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Reutilization of low-grade magnesium oxides for flue gas desulfurization during calcination of natural magnesite: A closed-loop process

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HIGHLIGHTS

- Reuse of MgO by-products can achieve SO_2 removal with a 100% efficiency.
- 2.9 kg of by-product can completely neutralize 1 m^3 of SO_2 in diluted conditions.
- The alkali-to-sulfur ratio were the same order as other absorbents and technologies.
- The minimum pH range for assuring total desulfurization was 5.2–6.3.
- The residual solids are a mixture of Mg/Ca compounds with $CaSO_4{\cdot}2H_2O$ and $MgSO_4{\cdot}6H_2O$.

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ABSTRACT

The European Commission is encouraging the Cement, Lime and Magnesium Oxide Manufacturing Industries to reutilize collected particulate matter or wastes in the emission control of SO_2 with a 100% removal efficiency. Following this directive, three different by-products from the calcination of natural magnesite were selected in order to evaluate their desulfurization capacity. The saturation time, defined as the time for the total neutralization of SO_2 was used to determine consumption values at laboratory scale with 100% removal efficiency. The by-product LG-MgO (~68% MgO) presented the lowest consumption value, with 2.9 kg per m^3 of SO_2, three times the corresponding to the widely used high grade $Ca(OH)_2$. The liquid-to-gas (*L*/*G*) ratio was used for comparison to the industry and taking this into account, the final pH range before achieving saturation was 5.1–6.3. The residual solids obtained at the end of the process were mainly composed of unreacted magnesium and calcium compounds and reaction products $CaSO_4{\cdot}2H_2O$ and $MgSO_4{\cdot}6H_2O$ which can be used as fertilizers. Therefore, the reutilization of these by-products in a wet flue gas desulfurization process is a feasible and sustainable choice that allows extending their life-cycle.

1. Introduction

From an economical point of view, the use of fossil fuels is still going to prevail in the energy mix for a few years [1]. In fact, fossil fuels will continue to supply almost 80 percent of world energy use until 2040 [2]. Among these, coal-fired boilers and kilns are the most preferred option for providing heat, because of the high density of energy that can be obtained at a moderate cost compared to oil or natural gas. In this aspect, coal contains sulfur in the range of 2–5%, whereas less than 1% can be found for the low-sulfur type [3]. During the combustion process, the sulfur released to the atmosphere oxidizes to form SO_2 and further SO_3, which is highly soluble in water and is one of the key precursors to acid rain [4].

In this aspect, the abatement of SO_2 emissions has been an issue of great concern among EU member states for more than two decades because of its economic and environmental implications and more important because of the human health effects. For this reason and in order to prevent atmospheric deterioration, many countries around the world have imposed tight regulations on coal-fired industries and power plants, with those in the EU member states and Japan being characterized as the most stringent [5].

The commonly used desulfurization processes are mainly classified as pre-combustion and post-combustion processes [6]. At present, the most effective technique to control SO_2 emissions is flue gas desulfurization (FGD) [4]. It consists of scrubbing the

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Nomenclature

L/G	liquid to gas ratio (liters of slurry per $m^3$of gas)
t	time (min)
W	mass of water (g)
S	mass of by-product (g)
L	mass of slurry (g)
S/W	by-product per water ratio (%)
t_s	saturation time (min)
AKS	alkali-to-sulfur ratio (molar basis)
f	gas flow ($L \cdot min^{-1}$)
ρ_s	density of the slurry ($kg \cdot L^{-1}$)
$(Ca + Mg)_{total}$	sum of Mg and Ca in each by-product in a molar basis
S_S	sulfur as impurity in each by-product (mole)
S_{SO2}	sulfur from the SO_2 of the gas flow (mole)

exhaust gases with an alkaline component. As an absorbing reagent, magnesium and limestone suspensions can be used. The former has a higher removing efficiency but the latter has a lower cost and therefore its more widely used [7,8]. There are many categories of FGD, although the wet-type is nowadays the most promising and the most widespread owing to the low operating cost and more stable operation [9]. Wet scrubbers, especially the limestone-gypsum process, are the front-running FGD technologies [10]. When selecting the adequate FGD process, economic viability and more importantly the disposal of generated wastes are the main factors to be taken into account. In this aspect, the research and development in the past years have been focused in the improvement of the removal efficiency and the minimization of water consumption as well as the management of the solid by-product produced [11]. However, a new era in what sustainability and waste management concerns have redirected all industrial processes.

