

# A Short Review: Hydrogen Reduction of Copper-Containing Resources

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## ABSTRACT

The trend of global copper production has prospectively increased over time. Based on typical mined ore grades, one tonne of copper ore generates approximately 6 to 10 kilograms of copper, which requires much energy, usually in the form of metallurgical coke. Copper production using carbon as a fuel and reductant contributes up to 0.3% to global greenhouse gas (GHG) emissions. As a result, research into decarbonisation processes applicable to reducing low-grade copper sulphide ores, copper oxides, electronic wastes, and other alternative complex Cu-rich materials has increased. Alternative fuels for reducing carbon-rich emissions in pyrometallurgical copper processing include methane, ammonia, biomass, solar and wind power, but in recent times increased focus has been on hydrogen as a potential fuel and reducing agent for materials such as oxidized copper scrap,  $\text{Cu}_2\text{O}/\text{CuO}$ , and Cu-rich slags/e-wastes. From a thermodynamic perspective, hydrogen exhibits a significantly more negative standard Gibbs free energy ( $\Delta G^\circ$ ) than copper oxide making it a suitable reductant and the exothermic thermal effect from reaction between hydrogen and  $\text{Cu}_2\text{O}/\text{CuO}$  may be used to control process parameters. These characteristics renders hydrogen an ideal gas for reducing copper oxides and copper-containing slags/e-wastes. This review article assesses previous research on utilizing hydrogen for producing and refining copper from primary and secondary feed materials.

## INTRODUCTION

Worldwide copper production increased marginally from 24.99 million tonnes in 2022 to 25.34 million tonnes in 2023 and is predicted to rise to 26.17 in 2024 (ICSG, 2023). The global copper demand predicted to rise by 350% in 2050 (Elshkaki et al., 2016). Currently, there are two significant sources of copper able to meet the demand. Natural ores containing primary copper-bearing minerals such as chalcopyrite ( $\text{CuFeS}_2$ ) and chalcocite ( $\text{Cu}_2\text{S}$ ), as well as less abundant alteration minerals including Cu-rich sulphates, hydroxy-silicates, oxides, and carbonates. Secondary resources, including scrap copper, copper alloys, and copper-containing resources, such as slag (Schlesinger et al., 2021). The carbon emissions generated by the process heat requirement and the Cu reduction, and ultimately how hydrogen can potentially be incorporated, will depend on the copper resource input used and the process route selected to manufacture the copper.

In conventional primary copper production, for example through a flash smelting route as shown in Figure 1, the copper concentrate is oxidised in a flash furnace to form matte. The matte is further oxidised in a converter to produce blister copper with 99 wt.% purity, while the slag from smelting is processed in a slag cleaning furnace. The heat for the smelting and converting are supplied mainly by the oxidation reactions themselves. The blister copper is further refined in an anode furnace before going into electrolytic refining. Figure 1 also shows opportunities for decarbonising the process by using hydrogen in specific unit processes. For example, hydrogen can be used as a reducing agent or for generating process heat and can potentially be introduced in the slag cleaning furnace and anode furnace (Schlesinger et al., 2021; Roben et al., 2021).

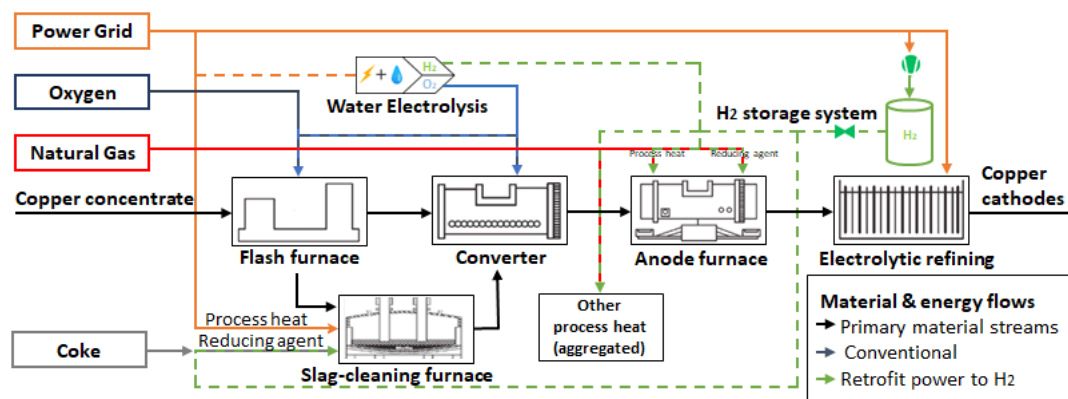


FIG 1 - Flowsheet of primary copper production process, showing possible decarbonisation/hydrogenation approaches (Roben, 2021)

