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Slaggreduktion med vätgas	
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Slag reduction with hydrogen gas	
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Sammanfattning

Denna rapport beskriver det gemensamma projektet "Slaggreduktion med vätgas". Projektet är ett samarbete mellan Swerim, Boliden och Linde med stöd från Energimyndigheten genom Industriklivet. Syftet med projektet är att förstå effekten av injicering av vätgas i smält slagg, eftersom det kan vara ett sätt att ersätta fossilt kol i Bolidens zinkprocess och andra metallurgiska processer.

Pilotförsök gjordes i Swerims universalkonverter med två olika injektionstekniker för väteinjektion i smält zinkinnehållande slagg från Boliden Rönnskär: (i) formor/dysor och (ii) coherent jet (CoJet)-teknologi utvecklad av Linde. Försöken har jämförts med referensförsök med injicering av kol genom formor/dysor. 1,8 eller 2,5 ton slagg användes för varje försök och vätgasflöde var som högst 1,2 Nm3/min. När man använder kol som reduktionsmedel används kol också som energi. Vätgasförsöken var designade för att använda propan som energikälla.

Resultaten visar att det är möjligt att injicera väte i flytande metallslagg på ett säkert sätt med båda teknikerna. Den totala zinkreduktionshastigheten, mätt som massan Zn som avlägsnats från slaggsmältan per försök, var liknande för det bästa forma/dysa-försöket och CoJet-försöken med 0,6 kg/min (bästa CoJet-försöket nådde 0,8 kg/min) jämfört med 1,3 kg /min för referensen med kol. Det faktum att reduktionen under ett försök fortsatte i oförändrad takt efter att vätgasflödet avbröts, tyder på att vägas inte var det enda reduktionsmedlet i processen.

Om man antar att vätgas var det huvudsakliga reduktionsmedlet, nådde vätgasens effektivitet maximalt 31 % för det bästa försöket förutsatt att Zn-, Pb- och Cu-oxider reducerades av vätgasen. Motsvarande tal för kol var 19 %. Det går dock inte att jämföra detta rakt av, eftersom den kolbaserade processen även använde kol som energikälla, medan vätgasprocessen använde propan som energikälla. Den totala energieffektiviteten, definierad som energi som används för att reducera zink per energi tillsatt som väte och propan eller som kol under reduktionsfasen, nådde 7–8 % för kol, 0–1 % för forma/dysa och 2–3 % för CoJet-injektionen för vätgasförsöken.

Att byta från ett fast till ett gasformigt reduktionsmedel är en väsentlig processförändring och kommer att kräva mer forsknings och utveckling.

Summary

This report describes the pilot campaign in the joint project "Slag reduction with hydrogen gas". The project is a cooperation between Swerim, Boliden and Linde with support from Energimyndigheten through Industriklivet. The aim of the project is to understand the effect of injection of hydrogen gas into melted slag, as this could be a way of replacing fossil carbon in Boliden's zinc fuming process and other metallurgical processes.

Pilot trials were made in Swerim's universal converter using two different injection techniques for hydrogen injection into liquid zinc-containing slag from Boliden Rönnskär: (i) tuyère injection and (ii) coherent jet (CoJet) technology developed by Linde. The trials have been compared with reference trials with injection of coal through tuyères. 1.8 or 2.5 tons of slag were used for each heat, and a maximum hydrogen flowrate of 1.2 Nm^3/min. When using carbon as a reducing agent, carbon is also used as energy. The hydrogen cases were designed to use propane as the energy source.

The results show that it is possible to safely inject hydrogen into liquid metal slag using both techniques. The overall zinc reduction rate, measured as mass of Zn removed from the slag melt per time, was similar for the best tuyere trial and the CoJet trials with 0.6 kg/min (best CoJet-heat reached 0.8 kg/min) compared to 1.3 kg/min for the reference using carbon. The fact that during one heat, the reduction continued at an unchanged rate after the hydrogen flow was discontinued, indicates that hydrogen was not the only reducing agent in the process.

Assuming that hydrogen was the main reducing agent, the efficiency of hydrogen gas reached maximum 31% for the most successful heat assuming that Zn, Pb and Cu oxides were reduced by hydrogen. The correlating number for carbon was 19%. This is not to be directly compared, since the carbon-based process also used carbon as energy source, while the hydrogen process used propane as energy source. The overall energy efficiency, defined as energy used for reduction of zinc per energy added as hydrogen and propane or as carbon during the fuming stage, reached 7-8% for carbon, 0-1% for the tuyere injection and 2-3% for the CoJet injection for the hydrogen cases.

Changing from a solid to a gaseous reducing agent is a substantial change of operations and will require more evaluation and experiments.

Introduction

Hydrogen gas has been identified as one of the key enablers in the industrial transition. Hydrogen gas is being investigated as a reducing agent and an energy carrier in traditionally fossil-carbon based processes, such as iron ore reduction and re-heating applications as well as many other metallurgical processes.

Zinc fuming is a liquid-solid-gas reduction system, where the material that is reduced is in liquid form, while the reducing agent is a solid that is gasified in the process.

In iron ore reduction, the reduction is done in a solid-solid-gas system, where the material that is reduced is in solid form (iron ore pellet, lump or sinter) while the reducing agent is injected primarily as solid carbon that is gasified (blast furnace

process – although gases are used to some extent) or as a gas (DR process). To replace a solid reducing agent such as coal with a gas in a liquid has many challenges. Although many alternatives have been investigated, gas-based zinc fuming has not yet been commercialized. Injection of hydrogen is challenging since it is a very light molecule that makes it difficult to achieve enough impact to penetrate the slag bath. This study aimed at evaluating two different injection techniques for injection of hydrogen into liquid slag and compare the results to the traditional coal-based zinc fuming process.

This report describes the pilot campaign in the joint project "Slag reduction with hydrogen gas". The project is a cooperation between Swerim, Boliden and Linde with support from Energimyndigheten through Industriklivet. The aim of the project is to evaluate the effect of replacing fossil carbon in Boliden's zinc fuming process with hydrogen gas. The project is based on the pre-study "Advanced state-of-the-art industrial Electrolysis – a pre-study" (Wolf & Nordberg, 2021) that was conducted 2020 together with RISE, Höganäs and a large consortium, based on the Swedish Hydrogen Development Centre's identified research needs. The pre-study performed thermodynamic calculations that showed promising results to scale up a process for slag reduction with hydrogen gas. The theoretical CO_2 savings based on the pre-study is 80 000 tons/a. The pre-study also evaluated different options for hydrogen injection into liquid slag and formed a base for a cost assessment for pilot trials. The pre-study suggested two different injection methods for further development: (i) tuyères and (ii) coherent jet (CoJet) technology.

Slag fuming process

Slag fuming is done at Boliden's Rönnskär plant in a box fuming process (Figure 1). The process is used to recover zinc from the slag produced in the copper smelting process. The box-fumer at Boliden is a water-jacketed reactor with 52 tuyères, 26 on each side. Fossil coal and pre-heated air is injected through the tuyères to perform the reduction work. There are 2 ladles of 45 tons, and 6 tons of coal is used for each heat of 45 tons of zinc slag. About 80 % of the zinc oxide in the slag is reduced, and the theoretical carbon yield for the zinc reduction itself is as low as 12 %.
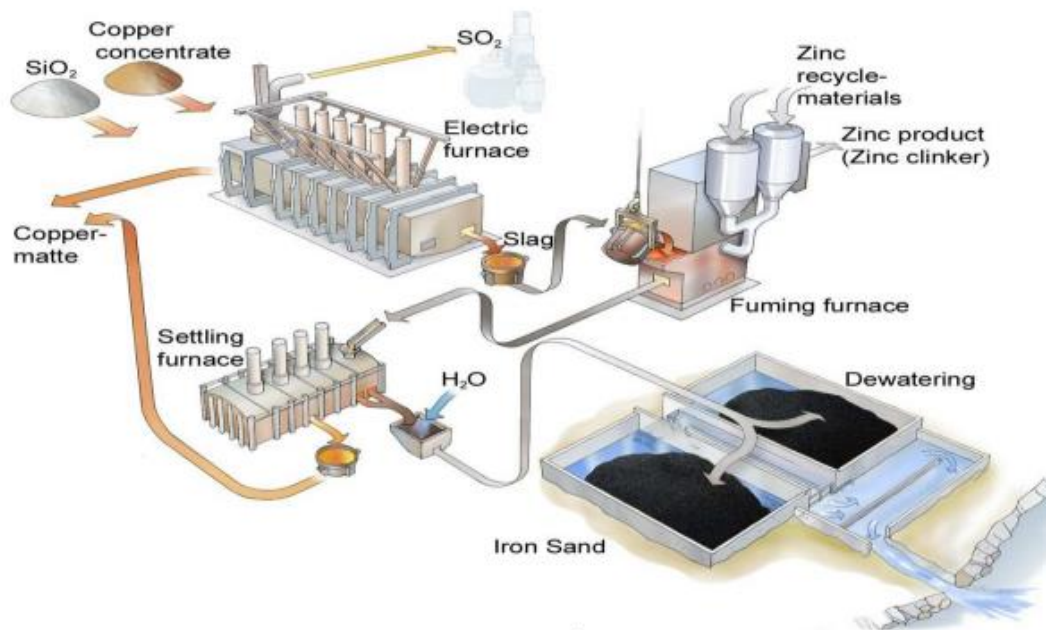
Figure 1. Slag fuming is one of the processes in Boliden's Rönnskär facility where copper is produced. The zinc fuming process is used to recycle zinc from the slag from the copper process.

