Energy 135 (2017) 182-194

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Technical and economic evaluation of a solar thermal MgO electrolysis process for magnesium production



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M. Korenko ^{a, c}, C. Larson ^a, K. Blood ^a, R. Palumbo ^a, S. Nudehi ^a, R. Diver ^b, D. Blood ^a, F. Šimko ^c, L.J. Venstrom ^{a, *}

^a Valparaiso University, 1900 Chapel Drive, Valparaiso, IN, 46 383, USA

^b Diver Solar LLC, 1112 Monte Largo NE, Albuquerque, NM, 87 123, USA

^c Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravska Cesta 9, Bratislava, 845 36, Slovakia

ARTICLE INFO

Article history: Received 1 February 2017 Received in revised form 3 May 2017 Accepted 8 June 2017 Available online 9 June 2017

Keywords: Thermal electrolytic process Magnesium electrolysis Solar thermal chemistry Economics Sodium heat pipes Molten salts

ABSTRACT

We present a techno-economic analysis of a 17,000–18,000 metric tons per year electrolytic process for producing Mg from MgO with and without out a concentrated solar thermal input. The solar thermal input is delivered via power tower technology and the evaporation and condensation of sodium. Energy requirements for the process at scale were based on thermodynamics and an extrapolation of laboratory measurements of the electrochemical kinetic and mass transport parameters via a finite-element numerical model. While technically possible, integrating a solar thermal input reduces energy operational costs from \$0.654/kg to as low as \$0.481/kg, but it also lowers the Mg production rate of the electrolytic cells such that more cells are required to achieve production capacity, which, in turn, increases capital and maintenance costs. The net operational savings are negligible. The estimated operational costs to produce Mg are ~\$2.46/kg. At this cost, the process without a solar thermal input is economically tantalizing vis à vis the current commercial processes for producing Mg, and its CO₂ emission level is 46% lower than that of the Pidgeon process, currently the predominant method for producing Mg.

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1. Introduction

1.1. The global context

Magnesium is an important commodity, particularly as an alloy for aluminum in the die-cast industry and as a lightweight alternative to steel in the automobile industry. It is also energy intensive to produce and results in the release of substantial amounts of carbon dioxide. When produced with the predominant hightemperature, low-pressure, ferrosilicon-based thermal reduction processes, magnesium requires at least 133 MJ/kg of energy to produce and releases 26 kg-CO₂/kg [1]. In comparison, the production of 1 kg of steel requires less than 36 MJ and releases less than 3 kg-CO₂ [2]. If Mg is to be a path to lightweight, fuel-efficient vehicles, a more environmentally friendly and energy efficient process to produce magnesium is highly desirable.

The electrolysis of magnesium oxide using concentrated solar

* Corresponding author. E-mail address: Luke.Venstrom@valpo.edu (LJ. Venstrom). thermal energy is such a process [3]. Magnesium is produced between 1200 and 1300 K by the following electrochemical reaction:

 $MgO(diss) + 0.5C(s) \rightarrow Mg(l) + 0.5CO_2(g)$ (1)

The feedstock MgO is dissolved (diss) in a molten fluoride salt (eutectic mixture of $MgF_2 - CaF_2$) and electrolyzed to liquid Mg(l) and gaseous $CO_2(g)$. The Mg(l) forms at a cathode and the $CO_2(g)$ forms at a consumable solid carbon anode C(s).

The electrolysis of MgO combines the best features of the two conventional production routes for magnesium: the MgO feedstock from the thermal reduction processes and the use of electrolysis from the MgCl₂ processes. The MgO feedstock is relatively easy to obtain by calcination of abundant ores such as dolomite and avoids the costly and complicated processing required to produce MgCl₂. Electrolysis is inherently energy efficient, operates at atmospheric pressure, and requires lower temperatures than thermal reduction processes. The result is greater energy efficiency and reduced emissions. Emissions can be further reduced with the integration of solar thermal energy.



Thermodynamics points to the promise of the process. The 1st and 2nd laws of thermodynamics give the energy requirements for the production of magnesium from magnesium oxide with carbon as a reactant (Fig. 1). The total energy required is the enthalpy of the process (ΔH_{rxn}), which includes the energy required to heat the reactants to the process temperature from 298 K, drive the reaction, and flash vaporize the liquid magnesium as a means of recovering it outside of the cell. Only a portion of the total energy, an amount equal to the change in the Gibbs free energy (ΔG_{rxn}), must be supplied as electric work. The remaining energy may be supplied in the form of process heat. Figure 1 illustrates that as the temperature of the reaction increases, one can substitute more and more thermal energy for valuable electric work. Under ideal conditions the thermal input at 1250 K is near 50% of the total energy required. To our knowledge, no industrial electrolysis process takes advantage of this thermodynamic fact. Rather, all of the required energy is supplied as electric work. From a thermodynamics perspective, the substitution makes sense: electric work is more valuable than process heat. We envision supplying the thermal energy with concentrated sunlight in order to avoid fuel costs and reduce operating expenses.

Although thermodynamics suggests the process has industrial potential, it is not enough to proclaim it as industrially viable. From a scientific perspective, one needs to consider the transport processes, which reduce the amount of thermal energy that may be substituted for electric energy (the overvoltage in Fig. 1). From an engineering perspective, one also needs a means of delivering concentrated solar energy at the top of a solar power tower to an electrolytic plant that, by its sheer size, dictates it being on the ground. From a commercial perspective, one needs to consider the cost of producing the metal and the cost of building the associated equipment. In this article, we address these concerns and we assess the industrial viability of the electrolysis of MgO process with and without a solar thermal input.

1.2. Review of the literature

The pioneering idea to produce valuable commodities like Mg, Zn, and H₂ in a high temperature solar thermal electrolytic process was first articulated by Professor Edward A. Fletcher from the University of Minnesota in the early 1980's. References [4–7] provide samples of this literature. In them he argued from a thermodynamic perspective that it made sense to investigate the use of high temperature solar process heat as a substitute for valuable electric work. We agreed with his premise that electric work is more valuable than process heat, and that it is thus worth probing whether a solar thermal electrolytic process for the production of metals from their oxides could be economically viable. In this study we focus on the Mg from MgO process. Our results will thus be specific to a particular industrial process, but our method of analysis may serve as a template for answering the economic question for other processes.

Our study adds to the literature in several important ways. Firstly we conduct a techno-economic analysis of a 17,000–18,000 metric ton per year Mg from MgO electrolytic plant. Secondly, the techno-economic analysis is based not only on thermodynamic arguments, but includes the impact of electrochemical cell kinetics and mass transfer on cell performance. In previous articles, we published a fundamental study in which we established the kinetics of the electrochemical reactions, the diffusion coefficients of the electroactive species, the ionic conductivity of the electrolyte and the solubility of MgO in the electrolyte [3,8]. In this study we present a finite-element model of the cell that quantifies how these transport properties force the electrical energy required for a

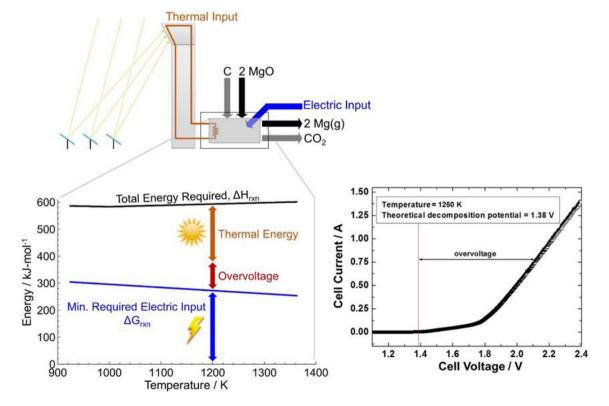


Fig. 1. Schematic showing the concept of the process: driving the electrochemical reaction with a thermal and electrical input. The thermal input is maximized by minimizing the overvoltage. Both reactants start at 298 K. Also shown is current as a function of cell potential; Electrolyte: $(MgF_2 - CaF_2)_{EUT} - MgO(sat)$, cathode: Mo, anode: graphite. The overvoltage is defined as the voltage difference between a data point and the vertical line at 1.38 V.

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