For secondary copper resources, such as black copper smelting, the material is either reduced then oxidised (or vice versa depending on the input composition and type), before being electro-refined. Figure 2 shows a generic process flowsheet showing where hydrogen can be potentially implemented as a reductant and fuel for heat requirement (e.g. in a reduction stage). Mairizal et al. (2023) evaluated the prospects for hydrogen incorporation through a preliminary thermodynamic analysis and found that 82.17% Cu can be obtained in the reduction stage while 94% Cu purity can be achieved from the oxidation stage. In the reduction stage scenario, 59 kg H<sub>2</sub>O off-gas is generated with zero CO<sub>2</sub> emissions. In an alternative scenario using copper slag as a feed, PCB as the reductant and H<sub>2</sub> gas as the heat supply, producing 46.6kg H<sub>2</sub>O off-gas and 33.7kg CO<sub>2</sub> formed.

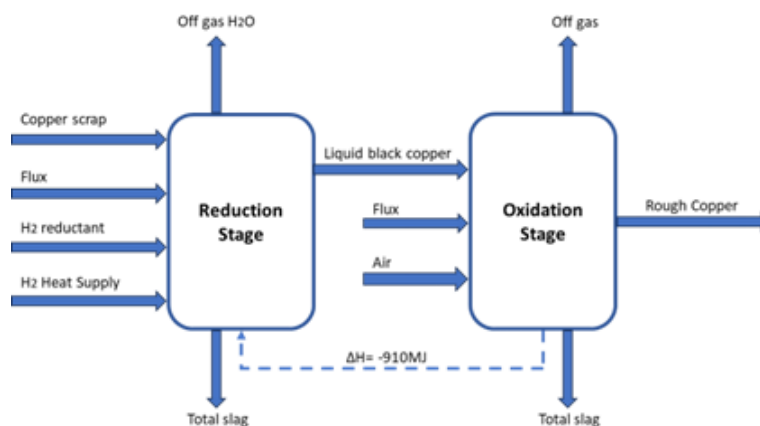


FIG 2 - Process flow sheet for secondary CU sources using hydrogen as both fuel and reductant (Mairizal et al., 2023).

Although some work has commenced, there is a need for a fundamental understanding of the detailed hydrogen reduction mechanism for the different copper sources to optimize its implementation in future processes. This article reviews the use of hydrogen as a reductant for copper-containing materials. The paper starts with a thermodynamic analysis, showing the feasibility of using hydrogen for the critical reactions involved in Cu reduction in the relevant processes. The paper continues with a review and discussion of previous studies that focus on the hydrogen reduction of chalcopryrite, chalcocite, Cu<sub>2</sub>O/CuO, and complex copper-containing secondary resources, both in the solid and liquid states. Most of these works were carried out only at a laboratory scale. Nevertheless, they provide the baseline for future industrial applications.

## THERMODYNAMICS OF HYDROGEN REDUCTION OF COPPER-CONTAINING RESOURCES

From a thermodynamic perspective, hydrogen reduction reactions have significantly lower standard Gibbs free energies ( $\Delta G^\circ$ ) compared to copper oxidation reactions, as shown in Figure 3. Hence, hydrogen makes an excellent reducing agent for reducing copper-containing ores and slag/e-wastes. Figure 3 also illustrates reaction equilibria for the traditionally used carbon and for plasma hydrogen (H and H<sup>+</sup>) which are potentially other hydrogen reducing sources. Eqns 1 and 2 show the reactions involved for the reduction of a metal oxide to its lower oxide and/or metal state by molecular hydrogen (Rukini et al., 2023).