The process separates zinc from the copper slag by reducing zinc oxide to elemental zinc. The zinc evaporates and re-oxidises in the free board and is collected in the off-gas duct (Figure 2).
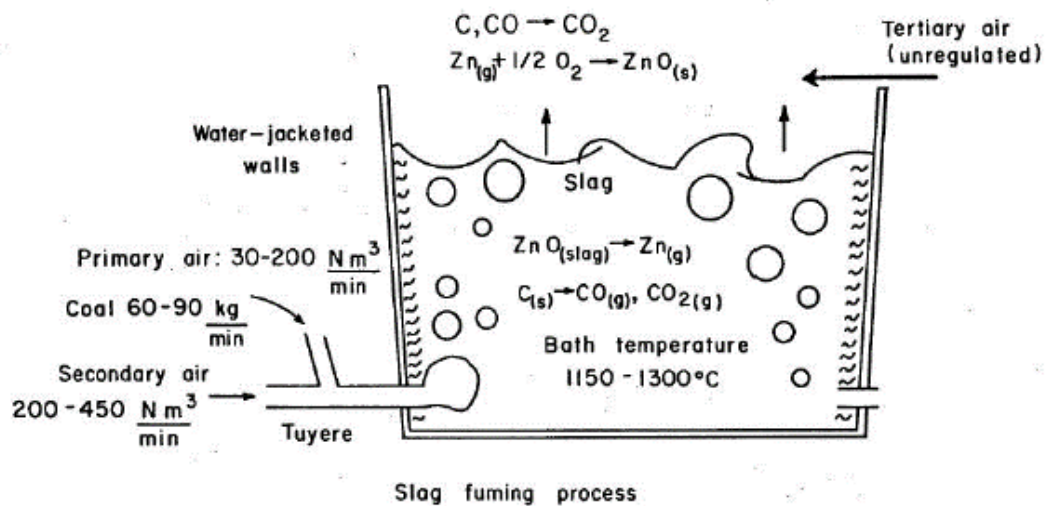

Figure 2. The slag fuming process is traditionally based on fossil carbon and preheated air that reduces the ZnO and other oxides from the slag. Schematic cross-section from (Richards G. G., 1979).

The reduction reactions are endothermic, which means that additional heat needs to be added to the process. Carbon has two purposes in the process, both to contribute heat to maintain the temperature at 1150-1300°C and to perform the reduction work. Some of the carbon will leave the process without having taken part in any reactions

and is post-combusted above the bath. Although the yield of carbon for reduction purpose is as low as 12 %, the total coal utilization is much higher since it contributes heat to the reactor.

The typical zinc fuming cycle lasts for around 2 hours and consists of three phases: smelting, fuming and tapping. At Boliden, the slag is added to the box-fumer in liquid form. During the fuming phase, the reduction is slow during the first 10-15 minutes but then reaches a steady linear reduction. The zinc fuming continues at a linear velocity until a new stage is reached, typically when the amount of zinc oxide reaches around 3.5 wt% (Richards & al, Kinetics of the Zinc Slag-Fuming Process: Part I. Industrial Measurements, 1985) (Sundström, 1969) (Richards & al, Kinetics of the Slag-Fuming Process: Part III. Model Predictions and Analysis of Process Kinetics, 1985). The temperature profile of a zinc fuming cycle shows that a reduction temperature between 1150°C and 1300°C is optimal (Richards & al, Kinetics of the Zinc Slag-Fuming Process: Part I. Industrial Measurements, 1985). Too high temperatures will increase the wear of the furnace and negatively affect the overall energy efficiency. Furthermore, the viscosity of the slag decreases with higher temperature which affects the process negatively.

Already in 1955, Bell et al. published an article on a thermodynamic study of alternative gases for zinc reduction/fuming purposes (Bell, Turner, & Peters, 1955). The study varied the amount of C, CO and H_2 and suggested that hydrogen is a strong reducing agent in zinc reduction, since increasing hydrogen concentration indicated a more efficient zinc fuming process. The hypothesis was strengthened by the fact that highly volatile carbons showed a more efficient fuming process than a less volatile carbon in industrial operations. On the other side, as pointed out by (Das & Sarkar), researchers are debating whether solid carbon is an essential parameter for efficient zinc fuming or not. The theory to support this is that the solid carbon could play an essential role in the zinc fuming process for the kinetics of the reactions, since it creates a large enough area for contact between reducing gas and slag (Richards & al, Kinetics of the Slag-Fuming Process: Part III. Model Predictions and Analysis of Process Kinetics, 1985) (Richards & al, Kinetics of the Zinc Slag-Fuming Process: Part I. Industrial Measurements, 1985). The use of a fully gaseous zinc fuming process has not yet been industrialized, although several initiatives are currently evaluating the options.
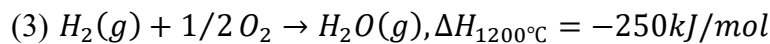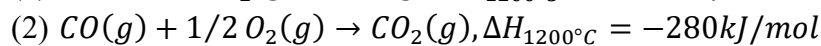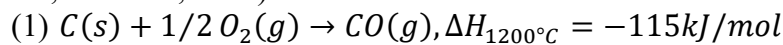
Several alternative reducing agents have been suggested and evaluated to replace fossil carbon. Alternative reducing agents such as plastics (Lotfian, et al., 2019) and ammonia (Khartcyzov & al, 2023) have been studied at Boliden. In (Lotfian, et al., 2019), successful industrial trials using plastic residues were conducted with indications that plastics could be used as a reducing agent with similar efficiency as carbon and that amount of reducing gases in the injected material is not the only parameter that influences the fuming rate. In (Khartcyzov & al, 2023), the thermodynamic modelling suggests that ammonia can replace carbon as a reducing agent and could improve the removal of minor elements such as Sb and As from the slag. However, the thermodynamic model does not take kinetic changes into account.

Hydrogen as reducing gas in the zinc fuming process is currently being investigated by other research teams in Europe: the HARARE project and by Aalto University, Finland. Both teams are working with small scale experiments. Aalto University
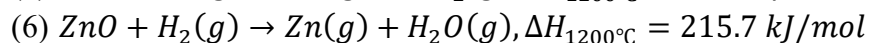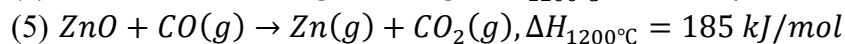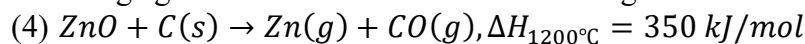
has performed gram-scale experiments, showing that hydrogen is thermodynamically a good reducing agent for zinc fuming applications (Attah-Kyei & al, 2022). The HARARE project has performed small scale experiments with zinc fuming with hydrogen gas. The scale of the trial was 1.5 kg of zinc slag using 90 l of hydrogen (Hovsestad, 2023). In April 2023, they reported successful trials where the fuming with hydrogen behaved as expected. However, the efficiency of the hydrogen was maximum 31%. The efficiency was higher for lower H_2 concentrations for experiments with the same total flowrate, while it was little effected by the change in flowrate for the experiments with 100% hydrogen.

The thermodynamic calculations used in this project are based on the assumptions given below:
The reduction potential is controlled by α =O/C in the following reactions (Bell, Turner, & Peters, 1955).

(1) $C(s) + 1/2\,O_2(g) \rightarrow CO(g), \Delta H_{1200°C} = -115 kJ/mol$

(2) $CO(g) + 1/2\,O_2(g) \rightarrow CO_2(g), \Delta H_{1200°C} = -280 kJ/mol$

(3) $H_2(g) + 1/2\,O_2 \rightarrow H_2O(g), \Delta H_{1200°C} = -250 kJ/mol$

The reducing agents reduce the zinc oxide according to the following reactions:

(4) $ZnO + C(s) \rightarrow Zn(g) + CO(g), \Delta H_{1200°C} = 350\ kJ/mol$

(5) $ZnO + CO(g) \rightarrow Zn(g) + CO_2(g), \Delta H_{1200°C} = 185\ kJ/mol$

(6) $ZnO + H_2(g) \rightarrow Zn(g) + H_2O(g), \Delta H_{1200°C} = 215.7\ kJ/mol$

In traditional zinc fuming with solid carbon injection, a more efficient process can be achieved by increasing the injection pressure (Cockcroft & al, 1989), pre-heating the blast to increase the reaction efficiency with regard to fuel efficiency (Blaskett & al) or oxygen enrichment (MvNaughton & al, 1949).

