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Cost effective decarbonisation of blast furnace – basic oxygen furnace steel production through thermochemical sector coupling

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ABSTRACT

We present here a first-principles study of the sector coupling between a thermochemical carbon dioxide (CO_2) splitting cycle and existing blast furnace – basic oxygen furnace (BF-BOF) steel making for cost-effective decarbonisation. A double perovskite, $Ba_2Ca_{0.66}Nb_{0.34}FeO_6$, is proposed for the thermochemical splitting of CO_2, a viable candidate due to its low reaction temperatures, high carbon monoxide (CO) yields, and 100% selectivity towards CO. The CO produced by the TC cycle replaces expensive metallurgical coke for the reduction of iron ore to metallic iron in the blast furnace (BF). The CO_2 produced from the BF is used in the TC cycle to produce more CO, therefore creating a closed carbon loop, allowing for the decoupling of steel production from greenhouse gas emissions. Techno-economic analysis of the implementation of this system in UK BF-BOFs could reduce steel sector emissions by 88% while increasing the cost-competitiveness of UK steel on the global market through cost reduction. After five years, this system would save the UK steel industry £1.28 billion while reducing UK-wide emissions by 2.9%. Implementation of this system in the world's BF-BOFs could allow the steel sector to decarbonise in line with the Paris Climate Agreement to limit warming to 1.5 °C.

1. Introduction

The iron and steel sector is a major greenhouse gas emitter, releasing up to 9% of global CO_2 emissions (IRENA, 2020). Steel is firmly in the category of hard-to-decarbonise sectors due to the inherent carbon-intensive nature of its production. Indeed, more carbon dioxide is released on a weight basis than steel produced, with 1.89 tonnes of CO_2 released for every tonne of steel produced. The main reason for this is the use of coking coal as an energy source and structural support, making up a 74% share of the total energy feedstock and accounting for 15% of the total global coal consumption (World Steel Association, 2011). Nevertheless, the sector must achieve 54% or 90% emissions reduction by 2050 to limit warming to 2 °C and 1.5 °C, respectively (IRENA, 2020). If the currently operational assets are run for their natural 40-year lifetimes, it would constitute entrenched emissions of 65 Gt of carbon dioxide equivalents[1] (CO_2e). On an annual basis, the steel industry uses 2 billion tonnes of iron ore, a billion tonnes of metallurgical coal, and 575 million tonnes of recycled steel to produce

1.7 billion tonnes of crude steel (World Steel Association, 2011). This requires 32 EJ of final energy (IRENA, 2020). There are currently two main methods of steel production, the blast furnace-basic oxygen furnace (BF-BOF) route accounting for 71% of production, and natural gas-based direct reduction of iron followed by an electric arc furnace (DRI-EAF) making up the other 29%. The BF-BOF route will be discussed in detail below but, both methods consist of two steps. Firstly, iron ore is reduced to metallic iron in the blast furnace (BF) or direct reduced iron (DRI) before being converted to steel by reducing the carbon content in the metal in the basic oxygen furnace (BOF) or electric arc furnace (EAF).

There are a few technologies that are being researched to decarbonise the steel industry (Managi and Kaneko, 2020). The first option is to close the old BF-BOFs and replace them with DRI-EAFs. If the EAF is powered by renewable electricity, it has the potential to save 1.5 Gt of CO_2 emissions annually (IRENA, 2020). However, a DRI-EAF plant costs between $1.1 and $1.7 billion to build (Moggridge, 2021), which combined with the stranded assets of the old BF-BOF plant, makes this

switch economically unfeasible in the short time period needed to meet the Paris Climate Agreement (United Nations, 2015). A second option is to increase the scrap recycling rate. Steel is already one of the most recycled materials, with an 84% recycling rate in 2017 (IRENA, 2020). In 2019, 32% of all inputs were scrap (Managi and Kaneko, 2020). Scrap recycling results in a 90% reduction of CO_2 emissions and 70% energy savings compared with virgin iron ore in a BF-BOF. Additionally, each tonne of scrap steel reused displaces 1400 kg of iron ore, 740 kg of coal and 120 kg of limestone (World Steel Association, 2011). The proportion of scrap steel in the input can be up to 100% in an EAF while 20–25% is currently the maximum input for a BF-BOF. It is expected that the share of scrap in inputs could increase to 46% by 2050 and although this is not sufficient to decarbonise the sector alone, it could result in significant CO_2 emissions reduction. Another decarbonisation option is to use hydrogen for the direct reduction of iron (HDRI), followed by EAF (World Steel Association, 2011). If renewable electricity is used to power an electrolyser to make green hydrogen, this could dramatically reduce emissions. However, this requires new DRI plants to be built to replace BF-BOFs and has a Technological Readiness Level (TRL) of 5–7, meaning the technology has been demonstrated but is not industrially operational. The TRL allows for consistent comparisons of the maturity of different technologies, with a scale of 1–9 where 9 is the most mature and has been proven in the operational environment. It has been estimated that a carbon price of \$67/tCO_{2eq} would be needed to enable HDRI to produce steel at the same price as a traditional blast furnace, provided there is sufficient low-cost renewable electricity (IRENA, 2020). Additionally, reducing iron with hydrogen is less efficient at lower temperatures than carbon monoxide, with the reduction from Fe_2O_3 to Fe_3O_4 occurring more readily under CO (Abu Tahari et al., 2019). Conversely, the reduction of Fe_3O_4 to Fe at higher temperatures occurs more readily under hydrogen. Modelling suggests that hydrogen-based DRI could reduce emissions in the EU steel industry by 35% at current grid emission levels while requiring 3.72 MWh per tonne of liquid steel produced (Bhaskar et al., 2020). For reference, BF-BOF uses 3.48 MWh/t. The cost of hydrogen production remains prohibitive.