In the case of copper oxides, the reactions and associated free energies for the reduction of Cu<sub>2</sub>O and CuO at 250°C are shown in Reactions 3 and 4 (Gargul et al., 2013)



The  $\Delta G^\circ$  of the reduction reaction for CuO is lower compared to that of Cu<sub>2</sub>O, which indicates greater thermodynamic feasibility for the reaction at the same temperature. Kinetically the observed activation energy for reduction of CuO is 14.5 kcal/mol, meanwhile Cu<sub>2</sub>O is 27.4 kcal/mol (Kim et al., 2003).

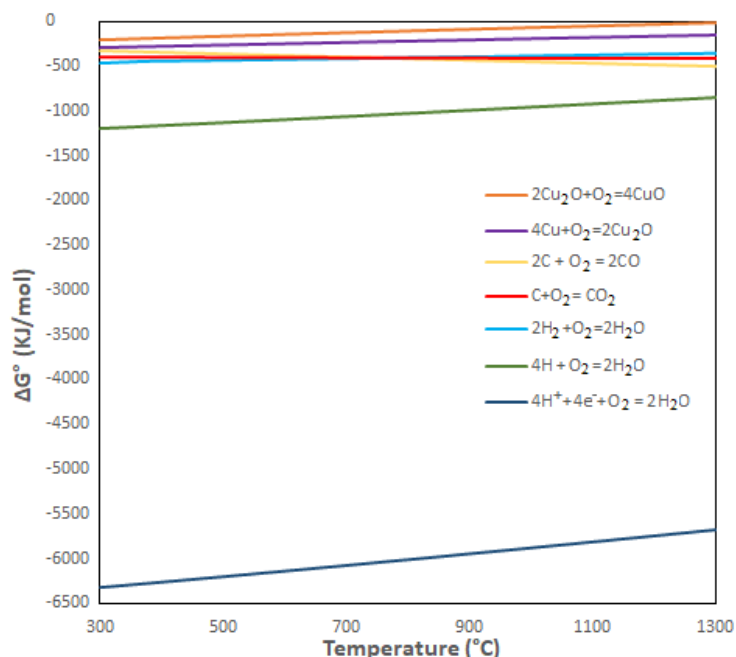
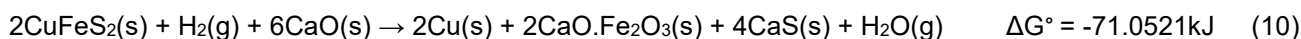
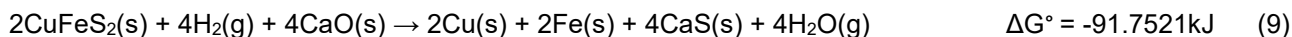
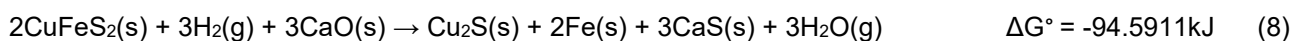
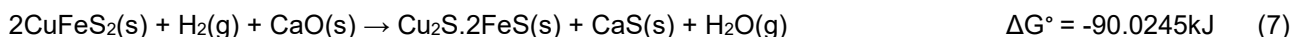


FIG 3 - Ellingham diagram of Cu reduction reactions and including reactions involving carbon, molecular and plasma hydrogen.

Chalcopyrite and chalcocite are the most common ores used for the primary production of copper. As discussed in the previous section, there is possibility for hydrogen reduction of these primary sulphide sources. However, analysis indicates that direct hydrogen reduction of metal sulphides has unfavourable thermodynamics. The equilibrium constant for Reaction 5 at 800°C ranges from  $2 \times 10^{-3}$  to  $6 \times 10^{-3}$  for Cu, Ni, Co, and Fe sulphides. Shifting the equilibria to the right can boost metal yield by removing hydrogen sulphide (H<sub>2</sub>S) immediately after the reaction. This can be achieved by adding a flux with a strong H<sub>2</sub>S affinity to the sulphide compound (Reaction 6). CaO is a flux that favours the reduction of chalcopyrite by hydrogen at 800°C and this can be achieved through additions of different amounts of CaO as shown in Reactions 7-10 (Habashi et al., 1974; Habashi et al., 2014).