Although the zinc fuming process is designed to reduce zinc oxide, many other oxides are present and will be affected by the reduction work of carbon, CO and H_2 or other reducing agents present in the furnace. Other metals present are typically lead, copper and different iron oxides. The lead is usually fumed similarly to zinc, while the iron oxides have a complex influence on the fuming process itself. Different researchers have debated whether or not the system is in equilibrium and is limited by thermodynamics, or if it is in fact limited by kinetics highly influenced by the reactions of the iron oxides (Kellogg, 1967) (Quarm & al, 1965). An explanation in favour of the latter is that during the melting phase or during other moments in the process where no reduction should take place, sometimes Zn (g) can be found in the off-gases or a measurable zinc fuming can be identified. This was noted early by (Kellogg, 1967) (Quarm & al, 1965) in experiments where coal injection was stopped for a short time during the process while the zinc fuming still took place, and with general monitoring of industrial process procedure. It is believed that FeO may reduce ZnO and form magnetite, Fe_3O_4, which then uses the CO(g) to be reduced back to FeO (Quarm & al, 1965) (Kellogg, 1967). Laboratory experiments were done by (Reddy & al, 2003) showing that stirring the melt improved the reduction of ZnO even with no available reducing agent, supporting the theory that FeO was reducing ZnO. Later researchers conclude that depending

on the stage of the fuming process, either thermodynamics or kinetics can limit the reactions. Typically, equilibrium is reached in the early fuming stage, while kinetics are rate limiting towards the end of the cycle when the ZnO concentration is lower (Nagraj, 2022). Stirring in itself could also facilitate the reactions according to Le Chatelier's principle where removal of the gaseous product decrease of the partial pressure of $Zn(g)$ and drives the reaction towards forming $Zn(g)$ according to the reactions 4-6. The ZnO could also be removed directly caused by additional stirring without the reduction to $Zn(g)$ taking place.

Tuyère injection

Tuyère injection is a state-of-the-art technology for the metal industry. It is a side-blown lance that injects the selected material or gas into the reactor (Figure 3). In zinc fuming, the tuyères injects the material/gas into the bath (under the slag surface) while in blast furnace ironmaking, the injection is done above the bath surface.
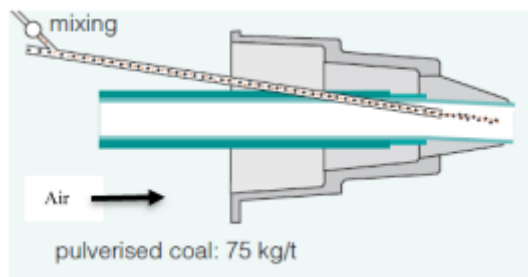

Figure 3. A schematic sketch of a tuyère.

CoJet® technology

The CoJet® technology was developed by Linde (previously Praxair) and commercialized, in part, as an injection method for oxygen in the EAF (electric arc furnace – a steelmaking process). A supersonic coherent jet is created by surrounding an internal jet with a reacting shroud flame, thereby achieving a laser like injection method (Figure 4). The technology has previously mostly been used in oxidizing conditions, while it was applied for reducing conditions in this project. The very low molecular weight of hydrogen gas makes injection challenging. It is difficult to achieve a large enough impact, since the low weight causes it to rise in the atmosphere rather than penetrating a liquid bath. The coherent jet technology has proven useful to achieve a more focused injection jet, which could be useful especially for light gases.
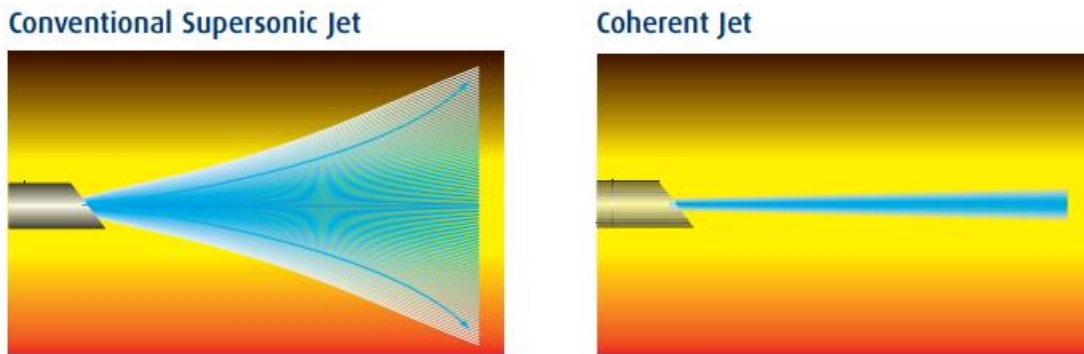
Figure 4. Comparison of traditional supersonic jet and coherent jet. (linde-gas.com)

The water-cooled CoJet® lance can be used both as a burner and as an injector. The different modes are taken into consideration in designing the lance. When in burner mode, nitrogen is injected through the center and relatively higher rates of liquefied propane gas (LPG) and oxygen are passed through the outer shroud ring. When used as a supersonic injector, the H_2/N_2 mixture is injected through the center and LPG and oxygen used as shrouding gases optimized to maximize the supersonic jet length. A schematic cross-section of the CoJet lance is shown in Figure 5.
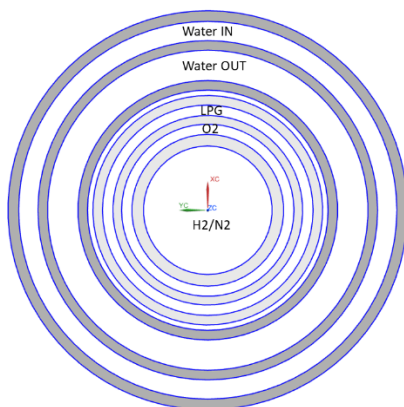
Figure 5. A schematic sketch of a CoJet® lance, showing the water cooling and the ports for LPG, O_2 and injectant (H_2/N_2).

Work-plan

The project started with a planning phase to ensure timely delivery of all necessary equipment. Thermodynamic calculations from the pre-study were updated. Design of experiments and experimental set-up were based on the thermodynamic calculations and the infrastructure at Swerim.

Experimental set-up

The experiments were done in the universal converter at Swerim (Figure 6). The converter was bricked with chrome magnesite bricks for the trials.
New hydrogen and nitrogen control systems were designed and constructed at Swerim (Figure 7). A HAZOP analysis was performed to identify risks and suggest

risk management measures. Flow meters and valves were identified and acquired based on identified risks. A data management system was prepared to enable data acquisition for evaluation of the trials.
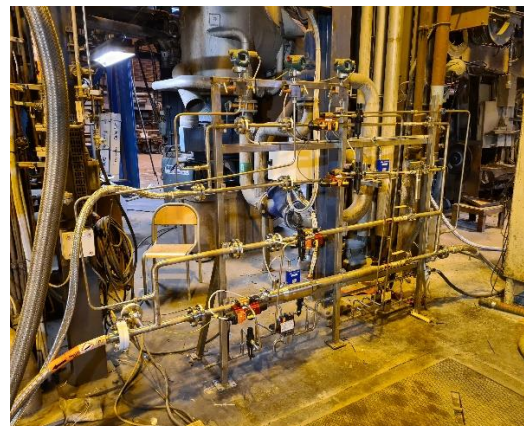

Figure 6. Swerim's 3-ton universal converter

Figure 7. New control systems were installed for hydrogen (left) and nitrogen (right).

Design of tuyeres

The tuyeres were designed and constructed at Swerim based on the requirements for the pilot trials. The tuyeres were installed at the bottom of the converter. The mixture of nitrogen gas and hydrogen gas goes in the inner gap of the nozzles while pure nitrogen gas goes in the outer gap. Figure 8 shows the tuyère from the side and a cross-section.

Figure 8 Hydrogen tuyeres from the side (left) and cross-section (right).

Design and testing of CoJet lance

The design of the CoJet lance was done to accommodate the existing infrastructure at Swerim and the updated hydrogen nitrogen control systems in combination with the thermodynamic calculations for the specific experiments. The lance was factory acceptance tested (FAT) at Linde's combustion lab for both burner mode (only propane and oxygen) and CoJet injection mode (nitrogen and hydrogen injection) using the following set-up. Jet length was measured by pitot tube probe at 45.7 cm (18 inches) and at 30.5 cm (12 inches) from the nozzle opening. The hydrogen concentration was measured at the top of the flame (45.7cm from the nozzle opening).