A related technology is a natural gas-powered DRI with carbon capture, use and storage (CCUS), which also has a TRL of 5–7. Although several methods of CCUS have been demonstrated and a few industrial CCUS facilities are operational, the cost is expected to be \$100 per tonne of CO_2 for capture and \$160 per tonne for transport and storage by 2030, with costs falling moderately by 2050 (Managi and Kaneko, 2020). Given the extremely high emissions from iron and steel facilities, large CCUS plants would be required but emissions reductions are estimated to be between 20 and 80%. Finally, another proposed solution is iron ore electrolysis, which has a TRL of 6. This technique is already used on a large scale for the manufacture of aluminium, so the technology has been proven on an industrial scale (Haraldsson and Johansson, 2018). Optimisation of the electrodes and electrolyte are needed for the efficient reduction of iron.

In summary, steel production accounts for 9% of global CO_2 emissions and must be rapidly decarbonised to limit warming to 1.5 °C. 70% of existing iron and steel facilities rely on the extremely energy-intensive and emission-heavy BF-BOF route. Most of the current methods of decarbonising this sector rely on the phase-out of these BF-BOF plants and the implementation of lower carbon methods such as EAF and DRI plants. This will be extremely costly. This paper proposes another way to decarbonise the sector, namely by coupling a thermochemical carbon monoxide plant with a BF-BOF facility creating a closed carbon loop to produce steel. The existing BF-BOF technology will first be examined to determine the optimal coupling. The first-principal calculations of the sector coupling will then be proposed by exploring the mass and energy implications. Next, the expected emissions reduction and cost estimates of rolling out this coupling to UK BF-BOFs will be performed using techno-economic assessment. Finally, the superiority of this technology compared with existing decarbonisation solutions will be discussed. In conclusion, this paper aims to demonstrate the first principal

calculations of coupling a thermochemical carbon dioxide splitting cycle with a steel production facility for cost-effective steel decarbonisation.

2. Blast furnace – basic oxygen furnace

Modern blast furnaces can produce 10,000 tonnes of hot metal a day in furnaces as large as 15 m in diameter and 35 m tall (Yang et al., 2014). The top of the furnace is around 200 °C while the bottom can reach temperatures above 1600 °C (Hosford, 2012). Iron ore and coke are added to the furnace in layers. Air or oxygen-enriched air also called the blast, is injected at the bottom of the furnace, having been preheated to 1100–1350 °C by regenerative heat exchangers known as hot stoves (Yang et al., 2014). This hot blast provides most of the heat needed in the furnace. The hot blast reacts with the layers of coke, producing large volumes of carbon monoxide (CO). The CO rises through the furnace, reducing the iron ore to metallic iron and transferring heat to the material higher up in the furnace. Once the iron ore has been reduced to metallic iron, the liquid metal collects lower in the furnace to be tapped or removed, from the furnace. Iron ore is often impure; therefore, limestone and other additives are used to separate these impurities from the liquid metal. For example, limestone removes sulphur from iron sulfide (FeS) to give metallic iron and calcium sulfide (CaS) (Hosford, 2012). The CaS, having a lower density than metallic iron, rises in the furnace and forms a layer of molten slag which also contains other impurities such as SiO_2, Al_2O_3, MgO and CaO. The slag is tapped from the furnace at 1650 °C, and up to 65% of this heat can be recuperated (Barati et al., 2011). Around 0.275 tonnes of slag are produced per tonne of steel produced. The blast gas, mixing with carbon monoxide and carbon dioxide within the furnace, rises to the top of the furnace and is known as top gas. This top gas leaves the furnace at around 200–300 °C and has a lower heating value of 3–4 MJ per Nm^3, much of which is recovered by regenerative heat exchangers (Yang et al., 2014). This heat, along with additional heat obtained through the combustion of this top gas is used to heat the blast to over 1100 °C, as discussed above.

