# Hydrogen Plasma in Extractive Metallurgy Application

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Keywords: hydrogen plasma, extractive metallurgy, metal oxide reduction, plasma reactor

# ABSTRACT

Metal production have long been using carbon sources as both reducing agents and energy sources. Consequently, the global extractive metal sector contributes significantly to greenhouse gas emissions, accounting for approximately 9.5%. Hydrogen gas offers as a promising eco-friendly alternative to carbon in metallurgical processes, serving as both a reductant and energy supplier with a by-product being only water vapor. However, the implementation of molecular hydrogen faces certain challenges related to the thermodynamics and kinetics of metal oxide reduction. In addressing these challenges, researchers have explored the application of hydrogen plasma, generated by subjecting molecular hydrogen to high energy to produce atomic, ionic, and excited hydrogen species. Hydrogen plasma offers thermodynamic and kinetic advantages over molecular hydrogen and carbon-based reductants, exhibiting lower standard Gibbs free energy of reaction and activation energy. Therefore, hydrogen plasma can produce metal in fewer steps, process any oxide feed and feed size, and even be used to refine metals. Despite these advantages, challenges exist in utilizing hydrogen plasma in extractive metallurgy, including electricity costs, potential reverse reactions, and industrial-scale implementation. This study provides a mini review of prior research on hydrogen plasma for metal oxides reduction, particularly iron oxide, as well as state-of-the-art techniques for its use in extractive metallurgy applications by mentioning several reactor types. Future prospects and scale-up possibilities of the hydrogen plasma in extractive metallurgy will also be presented.

# INTRODUCTION

The field of extractive metallurgy continues to grow, driven by the growing demand for metals in human needs. Traditionally, carbon-based reductants and energy sources have been heavily relied upon due to their affordability and abundance. However, this reliance contributes to climate change, with carbon dioxide ($CO_2$) emissions accounting for a significant 9.5% of global greenhouse gas emissions (Mackenzie, 2023). Recently, there is a rising interest in hydrogen as a sustainable alternative for various sectors, including extractive metallurgy, as it holds the potential to eliminate scope 1 $CO_2$ emissions. Unlike traditional methods, using hydrogen in metal production results in the production of water vapor as a byproduct. Despite its promise, hydrogen faces challenges as a weaker reductant compared to carbon at higher temperatures based on thermodynamics. One alternative to address this challenge is the utilization of hydrogen plasma, a higher state of hydrogen gas. Hydrogen plasma is achieved by subjecting molecular hydrogen to high energy until it transforms into excited ($H_2^*$), atomic (H), and/or ionized ($H^+$) hydrogen. The main advantages of hydrogen plasma include its ability to enhance the feasibility of metal oxide reduction and its reaction rates. Its high thermal conductivity facilitates efficient heat transfer, while low viscosity enables rapid mass transfer (Sahu, 2014). This mini review paper systematically compiles and reviews recent and current studies on the application of hydrogen plasma in the context of extractive metallurgy. The aim is to provide information that supports future scale-up efforts. A more comprehensive and complete review on the topic is presented by the authors elsewhere (Satritama *et al.*, 2024).

# OVERVIEW OF HYDROGEN PLASMA

To generate a plasma state in a specified reactor, energy in the form of DC or AC electricity and/or electrodeless microwave electromagnetic must be applied to the gas. When an electric arc forms between two electrodes or an electromagnetic field is present in the gas, the gas becomes electrically conductive, leading to excitation, dissociation, and eventual ionization. Hydrogen fully dissociating into H atoms at 5,000°C and complete ionization occurring at 25,000°C under atmospheric pressure (Satritama *et al.*, 2024). Lowering the pressure significantly decreases the required temperatures for both dissociation and ionization. Plasma is broadly categorized as thermal or non-thermal, also known as non-equilibrium or cold plasma. Thermal plasma is characterized by uniform temperature among all plasma particles (electrons, ions, and neutral atoms), while non-thermal plasma exhibits a temperature differences, with heavy particles ($T_i$ and $T_n$ denoting ions and neutral species temperature) significantly lower than free electrons ($T_e$). This temperature difference arises from low particle collisions at low pressure conditions, typically lower than 1 atm (Inui *et al.*, 2010). There are a few plasma reactors used for metallurgical application which include batch, continuous feeding, and in-flight reactors (Fig. 1). The difference between continuous feeding and in-flight reactors is that in-flight reactors combine continuous feed and plasma gas into a single stream.

