching or stepwise leaching with sulfuric and hydrochloric acid. Also oxalic acid has been used as it forms stable Ga and Ge complexes and therefore selectivity towards Zn, Cu and Si can be achieved. Extraction of Ga and Ge can further be conducted e.g. by tri(octyl-decyl) amine (N235). However, in industrial processing, sulfuric acid based processes dominate. Furthermore, the extracted Ga(III) and Ge(IV) can be almost completely separated by sequential stripping using sulfuric acid and NaOH. In order to reduce the amount of oxalic acid, a novel two-stage leaching process has been adopted; zinc refinery residues are first leached with low concentration sulfuric acid resulting in selective Zn(II) and Cu(II) dissolution, whilst Ga(III) and Ge(IV) are enriched to the high silicon residues to be further dissolved by oxalic acid.

Recovery from dilute solutions (<1 g/L) of Ga and Ge can be conducted by various methods, such as tannin precipitation, neutralization (hydrolysis) and cementation with Zn powder. Although tannin precipitation can achieve selective separation of Ge, its decomposition products challenge the following zinc electrolysis operation by decreasing the current efficiency. Increasing tannin from 10 mg/L to 50 mg/L can decrease the current efficiency from 89 % to 78 %. Further, the presence of tannin may decrease the final Zn product quality making the product brittle. Methods for tannin management in the electrolyte are decomposition by $KMnO_4$ or the addition of Mn^{2+} (15 g/L) into the solution. Tannin-germanium residues are often treated by using traditional processes such as oxidative roasting and chlorination distillation. Recently, also oxalate conversion has been suggested.

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20 THE MODELLING OF NEUTRAL ELECTROLYTIC PICKLING

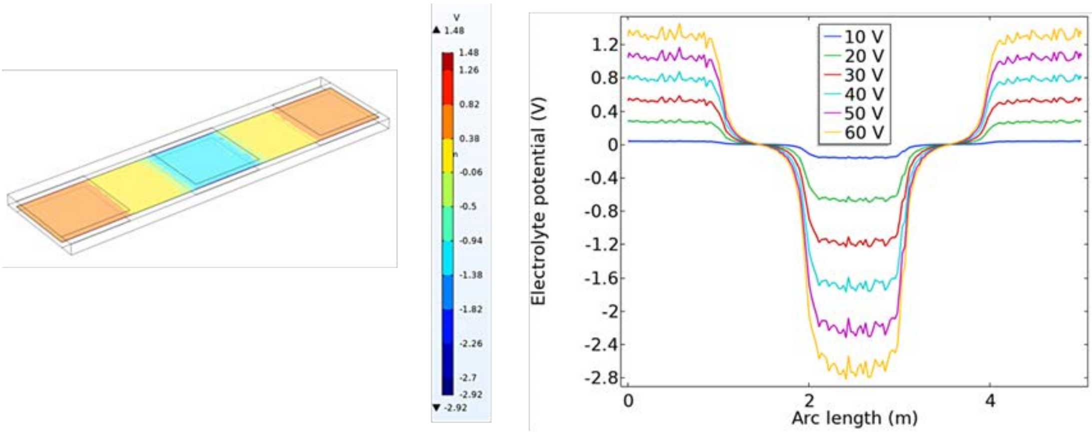

Figure 23. **Comsol model of Neutral Electrolytic Pickling. The polarization of steel strip surfaces requires large cell voltages and polarization is largest just opposite the anodes and cathodes.**

Description

Oxide scale is formed on stainless steels when they are heated up during the manufacturing cycle. The removal of the oxide scale and chromium depleted subscale by pickling is necessary to maintain surface quality. In electrolytic pickling using neutral sodium sulfate solution, the steel strip is not electrically connected to a current source, and the moving strip acts as a bipolar electrode between alternating anode and cathode banks. The challenge is to produce rapid and large polarization that can assist scale removal. The aim of the study was to evaluate how the geometry of the cell, and the electrolyte conductivity, will affect the strip polarization. The main target was to increase the current efficiency of the process.

Application

The actual current density at the coil surface is difficult to estimate as not all current passes from the cathodes to the anode through the coil and some of the current will flow through the electrolyte directly from the cathodes to the anode. The primary current distribution determines how much current is available to the descaling reactions. This is affected by electrode arrangements and conductivity. Polarization and conductivity modelling were used to determine the required strip surface polarization.

Results

The necessary polarization was measured to be approximately 2 V in the anode side and 1 V in the cathode side. The polarization must develop in seconds due to the high speed of the strip. This requires current density in the order of 100 A/m^2 or more on the strip surface. The conductivity of the electrolyte was 170 – 250 mS/cm in the test range 150 – 200 g/dm^3 Na_2SO_4 and 60 – 80 °C and the conductivity is not expected to have a major effect on current distribution.

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21 THE DYNAMIC MODELLING OF THE MIXED-ACID PICKLING PROCESS

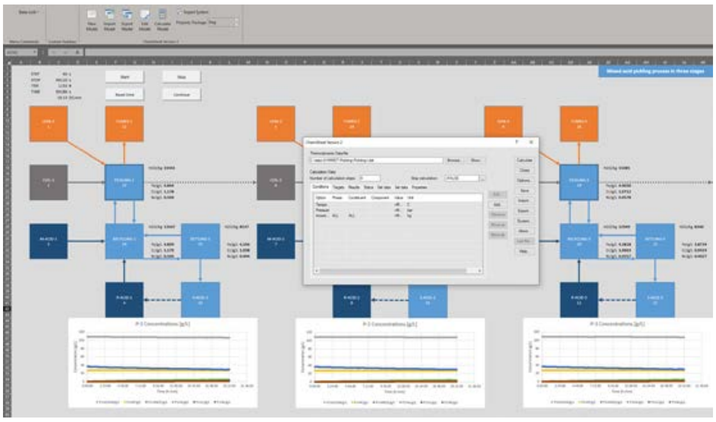

Figure 24. **Flowsheet of the pickling process and ChemSheet dialog window.**

Description

Production scheduling and control of the pickling process are needed to minimize the hazardous materials in the effluent and to maintain the optimal concentration of acid solution in the tanks. The goal of this work was to make a dynamic simulation model that can be used for the improved understanding of the mixed acid pickling process. The simulation model was implemented in Microsoft Excel by using ChemSheet version 2 and Excel macros.

Application

In the last phase of steel production, metals are rolled and subsequently annealed to achieve desired properties and structure. The annealing processes occur in the presence of air that creates a film of chromium, iron and other metal oxides on the steel surface. Pickling processes that consist of series of acid baths are made to remove these oxides from the metal surfaces. The mixed solution of fluoric acid, nitric acid and sulfuric acid is used as a pickling acid in Outokumpu HP4 pickling for austenitic steels. The chemical species in the pickling system were compiled from VTT's aqueous database. The included elements are H, N, O, F, S, Fe, Cr, and Ni. The included phases are gas (air and volatiles), aqueous (water, dissolved acids and formed complexes) and a number of pure solid phases (coil metals and oxides). In the model, there are three pickling units in sequence and one pickling unit contains a pickling tank, a recycle tank, and a settling tank, corresponding to Outokumpu's process. Acids circulate between the pickling tanks and the recycle tanks, and the recycle tanks and the settling tanks. Spent acids are taken from the settling tanks to the acid regeneration and the regenerated acid is added back to the recycle tanks.