Attention will now be paid to the material flows in the BF. Modern steel production via the BF-BOF route uses 1370 kg of iron ore, 780 kg of metallurgical coal, 270 kg of limestone, and 125 kg of recycled steel to produce 1000 kg of crude steel (World Steel Association, 2011). The blast requires 1500 kg of air which is fed into the bottom of the furnace via tuyeres (nozzles) (Hosford, 2012). The metallurgical coal must be treated before it can be used in the BF, being heated to 1250 °C for 12 h using heat obtained from the top gas and the coke oven gas (COG). COG is the gas released from the pre-treatment of the coal once it has been quenched and cleaned. Typically, COG contains 60% hydrogen (H_2), 24% methane (CH_4), 6% CO, 6% nitrogen (N_2), and 4% CO_2 (Yang et al., 2014). COG is also used in the BF since hydrogen and carbon monoxide are excellent reducing agents of iron ore. Once treated, coke has a few main uses in a BF. Firstly, coke is a major energy source for the BF, with energy being supplied from the combustion of coke in the BF and making up 20–40% of total costs. Secondly, the coke reacts with oxygen to produce carbon monoxide, a good reducing agent for iron ore, then reacts with the carbon dioxide produced in the reduction to form more carbon monoxide according to the Boudouard reaction. Coke also adds carbon to the metallic iron. Finally, the coke acts as a support for the layers of iron ore and aids in gas movement through the furnace. Other reducing agents can also be injected into a blast furnace to reduce the amount of coke needed, such as pulverised coal (cheaper than metallurgical coal), hydrocarbons, waste plastics and biomass. Additionally, natural gas can replace some coke due to its decomposition into carbon monoxide and hydrogen provided it has a methane content above 80% (Yang et al., 2014). There is an accepted minimum theoretical fuel value of 465 kg per tonne of hot metal produced, with modern BF coming close to this with 500 kg per tonne.

Four main reactions are occurring in a BF regarding the reduction of iron ore (Yang et al., 2014). Iron ore is predominantly made of Fe_2O_3. Two reactions are occurring below 570 °C:

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \tag{1}$$

$$\Delta H_{843K} = -30.050 \text{ kJ}$$

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2 \tag{2}$$

$$\Delta H_{843K} = -44.478 \text{ kJ}$$

Once the remaining iron ore has started to drop lower in the furnace and the temperature increases above 570 °C, the following two reactions become dominant:

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \tag{3}$$

$$\Delta H_{1073K} = +9.707 \text{ kJ}$$

$$FeO + CO \rightarrow Fe + CO_2 \tag{4}$$

$$\Delta H_{1273K} = -15.653 \text{ kJ}, \Delta H_{1473K} = -16.484 \text{ kJ}$$

The reduction of FeO (Equation (4)) requires a CO concentration of at least 70%. The so-called pig iron is tapped from the BF and injected into the BOF, with up to 25–30% of scrap metal (Hosford, 2012). No heat must be added to the BOF, since when oxygen is blown through the molten metal, the carbon in the iron (often iron carbide (FeC)) reacts, forming carbon monoxide and carbon dioxide while releasing heat. This reaction increases the temperature to 1650 °C. The oxygen must be a minimum of 99.9% pure to allow for a large range of steel products to be made (Ghosh and Chatterjee, 2008). A total of 50–60 Nm^3 of oxygen per tonne of liquid steel (tls) is blown through a lance above the hot metal for 15–20 min, also called the blow. The steel will be tapped from the furnace every 40 min. Basic Oxygen Furnace Gas (BOF Gas) exits the furnace at around 1600 °C and 100 Nm^3/tls is produced, containing carbon dioxide and carbon monoxide. This BOF Gas has a heating value of around 8.8 MJ/Nm^3 (Ahmed, 2018), of which over 90% can be recovered as heat and chemical energy (Ghosh and Chatterjee, 2008). However, the gas will also contain dust, up to 20 kg/tls, made up predominantly of iron oxide and lime. A slag will also form in a BOF, containing carbon, silicon, sulphur and phosphorous. Slag-forming agents are added at the beginning of the blow such as lime and dolomite, as the fast formation of the slag is needed for the removal of impurities.

3. Thermochemical cycle

A thermochemical cycle consists of a reduction and oxidation reaction (redox). Many materials can undergo a thermochemical cycle, however, $Ba_2Ca_{0.66}Nb_{0.34}FeO_6$ (BCNF1) will be used here due to its superior properties including high yields, low reaction temperatures, 100% selectivity towards CO, and low activation energy of the oxidation reaction (Kildahl et al., 2022). BCNF1 is a double perovskite material with a cubic structure, where barium atoms are found at the A-site of the perovskite, calcium, niobium, and iron share the B-sites and oxygen atoms are found at the interstices. When BCNF1 is reduced at 700 °C under nitrogen, oxygen is lost from the crystal structure, forming oxygen vacancies, and releasing oxygen gas:

$$Ba_2Ca_{0.66}Nb_{0.34}FeO_6 \xrightarrow[700\ °C]{} Ba_2Ca_{0.66}Nb_{0.34}FeO_{6-\delta} + \frac{\delta}{2}O_2 \tag{5}$$
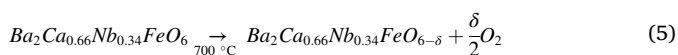
δ is equal to the degree of non-stoichiometry. The oxidation reaction occurs at 800 °C under carbon dioxide. CO_2 is split into CO, and the oxygen atom is used to fill the oxygen vacancy. This forms the original perovskite, allowing the cycle to be repeated, splitting CO_2.

