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CH₄-UTILIZATION AND CO₂-MITIGATION IN THE METALLURGICAL INDUSTRY VIA SOLAR THERMOCHEMISTRY

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Abstract- The industrial production of metals by carbothermic reduction of their oxides are high-temperature energy-intensive processes that release vast amounts of greenhouse gases and other pollutants to the atmosphere. A thermodynamic analysis and related experimental studies indicate the technical feasibility of reducing these emissions by combining the reduction of metal oxides with the reforming of natural gas for the co-production of metals and synthesis gas (as feed stock for methanol processing). Replacing fossil fuels with solar energy as the source of process heat further reduces CO₂ emissions to zero, and upgrades the calorific value of the products.

INTRODUCTION

About 50% of the world's total annual anthropogenic CO₂ emissions results from the combustion of fossil fuels for heat generation [1]. The extractive metallurgical industry is a major consumer of high-temperature process heat. Industrially, metals are extracted from their oxides ores either electrolytically, e.g. the Hall-Héroult process for aluminum production, or thermochemically, e.g. blast furnaces for iron production. In either case, an amount of energy equal to the Gibbs free energy change of the reaction, ΔG , has to be supplied as *high-quality* energy, for example in the form of electrical work in electrolytic processes, or in the form of chemical energy by introducing a reducing agent in thermochemical processes. The remainder of the required energy, $\Delta H - \Delta G$, may be supplied as *low-quality* energy in the form of heat, which has a lower exergy than electrical or chemical energy. However, in many commercial electrolytic processes and reducing furnaces, electrical and/or chemical energy are frequently used in excess of ΔG in order to supply for the process heat. The combustion of fossil fuels for supplying electricity or process heat to the extractive

metallurgy releases vast amount of contaminants to the environment. Iron production in blast furnaces is among the most intensive and concentrated anthropogenic sources of CO₂ pollution, with emissions at a rate of 2.2 kg of CO₂ per kg of steel produced [2]. Aluminum smelting also results in large CO₂ gas emissions from the production of fossil-fuel-generated electricity consumed during electrolysis (theoretically, 6.25 kWh per kg aluminum [3]) and from the combustion of the consumable carbon electrodes, with an estimated discharge of 22 kg of CO₂ per kg of aluminum [4]. Magnesium produced by electrolytic reduction of magnesium chloride is said to consume 40% more energy per unit weight of metal as compared to the aluminum production, ranging from 10-20 kWh per kg magnesium [5]. Assuming 0.9 kg CO₂ emitted per kWh for coal-fired electricity [1], that would translate to about 15 kg CO₂ emitted per kg magnesium produced. The production of zinc, which requires about 14 kWh per kg zinc when produced electrolytically, or 0.8 kg coke per kg zinc when produced carbothermally [6], has also high levels of CO₂ emissions. Considering the annual world production of iron, aluminum, magnesium, zinc, and other metals, the extractive metallurgical industry is responsible for approximately 10% of the annual global anthropogenic CO₂ emissions to the atmosphere [2,3]

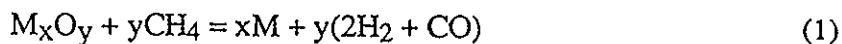
The amount of fuel needed to reduce metal oxides to metals could be substantially reduced if it were used exclusively as a reducing agent and process heat were supplied by an alternative clean energy source, e.g. solar energy, thus minimizing the build-up of greenhouse-effect gases and pollutants.

Solar Energy as High-Temperature Process Heat

The sun is equivalent to a 5800K heat reservoir. By concentrating the sunlight that reaches the earth and capturing that radiative energy in solar receivers, we can provide high-temperature process heat to drive endothermic reactions. The reduction of metal oxides, being high-temperature, energy-intensive reactions, are attractive candidates for solar thermochemical applications. Examples of metal oxides reduction processes that have been experimentally studied in solar furnaces include the production of Fe, Al, Mg, Zn, TiC, SiC, CaC₂, TiN, Si₃N₄, and AlN by carbothermic reduction of their oxides in Ar or N₂ atmospheres [7-12], high-temperature electrolysis of ZnO and MgO [13-15], and the thermal decomposition of Fe₃O₄, Mn₃O₄, and other oxides [16-18].