Results

The test simulation was done as a two week operation period with constant input starting from a situation where the pickling, recycling, and settling tanks were filled with acid mixture without dissolved metals. After the first time-step (each time-step equals one minute), the metals from the coil started to dissolve in the pickling tanks with a given rate, 40 % in the first stage, and 30 % in the second and the third stages. Two weeks' time was enough for the model to reach steady-state condition.

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AQUEOUS ELECTROLYTES THERMODYNAMICS

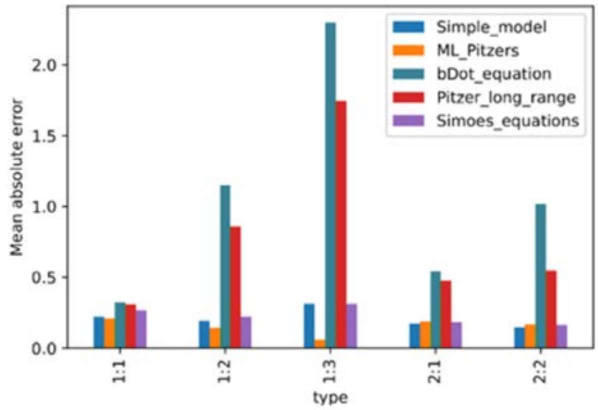

Figure 25. **Mean absolute error of in γ± for the different models, by electrolyte type.**

Description

The object was to develop thermodynamic methods applicable to the modelling of hydrometallurgical conditions. The task was divided into generating a theory and practical methods for aqueous phase diagrams, collecting thermodynamic data for pickling solutions and studying the suitability of the artificial neural network (ANN) model for predicting ionic interaction parameters in aqueous solutions.

Application

The collected thermodynamic data was entered into FactSage, a program for drawing phase diagrams illustrating the effect of the extent of the reactions, affinities and redox potentials on the thermochemistry of aqueous systems. For the prediction ionic interaction parameters, a neural net model was trained on a dataset of 123 ion pairs to predict the mean activity coefficients of binary electrolytes from ion specific properties.

Results

The new kinds of phase diagrams were shown to illustrate the various reactive domains in aqueous chemistry. The ANN-generated Pitzer parameters outperformed traditional activity coefficient expressions, such as the Davies equation. However, the improvements were slight compared to two expressions determined by more conventional regression analysis procedures, one derived in this work and the other found in literature both utilizing only the ionic radii and charges. The comparable performance of the neural net to these models may therefore imply that the ionic radii is the only ion specific feature tested with a strong relationship to the activity coefficient. Nevertheless, using neural networks for estimating Pitzer parameters was shown to be feasible. Accuracy is expected to improve with larger datasets.

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Publications

Kattelus, J. 2020. Artificial Neural Networks for Predicting Pitzer Parameters Based on Ion Specific Properties. Bachelor's thesis. Aalto University.

23 NOVEL METHODS FOR THE PRODUCTION OF VALUE-ADDED PRODUCTS FROM STEELMAKING SLAGS

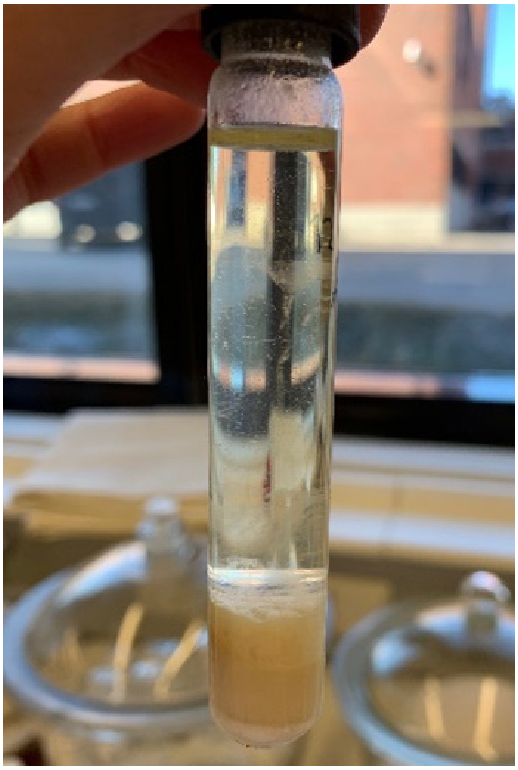

Figure 26. **Calcium soap precipitate formed in reaction with rapeseed oil.**

Description

In addition to their primary products, the iron and steelmaking industries produce slags containing mainly CaO, FeO, MgO and Al_2O_3 which are still partly landfilled. The aim of this task was to find novel methods for the treatment of steelmaking slags. Novel products beyond $CaCO_3$ were of interest.

Application

Industrial samples of blast furnace slag, desulfurization slag, as well as basic oxygen furnace slag and ladle slag were used. Alkali metal salts of low and high molecular weight organic acids were the selected products due to their novelty, market potential and environmental impact. Experiments were carried out in a batch reactor.

Results

A new route to calcium formate that does not use formic acid as a raw material was identified and demonstrated. Also, production of calcium soap from rapeseed oil (waste cooking oil) was demonstrated. The synthesis of each product was first successfully conducted using commercial reagents. With industrial slags, 34 % to 97 % conversion was reached depending on the slag. The yield varied greatly (31 % to 84 %) depending on the synthesis route even for a given slag.

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Publications

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24

THE PURIFICATION OF ANODE SLIME LEACHATES

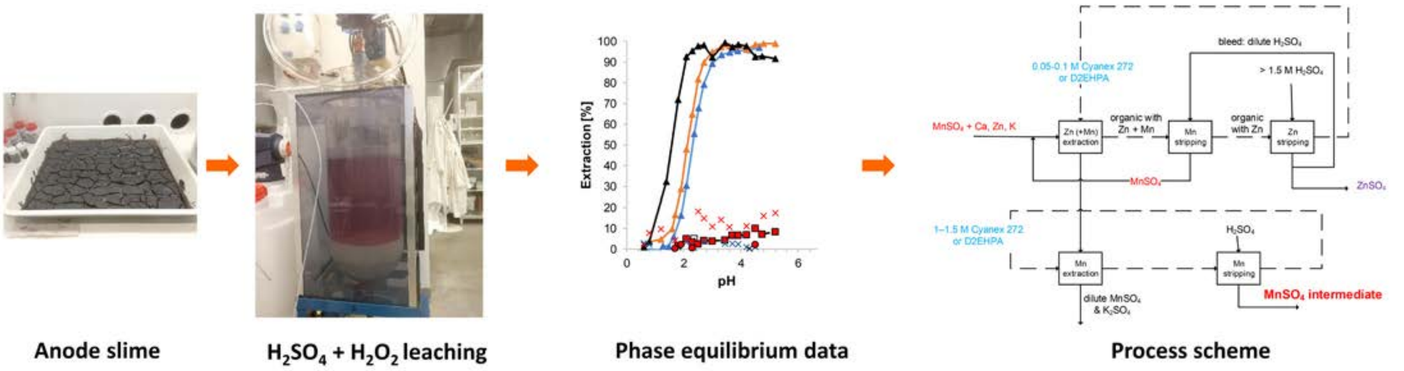

Figure 27. **From laboratory scale fundamental studies to process scheme development and experimental verification in LUT University's SYMMET subproject.**

Description

Zinc electrolysis anode slime could be a secondary source for manganese, the demand of which is increasing alongside the wider adoption of electric vehicles. In this task, the purification of anode slime leachate to high grade manganese was studied using liquid-liquid extraction.