$$Ba_2Ca_{0.66}Nb_{0.34}FeO_{6-\delta} + \delta CO_2 \xrightarrow[800\ °C]{} Ba_2Ca_{0.66}Nb_{0.34}FeO_6 + \delta CO \tag{6}$$
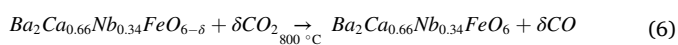
BCNF1 has been found to convert 10.1% of CO_2 to CO over five cycles. The scale-up to an industrial carbon monoxide production facility was calculated previously. A 150 m^3/h would produce carbon monoxide

for £0.19 per kg at an electricity price of £0.11/kWh. At an electricity price of £0.05 (the average US industrial electricity price), carbon monoxide would cost £0.11 per kg.

4. Thermochemical blast furnace- basic oxygen furnace coupling (TC-BF-BOF)

There exists a significant opportunity for sector coupling. The main reducing agent in a BF is carbon monoxide (currently obtained from the reaction of coke with air), with an output of large volumes of carbon dioxide responsible for the significant emissions of the system. The BOF requires large quantities of oxygen and releases carbon monoxide and carbon dioxide in the BOF Gas. Both the BOF Gas and BF top gas contain significant amounts of thermal energy. The BCNF1 thermochemical cycle has inputs of heat and carbon dioxide and outputs of carbon monoxide and oxygen. The TC-BF-BOF system proposed here is composed of two thermochemical reactors for the simultaneous production of oxygen and carbon monoxide. In one reactor the BCNF1 will be reduced, producing an oxygen stream. In the second reactor, reduced BCNF1 will be oxidised under CO_2, creating a CO stream. Once the reactions have proceeded to their optimum point, or in other words, the maximum non-stoichiometry has been reached in the first reactor and all oxygen vacancies have been filled in the second reactor, the gas flows in each reactor will be switched. The newly reduced BCNF1 in the first reactor will now produce CO and the second reactor will now undergo reduction.

4.1. Mass flows

The TC-BF-BOF system is depicted in Fig. 1, showing the mass flows of the system to produce 1 tonne of liquid steel.

The production of 1 tonne of liquid steel (tls) in the TC-BF-BOF system occurs as follows:

- The reduction of iron ore to metallic iron requires 3 mol of CO per mole of Fe_2O_3. This equals 23,800 mol of CO/tls.
- CO is injected into the BF via the tuyeres, with 1500 kg/tls of hot air-based blast.
- The iron ore is estimated to have 95% Fe_2O_3 and 5% impurities and 1.599 tonnes of iron ore are needed per tls (Bhaskar et al., 2020). 125 kg of recycled steel is added to the hot metal in the BOF.
- The usual slag-forming agents are used at the same rates as a typical BF-BOF.
- BF top gas is typically produced at a rate of 2.5–3.5 tonnes/tls and contains 20–30% CO, 20–25% CO_2 and 2–6% H_2 with the remainder being nitrogen (Huth and Heilos, 2013). The hydrogen content comes from the humidity in the blast furnace and the water content of the iron ore (Song et al., 2020). In the TC-BF, an estimated 1.5 tonnes/tls of top gas is produced, containing 5% CO, 45% CO_2, 2% H_2 and 48% N_2 due to the absence of coke and the stoichiometric volume of CO added.
- The BF top gas is separated into its constituent components. The CO is stored in the CO storage tank until it is needed. CO_2 is added to the BCNF reactor undergoing oxidation while the nitrogen and a small volume of hydrogen are added to the BCNF reactor undergoing reduction. The addition of hydrogen in the reduction step has been found to improve reduction extent and oxygen yields in other thermochemical materials (aJ Hare et al., 2018; bBryan J. Hare et al., 2018; Ramos et al., 2019).
- 50 m^3/tls of oxygen are blown into the BOF, producing BOF gas at 100 m^3/tls (Ghosh and Chatterjee, 2008). The BOF gas contains 90% CO and 10% CO_2 (Nutting and Wondris, 2019). The gas is separated, with the CO stored in the CO storage tank and the CO_2 being added to the BCNF reactor undergoing oxidation.
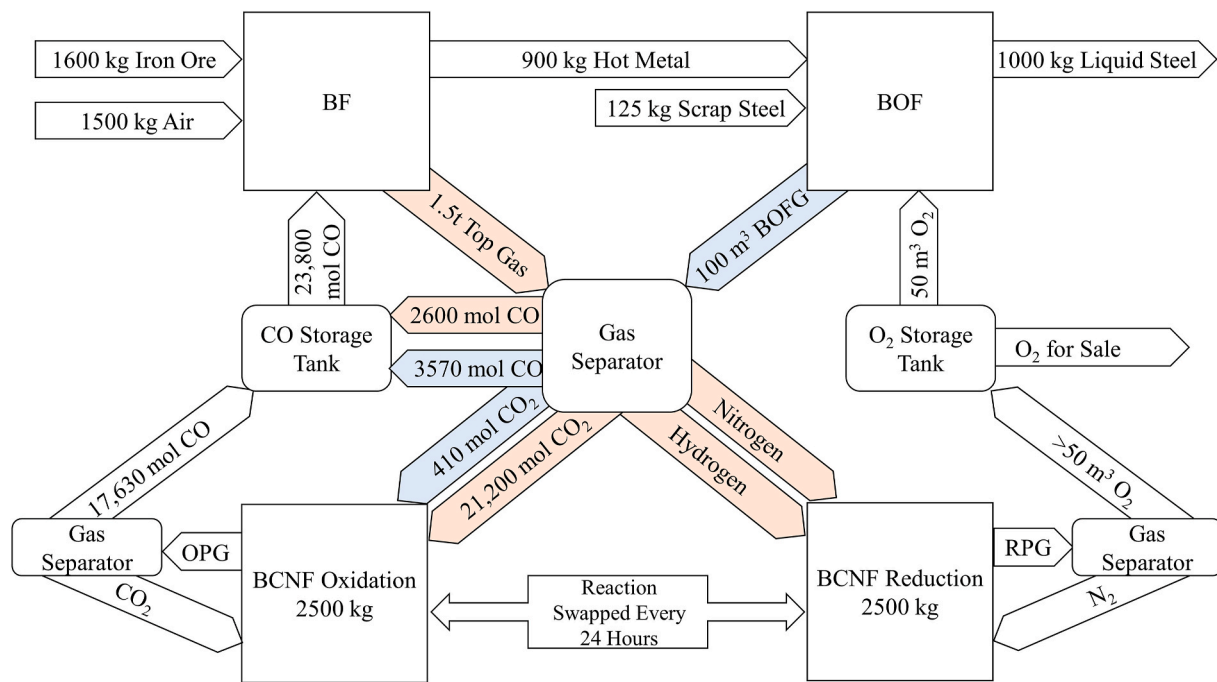
Fig. 1. *The TC-BF-BOF System with Mass* flows needed to produce *1 Tonne of Liquid Steel.*