Natural Gas as Reducing Agent

Carbothermic reduction processes make use of coke as the reducing agent and release CO₂, which is inherently derived from the chemical transformation. In contrast, the use of natural gas as the reducing agent of metal oxides has some intriguing advantages with respect to the gaseous products. Methane, the chief constituent of natural gas, can undergo catalytic partial oxidation to form synthesis gas (syngas, a mixture of primarily H₂ and CO), widely utilized in the chemical industry as feedstock for the direct production of methanol and other important organic chemicals. Most syngas is produced from natural gas using steam as the oxidant [19]. Alternatively, one can use a metal oxide as the donor of oxygen. This approach is formally equivalent to combining two processes, viz., the methane reforming to produce syngas, and the metal oxide reduction to produce the metal, into a single reaction, by reducing the metal oxide with CH₄. The overall stoichiometric reaction can be represented as:



where M denotes the metal, and M_xO_y the corresponding metal oxide. The products of this reaction, when brought to ambient conditions, consist of the metal in the condensed phase and a 2:1 mixture of H₂ and CO in the gas phase. The advantages would be threefold: 1) the reforming of methane, in the absence of catalysts and with proper optimization, may be made to produce high quality syngas suitable for methanol synthesis; 2) the evolved gases are sufficiently valuable commodities to justify their collection, eliminating inherent gas emissions to the environment; 3) the integration of the metal oxide reduction and the natural gas reforming into a single reactor could improve energy efficiencies through concurrent high-temperature reactions.

Metal and Methanol as Final Products

The potential for CO₂ mitigation by the combined reduction/reforming process is illustrated in Fig. 1, where only the CO₂ inherent in the stoichiometric chemical reactions is considered. The desired final products are the metal and methanol. These two important industrial commodities are conventionally produced by two independent processes: the metal is assumed to be obtained by the carbothermic reduction of its metal oxide, while methanol is assumed to be derived from synthesis gas obtained by the partial oxidation of methane. The CO₂ evolved from the overall chemical transformations is depicted in the upper box diagram. It shows that the carbothermic reduction of 1 mole of M_xO_y releases $y/2$ moles of CO₂, whereas the combustion of y moles of methanol releases y moles of CO₂. The total CO₂ contribution from these 2 *independent* processes is 1.5 y moles of CO₂ emitted per mole of M_xO_y reduced and per y moles of methanol produced. In contrast, the lower box diagram shows instead that, for the proposed combined process, only y moles of CO₂ are emitted per mole of M_xO_y reduced and per y moles of methanol produced. The CO₂ emissions of this combined process are, in the thermodynamic limit, only those resulting from the combustion of the methanol produced. This corresponds to a saving of 33% of the total CO₂ emissions for obtaining the same amount of desired final products. By this combined process, the $y/2$ moles of CO₂ derived from the carbothermic reduction of 1 mole of M_xO_y have been avoided. For example, if the reduction of Fe₂O₃ were to be combined with the reforming of methane, 3/2 moles of CO₂ per mole of Fe₂O₃ reduced could be avoided. For the reduction of ZnO or MgO with methane, 1/2 moles of CO₂ per mole of Zn or Mg produced could be avoided. By combining the CO₂-emitting reduction process with the CO₂-consuming reforming process, one can avoid the CO₂ emissions of the classic carbothermic reduction of metal oxides [20].