The lance was then installed and tested at Swerim (figure 9).

Figure 9. Installation of the CoJet lance at Swerim (left) and a close-up photo of the CoJet lance (right).

Experimental plan

Thermodynamic calculations

The thermodynamic simulations performed in the pre-study were updated to be suitable for the capabilities of the pilot facilities. The process model calculations were done in HSC Sim with the aim to calculate the need for externally added energy by propane burners during the trials. The experiments were downscaled from 100 tons of slag in the industrial application to approximately 2 tons in the pilot plant. The total gas flow rate was scaled down to 9 Nm^3 and the amount of carbon to 1.9 kg/min accordingly. The main difference in the box-fumer operation compared to Swerim's converter set-up is the preheated secondary air at approx. 450°C which combined with the primary air reached approx. 360 nm^3/ton and hour at 200°C. The hydrogen gas available for the experiments was 80 Nm^3/h based on the electrolyzer capacity at Swerim. The available flowrate of hydrogen was used to design the hydrogen injection trials. The simulations were made based on an average slag composition from Boliden.

During the reference experiments carbon supplied energy to maintain the heat in the vessel and acted as a reducing agent. During the experiments with hydrogen gas in the CoJet lance was used as a propane/oxygen burner to maintain the temperature of the slag. Cooling effects were estimated based on previous experiences and the

need for external energy from propane in burners during the experiments with hydrogen gas was calculated for the different cases.

The reference campaigns with carbon were done using tuyère injection, case 0. Hydrogen injection was designed in two set-ups: injection of reducing gas through tuyères (case 1) and injection of reducing gas through CoJet (case 2). The three cases are described in more detail below.

Case 0 – Injection of carbon through tuyeres

Carbon and oxygen were injected together with nitrogen gas as a carrier gas in the tuyères installed at the bottom of the converter. The flowrate of carbon was 1.9 kg/min, the flowrate of oxygen was 1.9 Nm^3/h, and the flowrate of nitrogen was 9 nm^3/min, giving α=0.71.

Case 1 – Injection through tuyeres

Figure 9 shows a principal picture of the set-up of the tuyère trials. The experimental design was made for two different concentrations of hydrogen gas in the inner gap, by varying the amount of nitrogen gas addition. The high concentration mixture was 25% H_2, and the low concentration mixture was 11% H_2. During the experiments with hydrogen gas in the tuyères, the CoJet lance was lowered to 90 cm above the slag bath and used as a propane/oxygen burner to maintain the temperature of the slag.
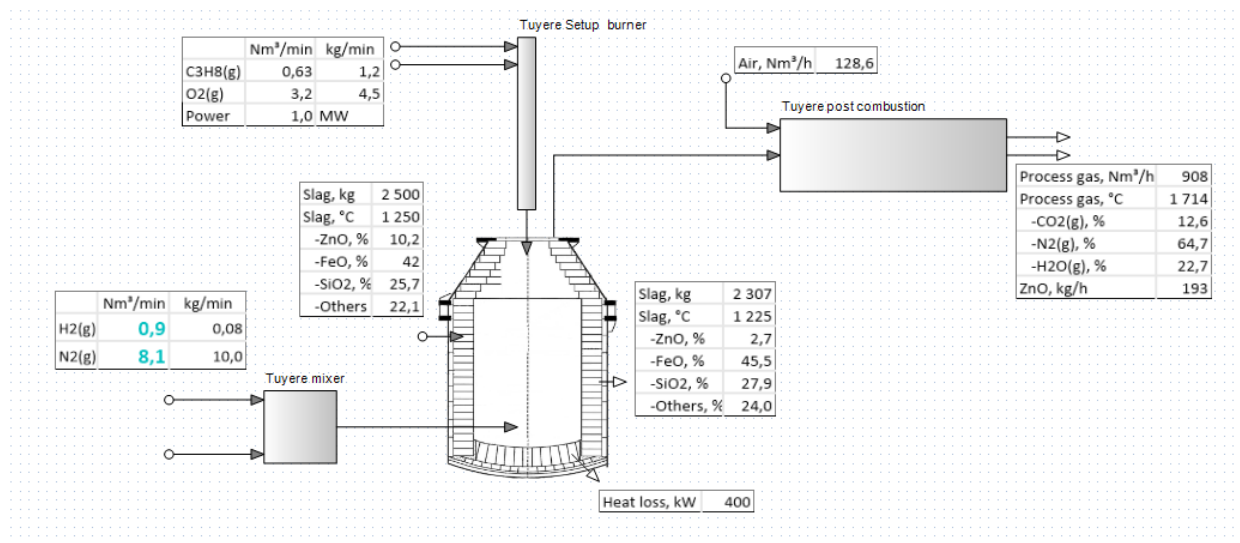
Figure 10 Experimental set-up of Case 1 – Injection of hydrogen by tuyères.

Case 2 – Injection by CoJet lance

During the experiments with the CoJet lance, the reducing gas (H_2/N_2) was added through the lance from the top of the converter (figure 10). The experimental set-up was designed to test the same H_2/N_2 mixtures as in case 1: high concentration 25%, and low concentration 11%. Propane/oxygen gas is added by the same lance through the outer gap to maintain the temperature of the slag. The lance was 20 cm above the slag bath.

Figure 11 Experimental set up of Case 2 - Injection by CoJet lance.

Experimental procedure

Each heat was charged with approximately 1800 or 2500 kg of zinc containing slag from Boliden Rönnskär's Electric Smelting Furnace. The zinc slag was continuously charged to the conver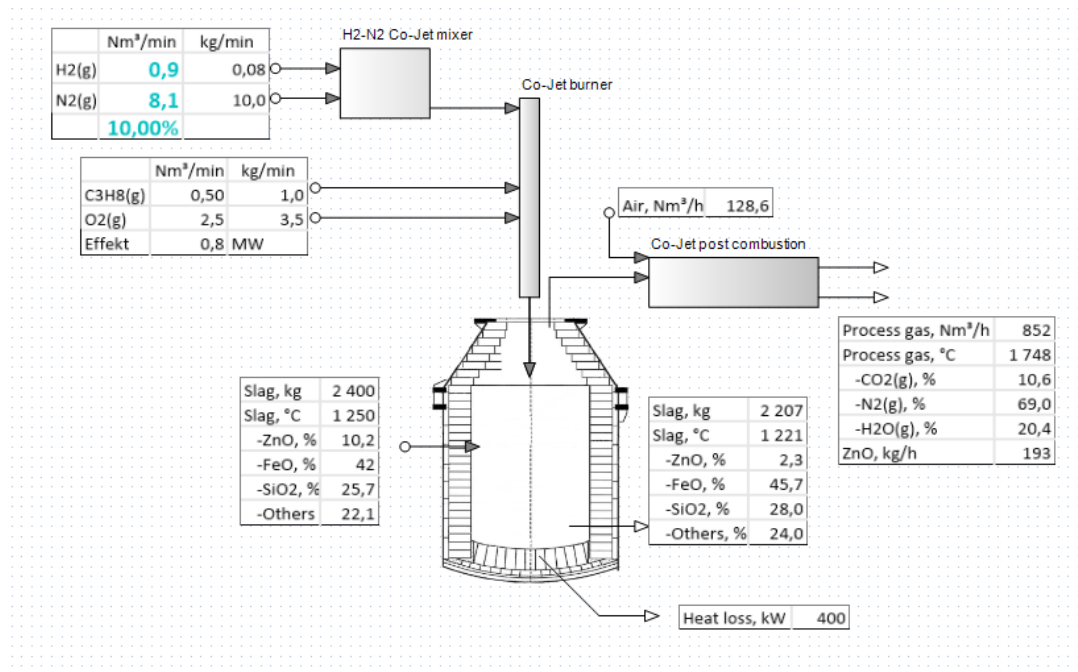ter and melted by propane/oxygen combustion. Target temperature of the melted slag was 1250-1300°C. Some heats took longer time to melt than expected due to formation of "icebergs" of solid slag. Adjustments were done to improve the melting procedure; the feeding rate was decreased to enable continuous melting of the added material and by lowering the lance initially and raising it slowly as the level of slag raised. The melting was done at stoichiometric conditions to maintain the slag's oxygen potential and properties.

When all material was melted and the target temperature achieved, a starting sample of temperature and composition was taken (S0). After S0, zinc fuming started by injection of the selected reducing agent (case 0, case 1 or case 2). For the current trial (case 1 and 2) the aimed fuming step was 60 minutes. Samples to measure the composition were taken every 15 minutes. The fuming ended by stopping the injection of carbon or hydrogen and retracting the burner lance.

The composition of slag samples was analyzed by X-ray fluorescence (XRF) with a Thermo Fisher Scientific ARL990 instrument calibrated for the particular type of slag using samples from Boliden Rönnskär. The composition is reported in weight-% (wt%) for pure elements (for example Zn, Pb and Cu) or oxides (for example CaO and SiO_2).