## PREVIOUS STUDIES ON SOLID STATE REDUCTION OF COPPER OXIDES

The kinetics of CuO/Cu<sub>2</sub>O reduction in H<sub>2</sub>/CO gas mixtures have mainly been studied on submicron-sized powder mixes (Rodriguez et al., 2003; Kim et al., 2003; Jelić et al., 2011; Yao et al., 2018), pressed powder pellets (Sabat et al., 2016), and nanoaggregates such nanoparticles, nanowires, rods, etc. (Pike et al., 2006; Shrestha et al., 2010). In micro- and nano-scaled assemblies, the building blocks (e.g., particles, rods, platelets) and their aggregates have broad size and shape distributions, resulting in very different surface morphologies, defect structures, and CuO:Cu<sub>2</sub>O phase fractions (Jelić et al., 2011). Different properties and characteristics of the Cu<sub>2</sub>O/CuO powders resulted in contradictive findings regarding the duration of incubation, reaction rates, and phase changes during the reduction. There was however, four main findings. Full transformation reduction CuO → Cu<sub>4</sub>O<sub>3</sub> → Cu<sub>2</sub>O → Cu was observed in the reduction of CuO by hydrogen plasma (Sabat et al., 2016). Meanwhile according to (Rodriguez et al., 2003; Kim et al., 2003; Tyagi, 2018) CuO → Cu directly reduced without any intermediate phase of Cu<sub>2</sub>O or Cu<sub>4</sub>O<sub>3</sub>. Sequential reduction of CuO → Cu<sub>2</sub>O →

Cu was also reported by some workers (Li and Mayer, 1992; Pike et al., 2006; Unutulmazsoy et al., 2022). Reduction occurring as a single step of  $\text{Cu}_2\text{O} \rightarrow \text{Cu}$  was studied by (Tilliander et al., 2006). A summary of previous studies in solid state reduction of  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  is presented in Table 1. All these studies were carried out at laboratory scale and the main findings are discussed below for each oxide.

## **Cu<sub>2</sub>O**

In secondary sources such as copper slag, the copper oxide form mainly is  $\text{Cu}_2\text{O}$ . Most  $\text{Cu}_2\text{O}$  reduction research has focused on catalysts and has been carried out only at a lab-scale. Reduction of  $\text{Cu}_2\text{O}$  with hydrogen is an autocatalytic process (Hamada et al., 1992). Recent investigations on  $\text{Cu}_2\text{O}$  reduction have focused on the kinetics and the mechanism of reduction. *In-situ* time-resolved XRD involving reducing  $\text{Cu}_2\text{O}$  thin films to metallic copper was studied by Unutulmazsoy et al. (2022). High-resolution scanning electron microscopy of the products showed the presence of nano porous copper formation after reduction. Copper film grain size, strain, and peak area were all found to be important parameters in real-time reduction kinetics data. Much slower than oxidation, reduction at  $300^\circ\text{C}$  was found to take 680s to 1800s to convert  $\text{Cu}_2\text{O}$  to Cu. A single-phase  $\text{Cu}_2\text{O}$  film produced by thermal oxidation of a 300nm Cu film at  $275^\circ\text{C}$  was reduced at  $300^\circ\text{C}$  to measure  $\text{Cu}_2\text{O}$  to Cu transformation rates.  $\text{H}_2$  exposure causes grain boundaries and porosity at the  $\text{Cu}_2\text{O}$  film surface to behave as short-circuit diffusion routes, trapping hydrogen. Hydrogen diffusion along intergranular areas might cause compressive stress, reminiscent of how atoms diffuse along grain boundaries during the growth of films (Chason et al., 2002; Floro et al., 2001). Another study of the kinetics of reduction  $\text{Cu}_2\text{O}$  by hydrogen gas using thermogravimetric analysis (TGA) at temperatures  $300\text{--}400^\circ\text{C}$  was conducted by Tilliander et al. (2006). This study discovered that the stability of the oxide and the existence of other elements, such as nickel (Ni) or nickel oxide (NiO), did not influence the reduction process. The pace of reduction may be controlled by adjusting the hydrogen flow.