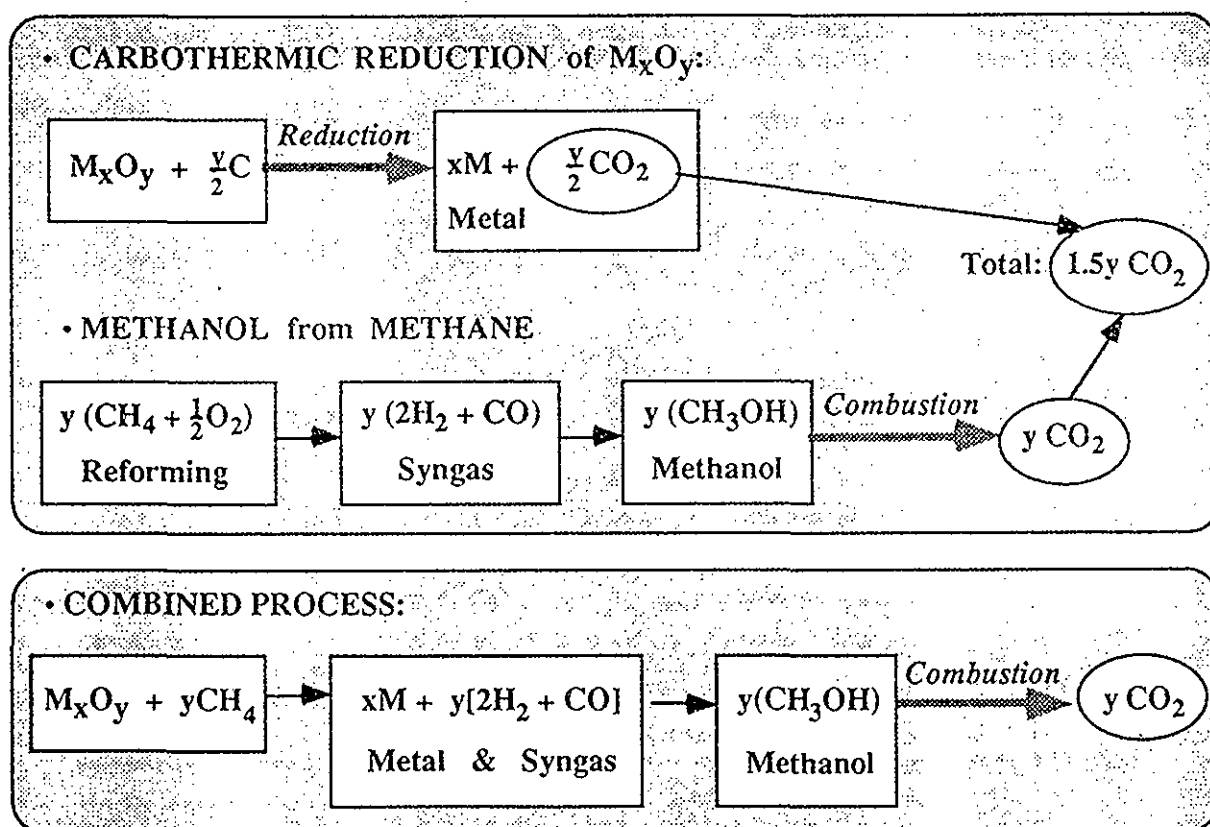


Fig. 1: CO₂ mitigation potential by the combined M_xO_y-reduction/CH₄-reforming process for producing metal M and methanol. Only the CO₂ derived from the stoichiometric chemical transformations is considered. The CO₂ emitted by the combustion of fuels for supplying the process heats is excluded.

The CO₂ mass balance of Fig. 1 only considers CO₂ derived from the chemical transformations, but it does not include the CO₂ emitted from the combustion of fuels which are needed for supplying the process heats for the endothermic reactions. The production of synthesis gas by reforming of natural

gas is also a major consumer of industrial process heat, and consequently a major contributor of anthropogenic CO₂ emissions. Replacing fossil fuels for solar energy as the source of process heat for conducting reaction (1) offers the possibility of simultaneously producing metals and synthesis gas without discharging CO₂ to the atmosphere. But aside from having value as a fluid fuel commodity, synthesis gas stores solar energy. The reverse, methanation, reaction proceeds catalytically in the 650-900K range. The amount of solar energy stored in reaction (1) is about the same as the heating value of the methane involved in this reaction, the exact value depending on the metal oxide reduced. Thus, driving reaction (1) by burning methane instead of using solar energy would about double the methane consumption. In the proposed process, methane is to be used only as a reducing agent. The use of solar energy to heat up the reactants from ambient temperature to the operating temperature and to provide for the ΔH would eliminate the cost of fuel consumption as well as the cost of removal and disposal of harmful pollutants. It adds, however, investment costs for the solar energy collecting systems.

THERMODYNAMICS

The thermodynamics of the system $M_xO_y + yCH_4$ have been analysed for various metal oxide/metal systems of practical interest, namely: Fe₃O₄/Fe, ZnO/Zn, MgO/Mg, SiO₂/Si, Al₂O₃/Al, and TiO₂/Ti [21]. Figure 2 shows the variation of ΔG° of reaction (1) with temperature [22]. The turning temperature, for which the corresponding chemical equilibrium constant equals 1, is about 900K for Fe, 1100K for Zn, 1800K for Mg, 1500K for Si, 1800K for Al, and 1600K for Ti. These temperatures are within the reach of large-scale solar collection facilities, such as central receivers, having concentrations of 1000 suns and higher (1 sun = 1 kW/m²). Calculation of the chemical equilibrium composition indicates that while several reactions have favorable free energies, only the reduction of Fe₃O₄, ZnO, and MgO with methane will result in free metal formation (Fe, Zn, and Mg, respectively). For the other M_xO_y/CH_4 systems examined, the formation of by-products, especially carbides, prevent the presence of the free metal in chemical equilibrium [21].