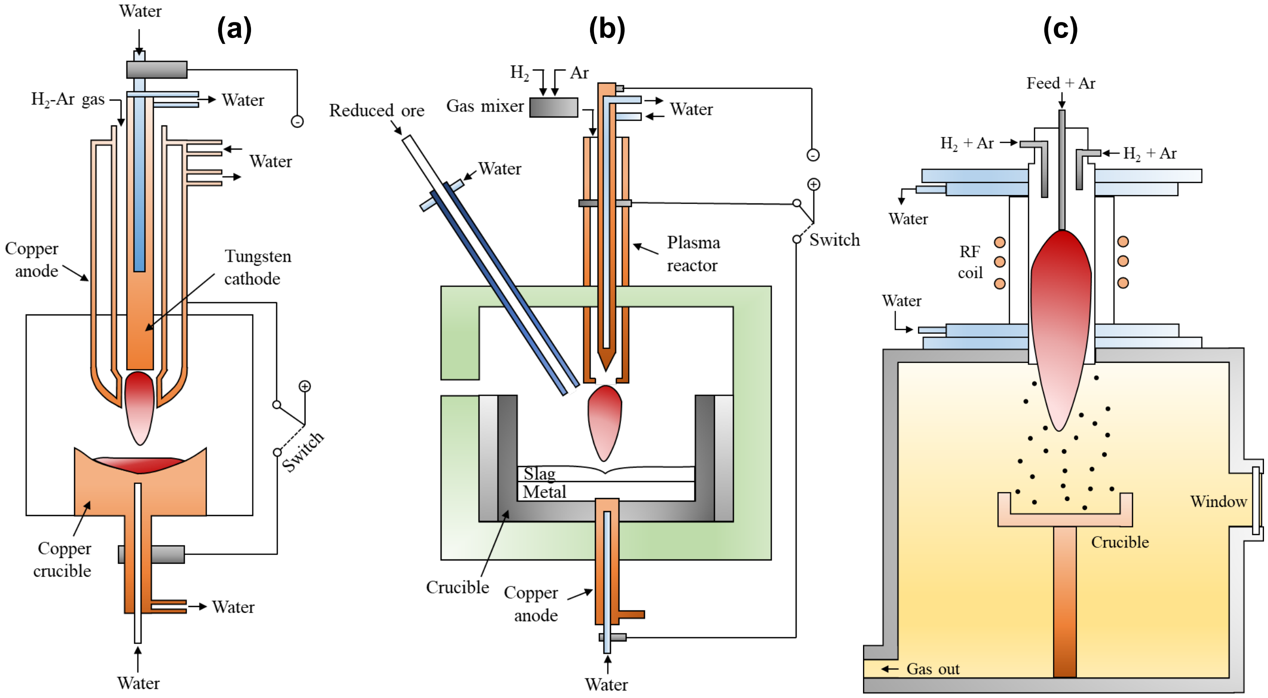

FIG 1 - Type of plasma reactors, including (a) batch DC non-transferred and transferred plasma, (b) continuous DC non-transferred and transferred plasma, (c) in-flight microwave plasma. Adapted from (Alexis Yvon *et al.*, 2011, De Sousa *et al.*, 2016, Rains and Kadlec, 1970) by (Satritama *et al.*, 2024).