## **CuO**

The exothermic reaction between  $\text{CuO}$  and  $\text{H}_2$  to produce metallic Cu and  $\text{H}_2\text{O}$  gas may be divided into induction, autocatalytic, and decreasing rate processes. The properties of the initial oxide influence the reduction rates in each step (Tyagi, 2018). Single phase  $\text{CuO}$  film reduction by 5% $\text{H}_2/\text{Ar}$  at  $300^\circ\text{C}$  was evaluated and the phase transformations involving  $\text{CuO} \rightarrow \text{CuO} + \text{Cu}_2\text{O} \rightarrow \text{CuO} + \text{Cu}_2\text{O} + \text{Cu} \rightarrow \text{Cu}_2\text{O} + \text{Cu} \rightarrow \text{Cu}$  was observed by *in-situ* XRD (Unutulmazsoy et al., 2022). Three phases, Cu,  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ , coexist together during the reduction after an incubation time of 1300s and with average grainsize 30nm within a 300nm thick Cu film. Contrary to this, for a 50nm  $\text{CuO}$  film with average grain size 20nm, the formation of Cu metal occurs only after the  $\text{CuO}$  is completely reduced to  $\text{Cu}_2\text{O}$  (Unutulmazsoy et al., 2022). As oxygen vacancies continue to form on the  $\text{CuO}$  surface,  $\text{Cu}^+$  and  $\text{Cu}^0$  coexist. Oxygen vacancies move to the subsurface and create a partly reduced  $\text{CuO}$  superlattice structure, allowing the  $\text{Cu}_2\text{O}$  phase to nucleate (Sun et al., 2021; Hao et al., 2016; Maimaiti et al., 2014). The reduction time for  $\text{CuO} \rightarrow \text{Cu}_2\text{O}$  can be reduced by increasing temperature and increasing the partial pressure of hydrogen (Rodriguez et al., 2003; Kim et al., 2003).  $\text{CuO}$  reduction occurs under two circumstances. First, Cu aggregates form around oxide defects on the surface or bulk in a nonuniform reduction. The reduction mainly occurs at the Cu- $\text{CuO}$  surface. Second, most  $\text{CuO}$  loses oxygen in stages until it becomes metallic copper. Further studies found that when exposed to a steady hydrogen supply with flow rates more than 15 ml/min at temperatures over  $200^\circ\text{C}$ ,  $\text{CuO}$  underwent straight reduction to Cu without forming intermediate suboxides (Kim et al., 2004; Rodriguez et al., 2003; Kim et al., 2003).

TABLE 1 – Summary of previous works on solid state reduction of Cu<sub>2</sub>O and CuO using hydrogen

