



## HIGH-TEMPERATURE SOLAR THERMOCHEMISTRY FOR CO<sub>2</sub> MITIGATION IN THE EXTRACTIVE METALLURGICAL INDUSTRY

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**Abstract** — The production of metals and synthesis gas are major consumers of high-temperature process heat and are responsible for about 10% of the total global anthropogenic CO<sub>2</sub> emissions to the atmosphere. These emissions can be substantially reduced by combining the reduction of metal oxides with the reforming of natural gas and by replacing fossil fuels with solar energy as the source of process heat.

### INTRODUCTION

Industrially, metals are extracted from their oxidic 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  $\Delta G$  needs to be supplied as *high-quality* energy. This energy is supplied, 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 delivered in the form of heat. However, in many commercial electrolytic processes and reducing furnaces, electricity and/or reducing agents are frequently used in excess of  $\Delta G$  in order to compensate for the process heat.

The extractive metallurgical industry is a major consumer of high-temperature process heat. It is, consequently, a major contributor of CO<sub>2</sub> emissions derived from the combustion of fossil fuels for heat and electricity generation. Table 1 gives an estimate of CO<sub>2</sub> emissions discharged during the production of iron, aluminum, and zinc: column 1 shows the annual world metal production;<sup>1</sup> column 2 shows the annual world CO<sub>2</sub> emissions for iron,<sup>2</sup> aluminum<sup>‡</sup>, and zinc<sup>§</sup>; and column 3 shows the percentage contribution to the world's total anthropogenic CO<sub>2</sub> emissions ( $\approx 20.7 \times 10^{12}$  kg).<sup>5</sup>

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‡ Assuming the use of fossil-fuel-generated electricity and the GWPs of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>.<sup>3</sup>

§ Assumptions: zinc production is 85% by electrolysis and 15% in an imperial smelting furnace (ISF);<sup>4</sup> CO<sub>2</sub> total emissions from electrolysis are estimated assuming 0.87 kg CO<sub>2</sub>/KWh<sub>e</sub> for coal-fired electricity<sup>5</sup> and energy consumption of 50 GJ/ton Zn produced; CO<sub>2</sub> total emissions from ISF assuming carbon consumption of 0.78 ton C/ton Zn produced.<sup>6</sup>

Table 1. Annual world production and corresponding CO<sub>2</sub> emissions for the production of iron, aluminum, zinc, and synthesis gas.<sup>1-6</sup>

	Annual Production [kg]	Annual CO <sub>2</sub> -emission [kg]	% of Total World CO <sub>2</sub> -emission
Iron (Blast Furnace)	$505 \times 10^9$	$1.11 \times 10^{12}$	5.4 % of Total
Aluminium (Hall-Electrolysis)	$14 \times 10^9$	$0.52 \times 10^{12}$	2.5 % of Total
Zinc (Electrolysis + ISF)	$6 \times 10^9$	$0.07 \times 10^{12}$	0.3 % of Total
Synthesis gas (Natural Gas Reforming)	$2 \times 10^{11} \text{ m}^3$	$0.30 \times 10^{12}$	1.4 % of Total

### Carbothermic processes

Coal as coke is a preferred reducing agent in blast-furnace processes because of its availability and relatively low price. However, carbothermic reduction processes usually use coke not only as the reductant but as the primary source of process heat as well. The combustion of coal and other conventional fossil fuels in air releases a great deal of nitrogen contaminated with CO, CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub>, and other pollutants. Carbothermic reductions occurring in commercial blast furnaces are complex, but their overall reaction may be represented by†



For example, for the reduction of hematite, Eq. (1) becomes



If carbon were used exclusively as a reducing agent according to Eq. (2), the stoichiometric mass ratio of carbon consumed to iron produced should be 0.16. In contrast, real blast furnaces use 0.9 ton of coke to produce 1 ton of pig iron and release vast amounts of greenhouse gases and other contaminants. For the carbothermic reduction of zinc oxide, Eq. (1) is



Similarly, if carbon were used only as a reductant according to Eq. (3), the stoichiometric mass ratio of carbon consumed to zinc produced should be 0.09. In contrast, commercial smelting furnaces use 0.8 ton of coke to make 1 ton of zinc while causing concomitant environmental pollution.

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. Concentrated solar radiation can provide the high-temperature process heat required to drive these highly endothermic reactions. Examples of metal oxides reduction processes that have been studied experimentally in solar furnaces include the production of Fe, Al, Mg, Zn, TiC, SiC, CaC<sub>2</sub>, TiN, Si<sub>3</sub>N<sub>4</sub>, and AlN by carbothermic reduction of their oxides in Ar or N<sub>2</sub> atmospheres,<sup>7-11</sup> high-temperature electrolysis of ZnO and MgO,<sup>12,13</sup> and the thermal decomposition of Fe<sub>3</sub>O<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub>, and other oxides.<sup>14-16</sup> An idealisation of a *solar blast furnace* is given in Ref. 7.