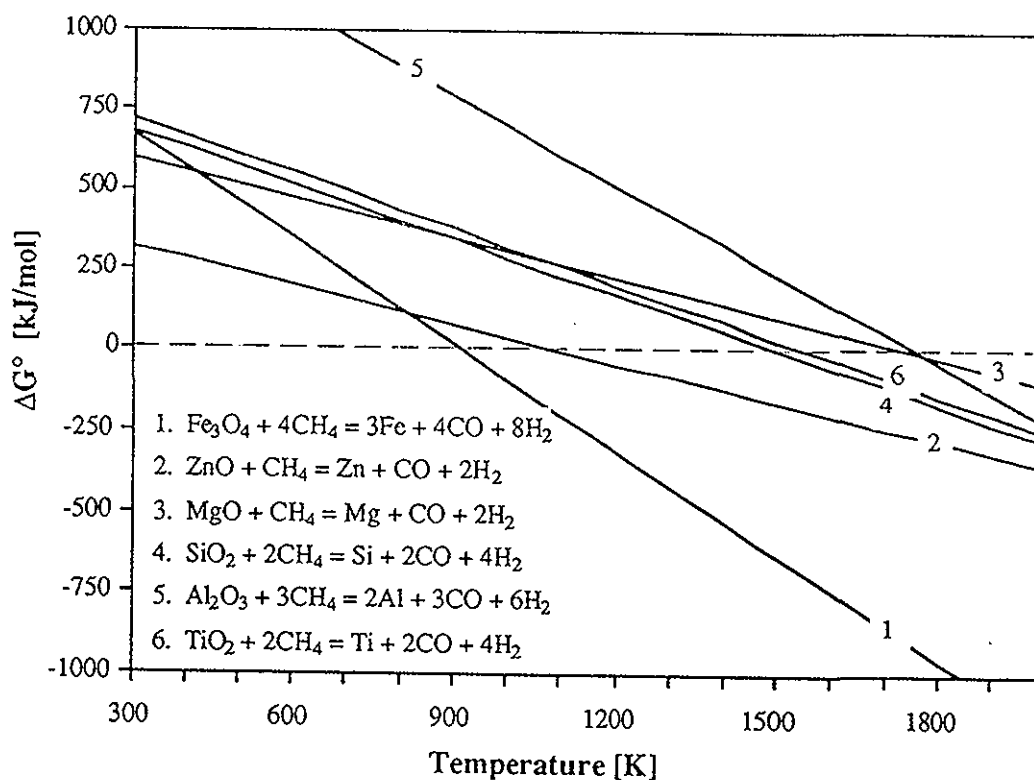


Fig. 2. Variation of ΔG° with temperature for the general reaction: $M_xO_y + yCH_4 = xM + y(2H_2 + CO)$

The kinetics of the reduction of Fe₂O₃, Fe₃O₄ and ZnO with CH₄ have been experimentally investigated in laboratory electric furnaces [23-28]. The Fe₃O₄-CH₄ and ZnO-CH₄ systems have also been demonstrated at The Paul Scherrer Institute solar furnace using concentrated solar radiation [29-30]. The reactions were conducted at 1300 K in a small-scale fluidized bed reactor. Directly

irradiated metal oxides particles, fluidized in methane, acted as energy absorbers, heat transfer, and chemical reactants, providing efficient heat transfer directly to the reaction site. These preliminary experiences indicate that the solar process technology for the proposed processes can be developed.

H₂ / Electricity / Methanol Scheme

A thermochemical scheme for the production of methanol, H₂, and electricity using methane and water as feedstock, solar energy as the source of process heat, and a metal as the energy carrier, is shown in the diagram of Fig. 3 [30]. It consists of two main steps:

- 1) the metal oxide M_xO_y is reduced with CH₄ to form the metal and syngas in the first, endothermic, solar step; syngas (a 2:1 mixture of H₂ and CO) is fed to a conventional methanol producing plant.
- 2a) the metal is reacted with H₂O to form H₂ and M_xO_y in the second, exothermic, step, e.g.,
 water-splitting with iron: $3Fe + 4H_2O = Fe_3O_4 + 4H_2$, $\Delta H^\circ_{700K} = -120 \text{ kJ/mol}$;
 water-splitting with zinc: $Zn + H_2O = ZnO + H_2$, $\Delta H^\circ_{700K} = -108 \text{ kJ/mol}$.

Alternatively,

- 2b) the metal is oxidized back to M_xO_y in a metal-based battery to produce electrical work in the second step, e.g., Zn-Air battery: $Zn + 0.5O_2 = ZnO$; $\Delta G^\circ_{298K} = -316 \text{ kJ/mol}$.

In either 2a or 2b case, the metal oxide is recycled to the first step. The advantage of the proposed two-step scheme over the conventional steam reforming of methane lies on the intermediate storage of energy in the metal, as a clean, compact, and transportable solid fuel, and the subsequent flexibility of its utilization to produce either H₂ or electricity. Emissions of CO₂ arising from this thermochemical scheme are only the ones resulting from the combustion of methanol; however, methanol, hydrogen, and electricity are produced with zero-CO₂ emissions.

