# Pyrometallurgical treatment of nickel smelting slag with biochar

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## ABSTRACT

In this study, the use of carbon neutral biochars as reducing agents in the pyrometallurgical treatment of nickel slag was investigated at 1400 ℃ in order to recover valuable elements such as copper and nickel from the slag. A large amount of slag is generated during the nickel matte smelting. Nickel slag contains valuable elements such as copper, nickel, and cobalt, which can be recovered. Disposal of this slag results in loss of resources and may cause pollution of the environment. It is important to retrieve these metals for environmental and economic reasons.

In this study, the slag was reacted with non-fossil reducing agents (biochar) which were produced from hydrolysis lignin and black pellet biomass pyrolyzed at 600 and 1200 ℃, and with metallurgical coke for comparison. The reduction experiments were done at 1400 ℃ for 15, 30 and 60 minutes under inert gas atmosphere. The samples were quickly quenched and analysed with Electron Probe X-ray Microanalysis (EPMA). The results showed that the use of biochar resulted in faster reaction kinetics in the reduction process compared to coke. The fast reaction kinetics is attributed to the relatively high content of volatiles in this biochar, leading to gas formation and thus mixing of the sample material. Moreover, thermodynamic modelling was also performed using Factsage to simulate equilibria with different amounts of biochar. The metal to slag distribution coefficient calculated from the results of thermodynamic modelling were consistent with experimental results. In addition, thermodynamic calculations confirmed that nickel is reduced rapidly, and it deports to the metal alloy phase. As the reduction progresses or extra reductant is available for reactions, more iron is deported to the metal phase. The calculations also revealed that Zn vaporizes into the gas phase.

## INTRODUCTION

Nickel is an important non-ferrous metal which is widely used in machinery, architecture, steelmaking, military, and other fields due to its physical and chemical properties. During the pyrometallurgical production of nickel, about 6–16 tons of nickel smelting slag is generated per ton of nickel produced (Sun et al., 2021; Zhang et al., 2020). The slag usually contains some valuable elements such as copper, cobalt and nickel and these valuable metals can exist in the form of sulphides, oxides, or dissolved elements. It is important to effectively extract valuable elements from nickel slag to ensure environmental sustainability and efficient resource utilization since negligent disposal of this waste stream results in environmental pollution and loss of valuable elements (Zhang et al., 2020).

Dańczak et al., (2021) employed anodic graphite of spent batteries as reductant in nickel slag reduction at 1350 ℃. They reported that metal alloy, matte, and slag phases were formed after reduction, and concluded that the metal/matte to slag distribution coefficient increases with an increase in the amount of spent battery. Avarmaa et al., (2020), on the other hand, studied the reduction of nickel slag at 1400 ℃ with biochar and battery scrap mixture to recover valuable metals and compared the results to the reduction with coke. They reported that biochar enhanced reaction kinetics compared to coke and the presence of battery scrap greatly increased the distribution coefficients of valuable metals.

While nickel slag cleaning aims to recover valuable metals such as nickel, cobalt, and copper as much as possible in the metal alloy phase, it is important to minimize the iron content as it is very difficult to separate during downstream processes. Since some of the metals have similar reduction properties as iron, some losses of valuable metals are unavoidable in the slag cleaning (Jones et al., 2002).

The metallurgical industry consumes great amounts of fossil fuels such as coke, which is mainly used as fuel and reducing agent resulting in large emissions of carbon dioxide and other greenhouse gases. In recent times, the use of non-fossil reductants in metal production have gained more attention (Cholico-González et al., 2021; Guo et al., 2017). One such option of non-fossil reductant is biocoke or biochar obtained from pyrolyzed biomass. Since biomass absorbs $CO_2$ from the atmosphere during their growth, they release the absorbed $CO_2$ in the reduction process, thus creating a closed loop carbon cycle (Adrados et al., 2016; Suopajärvi et al., 2013) . Several research groups have investigated the use of biomass or biochar as reductant in metal production (Avarmaa et al., 2020; Demey et al., 2021; Wiklund et al., 2017).

Adrados et al., (2016) compared biocokes pyrolyzed from olive and eucalyptus trees with commercial reducing agents (metallurgical coke, petroleum coke and anthracite). They reported that based on proximate and ultimate analysis, olive, and eucalyptus biocokes (bioreducers) have better quality than the usual reducing agents, since the bioreducers have lower ash and sulphur contents. Moreover, the bioreductants used have much higher specific surface area and porosity than that of the commercial reductants, making them much more reactive. In their study on the effectiveness of using biomass-based reducing agent in blast furnace, Koskela et al., (2019) concluded that the utilization of biomass as raw material in blast furnace ironmaking can have an enormous contribution to the mitigation of $CO_2$ emissions in steelmaking. Moreover, Mousa et al., (2016) reported that the use of biomass as a source of energy and reducing agents provides a promising alternative solution for green steel production.

The aim of this study was to ascertain the potential and effectiveness of using biochar as reducing agent to recover valuable metals like Co, Ni, and Cu from nickel smelting slag as well as to understand the effects of reaction time.

## EXPERIMENTAL

### Materials

Industrial (ground) nickel smelting slag provided by Boliden Harjavalta Oy (Harjavalta, Finland) was used experiments. The slag used was XRF (X-ray fluorescence) as well as *magnetite content analyses (Satmagan) for the slag were conducted at Boliden Harjavalta Oy, see Table 1.

TABLE 1 - Composition of Ni slag by XRF and its *magnetite content.

| Fe | Ni | Cu | Co | Cr | Zn | S | $SiO_2$ | MgO | $Al_2O_3$ | CaO | *$Fe_3O_4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 37 | 3.62 | 0.77 | 0.42 | 0.08 | 0.08 | 0.11 | 33.7 | 7.6 | 2.1 | 1.74 | 22 |

Four different kinds of reductants were tested in the experiments, i.e., black pellets pyrolyzed at 600 ℃ (B600) and 1200 ℃ (B1200) and hydrolysis lignin pyrolyzed at 600 ℃ (L600) and 1200 ℃ (L1200). The ultimate and proximate analysis (shown in TABLE 2) of these reductants were done with Elemental Analyzer Flash 2000. Ash analysis of lignin and black pellet was conducted using inductively coupled plasma - optical emission spectroscopy (ICP-OES) and is shown in Table 3.

