SOLAR RECYCLING OF HAZARDOUS SOLID WASTE MATERIALS

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The thermochemical conversion and recycling of hazardous solid waste materials is investigated using high-temperature solar process heat. Electric arc furnace dust (EAFD), an important source of waste contaminated with heavy metals, is being considered. The chemical equilibrium composition and the energy required to process it, using carbon as reducing agent, is computed for temperatures in the range 300–2000 K. Zinc, lead and iron can be extracted from their oxides in reducing atmospheres at above 1300 K. The thermal energy requirement for converting EAFD at 1500 K is 3000 kJ/kg, and the solar exergy conversion efficiency can be as high as 67%. Major sources of irreversibilities are those associated with the re-radiation losses of the solar reactor and the heat rejected during the quenching. The use of concentrated solar energy as the source of process heat avoids emissions of greenhouse gases and other pollutants derived from the combustion of fossil fuels, and further offers the possibility of converting waste materials into valuable commodities for processes in closed and sustainable materials cycles.

1 INTRODUCTION

Solid waste materials such as by-products from the metallurgical industry contain hazardous compounds that cannot be discharged to the environment. They are usually disposed of in hazardous waste storage and landfill sites, where they need to be continuously monitored [1]. The chemical transformation of these materials into elemental components offers the possibility of converting waste materials into valuable feedstock for processes in closed materials cycles [2]. The current commercial thermal recycling techniques are major consumers of electricity and high-temperature process heat and, consequently, major contributors of greenhouse gas emissions and other pollutants [3]. Concentrated solar radiation can supply clean thermal energy at temperatures exceeding 1500 K for driving these endothermic processes. Greenhouse gases and other pollutants derived from the combustion of fossil fuels are avoided, and the chemical products can be used as fuels with a solar-upgraded energetic value.

We present a thermodynamic study of the recycling process of EAFD, to assist the solar reactor engineering design [4]. Chemical equilibrium compositions are computed over a wide range of temperatures for the carbothermal reduction process. A 2nd law analysis is conducted to determine the maximum solar exergy conversion efficiency and to identify sources of irreversibility. This information determines the constrains to be imposed on the design and operation of the solar chemical reactor.

2 CHEMICAL THERMODYNAMICS

The carbothermal reduction of metal oxides (using C(gr) as reducing agent), is a complex process but the overall reactions can be represented by:

$$M_xO_y + y\,C(gr) = xM + yCO \qquad (1)$$
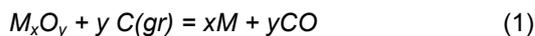
where M denotes the metal and M_xO_y the corresponding metal oxide. The chemical equilibrium composition for representative species compositions of EAFD was computed over the temperature range 300-2000 K using the code HSC Outokumpu [4]. Results are given in Figure 1. Species with less than 10^{-5} moles have been omitted from the graph.

Reactants: 3.46 mol ZnO, 0.91 mol $ZnFe_2O_4$, 0.12 mol Pb_3O_4, 7.56 mol C (reducing agent), 5.45 mol SiO_2 (main vitrification agent).
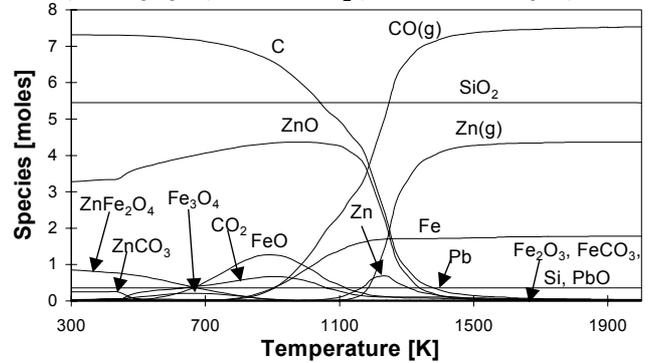

Fig. 1: Chemical equilibrium composition for the carbothermal reduction of EAFD.