Application

Approximately 60 L of anode slime leachate was produced from an industrial sample by sulfuric acid leaching under strongly oxidizing conditions in a batch reactor. The effects of extractant concentration, equilibrium pH, temperature and the extent of organic phase loading were studied in batch experiments. Continuous operation was demonstrated in a laboratory-scale mixer-settler.

Results

It was concluded that commercial solvent extraction reagents D2EHPA and Cyanex 272 (both organophosphorus acid derivatives) can remove Zn impurity efficiently, but Ca removal was not achieved since Ca/Mn selectivity was not good enough with such high Mn concentration. A process scheme was developed for producing high grade $MnSO_4$. $MnSO_4$ raffinates with less than 5 mg/L of Zn were obtained at O/A = 1, pH = 3, and 0.8 M extractant concentration in batch experiments under 25 °C with both of the extractants. Cyanex 272 had a higher Zn/Ca selectivity than D2EHPA. One significant part of the research was the characterization of the used MEAB MSU 0.5 mixer-settlers by determining the residence time distributions. Online conductivity and pH measurements were used to monitor the responses for stepwise tracer injections. The mean residence time within the mixer was found to deviate from nominal space time.

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THE REDUCTION OF ENVIRONMENTAL IMPACTS

Summary, key results and impacts

The technology teams 3 and 4 focused on topics related to renewable energy sources and non-fossil reductants, and the treatment of rejects. The activities consisted of literature studies, laboratory scale research, pilot tests and full-scale industrial trials, and measurement campaigns. The activities were conducted by research institutes (University of Oulu, Aalto University, VTT), SMEs and other domestic companies (Boliden Harjavalta Oy and Boliden Kokkola Oy, Outokumpu Stainless Oy, Outotec Finland Oy, Owatec Group Oy, SSAB Europe Oy). The research topics and main targets are summarized in the list below and the results are presented in the following Task Summaries.

Boliden Harjavalta: The testing and comparison of different reductants in copper and nickel smelting.

Boliden Kokkola: The use of non-fossil reductants in non-ferrous metals production residue treatments. Hydrometallurgical research on metal valorization from complex dusts.

Outokumpu: Online emission control and selective metal recovery.

Outotec: Replacing part of fossil reductants with non-fossil ones, and the application of Outotec DC technology for dust treatment.

Owatec Group: OwaGtube -method development and improvement, and a new water/sludge treatment process as well as an electrochemical water treatment method for cyanide waters.

SSAB: Research on LNG (liquefied natural gas) applications for improving iron and steel making processes, and proving validation data for CFD modelling.

Aalto University: Research on the use of non-fossil reductants in the cleaning of non-ferrous slags, including Cu slag reduction with CH_4 based reductants and Ni slag reduction with bio-based reductants. The pyrometallurgical treatment of steel-making dusts for investigating dust and refractory interactions.

University of Oulu: The mathematical and CFD modeling of the use of fine by-product stream, natural gas, and reagent injection in pig iron desulfurization. Experimental research on the effect of non-fossil raw materials on metallurgical coke properties. The study of possible non-fossil reducing agents, pyrolysis methods and a selection of non-fossil reducing agents related to the use of non-fossil reductants in non-ferrous metals treatment. The effect of LNG use on iron ore pellet reduction behavior in a blast furnace. Zinc and sulfur circulation in a submerged arc furnace, including HSC modeling. The recovery of precious metals from metallurgical slags and dusts in the zinc process, including the development of the hydrometallurgical process, as well as the recycling of zinc from sewage sludges.

VTT Technical Research Centre: Supporting the development of new hydrometallurgical methods for dust and sludge treatment by developing advanced thermokinetic models. The recovery of secondary and heavy metals from dust and waste, allowing the side streams to be valorized. Investigation of sources for non-fossil reducing agents in jarosite treatment.

SYMMET

THE REDUCTION OF ENVIRONMENTAL IMPACTS TASK SUMMARIES

25 THE UTILIZATION OF STEEL SLAG IN ZINC REMOVAL FROM THE SUBMERGED ARC FURNACE FLUE GAS WASH WATER

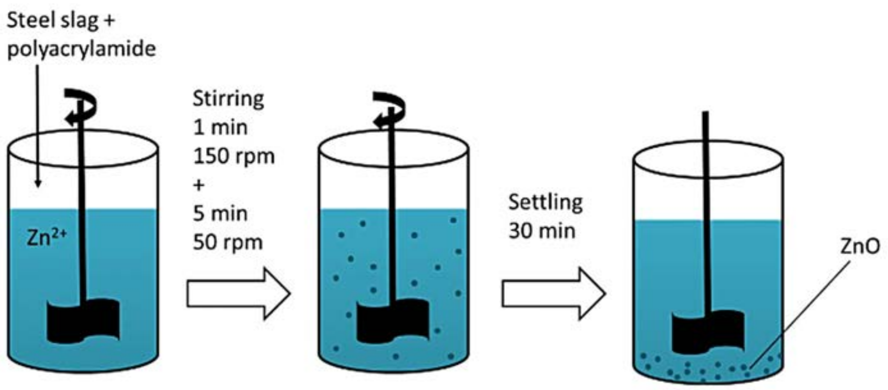

Figure 28. **A schematic diagram of zinc removal experiments using steel slag and polyacrylamide**

Description

In a ferrochrome production plant, zinc from the raw material chromite ore is transferred with the produced submerged arc furnace (SAF) flue gas to the flue gas wash water. The SAF flue gas wash water contains both dissolved and particulate zinc. The amount of zinc in the discharge water is regulated.

Application

A new method for improved zinc removal from the SAF flue gas wash water using steel slag, a side stream containing mostly argon oxygen decarburization slag, together with polyacrylamide, was introduced.

Results

The utilization of steel slag together with polyacrylamide for improved zinc removal from the SAF flue gas wash water compared to the current treatment with only polyacrylamide was investigated in laboratory scale. The results show that treatment with steel slag together with polyacrylamide is efficient for zinc removal from the SAF flue gas wash water with the main zinc removal mechanism precipitation as zinc oxide.

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Publications

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26 THE TECHNOLOGY FOR CYANIDE REMOVAL FROM SIDE STREAM WATERS

$$CN^- + O_3(l) \rightarrow OCN^- + O_2(l)$$
$$3CN^- + O_3(l) \rightarrow 3OCN^-$$

$$2OCN^- + 3O_3(l) + H_2O \rightarrow 2HCO_3^- + N_2(g) + 3O_2(l)$$
$$3OCN^- + O_3(l) + H_2O \rightarrow 2HCO_3^- + N_2(g)$$

Figure 29. **shows the proposed reactions of the cyanide with ozone.**

Description

Owatec Group Oy tested methods to oxidize the cyanide from the water. The tested methods were electrochemical oxidation (OwaReactor), aeration with a multi phase pump ($OwaO_2$), and ozone injection with a multi phase pump ($OwaO_3$).