† M denotes a metal; M<sub>x</sub>O<sub>y</sub> denotes the corresponding metal oxide.

### Combined $M_xO_y$ -Reduction/ $CH_4$ -Reforming Process

The use of natural gas as reducing agent for metal oxides offers some intriguing advantages with regard to the gaseous products. Methane, the main constituent of natural gas, can undergo partial catalytic oxidation to form synthesis gas (syngas, a mixture of primarily  $H_2$  and  $CO$ ). Syngas is widely utilized in the chemical industry as feedstock for the direct production of methanol and other organic commodity chemicals. Most syngas is obtained from natural gas using steam as the oxidant. Alternatively, one can use a metal oxide as oxygen donor. This approach is formally equivalent to combining two processes, viz., methane reforming to produce syngas and metal-oxide reduction to produce the metal. The overall reaction may be represented as



For example, for  $M = Fe, Zn,$  and  $Mg$ , Eq. (4) becomes



The resulting syngas mixture has a molar ratio of  $H_2$  to  $CO$  equal to 2, which makes it especially suitable for methanol synthesis. Thus, as opposed to carbothermic processes, the evolved gases are sufficiently valuable commodities to justify their collection, thereby eliminating the discharge of gaseous reaction products to the environment.

The chemical equilibrium composition of the system  $M_xO_y + yCH_4$  has been studied for various metal oxides of industrial interest.<sup>17,18</sup> The temperature for which the equilibrium constant equals 1 is 900 K for Eq. (5), 1100 K for Eq. (6), and 1800 K for Eq. (7). These temperatures are within the reach of large-scale solar collection facilities such as central receivers which have concentrations of 1000 suns and more (1 sun =  $1 \text{ kW}/\text{m}^2$ ).<sup>19</sup> Higher concentrations that permit delivery of energy at higher temperatures may be achieved in paraboloidal tracking dishes and by using non-imaging secondary concentrators. The  $CH_4$ -reduction of  $ZnO$  has also been proposed using process heat from gas-cooled nuclear reactors.<sup>20</sup> The kinetics of the reduction of  $Fe_2O_3$ ,  $Fe_3O_4$  and  $ZnO$  with  $CH_4$  have been investigated in laboratory electric furnaces.<sup>21-26</sup> The  $Fe_3O_4$ - $CH_4$  and  $ZnO$ - $CH_4$  reactions have also been studied experimentally at PSI's solar furnace and demonstrated to proceed at 1300 K in a small-scale fluidized bed reactor.<sup>27,28</sup> Directly irradiated metal oxide particles fluidized in methane acted simultaneously as energy absorbers and chemical reactants, thereby providing efficient heat transfer directly to the reaction site. These previous experiences indicate that solar production technologies may be developed for the proposed processes.

### $H_2$ /Electricity/Methanol Production Scheme

In an  $H_2O$ -splitting reaction, the metal is reacted with water at moderate temperatures to regenerate the metal oxide and form molecular  $H_2$  as the only product component in the gas phase, i.e.



For example, the water-splitting reactions with iron, zinc, and magnesium, are



Reactions (9) to (11) are thermodynamically favorable at temperatures below 1000 K. Preliminary experimental studies for iron and zinc have shown that these reactions proceed around 700 K and are exothermic. The heat liberated could be used in an auto-thermal reactor for conducting the water-splitting reaction at temperatures above ambient conditions. Alternatively, the metal may be used to produce electrical work directly in a fuel cell or in a metal-air battery (the reaction in a Zn-air battery is  $Zn + 0.5O_2 = ZnO$ ,  $\Delta G^\circ_{298K} = -316 \text{ kJ}/\text{mol}$ ).

An open process scheme for the production of methanol and H<sub>2</sub>/electricity, using methane and water as feedstock, solar energy as source of process heat, and a metal as energy carrier, is shown in the diagram of Fig. 1.<sup>28</sup> It consists of two main steps. In the first step, the metal oxide is reduced with CH<sub>4</sub> to form the metal and syngas in an endothermic, solar process [Eq. (4)]; syngas is sent to a conventional methanol-producing plant. In the second step, the metal is used to split H<sub>2</sub>O and form H<sub>2</sub> [Eq. (8)] or, alternatively, the metal is used in a metal/air fuel cell (or metal/air battery) to produce electrical work. In either case, the chemical product of the second step is the metal oxide which, in turn, is recycled to the first step. In this scheme, the *solar-made* metal serves as a clean, compact and transportable solid fuel. It may be utilized to produce directly either H<sub>2</sub> or electricity. The only emissions of CO<sub>2</sub> arising from this thermochemical scheme are those resulting from methanol combustion; on the other hand, methanol, hydrogen, and electricity are produced with zero-CO<sub>2</sub> emissions.<sup>†</sup>