3 2ND LAW ANALYSIS: SOLAR EXERGY CONVERSION EFFICIENCY

Solar chemical reactors for highly concentrated solar systems usually feature the use of a cavity-receiver type configuration. For a perfectly insulated blackbody cavity-receiver (no convection or conduction heat losses), the solar energy absorption efficiency of a solar reactor, $\eta_{absorption}$ is given by [5, 6]:

$$\eta_{absorption} = 1 - \left(\frac{\sigma T^4}{IC}\right) \qquad (2)$$

where I is normal beam insolation, C is the flux concentration ratio of the solar concentrating system, T is the nominal cavity-receiver temperature, and σ is the Stefan-Boltzmann constant. Since the net energy absorbed should match the enthalpy change of the reaction, the total solar energy required is

$$Q_{solar} = \frac{\Delta H_{rxn}}{\eta_{absorption}} \qquad (3)$$

The measure of how well the solar energy can be converted into chemical energy for the process is the

solar exergy efficiency, η_{exergy}, defined as

$$\eta_{exergy} = \frac{-\Delta G_{fuel\,cell}}{Q_{reactants} + Q_{solar}} \qquad (4)$$

where $Q_{reactants}$ is the heating value of the reactants, Q_{solar} is the total solar energy input given by Eq. (3), and $\Delta G_{fuel\text{-}cell}$ is the maximum possible amount of work that may be extracted from the products at ambient temperature. An ideal cyclic process (Figure 2) uses a solar reactor (assumed to be a perfect blackbody cavity-receiver), a quenching device, and a fuel cell.
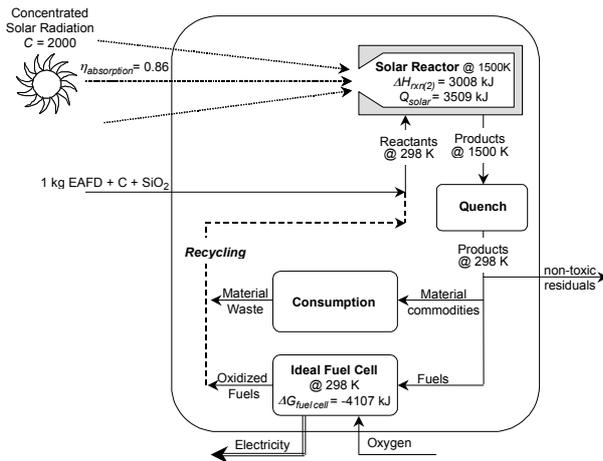

Fig. 2: Schematic of an ideal cyclic process for the solar carbothermal reduction of EAFD. Concentrated solar energy (solar flux concentration ratio = 2000) is the source of high-temperature process heat.

Table 1 is a numerical description of the components shown in Figure 2 for the solar flux concentration ratios 2000 and 5000.

$Q_{reactants}$ (heating value of reactants)		2975 kJ
Fuels in products		C, CO, Zn, Fe, Pb
$\Delta G_{fuel\,cell}$ (exergy of products)		-4107 kJ
ΔH_{rxn}		3008 kJ
$\eta_{absorption}$	$C = 2000$	0.857
	$C = 5000$	0.943
Q_{solar}	$C = 2000$	3509 kJ
	$C = 5000$	3189 kJ
η_{exergy}	$C = 2000$	0.63
	$C = 5000$	0.67

Table 1: Exergy efficiency for the solar carbothermal recycling of EAFD using the chemical compositions of Figure 1. The parameter is the solar flux concentration ratio, assumed to be 2000 and 5000. All values are normalized for 1 kg reactants.

The complete process is carried out at constant pressure. The reactants enter the solar reactor at 298 K and are heated to the reactor temperature at 1500 K. The products exit the reactor having the chemical equilibrium composition at 1500 K given in Figure 1. After quenching to 298 K, the fuels contained in the products are sent to an ideal fuel cell for calculating the exergy of the products, $\Delta G_{fuel\text{-}cell}$. Oxidized solid fuels and waste materials from consumer goods are recycled to the solar reactor. The energy demand for the transformation is 3008 kJ/kg, if the reactants are fed at 298 K and the products are obtained at 1500 K with the equilibrium composition of Figure 1.

For a solar concentration varying in the range 2000 to 5000, maximum exergy efficiencies vary between 63 and 67%. Major sources of irreversibilities are those associated with the re-radiation losses of the solar reactor and the heat rejected during the quenching. High efficiencies directly translate to lower solar collection area and associated costs of the heliostat field, which amount to 40-50% of the capital cost for the solar recycling plant. In general, it can be stated that the solar thermal technology for the recycling of highly contaminated waste materials is a favorable medium to long term prospect provided the cost of energy will account for the environmental externalities from fossil fuel burning such as the costs for CO_2 mitigation and other pollution abatement measures.

4   ACKNOWLEDGEMENT

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