Author	System and Parameters	Key Results
(Xu et al., 2022)	Cu <sub>2</sub> O powder-H <sub>2</sub> , thin film Cu <sub>2</sub> O T = 27-377°C, 30 min-23.4h pO <sub>2</sub> : 5.0×10 <sup>-7</sup> Torr, H <sub>2</sub> pressure: 1.54 - 1.64Torr	<ul style="list-style-type: none"> <li>• Activation energy for Cu<sub>2</sub>O '29'/Cu (111) reduction by H<sub>2</sub> was 23 kcal/mol, '29' stands for row structure of Cu<sub>2</sub>O, meanwhile (111) stands for orientation of the crystal structure.</li> <li>• Cu<sub>2</sub>O-'29'Cu and solid Cu were present on the surface before fully turning into Cu (111).</li> </ul>
(Unutulmazsoy et al., 2022)	Cu <sub>2</sub> O film - 5%H <sub>2</sub> /Ar Cu films: 50, 150, and 300nm T = 300°C, 30 min	<ul style="list-style-type: none"> <li>• Reduction of Cu<sub>2</sub>O to Cu was identified in 50nm thick CuO films with an average grain size of 20 nm.</li> <li>• Single-phase Cu<sub>2</sub>O and CuO films may be converted to porous Cu, whose size and shape depend on the original Cu-oxide phase's grain size and thickness.</li> </ul>
(Tyagi, 2018)	CuO powder-H <sub>2</sub> pO <sub>2</sub> : 76Torr CuO <sub>red</sub> T = 160°C-252°C, 40min CuO <sub>red</sub> 0.67 T = 160°C & 200°C, 100min	<ul style="list-style-type: none"> <li>• Activation energy of CuO<sub>0.67</sub> reduction was 10.2 ± 0.7 kcal/mol while CuO was 14.2 kcal/mol.</li> <li>• CuO<sub>0.67</sub> demonstrated a reduced density and faster reduction rate compared to CuO.</li> <li>• The reduction of CuO<sub>0.67</sub> occurs at 200°C and ranges from 2% to 85%. In the case of CuO, the reduction ranges from 0.75% to 90% at 150°C.</li> </ul>
(Tilliander et al., 2006)	Cu <sub>2</sub> O/NiO/Ni powder-H <sub>2</sub> /Ar T = 300-400°C, 42 min Heating Rates: 6,9,12,15,18 K/min Hydrogen flow rate: 0.6 L/min, Mass: 15 mg	<ul style="list-style-type: none"> <li>• Diffusion through the bed affected the decrease rate using different sample masses.</li> <li>• Presence of Ni/NiO did not affect the reduction kinetics.</li> <li>• Activation energy: isothermal Cu<sub>2</sub>O: 92±5 kJ/mol - non-isothermal Cu<sub>2</sub>O: 111±5 kJ/mol.</li> </ul>
(Jelić et al., 2011)	CuO powder-H <sub>2</sub> 25% H <sub>2</sub> -99.995% Ar 80 mL/min T = 300-450°C Heating rate: 2.5-30°C/min	<ul style="list-style-type: none"> <li>• Both synthesized CuO and commercial CuO with purity &gt;99% were reduced to Cu metal after a 19.7% loss of mass.</li> <li>• No intermediate copper oxidation was found.</li> <li>• Reduced copper particle size was temperature dependent and significantly increased due to sintering at 300-400°C.</li> </ul>
(Yamukyan, 2009)	CuO powder-H <sub>2</sub> Hydrogen pressure: 0.01 MPa-2.5MPa Sample density: 0.42-0.57 Combustion temperature: 400-600°C. Heating rate: 5-10K/s.	<ul style="list-style-type: none"> <li>• Self-propagating diffusion regime can reduce CuO by H<sub>2</sub>.</li> <li>• H<sub>2</sub> internal pressure range spans from 0.01 - 2.5 MPa, establishing a surface combustion regime.</li> <li>• The combustion temperature and velocity exhibited constancy at a constant H<sub>2</sub> pressure of 0.075 MPa while operating within a defined density range of 0.42 to 0.57.</li> </ul>
(Kim et al., 2004)	CuO powder - 5% H <sub>2</sub> /95%He T = 150–300°C	<ul style="list-style-type: none"> <li>• CuO reduced to Cu at H<sub>2</sub> flow 15 mL/min while forming intermediate phase Cu<sub>2</sub>O at hydrogen flow &lt; 1 mL/min.</li> <li>• H<sub>2</sub> flow rate did not influence intermediate phase presence.</li> </ul>
(Kim et al., 2003)	CuO powder - 5% H <sub>2</sub> /95%He T = 150 to 300°C, flow rate gas 5-15mL/min H <sub>2</sub> 2.5×10 <sup>-6</sup> m <sup>3</sup> /s, 150-400min	<ul style="list-style-type: none"> <li>• Pressure and temperature increase linearly with microwave power and hydrogen flow rate.</li> <li>• Best result for reduction efficiency is 94.5%.</li> <li>• Activation energy of CuO reduction is 14.5 kcal/mol, while Cu<sub>2</sub>O is 27.4 kcal/mol.</li> </ul>
(Rodriguez et al., 2003)	CuO powder - 5% H <sub>2</sub> /95%He, Gas flow rate 1-20 mL/min, 200–400°C, pH <sub>2</sub> 10 <sup>-4</sup> to 5Torr	<ul style="list-style-type: none"> <li>• Activation energy 27.4 kcal/mol.</li> <li>• Cu<sup>1+</sup> was not a stable intermediate in reducing CuO, resulting in a straight CuO to Cu transition.</li> </ul>

## PREVIOUS STUDIES ON LIQUID STATE REDUCTION OF CU-CONTAINING MATERIALS

### Slag

Each ton of copper produced produces 2–3 tonnes of primary copper slag with contains up to 1% copper by weight (Hovestadt et al, 2023; ICSG, 2023; Gilsbach, 2020) In 2021, copper production generated 57.2 million tons of slag (Jin et al, 2022). From an industrial point of view, the recovered copper content in the slag both from primary smelting and e-waste recycling can produce 350 kt/year copper with 70% recovery rate (Hovestadt and Friedrich, 2023).