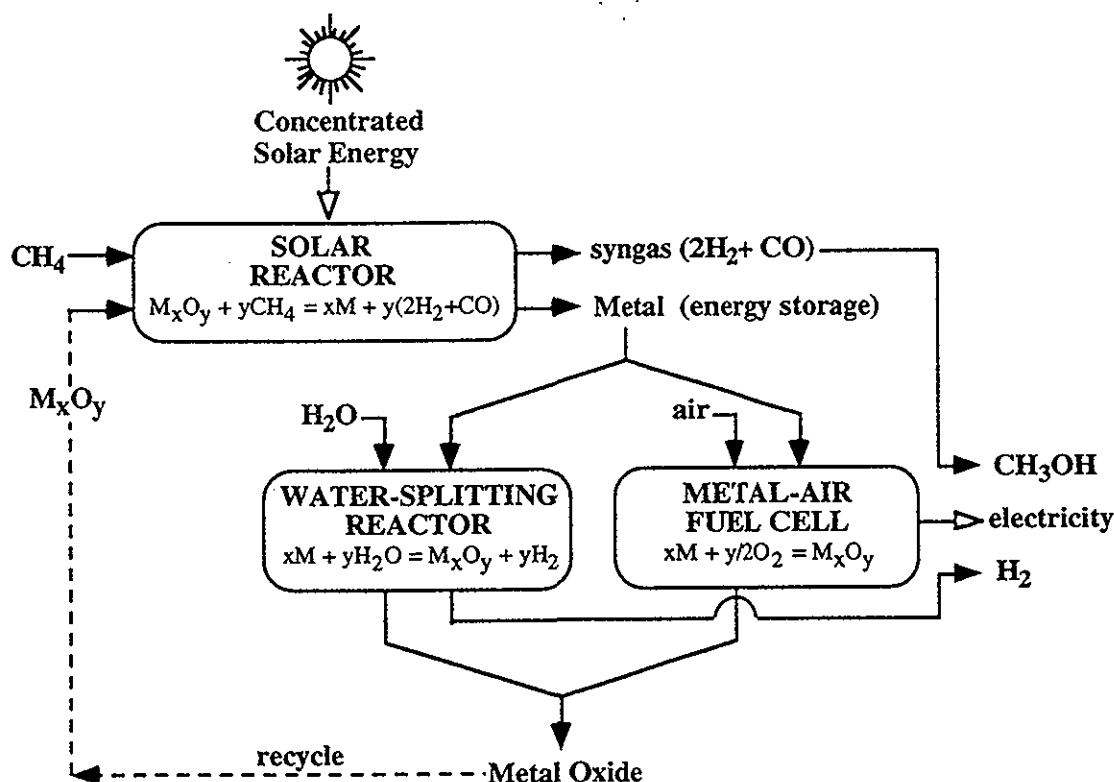


Fig. 1. Schematic of a methanol and H<sub>2</sub>/electricity producing process, using methane and water as feedstock, solar energy as source of process heat, and a metal as energy carrier.<sup>28</sup> *M* denotes a metal, *M<sub>x</sub>O<sub>y</sub>* denotes the corresponding metal oxide.

The potential for CO<sub>2</sub> mitigation by the combined reduction/reforming process is illustrated in Fig. 2, where the reduction of ZnO has been taken as a model.<sup>29</sup> Only the CO<sub>2</sub> involved in the stoichiometric chemical reactions is considered. The desired final products are zinc and methanol. These two important

<sup>†</sup> In this work, the CO<sub>2</sub> mitigation potential that may be achieved on the basis of idealized process steps is demonstrated. Technical realizations might involve additional energy consuming steps, e.g., associated with the recycling of the metal oxide.

industrial commodities are conventionally produced by two independent processes: zinc is assumed to be obtained by the carbothermic reduction of zinc oxide, while methanol is assumed to be derived from synthesis gas obtained by the reforming of methane.