# HYDROGEN PLASMA FOR EXTRACTIVE METALLURGY

## Thermodynamics and Kinetics of Hydrogen Plasma in Extractive Metallurgy

Hydrogen plasma demonstrates the ability to reduce a broad spectrum of metal oxides, overcoming limitations observed with molecular hydrogen. Thermodynamic calculations reveal that the use of molecular hydrogen for most metal oxide reductions tends to yield positive Gibbs free energy, hinders spontaneous reaction. In contrast, hydrogen plasma addresses this challenge due to its enhanced energy profile. An Ellingham diagram (Fig. 2) was generated using FactSage 8.2 database, illustrating the Gibbs free energy of metal oxide formation (from its elemental state with 1 mol of $O_2$) alongside reductants like carbon, hydrogen gas, and hydrogen plasma at a total pressure of 1 atm. It is evident that carbon can serve as a reductant for most metal oxides at high temperatures, while hydrogen gas can reduce specific metal oxides at all temperatures and others at higher temperatures. In contrast, the application of hydrogen plasma in the form of atomic H and/or H+ significantly broadens the range of reducible oxides, offering the additional advantage of lower temperatures favouring the reduction process.

In addition to meeting the Gibbs free energy criteria, the reactants must surpass the activation energy for a chemical reaction to take place. Activation energy ($E_a$) represents the minimum energy required for a reaction to proceed. The reduction of metal oxide to metal using molecular hydrogen may face challenges due to a high activation energy ($E_{a,1}$). Hydrogen plasma, in atomic ($E_{a,2}$) and excited atomic hydrogen forms ($E_{a,3}$), can significantly decrease the activation energy of the process, with the order $E_{a,1} > E_{a,2} > E_{a,3}$ (Sabat *et al.*, 2013). There is limited research on the kinetics of metal oxide reduction using hydrogen plasma. Cobalt oxide reduction involves multiple steps, with the activation energy from $Co_3O_4$ to CoO (26.2 kJ/mol) higher than from CoO to Co (13.3 kJ/mol) metal (Sabat *et al.*, 2015). Two kinetic studies on $Cu_2O$ reduction to Cu metal indicate that the activation energy is nearly four times lower at lower temperatures (300-400℃) (Ramos *et al.*, 2021), that is 19.06 kJ/mol, compared to higher temperatures (470-900℃) (Sabat, Paramguru and Mishra, 2016), that is 75.64 kJ/mol. These results align with hydrogen plasma's preference for lower temperatures as a reductant. A similar trend is observed in the study of $Fe_2O_3$ reduction to Fe metal by Rajput *et al.*, with the activation energy four times lower at lower temperatures (300-800℃) (Rajput *et al.*, 2014, Rajput *et al.*, 2013), that is 5.069 kJ/mol, compared to higher temperature (690-1150℃), that is 20.54 kJ/mol. Gonoring *et al.* reported a significantly higher activation energy for $Fe_2O_3$ reduction (68.5 kJ/mol), attributed to the lower frequency parameter of microwave plasma (3.4 kHz) compared to Rajput *et al.* (2.45 GHz), resulting in lower energy during the induction process by the microwave plasma and incomplete dissociation and/or ionization of hydrogen gas.