A study of primary fayalitic slag reduction using hydrogen was conducted to examine what happened when different flow rates and hydrogen concentrations were added to two slags containing 1% and 2% Cu by weight. Experimental work was conducted at 1300°C with a variation in hydrogen concentration of 15–100% and with a flow rate of around 1-2 l/min. Copper concentration in slag was lowest at 0.3 wt.%. Turbulence increased the response rate by 40%, suggesting liquid transport was the rate-limiting step (Hovestadt et al, 2023). Furthermore, the presence of hydrogen gas in slag facilitates the evaporation of zinc and lead. Hydrogen produces equal Zn and Pb levels throughout a broad range of reduction gas concentrations. Thus, increasing hydrogen concentration might significantly reduce the processing time. Zinc concentrations declined linearly over a threshold and decreasingly below 1 wt%. Fumigation promoted slag zinc oxide diffusion (Hovestadt, 2023). From thermodynamic point of view, Cu, Zn, and Pb oxides were easily reduced, but reducing sulphides was more challenging. The optimal conditions for reducing copper slag were 1450°C, 1.2 alkalinity, and 0.225 reducing agent ratio. The newly developed procedure recovered 95.49% copper and iron from slag, as well as 83.54% Pb and 98.30% Zn (Zhang, 2022). Table 2 represents previous studies of liquid state reduction of copper-containing resources using hydrogen.

### Preliminary industrial studies/trials

Current initiatives in Cu metal production by industry seek to use hydrogen to decarbonize copper manufacture. For example, the main Hamburg Cu smelter operated by Aurubis, which features two anode furnaces with a capacity of 270 tonnes/batch, has been supplied by hydrogen from September to December 2021. Before this, natural gas treated unwrought copper, emitting much CO<sub>2</sub>. Using hydrogen (H<sub>2</sub>) as a reducing agent is expected to reduce the Hamburg plant's CO<sub>2</sub> emissions by at least 5,000 t/year. Tests using two new anode furnaces showed that the furnaces functioned more effectively and used 30% less natural gas, saving roughly 1.2 tonnes of CO<sub>2</sub> per year and decarbonized Aurubis output before enough hydrogen was available. Replacing anode furnaces improves metal extraction from metal concentrates and recycling, in addition to climate advantages (Aurubis, 2023; Edens et al, 2022).

TABLE 2 – Summary of previous works on liquid state reduction of copper containing resources using hydrogen