Table 2 shows that a biomass pyrolyzed at a higher temperature has higher fixed carbon and lower volatile matter contents. In addition, the ash content of black pellet is much higher than that of lignin. The ash analysis revealed that black pellets contain relatively high concentrations of Ca, K and Si. Most of the elements in the ash deport to the slag phase during reduction reactions. It can be seen in Table 2 that lignin has higher fixed carbon content compared to black pellet. The analysis reveals that biochar pyrolyzed at higher temperature contain higher carbon and lower hydrogen and nitrogen composition (TABLE 2). When biochar is employed as fuel or reducing agent in some metallurgical industries, low ash contents and high volatile matter may be advantageous (Wiklund et al., 2017) .

TABLE 2 – Ultimate and Proximate analyses of biochar.

| | Properties | B600 | B1200 | L600 | L1200 |
|---|---|---|---|---|---|
| **Ultimate Analysis** | C | 76.62 | 81.21 | 87.90 | 96.73 |
| | H | 1.56 | 0.00 | 1.73 | 0.07 |
| | O | 7.33 | 5.73 | 8.50 | 2.15 |
| | N | 0.47 | 0.12 | 0.97 | 0.13 |
| | S | 0.00 | 0.00 | 0.00 | 0.00 |
| **Proximate Analysis** | Volatile matter | 10.82 | 3.57 | 6.39 | 1.31 |
| | Fixed Carbon | 76.16 | 83.19 | 91.62 | 97.54 |
| | Ash content | 12.32 | 12.83 | 1.29 | 0.92 |

TABLE 3: Ash analysis of biochar used for the reduction study.

| Element | | Ca | Mg | Na | K | P | S | Fe | Al | Si | Mn | Ba |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lignin | mg/kg | 290 | 51.0 | <10 | 130 | 74 | 1100 | 810 | 14 | <10 | 41 | 4.8 |
| Black Pellet | mg/kg | 13900 | 960 | 210 | 2600 | 560 | - | 680 | 680 | 7400 | 400 | 200 |

The stoichiometric amount of carbon required for reduction was calculated based on the composition of nickel slag after converting the metal concentrations to oxides, as shown in equations (1) to (5). The stoichiometric mass of carbon to be used was calculated using equations (6) to (11). The amount of reductant needed was calculated from the amount of carbon required.

$$2Cu + 0.5O_2 = Cu_2O \quad (1)$$

$$Zn + 0.5O_2 = ZnO \quad (2)$$

$$Ni + 0.5O_2 = NiO \quad (3)$$

$$Co + 0.5O_2 = CoO \quad (4)$$

$$2Cr + 1.5O_2 = Cr_2O_3 \quad (5)$$

$$Fe_3O_4 + C = 3FeO + CO \quad (6)$$

$$Cu_2O + C = 2Cu + CO \quad (7)$$

$$ZnO + C = Zn + CO \quad (8)$$

$$NiO + C = Ni + CO \quad (9)$$

$$CoO + C = Co + CO \quad (10)$$

$$Cr_2O_3 +3C = 2Cr + 3CO \quad (11)$$

## Method

The vertical-tube furnace (FIG 1) used was Lenton LTF 16/450 (Lenton Furnaces & Ovens, Hope Valley, UK) The furnace temperature was set to 1400 ℃. The furnace was purged with argon gas (99.999 vol% purity, Wiokoski Oy, Finland) with a flow rate of 300 mL/min, controlled by a rotameter (Kytölä Instruments, Jyväskylä, Finland ±5% full scale) during the experiments. The cone-shaped silica glass Heraeus HSQ®300 crucibles (fused quartz with purity of >99.998 wt% by Finnish Special Glass Oy, Espoo, Finland), with a diameter of 25 mm and height of 15 mm were employed for nickel slag containment.

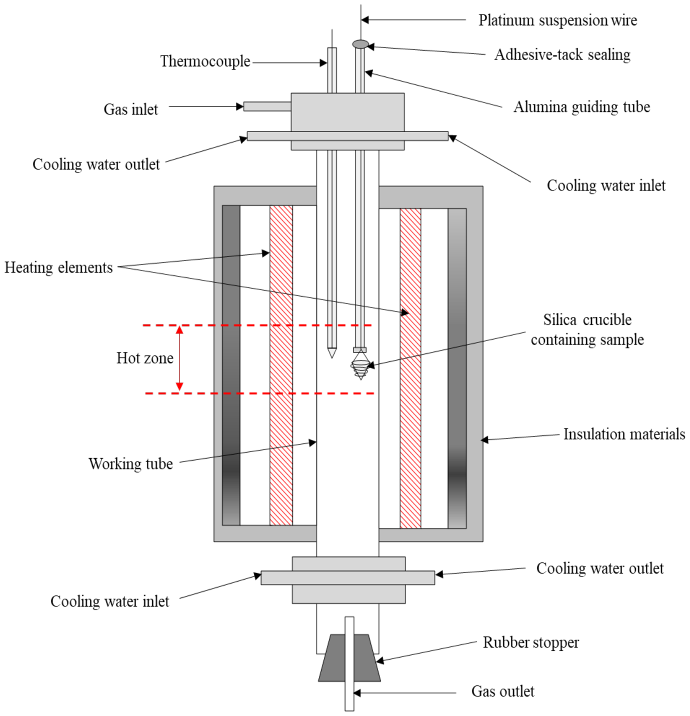


FIG 1 – Schematic of the vertical furnace used for nickel slag reduction experiments.

The drop-quench technique which have been employed by Avarmaa et al., (2020) was used in this study. One gram of the slag was mixed with the calculated amount of biochar, pelletised and placed in a crucible. The crucible was placed in a basket and attached to platinum wire hanging from inside of the furnace and subsequently lifted to the lower end of the furnace of the furnace before sealing the work tube with a rubber plug. 300 mL/min argon gas was used to purge the furnace to create an inert atmosphere. After about 15 min, the sample was lifted to the hot zone where the reduction reactions took place. After reaching the desired reaction time, the sample was dropped into ice water by pulling the platinum wire, which caused the sample-basket assembly to detach and fall. Reduction experiments were carried out at 1400 ℃ for 15, 30 and 60 minutes for each of the reductants.

## Characterization of Sample

The samples were dried and cast in epoxy resin and after curing, they were cut in half and again mounted in epoxy resin and cured. The samples were then polished, and carbon coated for scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). Mira 3 Scanning Electron Microscope (Tescan, Brno, Czech Republic) equipped with an UltraDry Silicon Drift Energy Dispersive X-ray Spectrometer (EDS) was used to perform preliminary elemental analyses and microstructural imaging. The compositions of the metal and slag phases were measured using EPMA with an SX100 (Cameca SAS, Gennevilliers, France) microprobe equipped with five wavelength dispersive spectrometers (WDS).

# RESULTS AND DISCUSSION

## Reduction Experiments

At the hot zone of the furnace (1400 ℃), the sample melts. Metal oxides (MeO) present in the slag react with the carbon in biochar producing metal (Me) as shown in equation (12). Carbon monoxide produced may also take part in the reduction of metal oxides (see equation (13)). As time progresses, more carbon and carbon monoxide react leading to a decrease in concentration of metals in the slag. The metal species produced from reduction of metal oxides as well as the mechanically droplets entrapped grow and form a metal alloy.

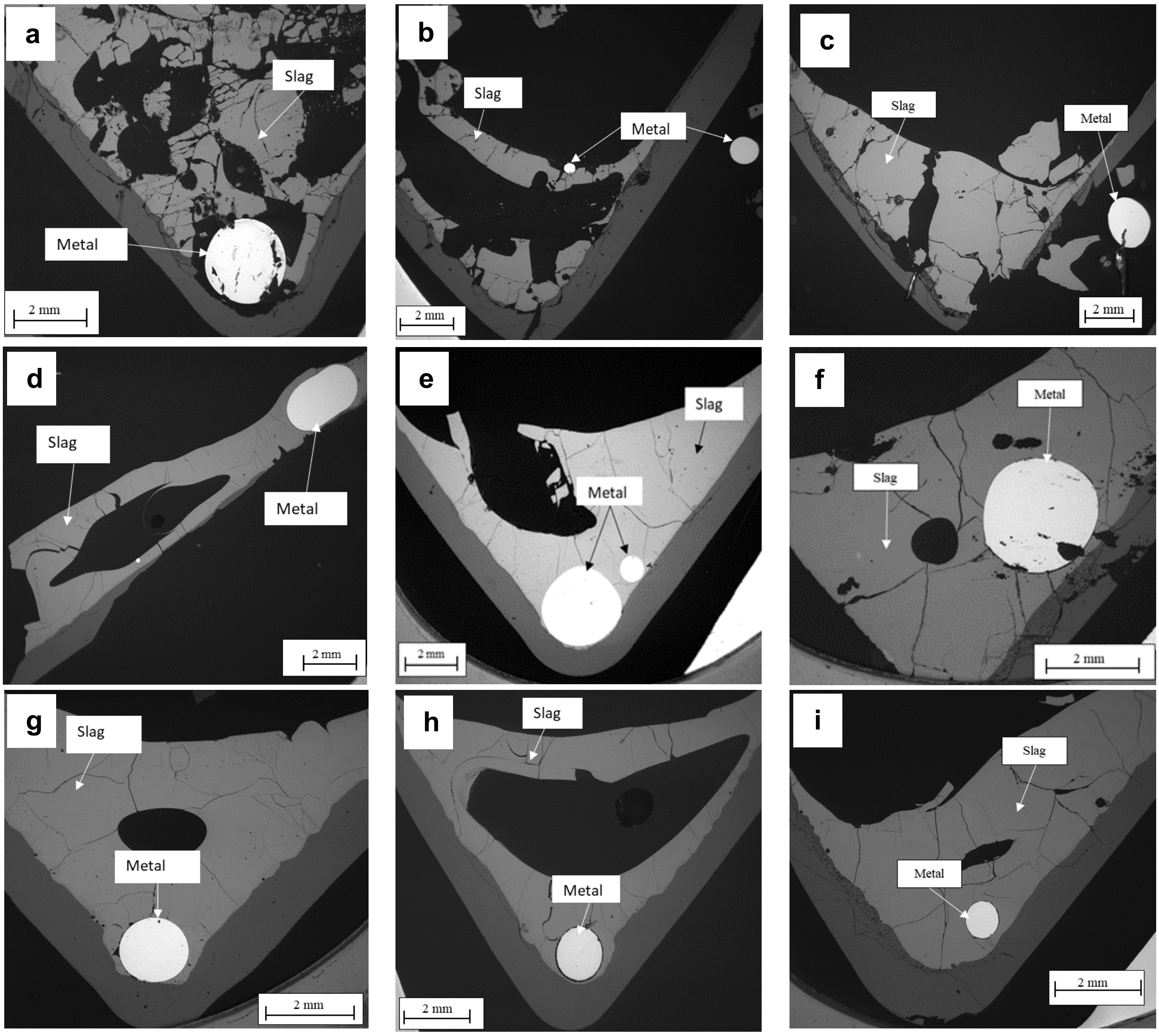
$$\mathrm{MeO(l) + C(s) = Me(l) + CO(g)} \qquad (12)$$

$$\mathrm{MeO(l) + CO(g) = Me(l) + CO_2(g)} \tag{13}$$

Figure 2 shows the SEM micrographs of sample polished sections prepared from nickel slag reduction with biochar at 15, 30 and 60 minutes. It can be observed that a metal alloy droplet was obtained with every contacting time, which suggests that the contact between the slags and reductants was good, and the reactions proceeded rapidly. The round shaped bright regions seen in the images are the metal alloy droplets and the grey regions are the slag areas (see FIG 2). The samples from reduction were rapidly quenched (< 3 s) and the slag phase was generally homogenous.

Since some of the slags were brittle because of rapid quenching, the metal droplets as well as slag pieces were sometimes detached from the rest of the sample while cutting. The dark regions (epoxy) found within the slag are attributed either to this or to gas formation within the melt.