The temperature was measured at various occasions throughout the experiments and always before a slag sample was taken. In case of temperature deviations, the stoichiometry for the burner was adjusted during the fuming stage. The average temperatures are found in Table 2 and Table 3. Additional temperature measurements are found in Appendix 1.

The experimental plan was updated as the results from the previous heat were evaluated. For example, a third repetition of setting 1, case 1, was excluded in favor of higher partial pressure of hydrogen. The reference experiments are summarized in Table 2 and the hydrogen experiments are summarized in Table 3.

Table 1. Summary of reference trials (case 0).

ID	Slag (kg)	Temp. (°C)	Fuming time (min)	C feed (kg/min)	Flow rates (Nm^3/min)	
					N$_2$	O$_2$
2117	1800	1257	116	1.9	7.1	1.9
2119	1800	1224	113	1.9	7.1	1.9
2120	1800	1215	117	1.9	7.1	1.9

**Table 2. Summary of hydrogen injection experiments (case 1 and 2). Slag weight for charge S2148 is estimated.**

ID	Slag (kg)	Temp. (°C)	Fuming time (min)	Flow rates (Nm^3/min)				
				H$_2$	N$_2$	Total	Propane	Oxygen
2141	2500	1291	70	0.9	7.1	9	0.63	3.2
2142	2688	1308	64	0.9	7.1	9	0.63	3.2
2143	2542	1360	61	0.9	2.1	4	0.50	2.4
2144	2558	1369	53	1.2	1.8	4	0.50	2.4
Change to H$_2$/N$_2$ injection through CoJet lance								
2145	2326	1196	65	1.2	7.8	9	0.60	1.5
2146	2320	1295	66	1.2	7.8	9	0.90	2.5
		1213	46	0	7.8	7.8	0.90	2.5
2147	2395	1280	55	1.2	8.9	10.1	0.80	2.24
2148	2500*	1310	60	1.2	5	6.2	0.90	2.5

Evaluation of the experiments

The experimental data was evaluated with respect to zinc reduction rate through visual plots and regression analysis. Yield was calculated based on molar fractions of ZnO, PbO and CuO that was reduced during the fuming stage per added mole of reducing agent (carbon or hydrogen). The yield for the reference case is based on 79.8 wt% of the injected coal being actual elemental carbon (according to the material sheet.). Energy efficiency was calculated as the amount of energy used to reduce zinc, per added unit of energy during the fuming stage. For case 0 carbon was used for both reduction and heat, while for cases 1 and 2, the energy input from LPG also needed to be considered.

The energy efficiency and the amount of energy needed per kg of Zn reduced has been calculated to allow comparisons between case 0, where carbon was used both for reduction and heating, case 1 and 2 where the hydrogen was used for reduction

and propane for combustion. The material data sheet for the injected carbon states an energy content of 31.86 MJ/kg, which was multiplied with the mass of injected carbon to obtain the ingoing energy. The reaction of interest was the reduction of ZnO to Zn by C, and assuming that C is fully oxidized to CO_2 this corresponds to the sum of reactions (4) and (5) from section 1:

$$(7)\ 2\,ZnO + C(s) \rightarrow 2\,Zn(g) + CO_2(g),\ \Delta H_{1200°C} = 535\ kJ/mol$$
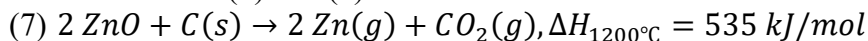
The enthalpy change was thus 187.5 kJ per mole of zinc, and the total energy for zinc reduction during the heat is used as the output energy which was compared to the input energy to give an estimate of the energy efficiency.

In the hydrogen fuming trials, hydrogen gas was used for reduction and propane for the temperature. The ingoing energy was thus taken as the sum of the energy from both sources. The energy content for propane is 88.4 MJ/Nm³, and for H_2 it is 120 MJ/kg. The enthalpy for the desired reaction (reaction (6) in section 1) was 215.7 kJ per mole of zinc, which was used to calculate the output energy and thus the energy efficiency.

Parameters for evaluation are summarized in Table 3.

Table 3. Parameters for evaluation of the experiments.

Parameter	Method for evaluation	Comment
Hydrogen concentration/partial pressure	Changing N_2 flowrate	Small room for increasing H_2 flowrate further in existing system.
Injection impact	Increasing N_2 flowrate	Increasing the weight of the gas.
Injection method	Using two different methods	Difficult to evaluate because of other parameters that influence the process
Reduction rate	Linear regression of amount of zinc reduced over time	Regression performed for samples taken in the liner region
Yield	Calculated yield for Zn or Zn+Cu+Pb removed from the slag, assuming reduction from ZnO, Cu_2O and PbO by carbon or hydrogen respectively	Carbon: used for both heat and reduction Hydrogen: only used for reduction
Energy efficiency	Calculated energy used for zinc reduction per added energy during the fuming stage (carbon + hydrogen + propane)	No consideration of melting praxis or starting temperature.

Resultat

CoJet design tests

The CoJet was tested according to the plan in section 2.1.4. (test-rig in Figure 12).
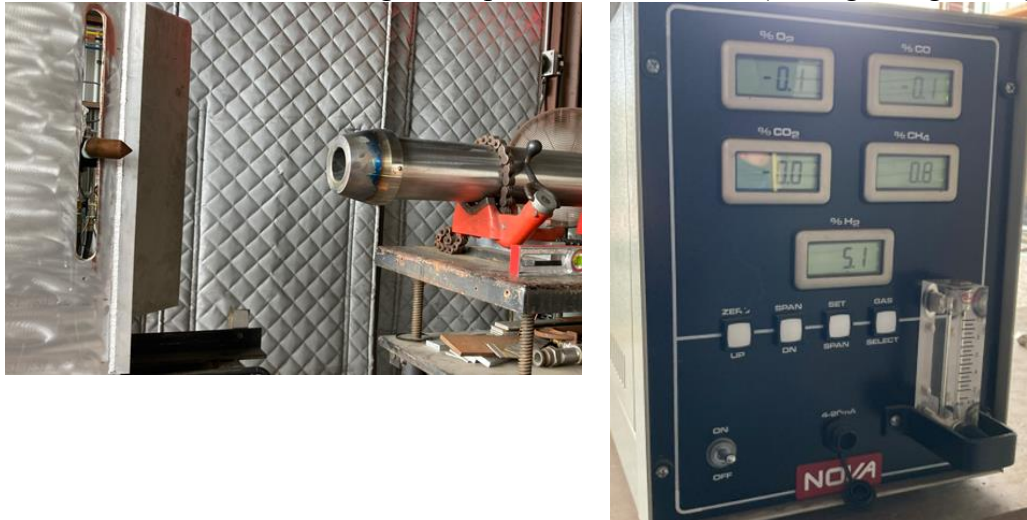

Figure 12 Set-up of the CoJet test rig.

A stable coherent jet was achieved for CoJet mode with hydrogen/nitrogen gas (figure 13).

Figure 13 Stable flame during testing of the CoJet lance.

The jet was sampled by suction through the pitot tube opening and the H_2 composition at 45.7 cm was determined to be 5%. No products of combustion, from the oxy/propane shroud were measured within the supersonic coherent jet, which indicates that no significant amount of hydrogen had been consumed by the shroud flame. That is, the internal hydrogen jet remained intact at 45.7 cm from the face of the lance.

Pilot experiments

Carbon reference trials

The results from the reference trials using carbon as a reducing agent are shown in Figure 14 and Figure 15. In Figure 14, the amount of zinc reduced from the slag (in kg) is plotted as a function of time. The three reference trials show similar reducing rates of 1.25-1.29 kg/min, calculated by linear regression of samples Sl1-Sl4.
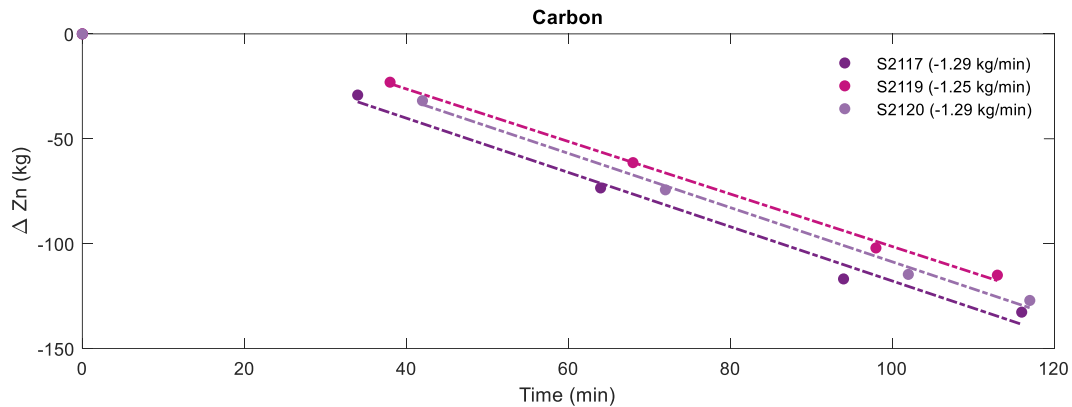

Figure 14. Linear regression to estimate the reduction rate (in kg/min) for reference case with carbon.