- Oxygen is blown into the BOF via a lance for 15–20 min, with liquid steel and slag being tapped every 40 min (Ghosh and Chatterjee, 2008).
- CO_2 is injected into the BCNF oxidation reactor, where 10.1% is converted to CO with each pass. The oxidation product gas (OPG) therefore contains 10.1% CO and 89.9% CO_2. The CO is separated and stored in the CO storage tank and the unreacted CO_2 is injected back into the BCNF oxidation reactor.
- The CO produced by the thermochemical cycle is set to replace 90% of the coke in the BF, based on the number of moles of iron ore needing to be reduced. The remaining 10% is supplied by biomass-based charcoal or recycled plastics to give a solid source of carbon for the Boudouard reaction. Theoretically, 100% of the injected coke can be replaced by charcoal at a rate of 200 kg per tonne of hot metal (thm), reducing CO_2 emissions by 40% and reducing slag volumes and sulphur content (Ahmed, 2018). However, the biomass must be injected via the tuyeres rather than top loading, due to the lower mechanical strength and a higher proportion of volatiles than coke. Waste plastics can also be used as a solid carbon source at a rate of 70 kg/thm.
- Nitrogen and a small volume of hydrogen obtained from the top gas are injected into the BCNF reduction reactor. The hydrogen actively reduces BCNF to form water and the nitrogen provides the low oxygen concentration necessary to passively reduce the BCNF. The reduction product gas (RPG) therefore contains nitrogen, oxygen, and water. The small volume of water is condensed out, the oxygen is stored in the O_2 storage tank, and the nitrogen is recycled to be used again during reduction.
- After 24 h, the rate of CO or O_2 production is found to decrease. The reaction conditions and gas flows are then switched. The reduced material now undergoes oxidation while the oxidised material now undergoes reduction.
- One kg of BCNF produces 5.8 mol of CO in 24 h, as determined experimentally (Kildahl et al., 2022)
- The TC-BF-BOF system would reduce CO_2 emissions by 94% compared to a typical BF-BOF, with the only emissions arising from the biomass-based charcoal. All carbon monoxide is produced from carbon dioxide, which can then be split again into carbon monoxide.

- Coke typically acts as a structural backbone in the BF, helping to ensure even gas flows throughout the iron ore. Research is needed to understand the impact of coke removal on the structural stability of the BF. Blast furnaces have been operated with 180 kg natural gas and 256 kg coke/thm, with coke rates decreasing when the natural gas is heated before injection via the tuyeres (Jampani et al., 2019).

4.2. Energy flows

The energy flows of the TC-BF-BOF system are shown in Fig. 2 and are described below.