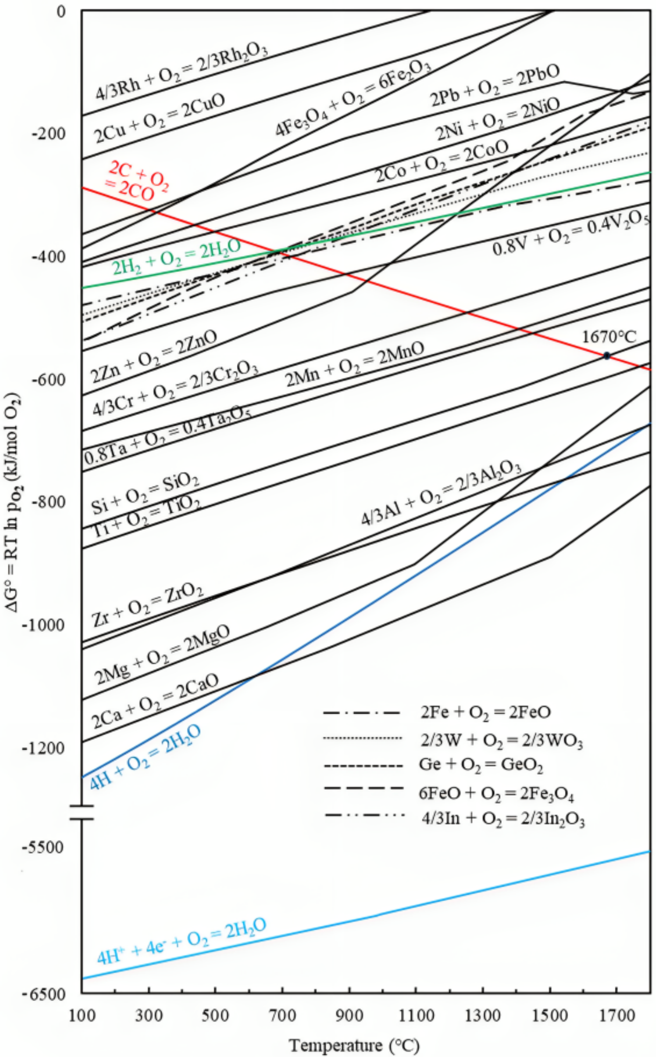

FIG 2 - Ellingham diagram of metal oxides stability in a function of temperature (Satritama *et al.*, 2024)

This mini review briefly discusses the utilization of hydrogen plasma for metal oxides reduction, where a more comprehensive discussion of its broader application in extractive metallurgy, which include for reduction, metals refining and wastes processing, is presented in other work (Satritama *et al.*, 2024).

## Reduction of Metal Oxides Using Hydrogen Plasma

The reduction of metal oxides using hydrogen plasma is categorized into heterogeneous reactions, involving the interaction between hydrogen plasma and solid/liquid metal oxides, and homogeneous reactions. Certain metals, such as aluminium and chromium, are efficiently produced through homogeneous reactions. This process involves vaporizing the metal oxide, breaking the metal-oxygen bond, utilizing hydrogen plasma to bind with the oxygen, and depositing the pure metal vapor in a cooler zone. Referred to as dissociative reduction, this method requires a water-cooled reactor wall and a quench probe that can optionally inject quench gas (Rains, 1968). General reaction mechanism is given in the Fig. 3 by distilling from several experimentation results (Sabat *et al.*, 2015, Sabat, Paramguru and Mishra, 2018, Sabat, 2019, Zarl *et al.*, 2022).

In the heterogeneous process, the initial step involves generating plasma by injecting gas between electrodes with different potentials, illustrated in the schematic mechanism using DC plasma. Microwave energy can also serve as a source to produce hydrogen plasma, as discussed earlier. $H_2$ plasma is formed through collisions with high-energy electrons sputtering from the cathode to the anode. These collisions elevate hydrogen to an excited state, leading to dissociation and ionization. Additionally, collisions with photons (*hv*) can occur, further enhancing the hydrogen state. Photons are generated when high-energy electrons collide with hydrogen gas, reducing their state and releasing photons. Heat transfer between gas molecules allows higher-state hydrogen to transfer energy to lower-state hydrogen, improving the equilibrium of hydrogen plasma. The hydrogen plasma then flows through a constricted anode into the sample. In many instances, argon is injected alongside hydrogen to broaden the radial distribution of plasma within the sample, as hydrogen's high specific heat results in a more constricted plasma arc.