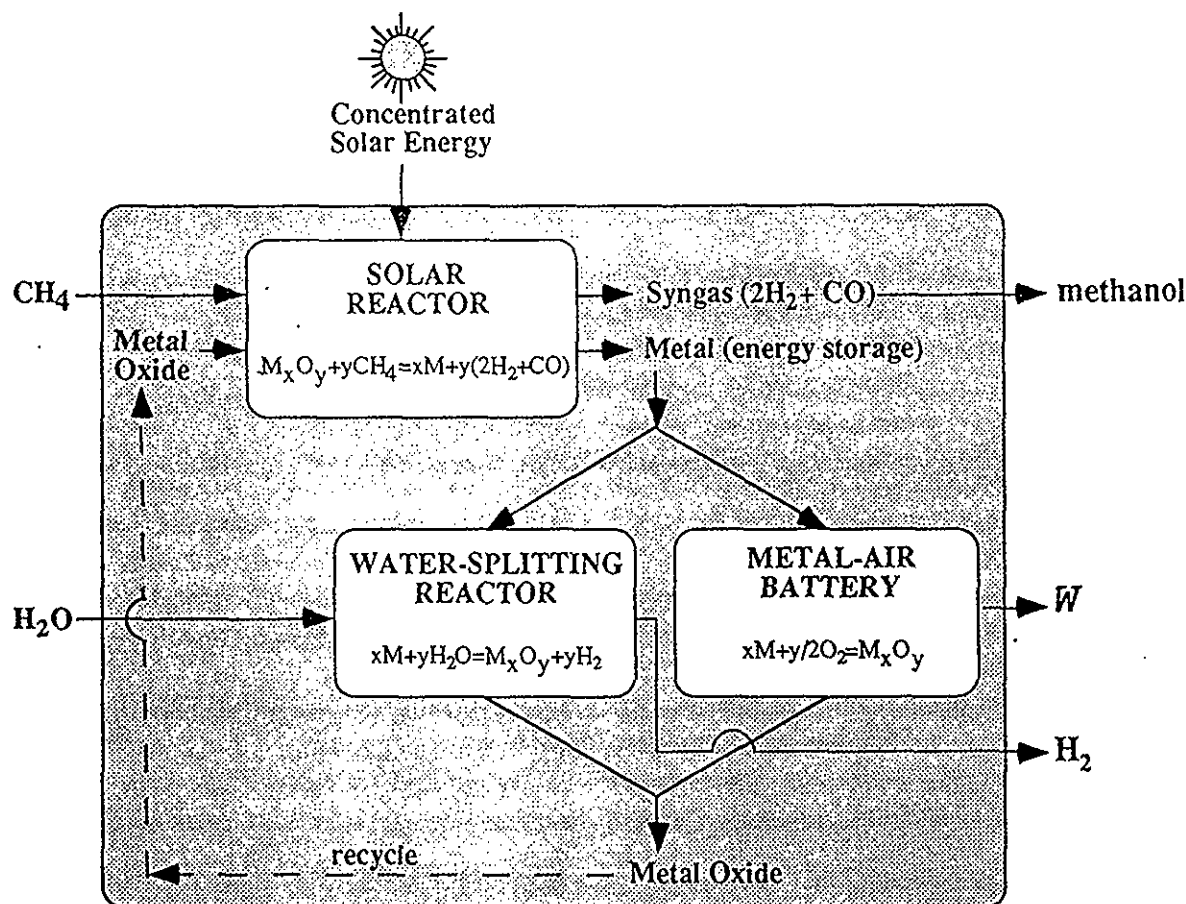


Fig. 3. Representation of a methanol and H₂/electricity producing scheme using methane and water as feedstock, solar energy as the source of process heat, and a metal as the energy carrier [30]. M denotes the metal, M_xO_y denotes the corresponding metal oxide.

CONCLUSION

This paper examined the potential for CO₂-mitigation and CH₄-utilization in the metallurgical industry by combining the reduction of metal oxides with the reforming of natural gas for the co-production of metals and synthesis gas. The CO₂ emissions of this combined process are, in the thermodynamic limit, only those resulting from the combustion of the methanol produced. This corresponds to an emission reduction equal to the amount of CO₂ derived in the classic carbothermic reduction of metal oxides. Further, by supplying solar energy to drive this endothermic process, the CO₂ emissions due to fossil fuel combustion are eliminated. The technical feasibility of conducting these reactions using concentrated solar radiation was demonstrated in solar furnace experiments. A thermochemical scheme for the production of methanol, H₂, and electricity with zero-CO₂ emissions is proposed using methane as feedstock, solar energy as the source of process heat, and a metal as the clean energy carrier.

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