- Removing coke from the BF decreases the energy available to heat the BF to the required temperature. Usually, the reaction between coke and oxygen is exothermic, releasing heat. The 10% biomass-based charcoal will help in this, but additional heating, from electric heaters, may be needed to reach the required temperatures. The iron ore could be preheated to aid in this.
- The blast will be preheated from the top gas and BOF gas, as in a normal BF-BOF. BF top gas and BOF gas contain 2.7 GJ/tls (Yang et al., 2014) and 0.8 GJ/tls (Ahmed, 2018), respectively, if 90% of the energy is recovered using the regenerative heat exchangers already in use in a BF-BOF (Ghosh and Chatterjee, 2008). This heat will be transferred from these gases before they are fed into the gas separator.
- The COG, BF top gas and BOF gas are usually combusted after the thermal energy has been extracted to produce the electricity needed for the BF-BOF. Given that COG does not exist in the TC-BF-BOF system and that top gas and BOF gas are now entirely recycled by the TC reactors, this electricity production is no longer possible. Electricity must therefore be imported.
- The carbon monoxide leaving the TC reactor is at a temperature of 800 °C, decreasing the heating requirements for a blast at 1200 °C. This may require the temperatures in the CO storage tank to be maintained at around 800 °C. This could be achieved by heat transfer from the oxygen produced in the reduction reactor since oxygen does not need to be heated before introduction into the BOF.
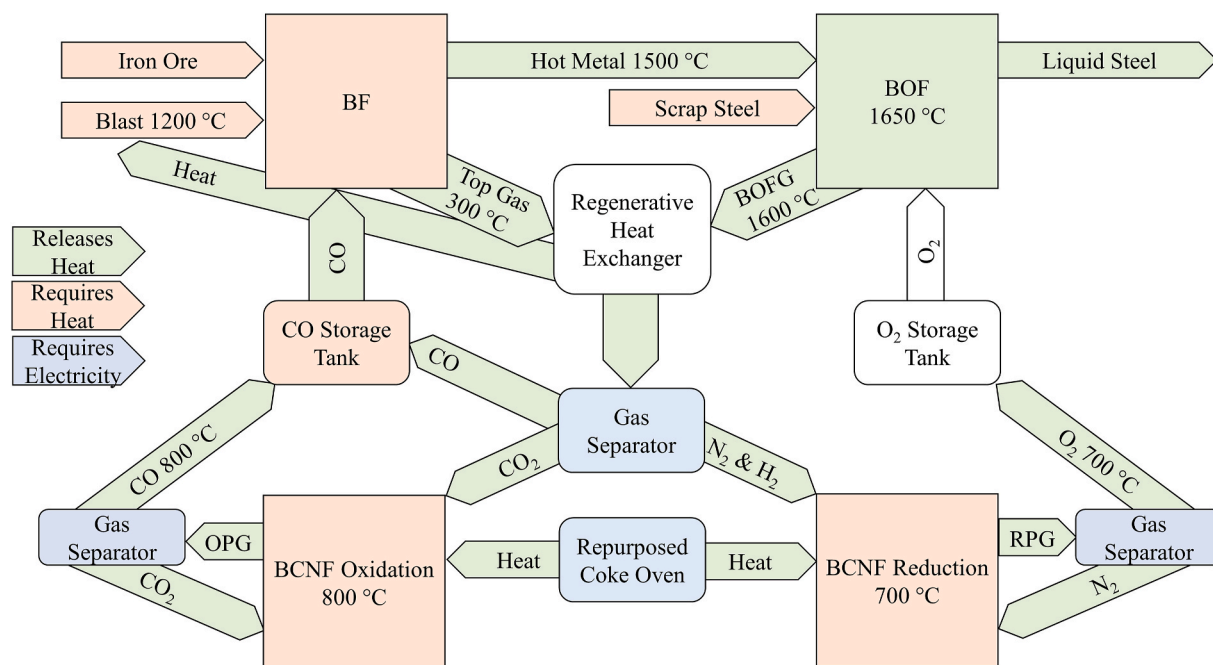
Fig. 2. *The TC-BF-BOF System with Energy flows needed to produce 1 Tonne of Liquid Steel.*

- The BOF does not require any extra heat or fuels since heat is generated by the reaction between oxygen and iron carbide (FeC).
- Liquid steel leaves the BOF above 1500 °C. Once the steel has been cast into its final shape, some heat could be recuperated for use in the TC-BF-BOF.
- The coke oven would no longer be needed for coke preparation, saving 1.1 GJ/tls of primary energy (Worrell et al., 2007). 2.2 GJ/tls is needed to power the TC reactors. This means the electricity and electric heaters previously used to heat coal to 1250 °C for 12 h could be repurposed to maintain the temperature in the TC reactors and to heat the BCNF1 from the reduction temperature of 700 °C to the oxidation temperature of 800 °C when the reaction conditions are being switched over. Therefore, an extra 1.1 GJ/tls of electricity used to power an electric heater is likely to be necessary to run the TC reactors.
- If the electricity needed to power the electric heaters and gas separators is procured from renewable sources, this would not add to the emissions of the TC-BF-BOF. The cost of this electricity, plus the electricity needed to power the gas separators, is more than accounted for in the savings from replacing the coke in the system.