Figure 15 shows the zinc removed from the slag, as a function of the injected carbon – both in mol. It also shows the yield, calculated assuming that ZnO or ZnO, PbO and Cu_2O were reduced to elemental metals while carbon was oxidized from C to CO_2. The yield was calculated to be 6-7% if including only zinc, and 8-9 % when copper and lead were included. This is in line with suggestions that down to 12% of the carbon was used for reduction.

The calculated energy efficiency in percent is 8% for S2117 and S2120 and 7% for S2119. The amount of energy needed per kg of Zn removed from the slag is 51, 58 and 52 MJ (for S2117, S2119 and S2120, respectively).
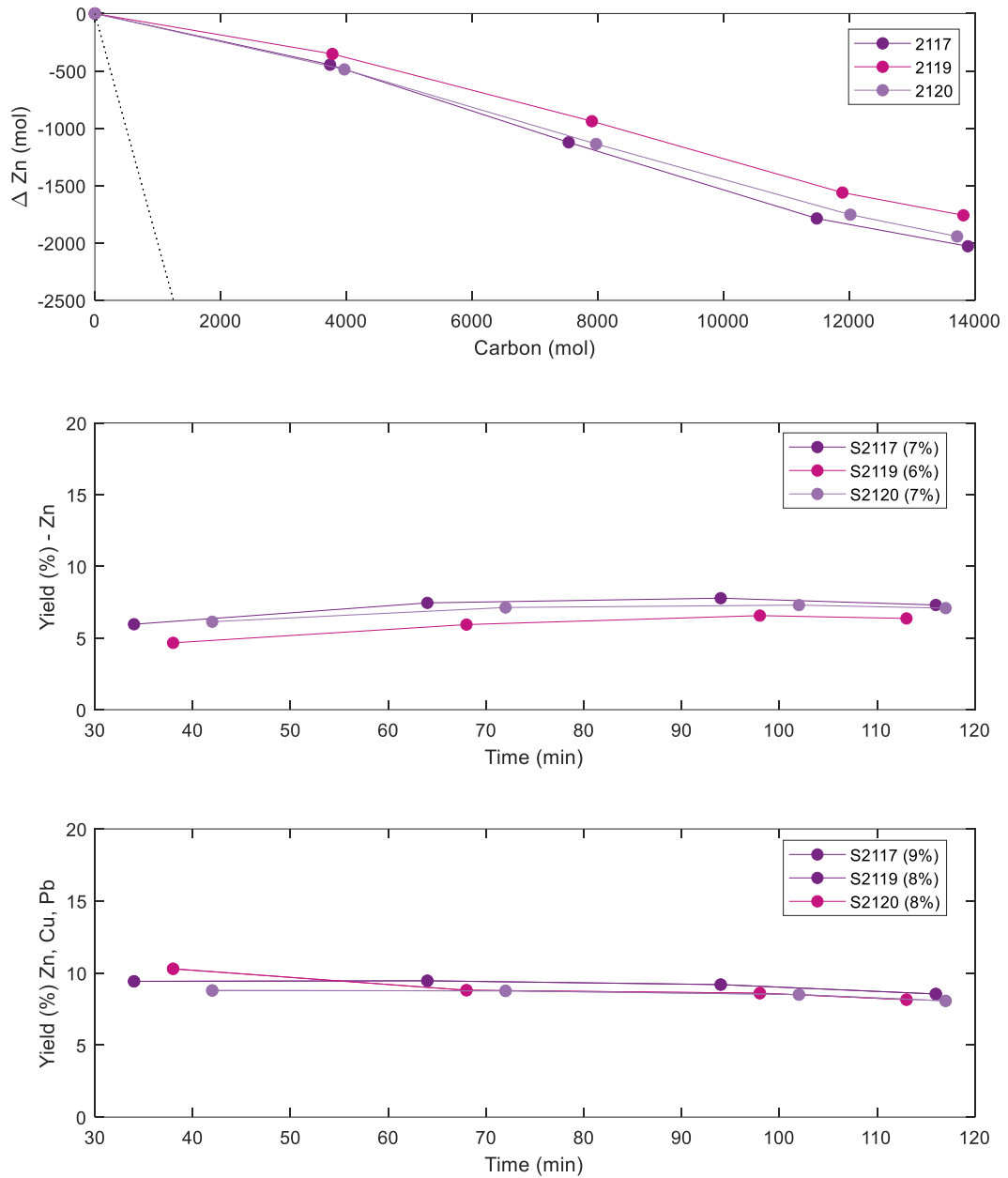
Figure 15. Top: Zinc reduced from the slag as a function of added carbon (both in moles) in the reference trials. Dotted reference line indicates a ratio of 2 mol Zn: 1 mol C.. Middle: Yield, based on change in Zn content and the amount of injected carbon in the reference trials. Bottom: Yield, based on change in Zn, Cu and Pb content (assuming reduction of ZnO, Cu_2O and PbO) and amount of injected carbon. In all cases, the total yield at the last point for each experiment is displayed in the legend.

Hydrogen reduction trials

Figure 16 shows the change of zinc content (in kg) as a function of time. Since the fuming rate is lower in the beginning in most experiments, the starting sample and the first sample after that are excluded from the regression.
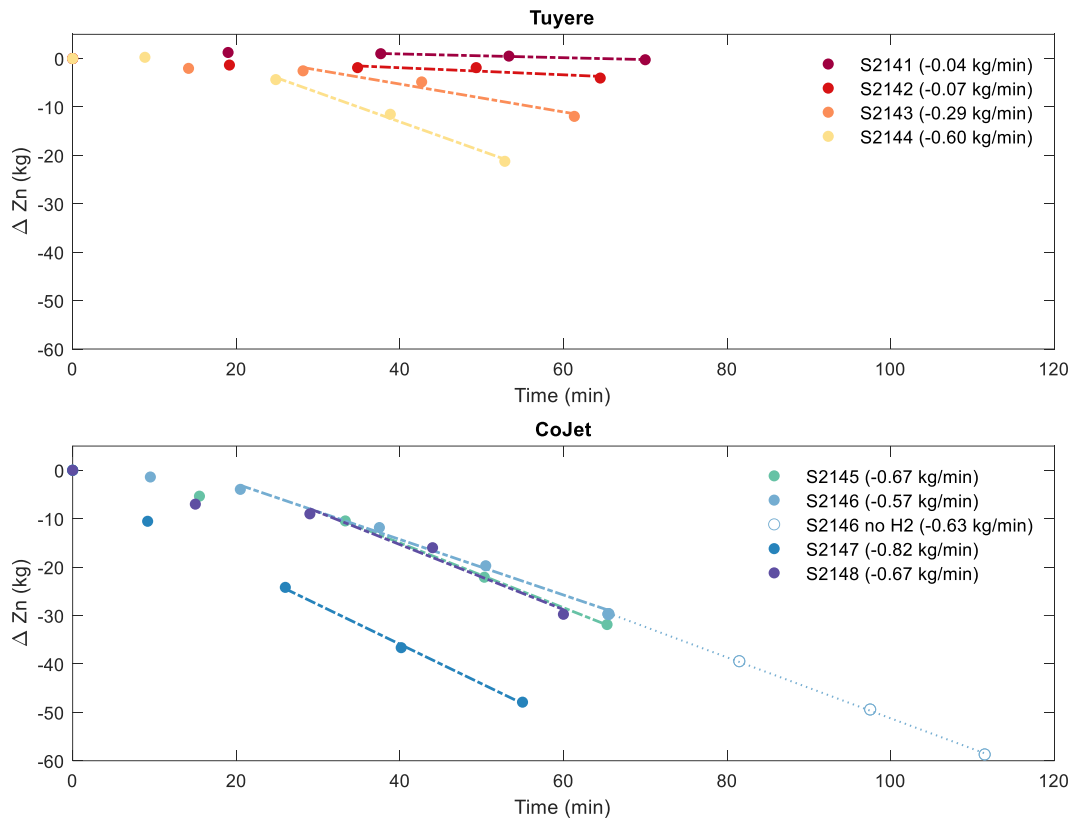

Figure 16. Linear regression to estimate the reduction rate (in kg/min) for hydrogen trials (case 1 with tuyères, and case 2 with CoJet).