OwaReactor is an advanced oxidation treatment technology. In OwaReactor O_2, O_3, and OH radicals ClO^- and H_2O_2 are generated and pollutants are oxidized from the water. There is also direct oxidation at the anode. Treatment is based on electrochemical oxidation that also creates nanobubbles. First the cyanide and cyano complexes become oxidized to form cyanate ions at the anode. The ions are then decomposed into carbon dioxide and nitrogen gas. Dissociated metal cations are reduced at the cathode.

Multi-phase pump generates microbubbles into the water. It simultaneously draws in air or other used gas and water, dissolves the air/gas with its turbine impeller and pumps the pressurized water to the reaction tank or other process stage. Like oxygen, ozone reacts with the cyanide to produce cyanate. Continued addition of ozone will convert the cyanate into carbonate and nitrogen gas.

Application

Verified methods would be needed in the future if the cyanide will not be oxidized any longer during slag granulation process.

Results

The tests were done at the Outokumpu Chrome plant with cyanide-containing water before its oxidation at the granulation process. The cyanide level in the water was 0,375 mg/l during the trial before any treatment.

All performed technologies/methods were capable of destroying / oxidizing the cyanide to rather low levels. The combination of electrochemical oxidation and multi-phase pump technologies gave the highest reduction (95 %) level.

Nevertheless, the $OwaO_3$ technology where ozone is mixed to the water with multi phase pumps has the best price – quality ratio. The reduction was 90 % to the concentration level of 0,038 mg/l. Figure 2 shows the water before and after the $OwaO_3$ treatment.

Because the method itself was proven in a small scale pilot, co-operation will continue with larger-scale trials to understand the operational performance of the system.

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27

THE USE OF REDUCTANTS IN THE PREVENTION AND REMOVAL OF BUILD-UPS

Figure 30. **Management of furnace lifetime is vital part of smelter operations. Boliden Harjavalta operates several furnaces.**

Description

Boliden Harjavalta has made full-scale trials with reductants in smelting furnaces. Reductants could help to keep furnaces and process parameters in control, reduce downtime during shutdown, and improve stability. The target with major maintenance overhauls is to lengthen the period between them and to shorten the duration overhauls.

Application

The build-ups in flash smelting furnaces are generally over-oxidized material like magnetite. The hypothesis of the study was that with the intelligent use of reductants, the removal of build-ups could be done during the smelting campaign.

Results

There were three full-scale test campaigns with a reductant during the SYMMET-project. In the full-scale tests, the used reductant was metallurgical coke. Based on the chemical analysis, the feed of the reductant did not show an effect on the copper matte-slag analysis. Some effect on the slag copper content was observed as a positive effect. The most interesting results were seen in the temperature measurements from the furnace bottom and with visual observations from the furnaces. These observations showed that the reductant had removed build-ups from the furnace.

To limit CO_2-emissions, a biobased reductant should be found for build-up removal.

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28 THERMAL TREATMENT OF JAROSITE LEACH RESIDUE

a) b)

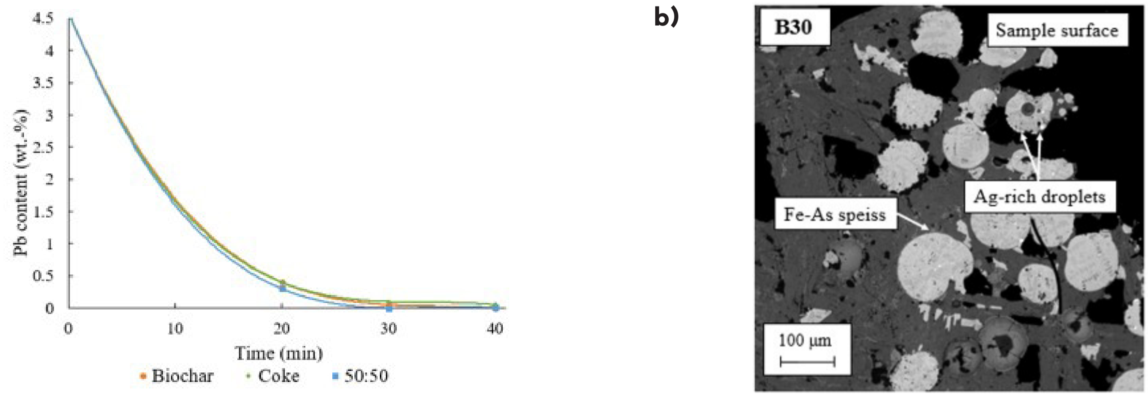

Figure 31. **Figure 27. a) Lead content (wt.-%) as a function of time in slag. b) Microstructure of a sample after the reduction step**

Description

Non-fossil reducing agents could possibly be used in jarosite treatment. The starting point for this research was to select the wanted non-fossil reducing agents. The focus was on investigating the processing options of jarosite containing precious metals such as Ag (150 g/t), Au (0.5 g/t), Zn (2 %), and Pb (3 %). A conversion method of hydrometallurgical iron oxide residue ('hydrated jarosite') in a pyrometallurgical process using non-fossil reductants into synthetic rock of acceptable environmental quality, to be used as gravel in the construction industry, was to be developed.

Application

Laboratory scale experiments were conducted to understand the elemental distribution between the different phases and their reaction kinetics at high temperatures as a function of process parameters and slag compositions with different non-fossil reductants. The optimal pyrometallurgical operating conditions were identified for producing safe-to-dispose slag and for the metallic (speiss) phase collecting of valuable metals.

Results

It was discovered that biochar can be used in place of the coke to convert joint waste residue into speiss, non-toxic slag and fume product. Due to uncertainties in the experimental setup and a high variation in phase compositions, no reliable conclusions could be drawn on whether biochar or coke is advantageous over the other, although the addition of biochar seemed to improve lead and zinc volatilization rates. The lead content was successfully decreased to near 0.0 wt.-% with both of the reductants and a bio-coke consisting half and half of biochar and coke, which shows that high-quality non-fossil biochar is indeed a viable reductant for the process despite the uncertainties.

The joint waste residue was lower in copper than in the previous studies, so the metallic phases after the reduction step were different. Instead of a copper antimonide speiss, the prevalent metallic phases were iron arsenide speiss and a lead-antimony-silver alloy. The metallic droplets were attached to molten iron oxides in a disperse layer on the bottom of the crucible, which shows that the silica fluxing had improved their settling behavior.

The initial plan was to conduct the experiments also with jarosite from the jarosite process, with the process optimized for joint waste residues, which turned out impossible due to the higher melting point of jarosite. Based on the microstructure of the oxidized material, jarosite contained zinc ferrite spinels, which have to be fluxed with both CaO and SiO_2 to effectively decrease the liquidus temperature.