Author	System and Parameters	Key Results
(Mairizal et al., 2023)	Modelling study, 1200°C-1400°C pO <sub>2</sub> ranged between 10 <sup>-7</sup> and 10 <sup>-9</sup> atm.	<ul style="list-style-type: none"> <li>• 73% reducing CO<sub>2</sub> emissions using hydrogen as a heat source.</li> <li>• PCBs significantly reduces carbon dioxide (CO<sub>2</sub>) emissions from 183.7 kg/h to 123.14 kg/h.</li> </ul>
(Hovestadt et al, 2023a)	Modelling and experimental study Primary slag & Slag mix (≤2%Cu) T = 1300°C, t > 150 min H <sub>2</sub> : 15%-100% & 1-2 l/min	<ul style="list-style-type: none"> <li>• Simulations showed after 0.5L hydrogen addition, Cu<sub>2</sub>O% reduced to 0.54wt.%.</li> <li>• Copper content decreased below the predicted limit of 0.49 wt.% across all concentrations.</li> <li>• Lowest slag copper content was 0.31 wt.% Cu.</li> </ul>
(Edens et al, 2022)	Industrial trial of 275-tonnes Cu Initial O <sub>2</sub> 0.9-1.2%, 60-97%H <sub>2</sub> /N <sub>2</sub> , H <sub>2</sub> flow rate 1400-2000m <sup>3</sup> /h, 150-190min	<ul style="list-style-type: none"> <li>• Hydrogen decreases O<sub>2</sub> oxygen content with 90% effectiveness.</li> <li>• Low gas H<sub>2</sub> efficiency is produced by unstable operation, such as blockage and leakages, which reduces valid measurements. Uninterrupted operation is predicted to be more efficient.</li> </ul>
( Hovestadt et al, 2023b)	1500g secondary copper smelter slag T = 1300°C, H <sub>2</sub> flow 0.5-2 l/min, H <sub>2</sub> 25-100%, H <sub>2</sub> 90l	<ul style="list-style-type: none"> <li>• Increased hydrogen injection volumes improve fuming and accelerate the reduction process.</li> <li>• Fuming process of H<sub>2</sub> did not follow a clear pattern with different concentrations (25, 50, 75% H<sub>2</sub>), but the quantity and turbulence of H<sub>2</sub> (0.5, 1.0, 1.5 l/min H<sub>2</sub>) did affect fuming and reduction.</li> </ul>
(Zhang et al, 2022)	Experimental Cu slag pellet with 10%H <sub>2</sub> -Ar H <sub>2</sub> flow 4 L/min, pH <sub>2</sub> 40%. T = 1500°C, 4 hours, CaO addition	<ul style="list-style-type: none"> <li>• Activation energy of H<sub>2</sub> copper slag reduction 29.107-36.082 kJ/mol.</li> <li>• Increasing the reducing gas flow rate improves the reduction ratio but after 4 L/min that the reduction process is controlled by internal diffusion, interface chemical reaction control, and mixed control.</li> </ul>
(Zhang et al., 2021)	Experimental work of copper slag T = 1100°C, t <1350s CO/H <sub>2</sub> Ratios (0-6 / 0-4)	<ul style="list-style-type: none"> <li>• Fastest response rates were seen when the entering gas was hydrogen gas for 300 seconds.</li> <li>• Primary cause of the loss of valuable components in the copper slags was the high magnetite content. Activation Energy = 58.8 kJ/mol.</li> </ul>
(Fasshauer et al., 2000)	Industrial trial of 145 tonnes Cu Initial O <sub>2</sub> 0.9%, 53-81%H <sub>2</sub> /Ar, gas flow 200-350m <sup>3</sup> /h, T = 1250°C	<ul style="list-style-type: none"> <li>• Optimal hydrogen volume percentage in the H<sub>2</sub>/N<sub>2</sub> combination was 60-72% by volume.</li> <li>• Preferable pressure of the reducing gas introduced into the melt at 8 to 12 bar.</li> </ul>
(Iwamura et al., 1991)	40 kg molten copper with O <sub>2</sub> 10ppm H <sub>2</sub> 5-50%/Ar, T = 1200°C, 10min	<ul style="list-style-type: none"> <li>• Increasing volume H<sub>2</sub> &gt; 50% reduce reaction efficiency.</li> <li>• Produced pure Cu with O<sub>2</sub> &lt; 3ppm by weight.</li> </ul>
(Fukunaka et al., 1991)	5mm Cu droplets with H <sub>2</sub> /Ar, T = 1697°C Initial O <sub>2</sub> 0.036-1.9wt%, pH <sub>2</sub> 4kPa Gas flow rate 2x10 <sup>-4</sup> m <sup>3</sup> /s	<ul style="list-style-type: none"> <li>• Deoxidation dropped droplet weight by a few percent and raised temperature in 30 seconds during vaporisation. Deoxidation rises with hydrogen partial pressure and gas flow rate (mixed rates control).</li> <li>• Copper droplets deoxidise faster at high oxygen levels and slower at low oxygen levels.</li> </ul>



## CONCLUSIONS

Recent investigations have shown significant advances regarding hydrogen's potential in reducing primary and secondary copper resources. The laboratory-scale investigations explicitly focused on the reduction kinetics and reaction mechanisms. More detailed investigations in a simple system (CuO and Cu<sub>2</sub>O) and a complex system (copper slag and copper-containing resources) at higher temperatures must be carried out to better understand interaction between phases during the reduction. Variations in the composition of the reductant gas mixture, temperature, and reduction time need to be further investigated since these parameters will vary the kinetic driving force. The influence of the H<sub>2</sub>/H<sub>2</sub>O ratio also needs to be determined to examine its effect on the kinetics and microstructures of the reduction process. Laboratory studies and industrial research indicate that hydrogen reduction can be applied to primary and secondary copper resources, contributing to industrial decarbonisation efforts. However, more research is needed to understand better the parameters impacting hydrogen reduction treatment.

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