The rate is higher for each subsequent heat in the first part with injection via tuyères. During the initial heats (S2141 and S2142), the zinc content was virtually constant. The flow rates were 0.9 Nm^3/min for H_2 and 7.1 Nm^3/min for N_2. Decreasing the N_2 flow rate to 2.1 Nm^3/min (S2143) resulted in a measurable decrease of the zinc content, and an increase of the H_2 flow rate and corresponding decrease of N_2 flow rate (S2144) further increased the rate. For injection via tuyères, a higher partial pressure of H_2 thus seems to be the governing factor for increasing the fuming rate. With injection through the CoJet lance, a larger decrease of zinc concentration in the slag was observed in all four cases (S2145-S2148). The calculated rates were similar to that of experiment S2144, which also had a H_2 flow rate of 1.2 Nm^3/min. An important observation was that even though the flow of H_2 was turned off after 66 min of fuming for S2146, the zinc concentration continued to decrease during the remaining time of the experiment. A similar rate was noted during the later part of S2146 even though there was no flow of H_2. This indicates that hydrogen was not the only reducing agent. S2147, with the highest total gas flow rate, had a slightly higher fuming rate than the others but also had the same rate already from the beginning, which makes the total amount of zinc reduced larger than in the other experiments.

The change of zinc content (in kg) in the slag as a function of accumulated injected H_2 (in Nm^3/h) can be seen in Appendix 2.

The amount of H_2 and Zn respectively during the experiments are shown in Figure 17. It can be noted that the amount of zinc reduced is far below the theoretically possible. Figure 18 shows the yield during the experiments assuming hydrogen as the only reducing agent. As described above, reduction can take place even without injection of H_2, which means that the true yield should be lower as H_2 is not the only reducing agent. Furthermore, copper and lead should also be reduced from oxide to elemental form. Figure 19 shows the yield when assuming that reduction also includes PbO and Cu_2O. However, the content of Pb and Cu is constant or even increasing during the first heats, meaning that the yield is lower and even negative when including Cu and Pb for the first heat (S2141) while for the CoJet experiments it was increased compared to only considering Zn.
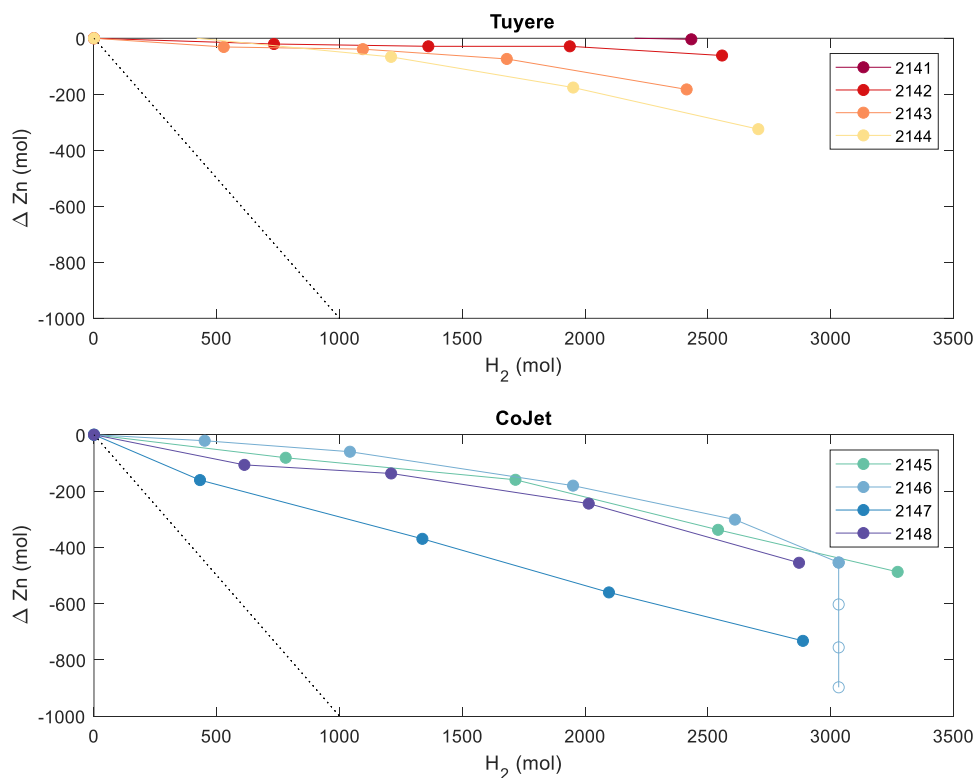

Figure 17. Zinc reduced from the slag (in moles) as a function of injected H_2 (also in moles). The dotted line represents 100% yield (assuming H_2 is the only reducing agent and ZnO the only oxide being reduced).

Figure 18. Yield, assuming H₂ to be the only reducing agent and ZnO the only oxide being reduced. For 2146, only the time with H₂ injection is included. Legend states the total yield at the last point for each experiment.
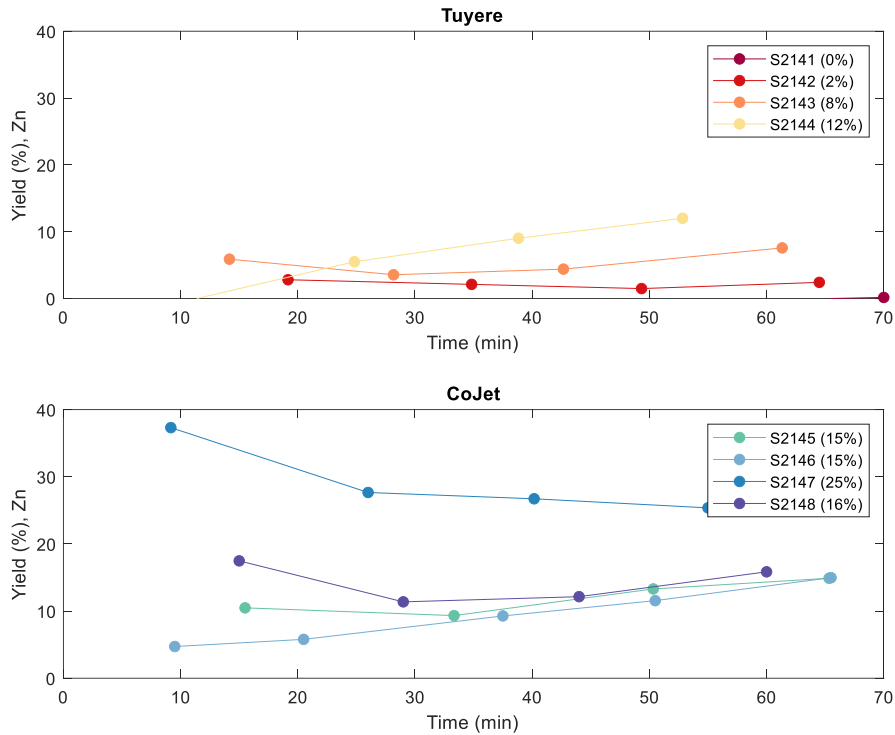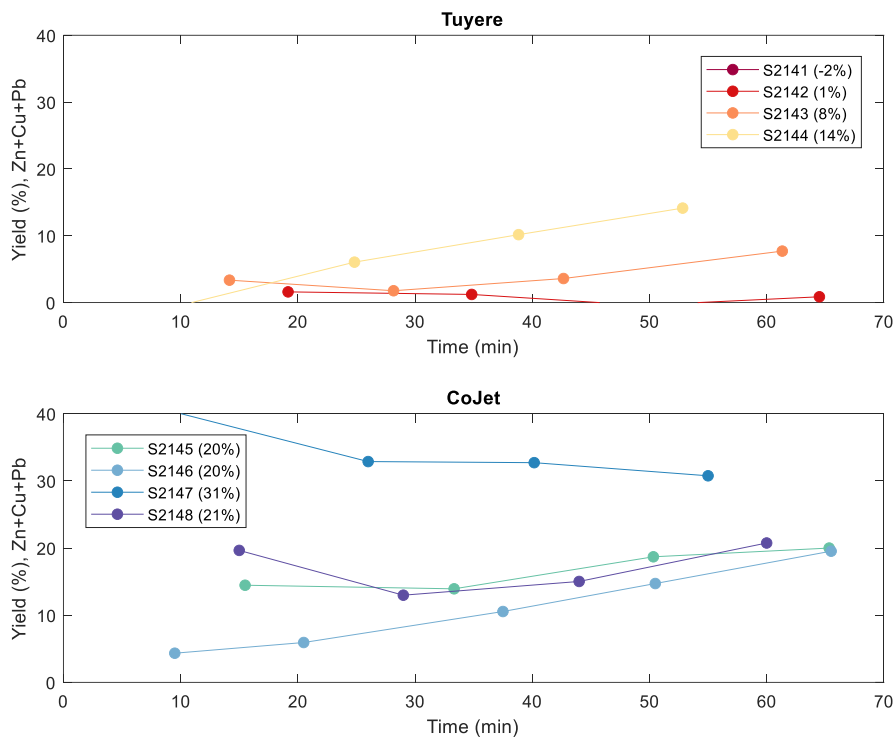

Figure 19. Yield, assuming H₂ to be the only reducing agent and ZnO, PbO and Cu₂O the oxides being reduced. For 2146, only the time with H₂ injection is included. Legend states the total yield at the last point for each experiment.