The formed metal generally settled at the bottom of the crucible although some smaller droplets were found in various locations inside the crucibles. Avarmaa et al., (2020) observed similar microstructures and attributed the presence of the smaller droplets found at the edges of the crucibles to the surface and interfacial tensions between the phases of the system. In some of the reduction tests, two metal droplets were found (a bigger one and a smaller one: see FIG 2 b 30 minutes). It is believed that the bigger droplet (>1 mm diameter) is the first metal that was formed and the smaller one(s) is(are) later generated. Analysis of the smaller metal droplets revealed that the nickel, cobalt, and copper concentrations were higher but iron concentration was lower compared to the bigger droplet.



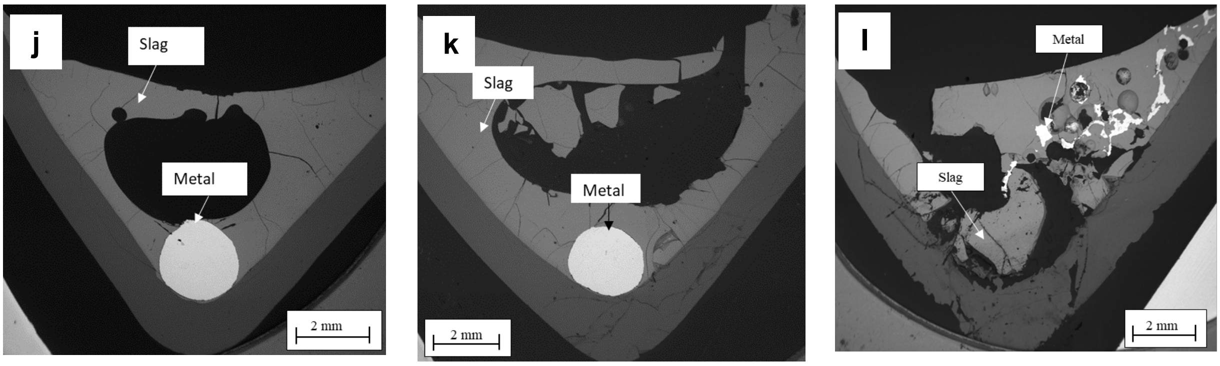


FIG 2 - SEM micrographs of sample polished sections of nickel slag reduction with (a) L1200 for 15 minutes, (b) L1200 for 30 minutes, (c) L1200 for 60 minutes (d) L600 for 15 minutes, (e) L600 for 30 minutes, (f) L600 for 60 minutes, (g) B1200 for 15 minutes, (h) B1200 for 30 minutes, (i) B1200 for 60 minutes, (j) B600 for 15 minutes, (k) B600 for 30 minutes, and (l) B600 for 60 minutes.

Nickel slag reduction was also conducted with metallurgical coke (FIG 3) to compare with the results from slag reduction with biochar. It was observed that biochar is a more reactive reducing agent compared to metallurgical coke. A large metal alloy droplet (~2 mm diameter) was formed (FIG. 2) when the different biochars were used, but such large alloy droplets were not found in the samples reduced with coke.

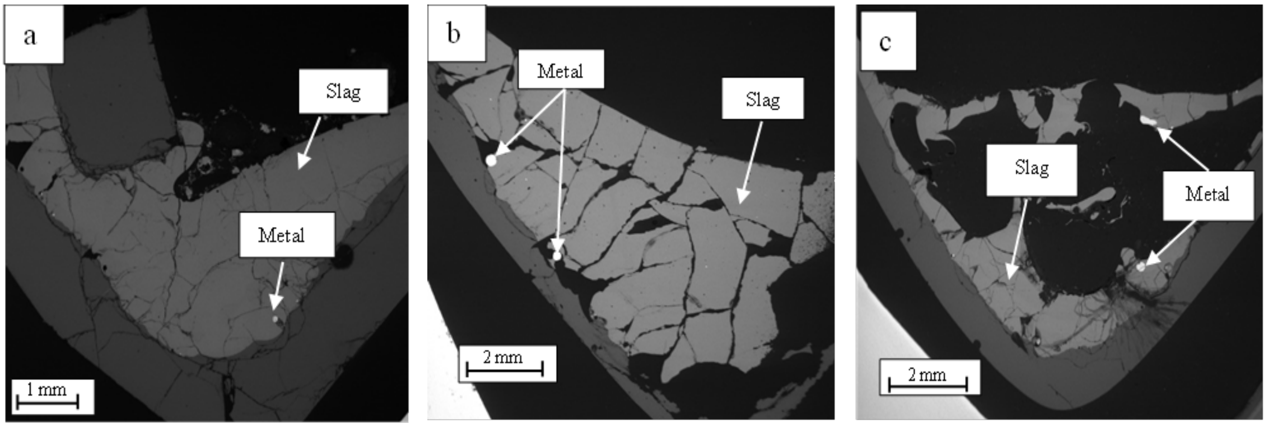


FIG 3 - SEM micrographs of sample polished sections of nickel slag with coke for (a) 15, (b) 30 and (c) 60 minutes.

Figure 4 shows the concentrations of nickel, cobalt, copper, and iron in the slag before (0 minutes) and after reduction (15, 30, and 60 minutes). This gives an indication of the amount of elements that have reduced to the metal phase or have been volatilized. The concentrations of nickel, cobalt and copper in the slag decrease as reduction time increases for all the biochar types. Within the first 15 minutes of the reduction, nickel concentration within the slag reduced from 3.62 to 1.06 wt% when metallurgical coke was employed. Higher metal removal was achieved when biochar was used, yielding nickel percentages in slag below 0.5 wt%. Biochars pyrolyzed at 600 ℃ (L600 and B600) showed higher reduction potentials than biochars pyrolyzed at 1200 ℃. When B600 and L600 were employed as reducing agents, the nickel concentration in the slag after 15 minutes was 0.06 and 0.07 wt%, respectively, while those for B1200 and L1200 were 0.48 and 0.24 wt%, respectively. While biochars pyrolyzed at 1200 ℃ have higher carbon contents, the higher volatile matter concentrations in L600 and B600 may be indirectly responsible for their higher reactivity, i.e., showed faster reduction kinetics.

It is commonly stated that in slag cleaning processes (at 1300-1400 ℃) and e.g., in titania smelting, volatiles are not contributing the reduction processes. This means that they are not considered when calculating the stoichiometric amounts of reductant needed in the process. However, the volatile matter upon moving to the gas phase increases the surface area for sufficient slag and reductant reaction (Lotfian et al., 2017). Moreover, compared to the coke and biochar pyrolyzed at 1200 ℃, more $CO_2$ is produced by biochar pyrolyzed at 600 ℃ which quickly reacts with solid carbon as shown in equation 14. (Boudouard reaction). Also, the generated CO take part in the reduction. Since reduction with solid carbon is slower compared to CO, the higher CO present during biochar reduction increases its effectiveness as reductant compared to coke (Lahijani et al., 2015).

$$CO_2(g) + C(s) = 2CO(g) \quad (14)$$

After 60 minutes reduction, the final concentrations of nickel in the slags were very close to each other with all reductants studied. Similar patterns regarding reduction kinetics of different reductants were observed for cobalt and copper as well, with the difference that the final concentration of cobalt in slag after 60 minutes was more than double with coke and B1200 compared to L600 and B600 reductants. Regarding iron concentration in slag, all the biochars behaved similarly, however, the use of coke resulted in the lowest iron concentrations.

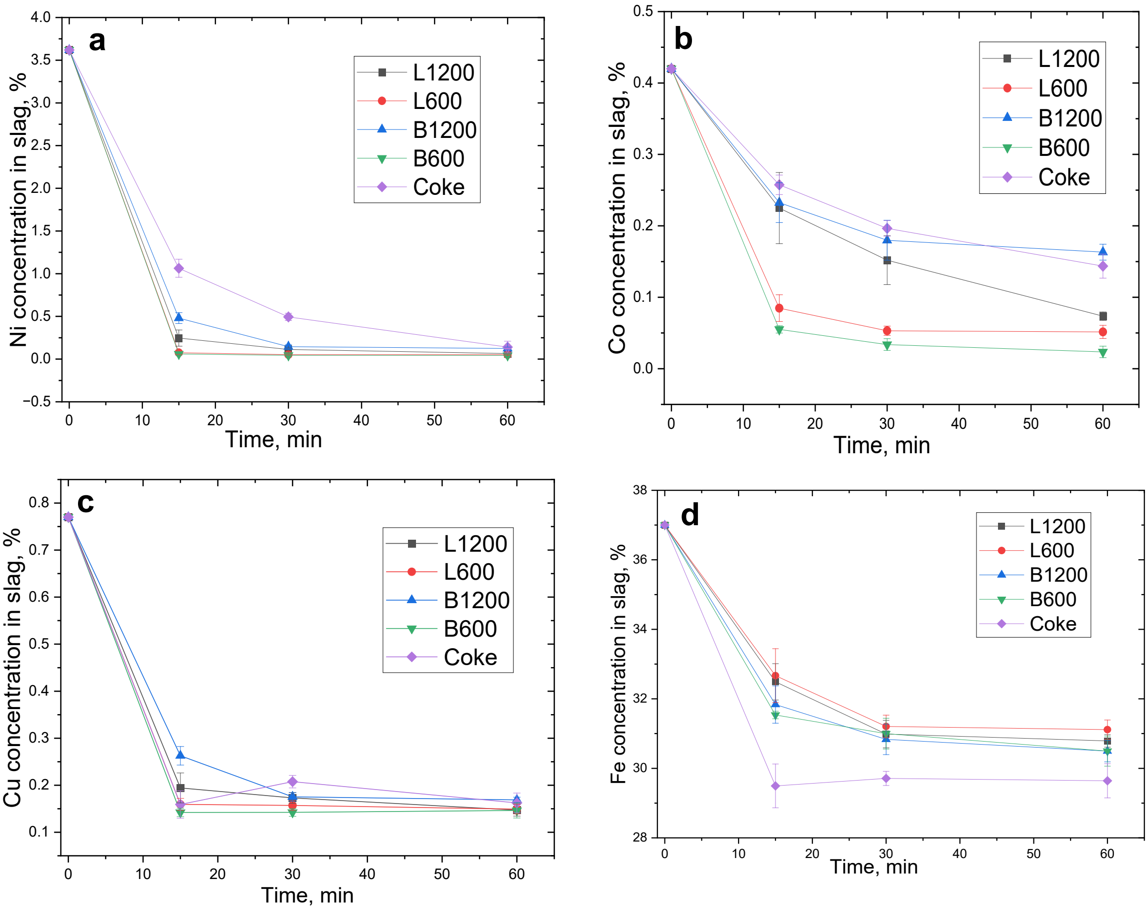


FIG 4 - Concentrations of (a) nickel, (b) cobalt, (c) copper, and (d) iron in slag as a function of time during nickel slag reduction with L1200, L600, B1200, and B600 biochar and metallurgical coke.

Biochar reactivity has been compared to that of coke. The reactivity of biochar was calculated from the ratio of volatile matter to fixed carbon (VM/FC) (Cui et al., 2023). Biochar with a high VM/FC ratio is more active and more advantageous in biofuel and chemical applications. It can be observed in Table 4 that the biochars are more reactive than metallurgical coke with B600 have reactivity close to 15 time that of coke.

TABLE 4 – Reactivity of reductant calculated from volatile matter and fixed carbon.

| **Reductant** | **B600** | **B1200** | **L600** | **L1200** | **Coke** |
|---|---|---|---|---|---|
| **Reactivity (VM/FC)** | 0.1420 | 0.0428 | 0.0697 | 0.01343 | 0.0097 |

## Distribution coefficients of the elements

The distribution coefficient is a parameter that is used to estimate the progress of the reduction reaction. It gives an indication of the behaviour of the various elements in the reduction study. In this work, the distribution coefficient between metal alloy and slag is used, and thus, a higher distribution coefficient indicates higher deportment to the alloy. The distribution coefficient of an element, Me, was calculated using equation (15) (Avarmaa et al., 2020)

$$L^{m/s} = \frac{wt\%\ Me\ in\ metal}{wt\%\ Me\ in\ slag} \tag{15}$$

where *m* represents the metal phase and *s* the slag phase.