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Publications

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29 A HOT METAL DESULFURIZATION SIMULATOR

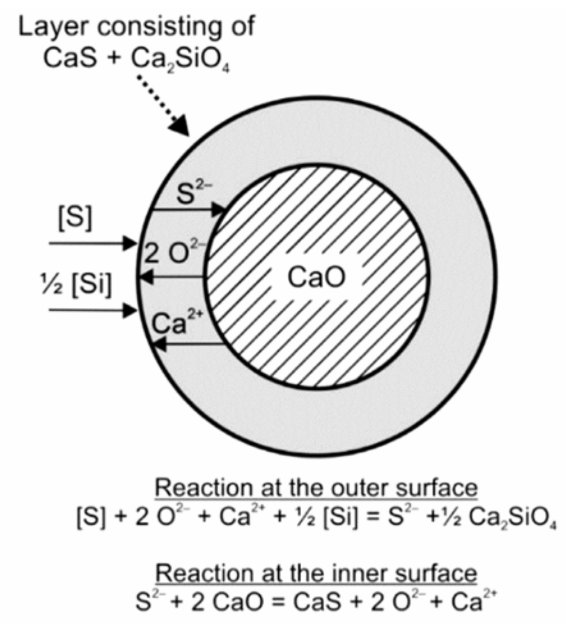

Figure 32. **The reaction mechanism of hot metal desulfurization with CaO in an inert atmosphere.**

Description

Sulfur is one of the main impurities in hot metal. Hot metal desulfurization is typically conducted in a ladle or a torpedo car by lance injection or in a mechanically stirred vessel. The long-term aim of the research work is to develop a hot metal desulfurization (HMD) simulator, which can be used to study and predict the effect of technological and operating parameters on the efficiency of desulfurization.

Application

The model is applicable for simulating hot metal desulfurization with lance injection. The model predicts the dynamic changes in metal and slag compositions due to metal-reagent and metal-slag reactions. One of the novelties of the model is that it accounts for the different rate-controlling mechanisms of the metal-reagent reaction separately for each size class.

Results

In SYMMET, the HMD simulator was improved with a new time integration method, an extensive thermochemistry module and a graphical user interface. A preliminary validation of the model for desulfurization with two lime reagents suggest a good agreement between the predicted and measured final sulfur contents. The model could also realistically predict the effect of particle size on the desulfurization efficiency. In further work, the model will be validated for lime-based reagent mixtures. Finally, an extensive review of the mathematical modelling approaches was published based on the experience gathered in the development of the HMD simulator.

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Publications

Visuri, V.-V., Sulasalmi, P., Vuolio, T., Paananen, T., Haas, T., Pfeifer, H., Fabritius, T. 2019. Mathematical Modelling of the Effect of Reagent Particle Size Distribution on the Efficiency of Hot Metal Desulphurisation. Proceedings of the 4th European Steel Technology and Application Days. Steel Institute VDEh, Düsseldorf, Germany.

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30 COMBINED PULVERIZED COAL AND LNG INJECTION IN A BLAST FURNACE

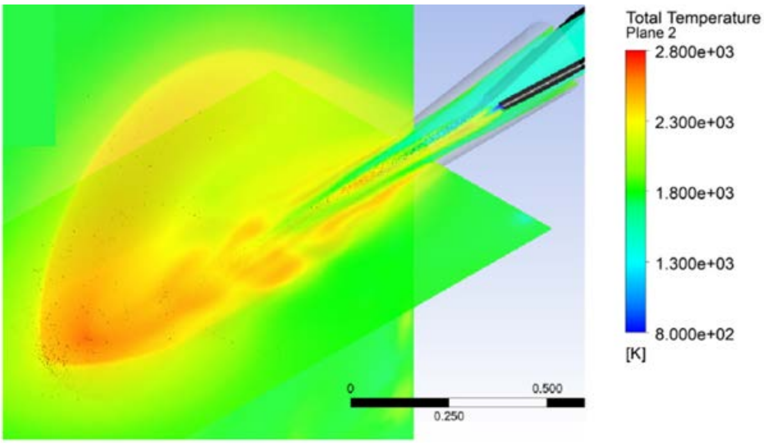

Figure 33. **Contours of temperature in combined PC and LNG injection**.

Description

Pulverized coal (PC) is currently used as an auxiliary fuel in the SSAB Raahe blast furnaces. The availability of LNG makes it possible to inject LNG together with PC. Currently, PC is injected with a double lance system with nitrogen used as a carrier gas. LNG can be injected as a carrier gas for PC or one lance can be used to solely inject LNG. The aim of the study was to investigate the combustion of LNG in the blast furnace tuyere-raceway area by utilizing Computational Fluid Dynamics (CFD).

Application

During the SYMMET project, a previously made CFD model for PC combustion was modified and applied for the LNG studies. The created model can be utilized to study any combination of PC and LNG injections in the blast furnace tuyere-raceway area. In the SYMMET project, the task was divided into three cases, 1) the standard PC case as a base case, 2) LNG as a carrier gas for PC, and 3) co-injection of LNG and PC with a double lance system.

Results

Based on the results from the three cases, it was clear that LNG had a positive effect on PC combustion efficiency in the blast furnace tuyere-raceway area. The base case resulted in a combustion efficiency of 69 %, LNG as a carrier gas provided 75 % combustion efficiency, and 84 % combustion efficiency was reached with LNG lance. The results indicate that LNG should be tested as an auxiliary fuel. The increase in the combustion efficiency could lower the amount of fine particulate matter inside the blast furnace, which would result in increased productivity. This could lower the need for the expensive coke and lower the iron production costs. Also, LNG has a higher hydrogen to carbon ratio than either of the currently used fuels and it would reduce the CO_2 emissions of ironmaking.

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Publications

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31 LABORATORY SCALE BIPOLAR NEUTRAL ELECTROCHEMICAL PICKLING

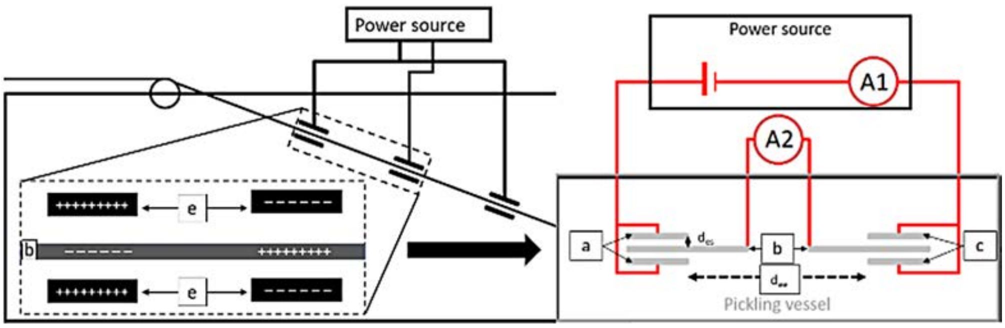

Figure 34. **Industrial- and laboratory-scale bipolar pickling device. Surrounding anodes and cathodes bipolarize stainless steel as the current passes the strip.**

Description

Neutral electrochemical pickling was used to rapidly dissolve the oxide layer before the final mixed acid pickling. Despite the apparent efficiency, both the main reaction and the industrial electrochemical cell have low current efficiency, leaving room for a significant increase. The majority of neutral electrochemical pickling studies have been conducted with a classical electrochemical cell where the sample acts as a working electrode and inert metal acts as a counter electrode. However, due to the high velocity of the steel strip in the industrial process, the steel strip is polarized indirectly by running it between the sets of electrodes as shown in **Figure 1.** A laboratory scale bipolar cell was constructed to simulate the industrial process more closely. Sets of anodes and cathodes surround samples, that are connected as a single bipolar electrode by amperemeter. A pump circulates the heated electrolyte from opposite ends to reduce gas bubbles on surfaces.