The energy efficiency as calculated according to chapter 2.2.3 is displayed in Table 4 and is about 0-1% for the tuyère injection and 2-3% for CoJet injection. The amount of incoming energy per kg of Zn is around 300 MJ for the tuyère cases where some reduction was achieved, and 100-200 MJ for the CoJet heats. For S2146, the number is calculated for the earlier part of the heat with active hydrogen injection.

Table 4. Energy efficiency (in %) and energy needed to reduce one kg of Zn.

ID	Energy efficiency (%)	Energy per kg of Zn (MJ)
2141	0	1717
2142	0.3	1103
2143	1.2	284
2144	1.3	263
2145	1.7	194
2146	1.6	204
2147	3.1	107
2148	1.9	171

Summary of results

The results from the trials are summarized in Table 5.

Table 5. Summary of results.

ID	Injection method	Carbon flow Rate (kg/min)	N_2 flow rate (Nm^3/min)	Fuming rate (kg/min)		Yield (%) (Zn, Pb and Cu)	Energy efficiency (%)
2117	Tuyère	1.9	9	-1.29		9	8
2119	Tuyère	1.9	9	-1.25		8	7
2120	Tuyère	1.9	9	-1.29		9	8
ID	**Injection method**	**H_2 flow rate (Nm^3/min)**	**N_2 flow rate (Nm^3/min)**	**Fuming rate (kg/min)**	**Fuming rate (kg Zn/Nm^3 H_2)**	**Yield (%) (Zn, Pb and Cu)**	**Energy efficiency (%)**
2141	Tuyère	0.9	7.1	-0.04	-0.04	-2	0
2142	Tuyère	0.9	7.1	-0.07	-0.08	1	0
2143	Tuyère	0.9	2.1	-0.29	-0.32	8	1
2144	Tuyère	1.2	1.8	-0.60	-0.50	14	1
2145	CoJet	1.2	7.8	-0.67	-0.61	20	2
2146	CoJet	1.2	7.8	-0.57	-0.55	20	2
		0	7.8	-0.63	-	-	-
2147	CoJet	1.2	8.9	-0.82	-0.68	31	3
2148	CoJet	1.2	5	-0.67	-0.56	21	2

The yield including Pb and Cu appears to be negative in the first heat and then increases throughout the campaign. This could be an effect of contaminated reactor vessel from previous campaigns (See Appendix 3) and should therefore not be given too much consideration in the evaluation.

Note that the yield is calculated based on the total amount of carbon, even though that carbon also serves as energy carrier, see definition in table 3. See also the discussion section.

Discussion

The experiments show that injection of hydrogen gas into liquid slag can be done in a safe manner. Either tuyères or CoJet technology may be used for injection of hydrogen. However, it was difficult to demonstrate efficient reduction using hydrogen as a reducing gas in slag fuming operations with the current set-up.

For the injection with tuyères, almost no effect was seen in the first heats. The reduction rate increased with higher partial pressure of H_2. The limiting factor in this case thus seems to be the available hydrogen gas. These experiments did not support that a total higher flowrate was also beneficial, as the experiments with high flow rates also had low partial pressure of H_2 due to limitations in H_2 availability in the current set-up.

The CoJet experiments showed higher reduction rate overall, but in the same range as the best tuyère heat where the hydrogen flowrate was the same. The reduction rate increased with total hydrogen flow rate. The amount of hydrogen gas was kept as high as possible during the last set of experiments, because there appeared to be a correlation between high hydrogen flowrate and reduction of zinc.

The rate of reduction using hydrogen was significantly lower for both tuyères and for CoJet compared to injection of carbon via tuyères in previous campaigns using the same converter. The reduction rate was 1.25-1.29 kg/min using carbon while only as low as 0.82 kg/min for the most efficient heat using hydrogen. Comparing the yield of the different reducing agents, the yield of carbon was 6-7% if only zinc reduction was accounted for (8-9% if Pb and Cu were added) while the yield for hydrogen was 0-12% (0-14% with Pb and Cu) for tuyeres and 15-25% (20-31% with Pb and Cu) for CoJet. The low yield for carbon was expected since the process is designed to use carbon for both reduction and for heat generation. The low yield of hydrogen is therefore even lower than it appears at a first view. The energy efficiency based on yield per unit of energy (carbon or hydrogen and propane) gives a more adequate view of the process. The energy efficiency was about 0-1% for the tuyere injection and 2-3% for the CoJet injection. The amount of incoming energy per kg of Zn is around 300 MJ for the tuyère cases where some reduction was achieved, and 100-200 MJ for the CoJet heats, compared to 7-8% for the carbon trials. For reference, reduction with hydrogen gas in other metallurgical processes is known to have rather low yield of hydrogen. In a closed shaft reactor such as a DR-shaft, the reducing gases can be recovered from the off-gases, while this is difficult to achieve in a more open furnace like a box-fumer, since the amount of oxygen in the atmosphere above the bath will combust any residual hydrogen to water.

The reactions continued even when the hydrogen injection ended during heat S2146 which suggests that hydrogen was not the only or even the dominant reducing agent in the reactor. Therefore, the results must be handled with great care. This phenomenon could be explained by two theories: either improved stirring or the presence of some other reducing agent. There are two potential reducing agents, one is the propane or the CO (g) generated from combustion of propane, and the other are iron oxides. The hydrogen could have reduced the oxygen potential in the melt overall leading to the elements in the iron oxides to reduce zinc oxide. This could not be evaluated within the project since there was no titration method available at the laboratories hired to make the analysis. For future experiments, a method could be planned in advance.

Based on a literature review, a few different theories can be developed to explain zinc reduction with hydrogen as there is likely a kinetic explanation to the lower efficiency. Stirring is known to improve the process efficiency. The lack of a solid carbon particle to create a large enough surface area to achieve good reaction may

be part of the explanation. The reaction is described as taking place in a bubble formation. Since H_2 is a light and small molecule it might not have enough residence time in the bath to react. A high enough temperature and thus pre-heating the blast are known methods for improving efficiency in metallurgical processes. Since the H_2/N_2 gas was injected at room temperature, it could have affected the reduction rate negatively.

Increased height of the bath could extend the residence time to enable higher conversion. The reference trials had slightly lower slag volume and thus lower height than the hydrogen injection trial, but still had higher yield/energy efficiency. Changing from a solid to a gaseous reducing agent is a substantial change of operations and will require more evaluation and experiments before it is rejected as not working. Co-injection of particulate matter (such as biocarbon or metallurgical dust) or other means to increase the impact of the injection or reaction zone for the reducing agent could improve the process efficiency. Pre-heating of the reducing gas is a potential improvement. A different reactor design could be beneficial for gaseous injectants. Injection could also be attempted with other methods. The pre-study suggested TSL (Top Submerged Lance) and bottom blown nozzles.

Conclusions

Changing from a solid to a gaseous reducing agent is a substantial change of operations and will require more evaluation and experiments. The initial tests show that it is possible to inject hydrogen gas safely into molten slag. Some reduction of the slag was achieved, but hydrogen was not the only reducing agent in the system. Propane and/or its combustion product (CO) was likely to influence the zinc reduction.

In general, it could be seen that higher hydrogen flow rate will likely increase the zinc reduction rate.

When only considering Zn reduction, the yield of carbon injection trials varies between 6-7% while the hydrogen injection trials vary between 0-25%. If Pb, Cu are also taken into consideration the yield of carbon is between 8-9% and 0-31% for the hydrogen trials. It is however difficult to compare these numbers since carbon addition is adapted to also contribute to the energy balance, while the hydrogen is only meant for reducing purposes. Therefore, the energy efficiency of the system was evaluated and was lower for hydrogen then for carbon.

There are ways to improve the efficiency, for example by pre-heating the reducing gas, using different reactor design, increasing the residence time by increasing bath level, different injection system and higher hydrogen gas flowrate.

Suggested continued work

- Pre-heating of reducing gas
- Higher partial pressure of hydrogen for injection
- Higher total gas volume

- Co-injection with particulate matter (such as biocarbon or metallurgical dust) or other means to increase the impact of the injection or reaction zone for the reducing agent
- Alternative injection method (bottom nozzle, TSL as suggested in the pre-study)
- Investigation of ferrous oxides
- Alternative reactor vessel design

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Bilagor

APPENDIX 1 Temperature measurements

APPENDIX 2 Additional results

APPENDIX 3 Other elements

APPENDIX 4 Administrativ bilaga