The uncertainty (*ΔL*) of the distribution coefficient was calculated using the relation below in equation (16),

$$\Delta L^{m/s} = \left\{\left[\frac{\Delta Me}{wt\%\ Me\ in\ metal}\right] + \left(\frac{\Delta Me}{wt\%\ Me\ in\ slag}\right)\right\} \times L^{m/s} \tag{16}$$

where *ΔMe* is the standard deviation of element Me calculated from the EPMA results.

Figure 6 shows the distribution coefficient of nickel, cobalt, copper, and iron between metal alloy and slag at 1400℃ as a function of time. The results from this work have been compared to other studies where battery scrap (Dańczak et al., 2021) and mixture of battery scrap and biochar (Avarmaa et al., 2020) were used as reductants for nickel slag reduction.

Generally, the distribution coefficients of all the metals using the various reductants increase with time. It can be inferred that the reduction proceeds quickly, and the metal oxides are efficiently reduced to the alloy already after 15 minutes reduction time since distribution coefficient values increase only slightly afterward. The use of B600 resulted in the highest distribution coefficients for nickel, cobalt, and iron, closely followed by L600 biochar. The distribution coefficients of nickel, cobalt, and iron had the lowest values with coke reduction, although these values have the highest increase as a function of time. This is attributed to the slower reaction kinetics of coke compared to the different biochars. The distribution coefficient values for Ni and Cu are similar for coke and the biochars after 60 minutes of reduction. It can be inferred from FIG 6 that in terms of the distribution coefficient values, the reductants can be ranked according to effectiveness or reactivity as B600 > L600 > L1200 > B1200 > Coke. This corresponds to reactivity of biochar that has been calculated.

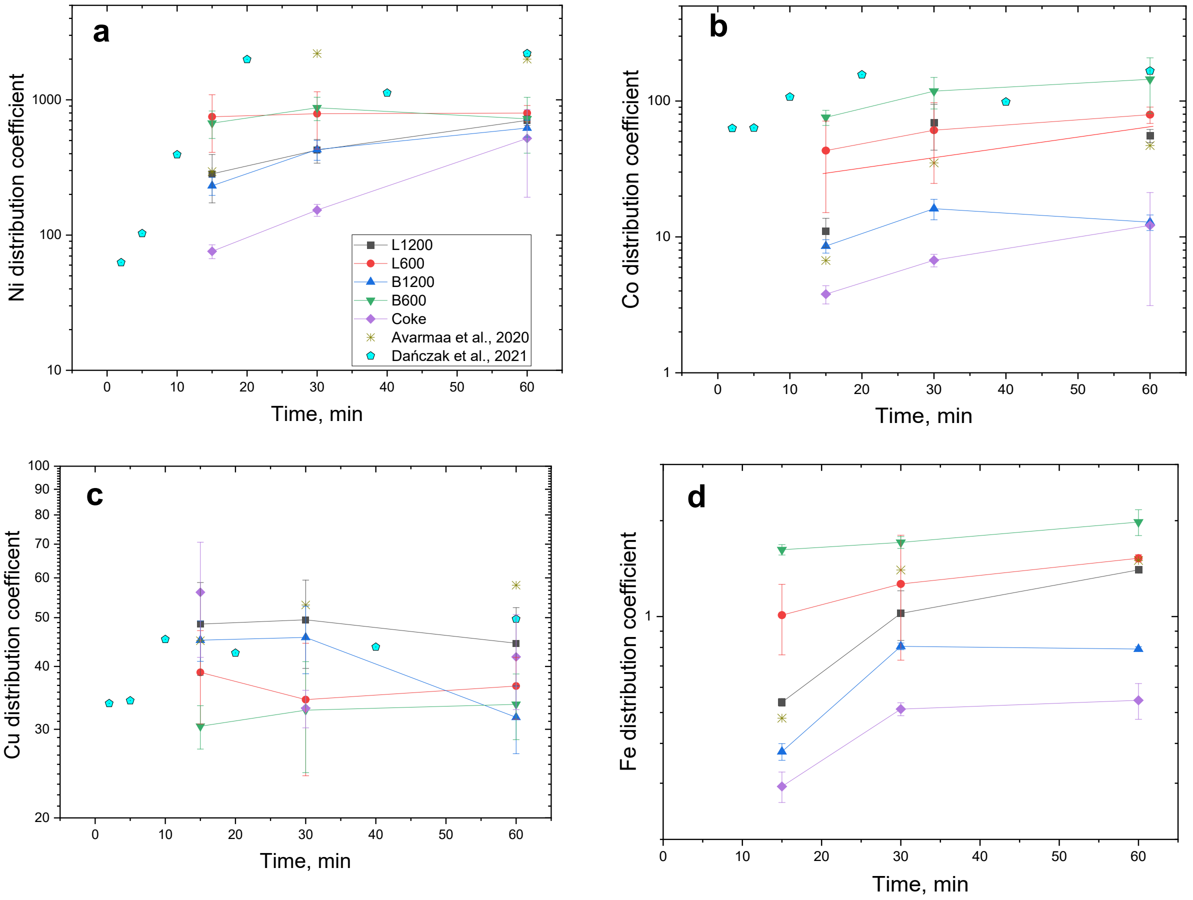


FIG 6 - Metal alloy to slag distribution coefficient of (a) Ni, (b) Co, (c) Cu and (d) Fe as time progresses at 1400℃. Note the difference in the y-axis scale.

## Thermodynamic Modeling

Factsage thermodynamic software package, version 8.0 was used in this study to investigate the effect of addition of biochar on the composition of metal and slag from nickel slag reduction. The composition of nickel slag, based on XRF analysis, as well as the ultimate and ash analyses of biochar were used as inputs in the software. The databases used for the calculations were custom collected based on the databases FactPS (pure substances), FToxid (optimized for oxide systems), and FSCopp (optimized for copper-containing solid and liquid alloys). The phases selected for the calculations were the spinel (solid solution phase with stoichiometry $AB_2O_4$, A, B = divalent and trivalent metals), slag (liquid oxide silicate phase), monoxide phase (solid solution), FCC, BCC, HCP-A3 (three solid multicomponent alloys), and liquid metal. Ideal gas and pure solids were also selected before the calculations were done at 1400 ℃.