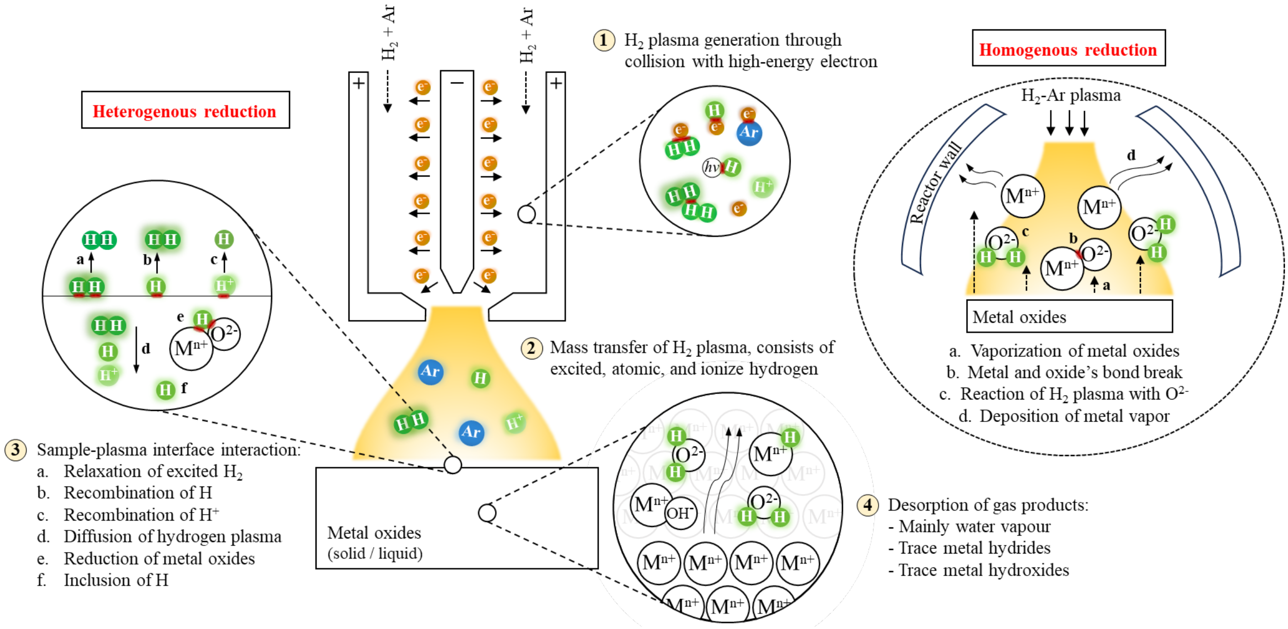

FIG 3 - General reaction mechanism of metal oxides reduction with hydrogen plasma (Satritama *et al.*, 2024)

The reduction process initiates from the upper interface of the solid/liquid-gas layer in the sample and gradually proceeds downward as more interfaces of metal oxides undergo reduction. The interaction between hydrogen plasma and the metal oxides interface is complex. Some hydrogen plasmas undergo relaxation and recombination at the interface, experiencing sudden temperature changes upon contact with the sample surface. These processes induce local heating on the sample's surface, enabling the energy to surpass the activation energy required for oxide reduction. Other types of hydrogen plasma can bind oxygen at the interface and diffuse further into the sample to reduce additional oxide. This process requires intensive control, as several studies have noted that reduction with hydrogen plasma may result in the inclusion of trace amounts of hydrogen inside the sample. A higher entrapment of hydrogen may lead to hydrogen embrittlement (Sabat, Paramguru and Mishra, 2018).

Certain metals are efficiently produced through homogeneous reactions with hydrogen plasma in the vapor state (Huczko and Meubus, 1988, Kitamura, Shibata and Takeda, 1993). A study by Kitamura revealed that hydrogen plasma can evaporate metal oxides much faster than argon plasma. Using hydrogen plasma, $Fe_2O_3$, $Cr_2O_3$, $TiO_2$, and $Al_2O_3$ can be evaporated in 1.4, 1.8, 2, and 5.9 ms, respectively (Kitamura, Shibata and Takeda, 1993). Once metal oxides evaporate, the bonds between metal and oxide break down, allowing hydrogen plasma to bind free oxygen. The resulting metal vapor can then be deposited in the cooler part of the reactor. Rains employed an additional quench probe inserted into the bottom of the vertical reactor, alongside its water-cooled reactor casing (Rains, 1968). This water-cooled quench probe injects cooled gas to enhance metal vapor deposition.

## *Iron Oxide Reduction*

Several studies have examined the effectiveness of different hydrogen plasma methods in reducing iron ore ($Fe_2O_3$) to metallic iron, positioning hydrogen plasma as a leading technology for oxide reduction compared to other metals. Microwave non-thermal plasma with $H_2$ has been particularly investigated, demonstrating rapid reduction of bulk $Fe_2O_3$. Bergh observed colour changes indicative of iron oxide reduction with atomic H at a relatively low temperature of 40°C, significantly lower than the 310°C required for molecular hydrogen. Rajput *et al.* achieved over 95% reduction within 2 hours using low power (500-1500 W), attributing this efficiency to the lower activation energy of hydrogen plasma compared to molecular hydrogen (Rajput *et al.*, 2014, Rajput *et al.*, 2013). Microwave power density (MWPD) emerges as a critical factor in microwave plasma reduction, influenced by reaction temperature and pressure, reflecting the efficiency of microwave energy absorption by plasma. Sabat's study estimated an MWPD of 4-9 W/cm³ in their process, translating to a mere 1-2% conversion of molecular hydrogen into atomic H based on Hassouni *et al.*'s findings (Hassouni, Grotjohn and Gicquel, 1999).

Extensive research on DC thermal plasma reduction with hydrogen plasma, commonly known as Hydrogen Plasma Smelting Reduction (HSPR), has been conducted at Montanuniversität Leoben as part of the SuSteel project, a collaboration between Montanuniversität Leoben and Voestalpine aimed at scaling up the process to a pilot scale (Seftejani *et al.*, 2020). Zarl *et al.* developed a promising six-step batch and continuous plasma reduction process using $H_2$ for potential industrial-scale applications. The process includes argon purging, pre-melting (electrode contact with a steel pin), pre-reduction to complete melting with $Ar+H_2$, reduction and sample charging, post-reduction until $H_2$ content in the off gas reached 40%, and $Ar/N_2$ flushing (Zarl *et al.*, 2022). Filho *et al.* examined a hybrid approach, combining molecular hydrogen direct reduction with hydrogen plasma (Filho *et al.*, 2022). This method resulted in complete conversion in just 15 minutes for the plasma step, as opposed to 40-70 minutes for direct reduction alone.

Increased microwave power and temperature generally result in higher rates and degrees of reduction (Gilles and Clump, 1970, Rajput *et al.*, 2013, Filho *et al.*, 2022, Gonoring *et al.*, 2022). However, accurately measuring temperature during hydrogen plasma reduction poses a challenge due to uneven heat distribution within the reactor. Kumar proposed an innovative method involving the placement of reflective aluminium foil beneath the sample and analysing the emitted light to estimate temperature based on black-body radiation principles (Kumar *et al.*, 2023). Beyond assessing reaction rate and degree, optimizing hydrogen utilization is critical for efficient reduction. Although higher hydrogen concentrations and flow rates enhance reduction rates, they typically lead to decreased utilization (Behera *et al.*, 2018, Plaul, Krieger and Bäck, 2005). Seftejani *et al.* observed an initial peak in hydrogen utilization (60%), followed by a gradual decline to near zero by the conclusion of the reduction process (Seftejani *et al.*, 2020).

## *Other Oxides Reduction*

The initial endeavour to reduce alumina using hydrogen plasma dates to 1970, conducted by Rains and Kadlec (Rains, 1968). They achieved a dissociative reduction, separating aluminium from oxygen through evaporation and the reaction of oxygen with hydrogen plasma. Subsequent studies have expanded on this work. Lyubochko *et al.* achieved a higher conversion of 50-60% in a batch system with higher power input, surpassing Rains and Kadlec, who achieved a 30% alumina conversion with an in-flight system (Lyubochko *et al.*, 2000). Rains and Kadlec successfully produced aluminium with a quench system and lower power input, while Kitamura *et al.* encountered challenges in producing Al due to reoxidation into alumina (Kitamura, Shibata and Takeda, 1993). This underscores the significance of an effective quenching system in homogeneous reduction.

Reduction of chromium oxide can occur through both heterogeneous and homogeneous reactions. Although prior studies reported incomplete reduction or the need for optimized parameters, homogeneous reactions generally exhibit higher efficiency. Huczko and Meubus found that vapor-phase reduction is more efficient than solid-vapor reduction, showing increased efficiency (up to 47%) with higher H2 flow rates (Huczko and Meubus, 1988). Their calculations indicated that the diffusivity of Cr in $H_2$-Ar plasma is higher than that of $Cr_2O_3$, with the value increasing with temperature. This suggests that Cr can more easily diffuse in the gas system, facilitating its deposition. Kitamura *et al.* stressed the importance of exceeding 2000K for Cr vaporization and subsequent quenching to form solid Cr. Dalaker and Hovig achieved a heterogeneous reaction, obtaining a metallic phase with 90% Cr, primarily due to the low reaction time (only 6 min, with 12 cycles of 30 s each), vacuum conditions, and relatively low current (30-100A), preventing Cr oxide from vaporizing (Dalaker and Hovig, 2023). They proposed a potential mechanism of Cr oxide reduction as $Cr_2O_3$ to CrO to Cr.

Although copper oxides can be reduced using molecular hydrogen, research has been conducted on their reduction with hydrogen plasma. The typical reduction steps for Cu oxides involve $CuO \rightarrow Cu_4O_3 \rightarrow Cu_2O \rightarrow Cu$ (Sabat, Paramguru and Mishra, 2016). Ramos *et al.* observed that the reduction step from $Cu_2O$ is directly to Cu, without the presence of metastable phases (Ramos *et al.*, 2021). However, Sabat *et al.* suggested a different reaction sequence, stating that the steps are $CuO \rightarrow Cu_2O \rightarrow Cu$ when iron oxide is added to the process (Sabat, Paramguru and Mishra, 2017). The reported activation energy for $Cu_2O$ reduction is 75.64 kJ/mol (Sabat *et al.*), while Ramos *et al.* reported an activation energy of 19.06 kJ/mol for $Cu_2O$ reduction. Furthermore, Ramos *et al.* found that the activation energy for $H_2$ plasma reduction was almost four times lower than that for molecular $H_2$ reduction (73.79 kJ/mol compared to 19.06 kJ/mol). Atomic hydrogen seems to be more efficient for reduction compared to molecular hydrogen, as observed by Bergh in 1964 (Bergh, 1965). They noted that the reduction temperature for $Cu_2O$ and CuO ranges from 225-450℃ and 100-225℃, with a colour change occurring at 265°C and 140°C, respectively. In contrast, the colour changes with H occurred at 25°C, consistent with findings by Fleisch (Fleisch and Mains, 1982).

Same case applies to nickel oxide as it can be reduced using molecular hydrogen, but some researchers also tried to reduce it with hydrogen plasma. Bergh observed a reduction in NiO occurring at a notably lower temperature (62°C) when exposed to atomic hydrogen, in contrast to molecular hydrogen (250°C) (Bergh, 1965). Sabat *et al.* achieved complete reduction of pure NiO within 5 minutes, employing a power input of 750 W. The reduction exceeded 100% due to excess lattice oxygen in non-stoichiometric NiO (Sabat, 2021). They calculated the specific enthalpy for NiO reduction as 32.8 kWh/kg, with the potential for reduction to 7.37 kWh/kg Ni when considering a 60% reactor power efficiency and simultaneous multi-pellet reduction. Despite these intriguing results, justifying the additional energy consumption of converting hydrogen to plasma for CuO and NiO reduction requires stronger arguments as these oxides are easily reduced with molecular hydrogen.