CO<sub>2</sub> evolved from conventional chemical processes is depicted in the upper box diagram. It shows that the carbothermic reduction of ZnO releases 1/2 mole of CO<sub>2</sub> per mole of zinc produced, whereas the combustion of 1 mole of methanol releases 1 mole of CO<sub>2</sub>. The total CO<sub>2</sub> contribution is 1.5 moles of CO<sub>2</sub> emitted per mole of zinc and methanol. In contrast, the lower diagram shows only 1 mole of CO<sub>2</sub> emitted per mole of zinc and methanol produced by the combined ZnO-reduction and CH<sub>4</sub>-reforming process. This change results in saving 33% of total CO<sub>2</sub> emissions while producing the same amounts of desired final products. By using the combined process, the production of 1/2 mole of CO<sub>2</sub> per mole of zinc derived from the carbothermic reduction of ZnO [Eq. (3)] has been avoided. Similarly, if reduction of Fe<sub>2</sub>O<sub>3</sub> is combined with methane reforming, 3/2 moles of CO<sub>2</sub> derived from the carbothermic reduction of 1 mole of Fe<sub>2</sub>O<sub>3</sub> [Eq. (2)] are avoided. In general, if reduction of M<sub>x</sub>O<sub>y</sub> is combined with methane reforming, y/2 moles of CO<sub>2</sub> derived from the carbothermic reduction of 1 mole of M<sub>x</sub>O<sub>y</sub> [Eq. (1)] may be avoided. The only CO<sub>2</sub> emissions of the combined process are those resulting from the combustion of produced methanol. This change corresponds to an emission reduction equal to the amount of CO<sub>2</sub> derived in the classic carbothermic reduction of metal oxides.

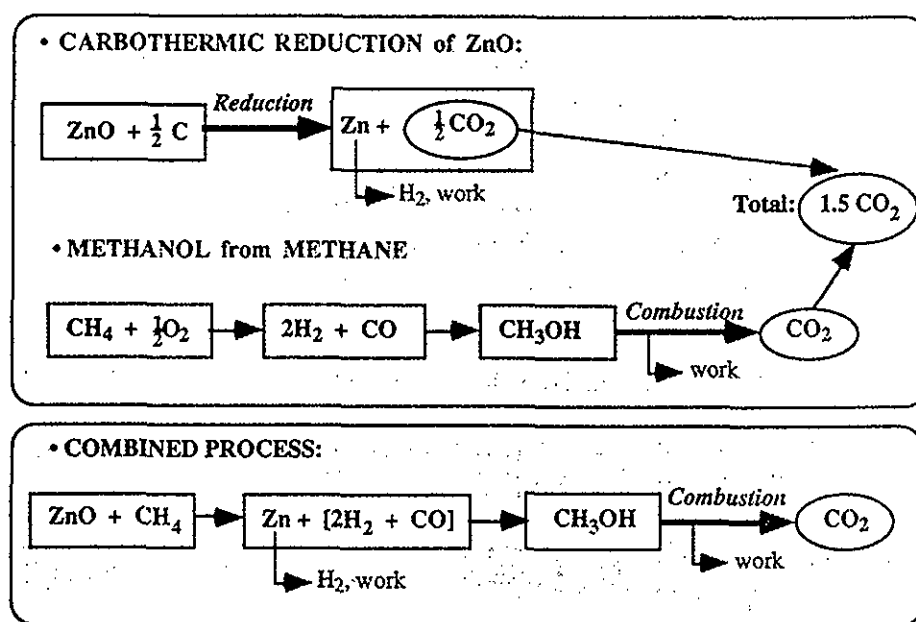


Fig. 2. CO<sub>2</sub> mitigation potential by the combined ZnO-reduction/CH<sub>4</sub>-reforming process for producing zinc and methanol.<sup>29</sup> Only the CO<sub>2</sub> derived from the stoichiometric chemical transformations is considered. The CO<sub>2</sub> emitted by combustion of fuels for supplying process heat is excluded.

The CO<sub>2</sub> mass balance of Fig. 2 allows only for CO<sub>2</sub> derived from chemical transformations. It does not include CO<sub>2</sub> emitted from the combustion of fuels which are needed to supply process heats. The combined M<sub>x</sub>O<sub>y</sub>-reduction/CH<sub>4</sub>-reforming is highly endothermic, as is indicated by ΔH in Eqs. (5-7). For example, if the combustion of natural gas were to be used for supplying process heat to the ZnO-CH<sub>4</sub> reaction, approximately an extra 1/2 mole of CH<sub>4</sub> would be required per mole of CH<sub>4</sub> reformed. The use of solar energy for heating reactants to the operating temperature and providing the ΔH of reaction further eliminates the discharge of greenhouse gases from burning fossil fuels.

### Concluding Remarks

Solar energy is essentially unlimited and its utilization is ecologically benign. It needs, however, to be stored and transported. Solar thermochemical processes provide a pathway for converting solar energy into storable and transportable fuels. Examples of candidate processes are the production of metals by the reduction of metal oxides and the production of syngas by the reforming of natural gas. These are high-temperature energy-intensive processes that contribute about 10% of the total global anthropogenic CO<sub>2</sub> emissions. Our results indicate the possibility of significantly reducing these emissions via a combined M<sub>x</sub>O<sub>y</sub>-reduction/CH<sub>4</sub>-reforming solar process for the simultaneous co-production of metals and syngas.

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