### *Effect of Addition of Biochar*

One gram of nickel slag was reacted with different masses of biochar. The phases formed during reduction, as predicted by Factsage, plotted as a function of addition of biochar are shown in FIG 7. It is observed that as the reduction progresses, the mass of slag decreases while the masses of metal and gas increase until about 0.15 g of biochar addition. After this point the masses of metal as well as the gas and slag remain constant. About 0.45 g of metal is formed with > 0.15 g of biochar addition. Moreover, the thermodynamic simulation reveals that relatively more gas is produced when L600 and B600 are employed as reductants compared to their respective biochars pyrolyzed at 1200 ℃.

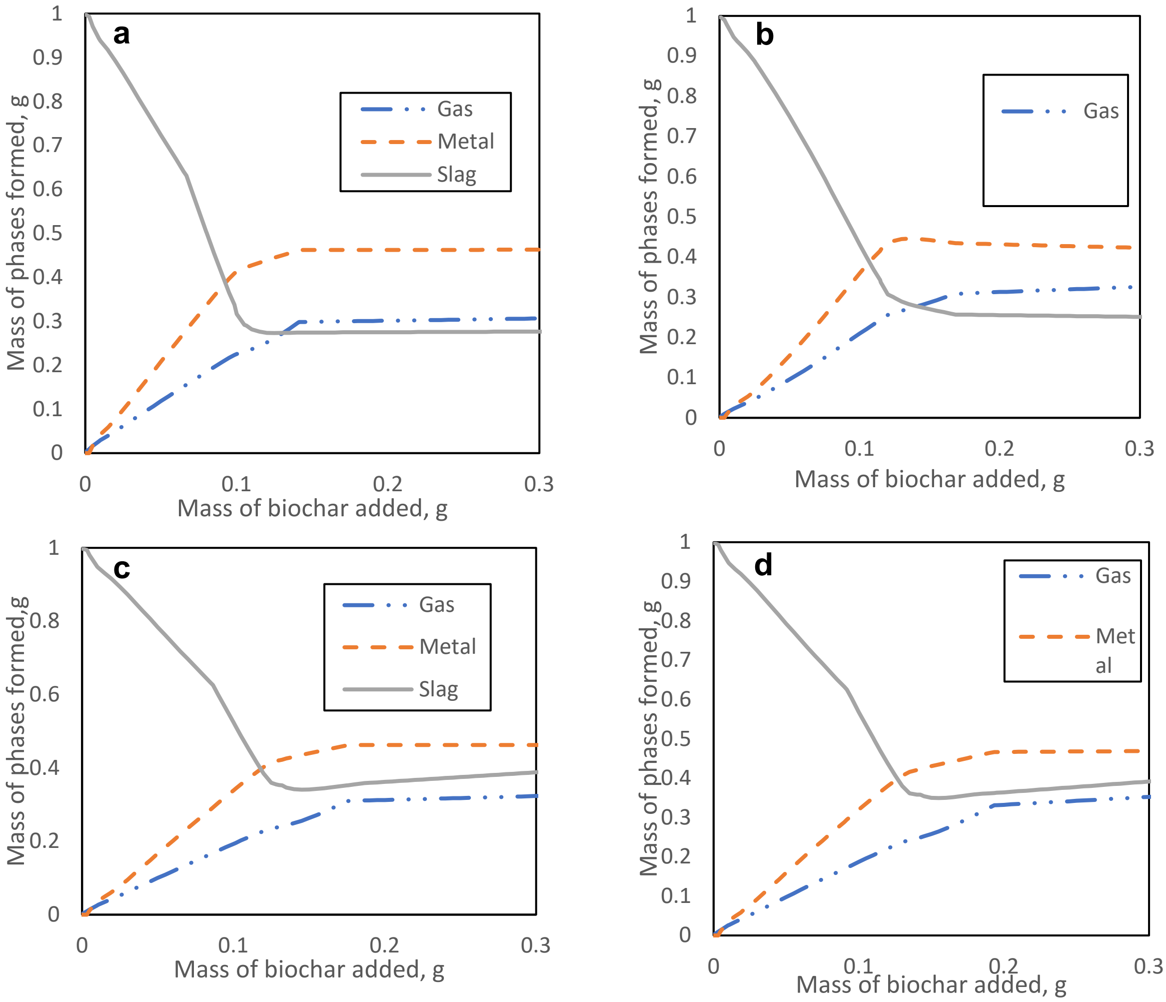


FIG 7 - Formation of gas, metal, and slag phases during nickel slag reduction with varying addition of (a) L1200 (b) L600, (c) B1200, and (d) B600 biochar to 1 g of nickel slag at 1400 ℃ as predicted by Factsage.

The mass percentages of selected metals (Zn, Cu, Ni, Co, and Fe) that were present in the gas, metal and slag phases have been shown in Fig. 8. The results from reduction of Ni slag with B600 have been selected for plotting since the calculated results were remarkably similar with all investigated biochars. When 0.01g of biochar is added to 1.0 g of nickel slag, at equilibrium, 80 wt% of the metal formed is nickel. This percentage continually decreases when higher amounts of biochars are added. Although the mass of nickel formed does not decrease with biochar addition, more iron is reduced, which consequently decreases the relative nickel concentration in the metal phase. In addition, the relative concentrations of copper and cobalt in the metal alloy increase to their highest values, 11 % and 4 % respectively, with less than 0.03 g biochar addition, after which they begin to decrease. The mass content and mass balance were not determined in the experimental section of this work, as it was not possible to separately collect all the phases from the quenched samples.

Nickel and copper have the highest concentrations of 80% and 10%, respectively, when 0.01 g of biochar is reacted with 1 g slag. The concentration of iron in the metal phase is the lowest at this addition. Since the formation of solid iron is undesired in industrial operation, it is important to recover other valuable metals like nickel and copper with low iron concentration.

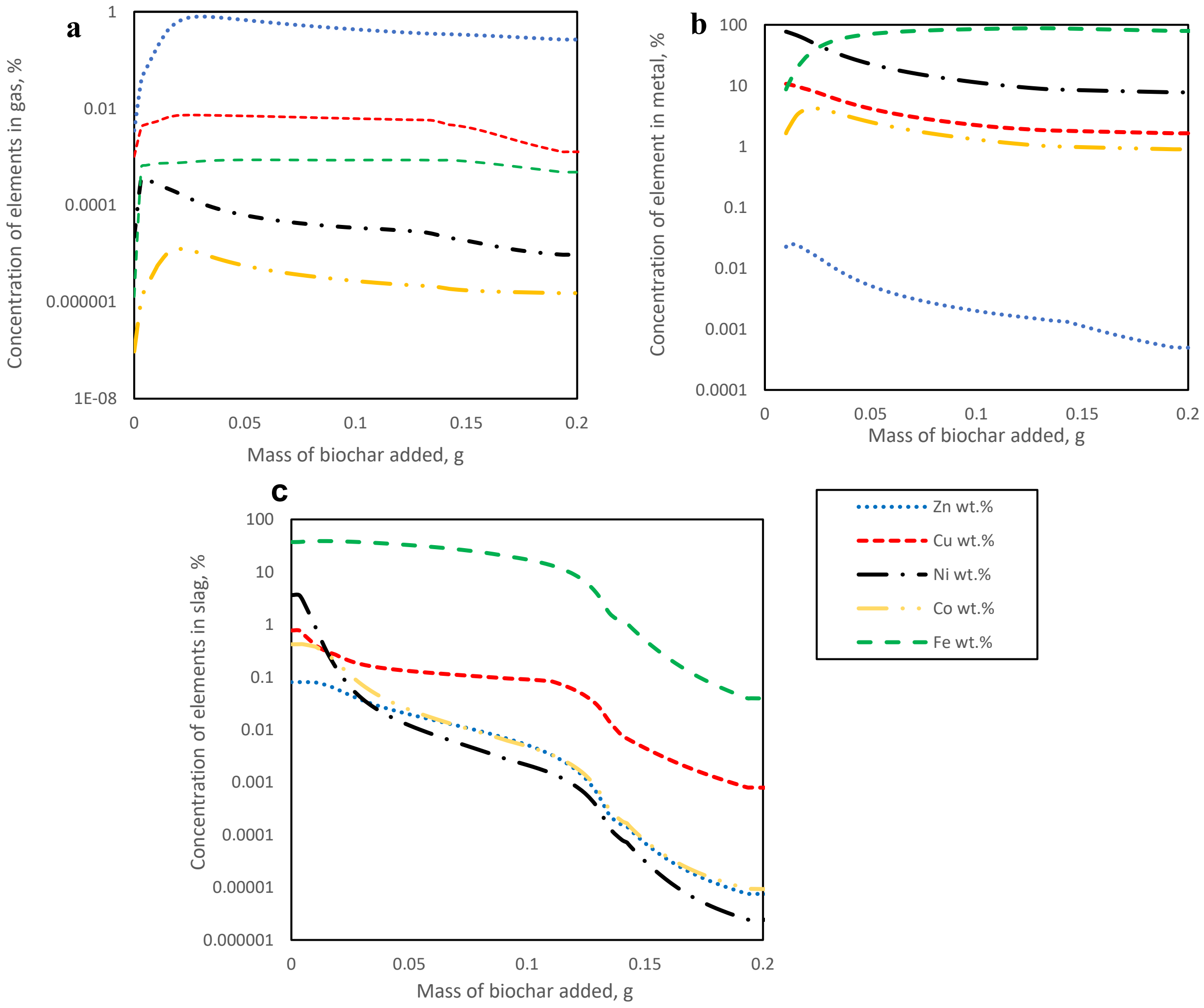


FIG 8 - Concentrations of copper, nickel, cobalt, zinc, and iron in (a) gas, (b) metal and (c) slag phase during nickel slag reduction with varying addition of B600 biochar to 1 g of nickel slag as predicted by Factsage

In the slag, nickel concentration plummets to about 0.1 wt% when 0.02 g of biochar is added to a gram of slag, and it continuously decreases until the nickel oxide in slag is almost completely reduced and Ni deported to the metal phase. Cobalt followed a similar trend as nickel in the slag. However, efficient copper oxide reduction from the slag requires a higher amount of reductant compared to nickel and cobalt. According to the calculations, approximately 0.15 g of biochar (to 1 g of slag) is enough to reduce all the iron oxides from the slag to metallic iron. As can be seen from FIG. 8 a, zinc evaporates into the gas phase.

## SUMMARY AND CONCLUSIONS

In this study, the use of carbon neutral biochars as reducing agents in the pyrometallurgical treatment of nickel slag was investigated at 1400 ℃ to recover valuable elements such as copper and nickel from the slag. Black pellet and lignin, each pyrolyzed at 600 and 1200 ℃, were employed as reductants and the recoveries of nickel, copper and cobalt were investigated, and compared to the results when using fossil coke as the reductant. The biochars pyrolyzed at 1200 ℃ had higher fixed carbon and lower volatile matter contents compared to those pyrolyzed at 600 ℃. While this may be preferred in industrial applications, the cost of energy required for pyrolyzing at higher temperatures might deter the use of biomass pyrolyzed at higher temperatures. B600 appeared to be the most efficient biochar, although it has lower carbon content compared to the other chars. The fast reaction kinetics is thought to be attributed to the relatively high content of volatiles in this biochar, leading to gas formation and thus mixing of the sample material. During the slag cleaning, biochars showed higher reactivity and faster reduction kinetics compared to coke. This, again, may be attributed to high concentration of volatile matter present. Although it is stated that at high temperatures (1300–1400 ℃) volatile matter do not contribute to the reduction process, it is possible that the volatiles create pores upon moving into the gas phase, increasing thus the surface area for reaction. In addition, $CO_2$ generated reacts with carbon (Boudouard reaction) resulting in more CO produced which takes part in the reduction reaction. Higher distribution coefficients between metal alloy and slag were obtained for Ni, Co and Fe using any biochar, compared to using coke.

Thermodynamic modeling was performed with FactSage© and the distribution coefficients calculated were compared to the experimental results, which were consistent with the thermodynamic modeling. In addition, thermodynamic calculations confirmed that nickel is reduced rapidly, and it deports to the metal alloy phase when enough ferric oxide has been removed from the slag. As the reduction progresses or extra reductant is available for reactions, more iron is deported to the metal phase. The calculations also revealed that Zn vaporizes into the gas phase.

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