5. Decarbonisation of the UK steel industry

The TC-BF-BOF system proposed above could be used to decarbonise the UK steel industry. The UK currently has five steel-producing companies; Tata Steel and British Steel which operate BF-BOFs, and Celsa Steel, Liberty Steels and Outokumpu which operate EAFs (MakeUK, 2022). Six million tonnes of steel products are made via the BF-BOF route out of the 7.65 million tonnes produced in the UK annually. BF-BOFs in the UK, therefore, account for around 94% of total emissions of the UK Steel sector based on an emissions intensity of 1.89 tCO$_{2eq}$/tls for the BF-BOF route and 0.44 tCO$_{2eq}$/tls for the EAF route (EVRAZ, 2016; UK Steel, 2020). EAFs can be more easily decarbonised with the use of renewable electricity and/or 100% recycled steel. On the other hand, decarbonising a BF-BOF is far more difficult due to the inherent carbon-intensive nature of the process. Their decarbonisation is crucial for the UK to reach its net-zero emissions goal by 2050.

Tata Steel and British Steel both produce around three million tonnes of steel a year at their Port Talbot and Scunthorpe sites, respectively.

Due to the similar production values, the same TC-BF-BOF system can be used in both cases, as described hereafter. Given that on average, 1.599 tonnes of iron ore is needed to produce 1tls, and the stoichiometry of equations (1)–(4), (124) million moles a day of carbon monoxide would be required. This would allow 90% of the coke to be displaced by the CO, with the remaining 10% swapped for a lower-emission solid carbon sources such as biomass-based charcoal. Given the yield of BCNF1-based thermochemical cycles, 42,500 tonnes of BCNF1 would be required in each of the UK's two BF-BOF sites. The BCNF1 at each site would be split into ten reactors that are 15m tall and 9.5m in diameter, with five reactors undergoing reduction and five undergoing oxidation at any one time. The raw materials to produce the required amount of BCNF1 would cost £210 million, which may need to be replaced every 5–10 years based on current estimates. In addition to the CO, these reactors would produce 1.3 million m^3 of oxygen a day, of which 420,000 m^3 would be required in the BOF. This excess oxygen production could generate £35,000/day. Additionally, the displacement of 90% of the coke by CO would save £187 million a year (Gielen et al., 2020). Therefore, the addition of a thermochemical cycle into either of the UKs BF-BOFs would reduce running costs and provide an additional, albeit small, stream of income in the form of oxygen sales, as shown in Table 1.

The energy required to power the TC cycle in the two UK BF-BOFs is 3.6 TJ per thermochemical reactor for a full cycle of reduction and oxidation over 48 h. The reduction reaction uses 85% of this energy due to the high endothermic enthalpy of reduction of 620 kJ/kg, while the enthalpy of oxidation is exothermic and therefore releases energy (−45.1 kJ/kg (Kildahl et al., 2021)). The implementation of the TC-BF-BOF system requires an additional 2.2 GJ/tls, whereas a typical BF-BOF requires between 19.8 and 31.2 GJ/tls (Yang et al., 2014). The

Table 1
Financial results of installing TC-BF-BOF into a UK BF.

Item	Financial Value
Perovskite Raw Materials Cost	-£209,000,000
Estimated TC Reactor Cost	-£150,000,000
Yearly Savings from Coke Replacement	£187,000,000
Yearly Oxygen Sales	£13,000,000
Balance Sheet after 1 Year	-£160,000,000
Balance Sheet after 5 Years	£640,000,000

now redundant coke oven could be repurposed, producing 1.1 GJ/tls of heat. As discussed above, there is substantial energy in the top gas and BOF gas. If 90% of this energy is recovered via the regenerative heat exchangers already in use in BF-BOFs, this equals 3.5 GJ/tls, higher than the energy use of the TC system. Alternatively, if the TC reactors were exclusively powered by electricity, it would require 607 kWh/tls, costing around £42/tls. This is drastically lower than HDRI which requires 3.72 MWh/tls (Bhaskar et al., 2020). If this electricity were taken from the UK grid, which has an emissions factor of 212 gCO$_{2eq}$/kWh, this would produce 129 kgCO$_{2eq}$/tls, equal to 6.9% of current emissions per tonne of liquid steel. Therefore, both financially and environmentally, using as high a share of renewable electricity as possible is beneficial.