Application

During SYMMET, the bipolar pickling device was constructed. The device can be used to quantify the effect of several key parameters for the current efficiency of the cell, as well as pickle samples suitable for FESEM-analysis.

Results

The temperature and cell potential increased cell efficiency by increasing the efficiency of the reaction, while increasing the sample-to-electrode distance and the electrolyte concentration decreased cell efficiency by increasing the electrode-to-electrode short circuiting. Unlike in a classical cell, lower electrolyte concentration was beneficial for the efficiency of the bipolar cell. Lower conductivity acts as a natural insulator between electrodes, decreasing the current lost to short-circuiting.

A sulfate solution from nickel precipitation was chosen for testing, as the nickel concentration would naturally increase during pickling. When compared to a reagent grade sodium sulfate of similar conductivity and adjusted pH, similar dissolution of the chromium oxide layer was observed. This suggests that conductivity is a more critical parameter than the chosen salt and that a secondary sulfate could be used in neutral electrochemical pickling.

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Publications

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32 SELECTIVE RECOVERY OF MANGANESE FROM THE ANODE SLUDGE

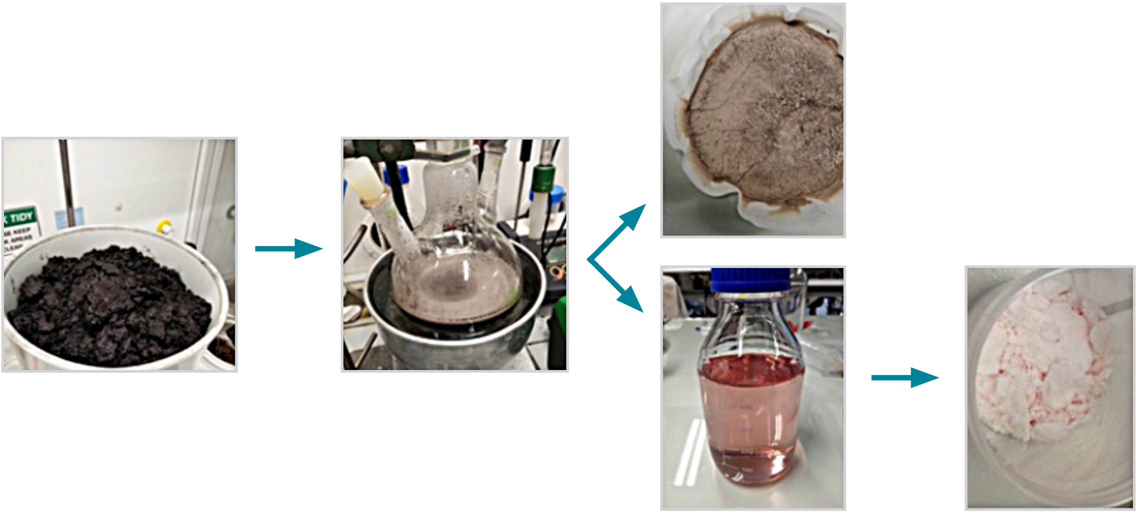

Figure 35. **Route from anode sludge to lead-rich leaching residue and manganese sulfate crystals.**

Description

Manganese-rich (Mn >40 %) anode sludge forms during the zinc electrowinning. Alongside with manganese dioxide, the anode sludge contains lesser amounts of lead, potassium, calcium and zinc. Manganese is an industrially important element with use cases in steelmaking, batteries and fertilizers.

Application

This work demonstrates a method for selective manganese recovery from a lead- and calcium-bearing manganese oxide side-stream.

Results

A hydrometallurgical process was developed for the recovery of manganese from the anode sludge. A concentrated manganese sulfate solutio could be obtained with high manganese yield, and low concentrations of lead and calcium. The purity of the manganese product was improved by pre-treating the anode sludge by acidic washing and removing transition metals after leaching by sulfide precipitation. Besides manganese sulfate, the process produces three other utilizable side-streams – acidic washing water, lead-rich leaching residue and zinc-rich sulfide precipitate.

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33

USING NON-FOSSIL REDUCTANTS IN NON-FERROUS METALS' SLAGS FOR METALS RECOVERY.

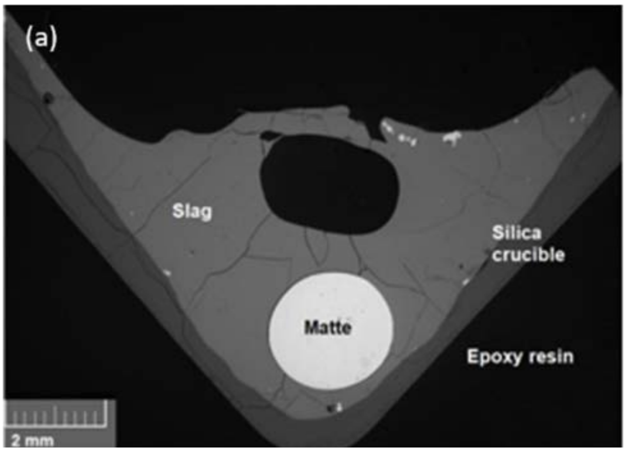

Figure 36. **SEM-BSE micrographs of slag + biochar sample**

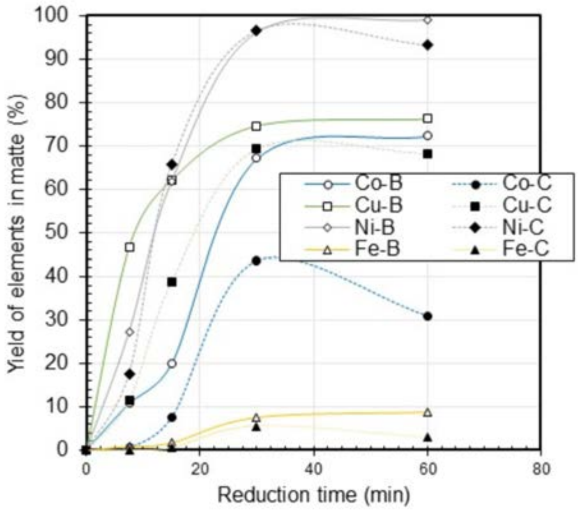

Figure 37. **The metal value recoveries in the nickel slag reduction by biochar (B) and coke with slag (C).**

Description

Bio-based reductants are considered as promising options to replace coal or coke in various metal reduction processes, including iron/steel making and non-ferrous processing. In ferrous metallurgy, the use of biochar or bio-coke (biochar mixed with coal) to partly or entirely replace the traditional coal/coke has become a research hotspot. The properties of biochar, such as calorific value, fixed carbon content and impurities, rely highly on its biomass source but especially its production technology. The different properties, such as porosity and impurities content, of biochar affects the kinetics of the slag reduction differently than if coke or coal is used as a reductant.

Application

The goal of the study was to find ways to improve the reduction of cobalt as well as valuable metals nickel and copper in nickel slag cleaning furnace conditions by using both traditional fossil-based coke and a more sustainable option, low-CO_2 footprint biochar, as reductants. A cobalt-rich fraction of battery scrap was also used as a secondary feed. The experimental technique consisted of reduction experiments with different times at 1400 °C in inert atmosphere, and with quick quenching and Electron Probe X-ray Microanalysis.

