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Thermodynamic modelling of the reduction of a saprolitic laterite ore by methane

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ABSTRACT

The recovery of nickel from the sulphide deposits is becoming more expensive and thus increasing attention is being paid to the nickeliferous laterite ores. One option being considered for the extraction of nickel would be the production of a concentrate by reduction and magnetic separation of the ferronickel alloy. The utilization of methane as a reducing agent offers some environmental benefits when compared to carbon. In this paper, thermodynamic modelling has been used to investigate the pyrometallurgical reduction of a saprolitic laterite ore by methane. The effects of methane additions, temperature, and ore composition on the nickel grade and nickel recovery were determined. It was found that nickel recoveries of 90% could be achieved at about 1000 °C with nickel grades of about 60%. The majority of the reduction was due to the carbon in the methane.

1. Introduction

1.1. Saprolitic laterite ore

As the nickel sulphide ore deposits become more difficult to mine, the nickeliferous laterite ores are becoming the major source for the global nickel metal supply (Dalvi et al., 2004; Mudd and Jowitt, 2014). In the sulphide ores, the nickel occurs in the discrete mineral pentlandite ($(Fe,Ni)_8S_9$), which although present in relatively small amounts, can be readily concentrated by conventional flotation techniques. Additionally, cobalt and some precious metals can often be recovered and the sulphur can be utilized as a fuel. However, the oxidic laterite ores cannot be beneficiated to any significant extent, since the nickel is widely disseminated in solid solution in the host rock. Furthermore, cobalt recovery is problematic and neither precious metals nor sulphur are present. Also, the mining and extraction of nickel from the oxidic ores may leave a larger environmental footprint than the sulphide ores (Mudd, 2009).

A typical nickeliferous laterite ore deposit consists of two primary nickel bearing layers: limonite and saprolite. For the purpose of this paper, the study will be limited to the saprolitic ores. In the saprolitic layer, the nickel is substituted for magnesium in the major mineral, garnierite ($(Mg,Fe,Ni)_3Si_2O_5(OH)_4$). Unlike the sulphide deposits, which typically occur at depth, the nickeliferous laterite deposits are formed by the weathering of ultramafic rock and thus can be mined at the surface. Several methods are currently being used for the processing of the saprolitic laterite ores. The saprolitic ores, which have higher nickel (2–5%) and lower iron (< 40%) contents, as well as significant amounts of magnesium silicates, are more amenable to pyrometallurgical processes such as smelting, to produce a high grade ferronickel product (Dalvi et al., 2004). These processes are costly since they involve the consumption of a large quantity of energy.

For this reason, it is of interest to investigate new processing techniques, which may offer a more economical and perhaps environmentally friendly route for extracting the nickel. For example, heap leaching or nitric acid leaching processes have been proposed and claim to offer reduced processing costs, but have not achieved commercial application (Mitchell, 2015; Oxley and Barcza, 2013). Another potential method is the selective reduction of the nickel oxide in the laterite ore to produce a high grade ferronickel alloy, which can then be concentrated by magnetic separation. This concentrate could then be sent for further upgrading, offering a potential reduction in either energy or acid consumption. Currently, significant research is being performed on the selective reduction of the nickeliferous laterites by coal, carbon monoxide, hydrogen and various mixtures of these reagents.

Worldwide, the metallurgical industry is a major contributor to the global emissions of carbon dioxide. In many pyrometallurgical processes, carbon based fuels are employed as a source of energy, but additionally carbon is used as a reducing agent. Carbon is abundant, has a high energy density but results in carbon dioxide emissions. In addition to the carbon dioxide generation issue, coals contain organics, sulphur and ash, which have additional environmental consequences. Alternative reducing agents include: other metals, hydrogen, and methane (CH_4). A more reactive metal can be used to reduce the oxide of a

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less reactive metal in metallothermic reduction reactions, but this is usually not economic, except for niche applications. Hydrogen has a major advantage in that the reaction product is water vapour. However, hydrogen must be manufactured from either water or methane and is therefore expensive and is also potentially explosive. Methane has received little attention as a reducing agent, primarily because of its high cost and limited availability (Domsa et al., 1966; Ghosh et al., 1986; Ostrovski and Zhang, 2006). However, it is becoming more readily available and in comparison to coal or coke, it offers significant environmental benefits. For example, if one considers the overall reduction of a typical metal oxide (MO) by carbon or methane then the reactions can be described as follows:

$$2MO + C = 2\,M + CO_{2(g)} \tag{1}$$

$$4MO + CH_{4(g)} = 4\,M + CO_{2(g)} + 2H_2O_{(g)} \tag{2}$$

For the production of an equivalent amount of metal, the utilization of methane should result in a fifty percent reduction in carbon dioxide emissions in comparison to carbon.

There is a paucity of information in the literature on the use of methane as a reductant for the nickeliferous laterites. The current work attempts to address this issue by developing a thermodynamic model to investigate the selective reduction of the saprolitic laterite ores by methane to produce ferronickel, which could be further concentrated by, for example magnetic separation. This model is based on previous models for the reduction of a laterite ore by carbon and hydrogen, and also on activity data available in the literature (Elliott et al., 2016; Hsieh and Chang, 1986; Pelton et al., 1979; Shirane et al., 1987; Swartzendruber et al., 1991). The model has been used to examine the effects of temperature and reductant to ore ratio on the recovery of nickel to the ferronickel phase, the nickel grade in the ferronickel, carbon deposition and the formation of magnetite.