Most importantly, implementation of the TC-BF-BOF system into the two UK BF-BOFs would reduce emissions from 5.7 million tonnes of CO$_{2eq}$ per site to 340,000 tonnes of CO$_{2eq}$. Even if no improvements in emissions were seen from the EAF plants in operation in the UK, implementation of this system alone would reduce UK steel emissions by 88% and the share of emissions from BFs would decrease from 94% to 48%. Currently, the Steel industry emits twelve million tonnes of CO$_{2eq}$ of the total 369 million tonnes of CO$_{2eq}$ of the UK, meaning steel represents almost 3.3% of UK emissions. Implementing the TC-BF-BOF system at the Tata Steel and British Steel plants would decrease the steel-based share of UK emissions to 0.38%. Therefore a 2.9% reduction in UK emissions can be realised with £720 million in capital expenditure, with an ongoing expenditure of £400 million every 5–10 years to replace the spent BCNF1 material once the activity has dropped. Additionally, there are significant operational expenditure reductions achieved from the implementation of this system, due primarily to the displacement of expensive metallurgical coal. The capital expenditure would be entirely repaid from these savings in 22 months, with total savings of £1.28 billion across both BF-BOF sites after 5 years. The possible minor increase in electricity consumption on implementation of this system would be easily absorbed in these savings. This system would also decrease the price of steel production, increasing the competitiveness of UK steel on the global market.

6. Advantages of the TC-BF-BOF system

The TC-BF-BOF system proposed here has several advantages over other methods to decarbonise the iron and steel sector. Firstly, since this system makes use of existing BF-BOFs, which make up 70% of steel production, this method prevents the formation of stranded assets. Given that the global switch to a net-zero economy is likely to create stranded assets in multiple sectors incompatible with net-zero, any system which minimises stranded assets while achieving drastic emissions reductions should be prioritised. Furthermore, the continued operation of BF-BOFs globally would ensure the preservation of highly skilled jobs and could create new jobs for the management and operation of the TC reactors. Secondly, the emissions reductions are evident as soon as the TC-BF-BOF retrofit is installed, rather than waiting years for a new DRI-EAF to be built or for decarbonisation of the grid for emissions reductions to be realised. This system operates a nearly perfect closed carbon loop, where any CO$_2$ produced in the BF or BOF is fed into the TC reactors to be split into more carbon monoxide for use in the BF. Additionally, the system provides an additional, albeit small, income in the form of selling the extra oxygen produced in the TC reactors, equal to around £13 million a year each for the UK's two BF-BOF plants. Another crucial factor is that since the TC-BF-BOF is economically viable and saves over £600 million per plant over five years, the cost of producing steel is lower than with a traditional BF-BOF. UK steel has historically been expensive on a global scale so this should allow UK steel to become more competitive. In addition to cheaper steel production, the steel produced could also be considered carbon-neutral steel, which is likely to fetch a premium as companies and governments try to reduce operational and entrenched emissions in a wide range of sectors. The emissions intensity of steel created via TC-BF-BOF could be up to four times

lower than a DRI-EAF plant. Most importantly, implementation of the TC-BF-BOF system does not exclude other efforts to decarbonise the sector such as efficiency improvements, the use of renewable electricity, increased scrap recycling or methods of improving the DRI-EAF route. Indeed, to maximise sector-wide emissions reduction, most of the scrap steel should be used in EAFs (where 100% scrap can be used) with the remaining scrap being used in the TC-BF-BOF.

7. Conclusions and further research

This research presents the first-principles calculations of the coupling of a thermochemical cycle with a BF-BOF to cheaply decarbonise the steel sector. Decarbonisation can be achieved by replacing 90% of typical coke use with carbon monoxide, produced from carbon dioxide. To produce the CO required for the BF, 5000 kg of BCNF1, split into two reactors, would be continually cycled. BCNF1 is an ideal TC material due to its low reaction temperatures, high CO yields and 100% selectivity towards CO compared to other TC materials. The addition of this system would add 2.2 GJ/tls of energy requirement, whereas a typical BF-BOF uses 19.8–31.2 GJ/tls and 3.5 GJ/tls of energy can be recovered from the BF top gas and BOF gas.

Further research is needed to understand the viability of this system under real-world conditions. One area of focus should be on the replacement of coke as a structural support in the blast furnace since the removal would likely lead to suboptimal heat and mass flows within the blast furnace. Another area of focus should be the separation of nitrogen and carbon monoxide gases in an energy-efficient manner. Finally, repeated cycling of the perovskite material under the reaction conditions over a period of years is needed to fully characterise the replacement rate of the perovskite in the TC-BF-BOF.

Six of 7.65 million tonnes of steel in the UK are produced via the BF-BOF route. Implementation of this system in the two BF-BOF steel plants in the UK could reduce steel sector emissions by 88%. This would require a capital investment of £720 million, which would be repaid in 22 months through the displacement of expensive metallurgical coal and sales of excess oxygen not required in the BOF. Within five years, implementation of the TC-BF-BOF would give total savings of £1.28 billion while reducing UK-wide emissions by 2.9%. Finally, through cost reduction, this system would increase the cost-competitiveness of UK steel on the global market. In conclusion, this paper details a novel method for cost-effective decarbonisation of BF-BOF steelmaking needed to meet the Paris Climate Agreement, while reducing the economic risk of stranded assets by utilising existing infrastructure.

CRediT authorship contribution statement

Harriet Kildahl: Conceptualization, Investigation, Writing – original draft. **Li Wang:** Validation. **Lige Tong:** Validation. **Yulong Ding:** Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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