Results

The use of biochar resulted in faster reaction kinetics in the reduction process, compared to coke. Moreover, the presence of battery scrap had a clear impact on the behavior and reduction kinetics of the elements and/or enhanced settling and separation of the matte and the slag. The addition of scrap notably increased the distribution coefficients of the valuable metals, but consequently also the iron concentration in the matte which is the thermodynamic constraint of the slag cleaning process.

In addition, the thermodynamic properties of the Ni-Fe-Co-C alloys have been modelled and databases have been developed.

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34 THE USE OF NON-FOSSIL REDUCING AGENTS IN THE MATERIAL TREATMENT OF NON-FERROUS METALS

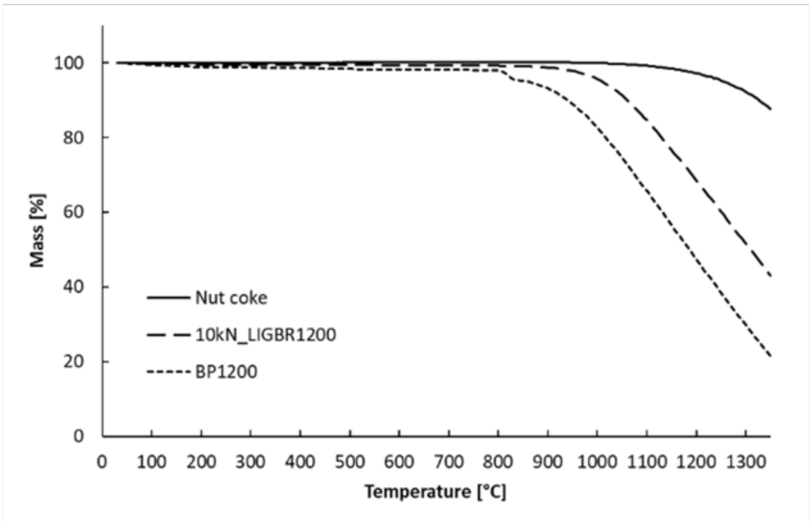

Figure 38.**The reactivity of the biochars and the nut coke.**

Description

Reductive treatment is usually performed by using a fossil-based, highly carbonaceous reductant e.g. metallurgical coke. The reductant is used for reducing oxidic material from the bulk raw material. Meanwhile the reducing agent becomes oxidized. This leads to the direct production of fossil-based carbon dioxide (CO_2) emissions. These CO_2 emissions could be considerably decreased by partly replacing the fossil-based reductant with bio-based reductants. In the reduction processes, the reducing agent is usually fed to the process either as mixed with the other raw material charge or fed to the melt during the process with different techniques e.g. through a lance. One of the main problems of directly switching the reductant from a fossil-based reductant to a bio-based reductant is the high reactivity of the bio-based reductant due to a higher surface area and a lower apparent density. The high reactivity of the material in high temperature processes may lead to the premature combustion of the reductant which leads to a low dissolution rate of the carbon content of the reductant of the melt.

Application

This goal of this study was to find solutions to suppress the reactivity of the bio-based reductant (biochar) in order to prevent the premature combustion of the reductant. Two different biomasses, hydrolysis lignin and black pellets, were used in the experiments. Hydrolysis lignin is a side product from enzymatic hydrolysis and the yeast fermentation process that are part of the process chain of bio ethanol production. Black pellets are a product from steam explosion and the pelletizing process of tree bark. Fossil-based nut coke was used as a reference material in the experiments.

The biomass was treated with slow pyrolysis in order to produce variable types of biochars. Three different pyrolysis temperatures, 450 °C, 600 °C, and 1200 °C, were applied in pyrolysis in order to find out the effect of the pyrolysis temperature to the material yield (wt%), reactivity, and density. Hydrolysis lignin was pyrolyzed in "as received"-form and in briquetted form. The non-briquetted hydrolysis lignin biochar was ground and sieved to a size fraction of less than 0.5 mm. Black pellets were pyrolyzed without pretreatment. The dynamic reactivity tests were run under a CO-CO_2-N_2 gas atmosphere for the produced biochars and nut coke from a room temperature up to a final temperature of 1350 °C.

Results

The results showed that the solid yield (char) of the biomass was not as significantly decreased when the pyrolysis temperature was raised from 600 °C to 1200 °C, as when the pyrolysis temperature was raised from 450 °C to 600 °C.

The briquetted char had a significantly lower mass loss degree in the reactivity tests than powdered char. Also, the pyrolysis temperature had a considerable impact on the reactivity of the char. The hydrolysis lignin char that was pyrolyzed at 450 °C, had a mass loss of 86.55 wt%, while the briquetted hydrolysis lignin char that was pyrolyzed at 1200 °C, had a mass loss of 56.55 wt% in the reactivity test in similar conditions. The nut coke had a mass loss of 12.21 wt% in the same reactivity test. According to these results, it can be concluded that the reactivity of the biochar was not suppressed to the level of the reactivity of the nut coke. However, with such a high suppression of reactivity of the biochar, it may have a potential to replace part of the coke for the purposes of a reducing agent.

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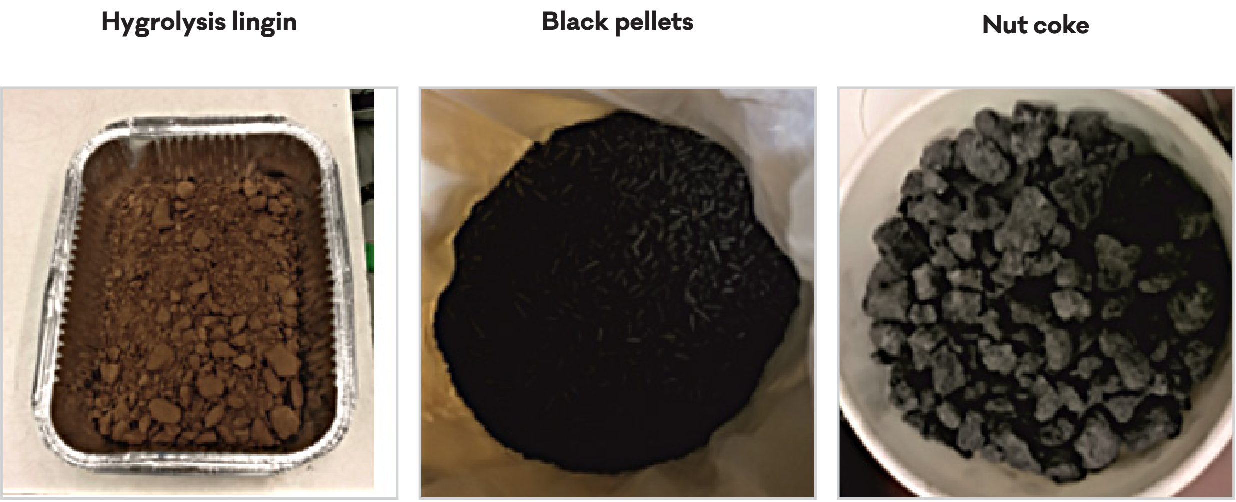

Figure 39. **Raw material used for the experiments.**

SYMMET

35 PYROMETALLURGICAL PROCESSING OF ELECTRIC FURNACE DUSTS

Description

Electric arc furnaces (EAF) generate significant quantities of dust which is considered as hazardous waste in most industrial countries as it contains toxic elements such as heavy metals. These dusts also contain valuable metals such as steel alloying elements, but the extraction and recovery of the valuables is difficult due to a complex composition of the dusts. Especially the high zinc content of the dust causes troubles in recycling, since it causes operational difficulties in the steelmaking processes. Direct recycling is further hampered by the alkali metals and halogens contained in the dust. Those elements have a deteriorating effect on the refractory materials.

Understanding the behavior of the dusts at high temperatures, combined with the effect of volatile components in the dusts on refractories is important for the efficient and safe operating of EAFs.

Application

The melting behavior of two EAF dusts and one Argon Oxygen Decarburization converter (AOD) dust was investigated at temperatures between 800 – 1400 °C under a reducing atmosphere. In addition, the effect of a synthetic dust, containing high concentrations of potassium, fluorine and chlorine, on four types of refractories was studied at 1300 °C.

After the experiments, the microstructure and phase compositions of the rapidly quenched samples were studied by SEM-EDS. In addition, image analysis was used to determine the amounts of different phases formed at certain temperatures during the melting behavior experiments.

Results

The melting of the EAF dusts started in the temperature region of 1250 – 1300 °C depending on the composition of the dust, whereas AOD dust had a molten fraction of about 30 % already at 1200 °C. In the AOD dust, high levels of fluorine were found in the liquid phase.

In the refractory – dust interaction experiments, it was observed that the chrome containing refractories were less affected by the synthetic dust. The potassium penetration depth to these refractories was much lower compared to the two other refractories and they also retained their original shape better.

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Publications

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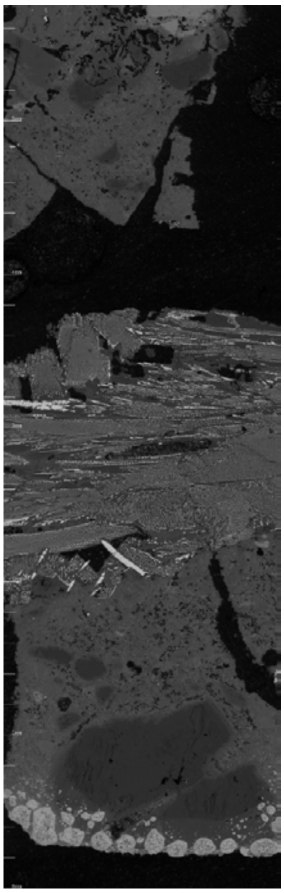

Figure 40. **BSE image of the cross section of the chromium containing refractory (bottom in contact with the synthetic exhaust gas**

SYMMET

36 REPLACING THE COAL USED IN STEELMAKING WITH BIOCARBON

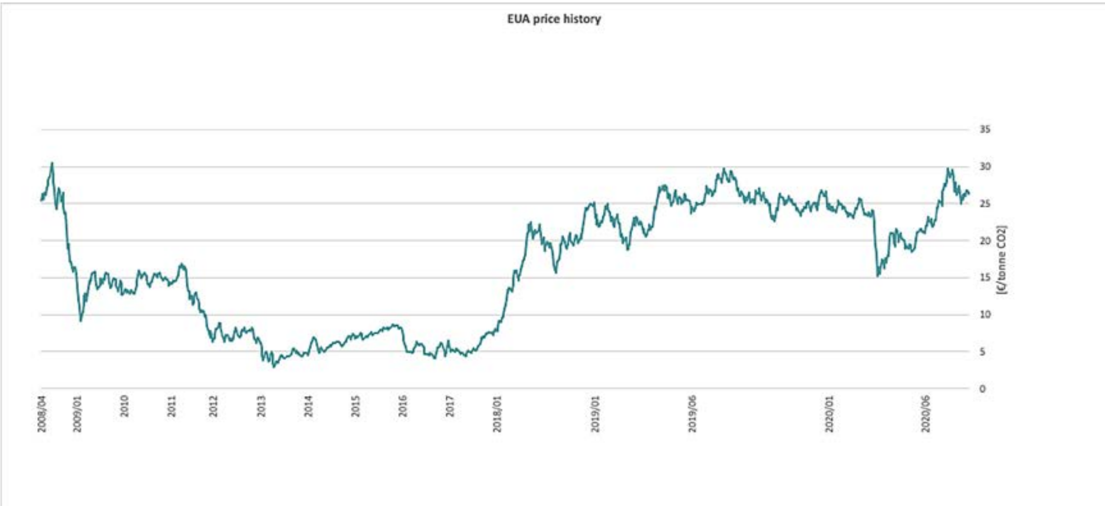

Figure 41. **The carbon market price history and the current situation. European Emission Allowance prices (Closing ECX EUA Future continuous contract prices.**

Description

Most of the CO_2 emissions in steel production occur during the reduction of iron ore to hot metal using coal and coke. Renewable carbon from the side streams of the forest sector is an asset for rapid reduction of these emissions. Slow pyrolysis is the most promising technology to upgrade biomass into a metallurgical reducing agent. The economic feasibility of the biomass conversion to biochar will depend on emission trading (Fig. 1.), fossil coal and raw material price, and on the integration of the excess energy from pyrolysis and available low-grade heat. The studies on applicability of biocarbon as a coal replacement begun in the FOR&MET project[1]. In SYMMET, optional Finnish sources for such bioreducers were outlined, and the techno-economical estimates were updated with appropriate sensitivity analyses for biocarbon production costs.

Application

The key focus of this study was to evaluate the direct substitution of fossil-based pulverized coal injection (PCI) in the blast furnace with biocarbon from sustainable sources. Black pellets (produced from softwood bark by steam explosion) and hydrolysis lignin (side product from 2nd generation bioethanol process) were selected for pyrolysis experiments. Using bark in pyrolysis was evaluated based on experiments and analyses of black pellets. Several scenarios were evaluated, based on biocarbon production as stand-alone (from lignin or black pellets) and as integrated to pulp (and paper) mill (from lignin or bark), including the transportation needs.

Results

Softwood bark, black pellets made of such bark, and hydrolysis lignin were found to be applicable sources for biocarbon production. Substitution of PCI coal in blast furnaces with biochar, set to a maximum of 20 wt% replacement share (based on alkali and phosphorus content), has the potential to reduce GHG emissions by about 20%. The utilization of excess pyrolysis gases (e.g. in a lime kiln) and available low-grade heat for raw material drying were found as key factors for reducing biocarbon production costs. Softwood

[1] Business Finland funded FOR&MET project (Added Value from Forest Industry for Metals Producing and Processing Integrates)

bark as a raw material for biocarbon production at an integrated pulp mill site will provide the best economic option within the forest-to-metal value chain, establishing an ample source, at a potential 95 k tonnes of biocarbon per year while ca. 8 k tonnes of biocarbon is produced in Finland today. Biocarbon replacement is yet to become an economically viable option, when fossil coal and emission trading costs are compared to the biocarbon production costs.

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