1.2. Previous thermodynamic studies

Several researchers have investigated the thermodynamics of the reduction of laterite ores by carbon, carbon monoxide or hydrogen (Canterford and Turnbull, 1980; Elliott et al., 2016; Hallet, 1997; Rhamdhani et al., 2009; Utigard and Bergman, 1992; Valix et al., 1995). In general, these studies have concluded that while truly selective reduction of the nickel oxide is not possible, it should be feasible to form a high grade ferronickel product at relatively low temperatures. In all cases, at a given temperature, the nickel recovery increased as the conditions became more reducing, but this lowered the grade due to the increased formation of metallic iron. Temperature was also reported to have a significant effect on the nickel grade and recovery, with recovery increasing with temperature, while the grade decreased again due to the coreduction of the iron. Several of these works also indicate potential kinetic limitations at temperatures below 600 °C. There is a paucity of information available in the literature regarding reduction by methane. Mohanty et al. (2008) performed a thermodynamic study of the feasibility of employing methane as a reducing gas, emphasizing its potential as a low cost alternative to hydrogen. The authors reported high conversions of nickel oxide to nickel from 600 to 800 °C, which were similar to that for an equivalent amount of carbon monoxide. The nickel grade in the ferronickel was not reported.

1.3. Previous experimental studies

Several previous works have examined the selective reduction of a laterite ore or similar material by coal, carbon monoxide or hydrogen (Antola et al., 1995; Cores et al., 1989; De Graaf, 1979; Díaz et al., 2015; Itao and Anacleto, 2011; Kawahara et al., 1988; Li, 1999; Utigard and Bergman, 1992; Utigard et al., 2005; Valix and Cheung, 2002). The findings of these studies have been in general agreement with the available thermodynamic predictions. In all cases, nickel was only present as part of a ferronickel alloy in the reduced ore, and increased temperature and reductant to oxide ratios improved nickel recovery but decreased grade. It is worth noting that the majority of these experimental works were conducted on saprolitic ores, while the majority of thermodynamic studies have been performed on the limonitic ores, which are simpler to model. Additionally, it has been recommended that the saprolitic and limonitic ores be treated separately, as the mineralogy of the saprolite requires higher reduction temperatures (Valix and Cheung, 2002). As with the thermodynamic studies, only limited work has been conducted on the reduction of laterites by methane gas.

Rashidi et al. (2013) performed a thermogravimetric study of the reduction of nickel oxide by methane gas in the temperature range of 600–750 °C. As expected from thermodynamic predictions, both an increased CH_4 to Ar ratio in the gas atmosphere and an increased reduction temperature resulted in an increased rate of reaction. A reduction atmosphere containing 20% methane and a reduction temperature of 660 °C was sufficient to achieve complete reduction of the nickel oxide in about fifteen minutes. The researchers also note that this reaction produces a valuable gas by-product (a blend of H_2 and CO), which may be suitable as a raw material for the synthesis of various hydrocarbons. If the reduction behavior of methane is sufficiently similar to hydrogen and carbon monoxide, Rashidi et al. (2013) suggested that the sale of this by-product combined with the relative cost of reductants could make methane an economically attractive option.

Some experimental work has also been conducted on the reduction of other metal oxides by methane, and by hydrogen-enriched methane. Khoshandam et al. (2004) studied the reduction of cobalt oxide by methane gas and observed deposition of solid carbon, which inhibits diffusion. This issue has also been noted by researchers working with carbon monoxide (Antola et al., 1995; Valix and Cheung, 2002). Ostrovski and Zhang (2006) studied the reduction of several metal oxides, including those of iron, by various methane, hydrogen and argon mixtures. The authors again noted the issue of carbon deposition with increasing reaction time.

1.4. Equilibrium considerations

The garnierite in the saprolitic ore will undergo dehydroxylation at temperatures between 550 and 650 °C as follows (Bunjaku et al., 2010):

$$(Mg,Fe,Ni)_3Si_2O_5(OH)_4 \rightarrow (Mg,Fe,Ni)SiO_3 + (Mg,Fe,Ni)_2SiO_4 + 2H_2O \tag{3}$$

The dehydroxylation of the saprolitic ore results in the formation of both pyroxene ($(Mg,Fe,Ni)SiO_3$) and olivine ($(Mg,Fe,Ni)_2SiO_4$). Once the crystalline water has been removed from the ore, then the reduction of the nickel oxide to metallic nickel can be achieved. The reactions for the reduction of the nickel oxide by methane in both olivine and pyroxene are as follows:

$$4NiSiO_3 + CH_{4(g)} \rightarrow 4Ni + 4SiO_2 + CO_{2(g)} + 2H_2O_{(g)} \tag{4}$$

$$2Ni_2SiO_4 + CH_{4(g)} \rightarrow 4Ni + 2SiO_2 + CO_{2(g)} + 2H_2O_{(g)} \tag{5}$$

Some iron oxide will also be reduced and a ferronickel alloy will be formed. For example, the reduction of the iron silicates, such as fayalite (Fe_2SiO_4), can be represented as follows:

$$2Fe_2SiO_4 + CH_{4(g)} \rightarrow 4Fe + 2SiO_2 + CO_{2(g)} + 2H_2O_{(g)} \tag{6}$$

However, this process requires elevated temperatures and increased reduction potentials. The decomposition of methane into carbon and hydrogen as well as the production of carbon monoxide in an actual reduction process leads to the majority of the metal oxides being reduced via these reducing agents. Carbon, hydrogen or carbon monoxide will reduce the hematite (Fe_2O_3) in the dehydroxylated ore to produce magnetite (Fe_3O_4). Under sufficiently reducing conditions, magnetite can be further reduced to wüstite (FeO) and metallic iron (Fe). This process is described by the following reactions: