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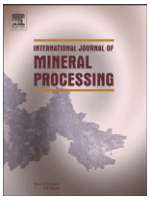

A feasibility study of carbochlorination of chrysotile tailings

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A B S T R A C T

This study examines the production of $MgCl_2$ from raw chrysotile tailings. The tailings were exposed to a dry carbochlorination reaction in a non-rotating oven. The effects of temperature, gas flow rate and time on the recovery of various cations were examined. Our results show that temperature is the determining factor for both the recovery of Mg (85%) and for limiting impurities. Reaction time can also be reduced to 30 min without affecting $MgCl_2$ recovery. Filtration trials during the carbochlorination reaction allow us to conclude that the main product is $MgCl_2$.

1. Introduction

The carbochlorination reaction is a process through which metallic chlorides are obtained in dry conditions and in the presence of a carbonaceous material (Habashi, 2002). Metal recovery from particularly refractory oxides such as MoO_3 or Nb_2O_5 (Ojeda et al., 2002) is possible and can be done at temperatures lower than those needed for direct chlorination. The rate of the reaction of carbochlorination is also faster than chlorination reactions at an equivalent temperature (Korshunov, 1992). The carbon, by providing an atmosphere with a low oxygen potential, reduces the propensity towards the formation of oxides and favours the formation of chlorides (Gamboa et al., 1999; Esquivel et al., 2003).

Magnesium oxide is present in high concentration in naturally occurring silicate minerals such as serpentine. Chrysotile fibers have been extracted from serpentinite in the Province of Quebec (Canada) since 1878. Chrysotile tailings, with almost 1.2 billion tons in open air tailing mounds (Huot et al., 2003), represent a rich source of industrially important metals and most notably magnesium.

The carbochlorination of natural silicate minerals is an interesting alternative for the production of magnesium chloride (Kanari et al., 1998):

$$Mg_3Si_2O_5(OH)_4 + 7Cl_2 + 7CO \rightarrow 3MgCl_2 + 2SiCl_4 + 2H_2O + 7CO_2 \qquad (1)$$

The comparison of Gibbs standard free energies (ΔG^0) of carbochlorination and chlorination reaction for $Mg_3Si_2O_5(OH)_4$, MgO and $Mg(OH)_2$ using the software package HSC 5.1 (Roine, 2002) is presented on Fig. 1.

$$MgO + Cl_2 + CO \rightarrow MgCl_2 + CO_2 \qquad (2)$$

$$Mg(OH)_2 + Cl_2 + CO \rightarrow MgCl_2 + H_2O + CO_2 \qquad (3)$$

$$Mg_3Si_2O_5(OH)_4 + 7Cl_2 \rightarrow 3MgCl_2 + 2SiCl_4 + 2H_2O + 3.5O_2 \qquad (4)$$

$$2MgO + 2Cl_2 \rightarrow 2MgCl_2 + O_2 \qquad (5)$$

$$2Mg(OH)_2 + 2Cl_2 \rightarrow 2MgCl_2 + 2H_2O + O_2 \qquad (6)$$

It shows that only the chlorination of brucite (Eq. (6)) is thermodynamically favourable above 150 °C with its ΔG^0 becoming negative. On the other hand, in the presence of carbon monoxide all reactions become thermodynamically feasible over the temperature range (Eqs. (1)–(3)).

Different processes exist for the production of magnesium chloride ($MgCl_2$). They involve the precipitation of seawater and brine or the leaching of carbonates or silicates (Duhaime et al., 2002). Most of these processes need a pre-treatment of the source materials at the beginning and an alternation of dehydration/filtration at the end. These steps are demanding in energy and add to the final cost of the $MgCl_2$.

The present study is aimed at producing $MgCl_2$ by carbochlorination of untreated chrysotile tailings, a residual material composed of different mineral phases. In this, this paper differs from most articles

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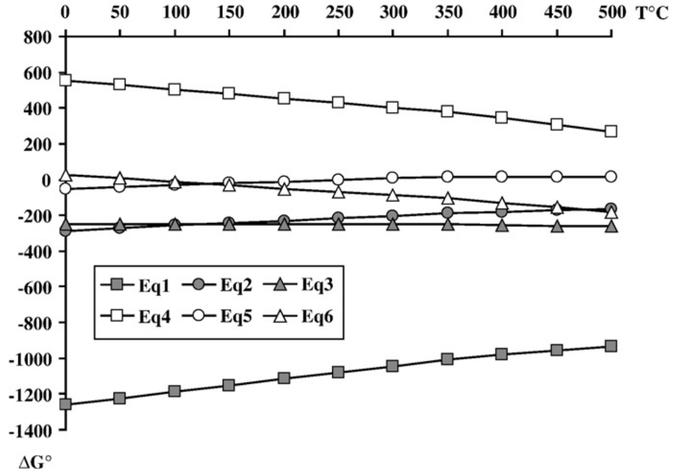

Fig. 1. Standard free energies as a function of temperature for various carbochlorination and chlorination reactions.

addressing the carbochlorination of magnesium silicate. After characterizing the tailings and evaluating the impact of different parameters on the reaction, the rate of recuperation of the magnesium and the quality of the produced $MgCl_2$ have been studied. This article focuses on the carbochlorination process while a future paper will address the mechanism of the reaction.

2. Materials and methods

2.1. Characterization of tailings samples

Samples of chrysotile tailings were taken from a non-homogeneous tailings mound at the Nationale Mine (Thetford Mines, Qc, Canada), combined and passed through multiple steps of grinding to achieve a grain size inferior to 40 µm (99.86%). X-ray diffraction (Siemens D5000) and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; Perkin Elmer Optima 3000), as well as a Scanning Electron Microscope (SEM; Zeiss EVO 50 XVP) with Energy Dispersive Spectrometer (EDS) probes, were used for the characterization. All of these analyses were performed in Laval University and INRS-ETE laboratories.

2.2. Magnesium extraction rate : effects of temperature, gas flow rate and time

The experimental setup is shown in Fig. 2. One gram of sample was placed in a ceramic nacelle (Coorstek 60032), then in the heat resistant tubing, and slid into the furnace. Once the target temperature was reached (30 min), a mixture of gaseous Cl_2 and CO was introduced for the duration of the exposure. Nitrogen atmosphere is provided before and after each step of the reaction. All weight measures were made with a Mettler AE200 scale (205 mg/0.1 mg).

The rate of magnesium extraction had been determined by the ratio between the extracted magnesium (solubilization of chloride salts) and the magnesium present in the original sample.

Temperatures tested were 600 °C, 675 °C, 725 °C, 750 °C and 800 °C, we used indications on chlorination of several metallic oxides (Kroll, 1952) and fusion and vaporisation points of subsequent metallic chlorides (CRC Press LLC., 2008; Hampden Data Services, 2008). Articles about chlorination and carbochlorination of various materials (Djona, 1994; Menad et al., 1997; Yang and Hlavacek, 1999), as well as necessity to not limit the reaction, led us to test a $Cl_2 + CO$ gas flow rate of 1 L/min and 1.2 L/min with a Cl_2/CO ratio comprised between 1 and 1.5.

Studies under optimal conditions were performed to give an indication of the reaction kinetics and to determine a minimum time for maximal magnesium recovery. Periods of time tested were 15 min, 30 min, 60 min, 90 min and 120 min.

The influence of temperature and gas flow rates on cation recovery was examined using a multiple analysis of variance (MANOVA) with $p < 0.05$, when the influence of reaction time was examined using analysis of variance (ANOVA) with a Tukey's Honestly Significant Difference (HSD) multiple comparison ($p < 0.05$). Statistical analysis was performed using the software package JMP 5.0. SAS Institute Inc, 2002.

2.3. Characterization of the products

Once removed from the oven, the chloride salts were separate from the rest of the samples by solubilization/filtration. The saline

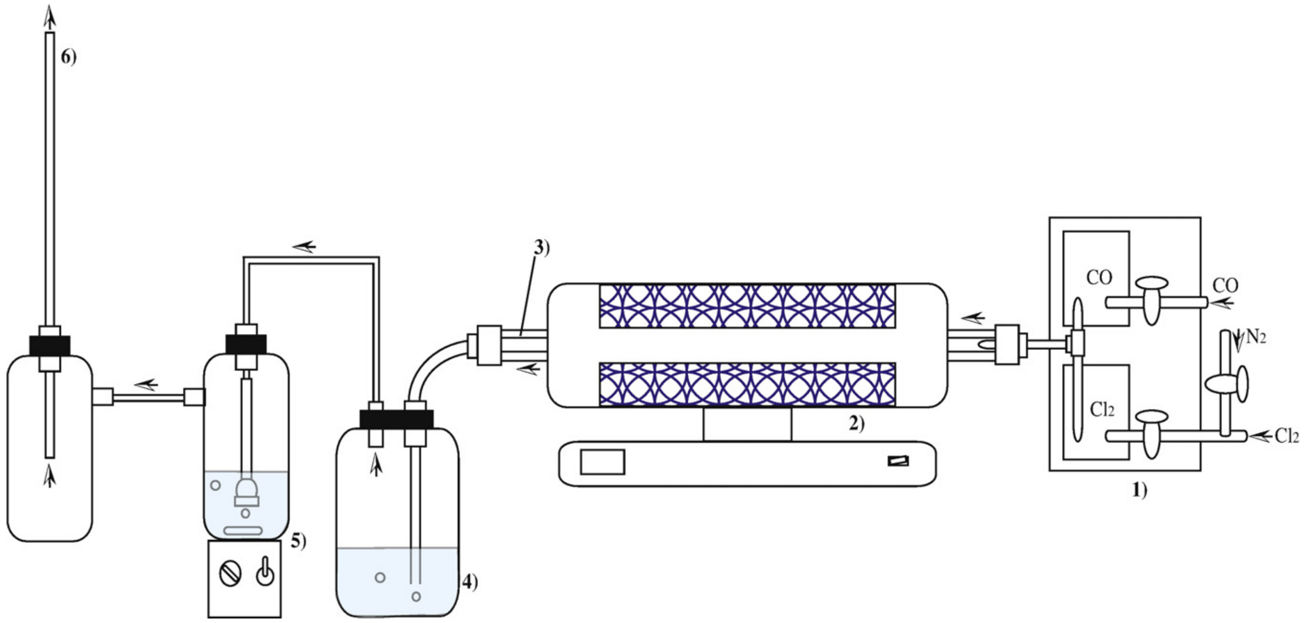

Fig. 2. Schematic representation of the experimental setup. 1) Gas mixing unit, 2) Non-rotating oven unit (Tube Furnace 21100 – Thermolyne), 3) Heat resistant Vicor© tubing, 4) Gas neutralizing bath: water, 5) Gas neutralizing bath: NaOH, 6) Outflow of neutralized gases.