The European Commission, through the Best Available Techniques (BAT) Reference Document of the Industrial Emission Directive 2010/75/EU, has established the associated consumption and emission levels for the Cement, Lime and Magnesium Oxide Manufacturing Industries, encouraging to follow certain key environmental issues in addition to fulfill efficiency standards. These can be encompassed in the reduction of the SO_2 emissions by the reutilization of collected particulate matter, by-products or wastes whenever practicable. Thus, the desulfurization standards could be achieved following the path to sustainability by minimizing the use of natural raw reagents while promoting the reutilization of waste and residues. However, this requires the research over suitable alternatives. In the framework of this issue, the literature has already described the enhancement in desulfurization when hydrated lime slurries are mixed with coal-fired fly ash [12]. This enhancement is mainly attributed to the presence of hydrated calcium silica $-(CaO)_x$-$(SiO_2)_y$-$(H_2O)-$ formed from the reaction between calcium and silicate found in the fly ashes [5]. Other alternatives include the use of waste cement particles as desulfurization agents with equivalent effectiveness to limestone and calcium hydroxide [5]. Therefore, the research in the reutilization of by-products or wastes promoted by the abovementioned directive seems to be the nowadays route to economic viability and sustainability.

On the other hand, the authors have already described the reutilization of some of the by-products obtained from the calcination of natural magnesite [13]. These by-products are usually referred to as Low-Grade magnesium (hydr)oxide (LG-MgO/$Mg(OH)_2$) and had proven to be effective in several environmental applications such as the stabilization of electrical arc furnace dust prior landfill, in the removal of ammonium and phosphates from industrial wastewaters, as ignifugant filler in polymers or for the formulation of Chemically Bonded Phosphate Ceramics [14–18]. Consequently, it can be stated that these by-products still have a profitable reuse at the end of their life-cycle, providing both an environmental benefit as well as economic. Nevertheless, its reuse as desulfurization agents has not yet been described.

These by-products are characterized for being a mixture of magnesium and calcium (hydr)oxides as well as different proportions of dolomite, siliceous materials and other impurities such as Fe and S, altering their alkaline behavior and therefore their acid neutralization capacity [19]. This would allow to treat the exhaust gases at the outlet of the calcination kiln with the own by-products generated after calcination, increasing the sustainability of the process and extending and closing their life-cycle.

The aim of this research work was to assess the desulfurization capacity of some of these magnesium oxide by-products. In particular, the study will focus on the flue-gas desulfurization from magnesite calcination, which would close the cycle of the process using the own by-products in the gas treatment system. Moreover, the drawing conclusions of this study could be extended to other industrial desulfurization processes. In order to carry out this research, several considerations were taken into account for evaluating the by-products potential use as desulfurization agents and resemble real conditions: (i) the exhaust gases from coal-fired industries are usually a mix of SO_2, NO_x, CO, CO_2 and O_2 in different proportions; (ii) although the particle size plays an important role as it is related to specific surface and thus the reactivity, no sieved was applied to the samples as no extra physical treatment to the solid would enhance economic viability; (iii) all experimental trials were performed at room temperature as previous studies have reported that the degree of desulfurization is practically independent of reaction temperature [10].

The development of a FGD process that fulfills both an economic and environmental compromise while accomplishing the BAT requirements is a task of great concern to the industry, especially from the point of view of sustainability. The reutilization of these by-products would establish an integrated process in the calcination system. In this regard, the authors believe that this study, carried out at laboratory scale, will contribute to give environmentally-friendly alternatives for the development of an industrial scale desulfurization process besides giving a valuable tool for assessing the desulfurization capacity of residues and wastes.

2. Materials and methods

2.1. Raw materials

Three different kinds of by-products were considered. The main differences between them are their particle size and the Mg/Ca content. Selected samples of around 25 kg each were supplied by Magnesitas Navarras S.A. located in Navarra (Spain). All samples were collected during the calcination process for obtaining magnesia, with their origin being described as follows. Once the magnesite ore is extracted from the natural deposits and selected, it is fed into two rotary kilns at 1200 °C and 1600 °C respectively for calcination. The gases generated from these two kilns are taken