Most research on $SiO_2$ reduction with hydrogen plasma primarily results in the formation of SiC (Salinger, 1972, Hollabaugh *et al.*, 1983, Meyer *et al.*, 1987, Asakami, Hokazono and Kato, 1988, Pirzada, 1990, Kong, Huang and Pfender, 1986), SiO (Kong, Huang and Pfender, 1986), or $Si_3N_4$ (Lee, Eguchi and Yoshida, 1990, Allaire and Dallaire, 1991) with the production of silicon metal proving challenging due to the complex behaviour of $SiO_2$ reduction. Only two studies, conducted by Watanabe *et al.* and Sousa *et al.* (Watanabe *et al.*, 1999, De Sousa *et al.*, 2016), have successfully produced silicon metal from silicon oxide samples. Watanabe *et al.* utilized a mixture of silica and alumina with argon and hydrogen plasma in a 4 kW DC non-transferred thermal plasma, discovering that argon plasma could generate silicon, while hydrogen was crucial for alumina reduction. Silicon with 98.3-99% purity was formed within a 15-minute treatment. Sousa *et al.* investigated the deoxidation of silicon kerf, a byproduct generated during wafer slicing in solar panel manufacturing, using in-flight DC non-transferred plasma. They found that the reaction time between hydrogen plasma and the silicon kerf sample was crucial. The deoxidation rate increased with an increasing nozzle diameter at low hydrogen content due to the resulting lower gas velocity. The oxygen wt% in silicon kerf decreased from 17.3-23.4% to 5.4-8.7%, and the deoxidation rate increased with an increasing nozzle diameter with low hydrogen content (<5 L/m).

## FUTURE PROSPECTS AND SCALE UP POSSIBILITY

While there is considerable research on metal oxide reduction with hydrogen plasma, its application to reduce complex ores, is still in the early stages of exploration. However, building on successful studies of pure metal oxides reduction with hydrogen plasma, there is potential to produce various metals from complex oxide ores by carefully controlling the process parameters. Future investigations should also consider exploring the use of hydrogen plasma for rare earth metal production to support advanced applications, as these metals often necessitate high temperatures or strong reductants for extraction. Implementation of in-flight plasma process holds promise for future applications. This method offers higher reaction times, leading to increased reduction degrees and enhanced hydrogen utilization, facilitated by the extensive surface area of the sample. Additionally, this approach appears economically viable for industrial-scale implementation, given its higher productivity compared to batch processing. When considering a larger-scale application, a thorough techno-economic assessment is crucial by evaluating cost-effectiveness, energy efficiency, and practical challenges associated with implementing hydrogen plasma technology. Furthermore, interdisciplinary collaboration between metallurgists and plasma physicists is essential to address existing knowledge gaps and facilitate the successful scale-up of hydrogen plasma technology in extractive metallurgy.

## CONCLUSIONS

Hydrogen plasma is emerging as a viable option for low-carbon extractive metallurgy, addressing the limitations associated with molecular hydrogen as a weaker reductant, particularly at elevated temperatures. Typically, hydrogen plasma is generated by subjecting molecular hydrogen to high energy, resulting in vibrationally and rotationally excited, atomic hydrogen and/or ionized hydrogen. This combination of species finds diverse applications in extractive metallurgy, particularly in the reduction of various metal oxides. While existing research predominantly focuses on the reduction of iron ore or iron oxides, numerous studies have explored the efficacy of hydrogen plasma in reducing oxides such as $Al_2O_3$, $Co_3O_4$, $Cr_2O_3$, CuO, NiO, $SiO_2$, and others, revealing promising results and showcasing its superiority over molecular hydrogen. Hydrogen plasma demonstrates effective reduction even for more stable oxides like $Al_2O_3$, $TiO_2$, and $SiO_2$. Less stable oxides such as NiO and CuO are more efficiently and sustainably reduced using molecular hydrogen, as it proves sufficient for less stable oxides. The added cost of electricity required to generate plasma does not justify the benefits in terms of reaction time, based on current research findings. Despite the manifold advantages, hydrogen plasma utilization in extractive metallurgy poses several challenges, which ongoing studies are actively addressing and must be further optimized in the future.

## ACKNOWLEDGEMENTS

This work was conducted as part of the PhD study of Bima Satritama and Dian Mughni Fellicia. Bima Satritama is co-funded by Swinburne University of Technology (SUT), Victorian Hydrogen Hub (VH2), and Commonwealth Scientific and Industrial Research Organization (CSIRO). Dian Mughni Fellicia is co-funded by SUT and CSIRO.

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