



# Low-grade magnesium oxide by-products for environmental solutions: Characterization and geochemical performance



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## ABSTRACT

The reutilization of the by-products from the calcination of natural magnesite for environmental solutions is conditioned by the availability of MgO, CaO and other compounds. In order to overcome their great heterogeneity, an exhaustive chemical and physical characterization is necessary in order to assess their potential applications. In this study, the acid neutralization capacity (ANC) test was used to categorize three types of by-products (LG-MgO, LG-D and LG-F), which mainly differed according to source ore and processing conditions. The experimental data concerning the leaching of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Fe^{2+}$  and  $SO_4^{2-}$  was corroborated with geochemical predictions using the modelling software Visual MINTEQ. Likewise, the main solubility-controlling mineral phases were also identified. According to the results, there is a buffer capacity within the pH 8–10 range, mainly dominated by the neutralization of  $MgO/Mg(OH)_2$ , equilibrium with a small contribution from the carbonate content at lower pH values. The release of sulphates showed a non-pH dependency attributed to the solubility of  $CaSO_4$  and elemental sulphur present in petcoke. For dust materials, leaching of Fe was minimal above pH 6 owing to the insoluble nature of the  $Fe_2O_3/Fe_3O_4$  pair. Accordingly, the by-products labeled as LG-D and LG-F are better suited for stabilizing solid wastes or wastewater that are acid while LG-MgO is more appropriate for alkaline residues such as contaminated soils. In both cases, a suitable pH range in which pH-dependent heavy metals and metalloids show minimum solubility can be obtained. The use of these by-products guarantees an environmentally friendly alkali reservoir for the long-term stabilization of heavy metals and metalloids at a very competitive price as a substitute for the widely used lime.

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## 1. Introduction

Magnesium oxide (MgO) is one of the most important raw materials used in the refractory industry (Salomão et al., 2007). It is predominantly produced by the calcination of natural magnesite ( $MgCO_3$ ) (Birchal et al., 2000; Demir et al., 2003; Zhu et al., 2013). During this thermal process, several by-products rich in magnesium are generated. In order to promote environmental sustainability and enhance the exploitation of these by-products, the three R's strategy (Reduce, Reuse and Recycle) should be promoted as an integral part of every industrial philosophy. The need to recover resources is not only related to benefits to the environment but also to the maintenance of natural resources. In this regard, the reuse of industrial by-products in environmental solutions by replacing other industrial products not only addresses issues of sustainability but also of greater environmental benefits.

After extraction from ore, the natural mineral is taken to classifiers and collectors for sieving, and the selected minerals are fed to the kiln

for calcination. Both the temperature of calcination and the time of residence are important for conditioning the quality of the MgO and thus its potential applications (Zhu et al., 2013). The so-called caustic magnesia is obtained at low temperature ranges (1200 °C) and shows high reactivity, while the dead-burnt magnesia is obtained at temperature ranges close to 1600 °C, and is less reactive than caustic magnesia because of the effect of sinterization on its crystalline structure. Regardless of the calcination conditions, the combustion gases generated at the outlet of the kiln are taken into the air pollution control system, consisting of fabric filters and cyclones, where a large proportion of the solid particles and flue-dust is retained. These components combine to form cyclone dust (CD), which is considered the bulkiest by-product obtained at the end of the calcination process. It is characterized for being a mixture of magnesium and calcium oxides as well as different proportions of dolomite, siliceous materials and other impurities that affect its alkaline behaviour and reutilization potential. CD is more widely known as Low-Grade MgO (LG-MgO). Its great heterogeneity complicates the post-treatment and without any reclamation, it is stored in the open. After 6–8 months, the natural spontaneous process of weathering hydrates LG-MgO to Low-Grade  $Mg(OH)_2$  (LG-Mg(OH)<sub>2</sub>).

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The reutilization of by-products from the calcination of natural magnesite is mainly conditioned by the availability of MgO, CaO, and other compounds. The main differences among these by-products are chiefly a function of both the raw materials and the thermal processes involved in their production, which condition their chemical and physical characteristics.

### 1.1. Reutilization routes of MgO by-products

With the aim of ensuring sustainable and beneficial use, previous studies carried out by our research group have highlighted the potential for reutilization of these low-grade magnesium (hydr)oxides in many applications despite their great heterogeneity. Fernández et al. (1999) described a method to obtain basic magnesium carbonates by means of the carbonation of LG-MgO slurries with the aim of using them as an additive for pigments and papermaking or as a flame retardant in polymers. In the same way, the use of LG-Mg(OH)<sub>2</sub> has been tested with very promising results as a flame retardant filler in polymers and as aggregates in the formulation of fire-protecting mortars (Fernández et al., 2009; Formosa et al., 2011).

In the environmental field, it is known that the leaching of heavy metals and some metalloids is strongly dependent on pH (Van Herreweghe et al., 2002). In this context, MgO acts as a buffering agent within the pH 9–11 range, minimizing heavy metal solubility and avoiding the re-dissolution that occurs when using only lime (García et al., 2004). In this context, and more precisely in landfill management, the use of different types of dolomitic limes with varying amounts of MgO equivalents has proved to be effective in the stabilization of electric arc furnace (EAF) dust as an alternative to the use of lime and/or ordinary Portland cement (Cubukcuoglu and Ouki, 2012; Fernández et al., 2003). In this regard, remediation of heavy metal contaminated soils is currently an important worldwide issue that is of great concern to many communities and municipalities (García et al., 2004; Peng et al., 2009; Yao et al., 2012). The use of magnesium (hydr)oxide by-products guarantees an alkali reservoir for the long-term stabilization of heavy metals and metalloids at a very competitive price. García et al. (2004) reported that contaminated soil stabilized with LG-MgO shows, independently of the quantity of stabilizer employed, a pH close to 9.2. Moreover, a reduction greater than 80% of the metals and metalloids released is feasible when applying this by-product. Another study carried out by the authors focused on the potential leaching of toxic trace elements from MgO by-products during their reutilization: even at very acidic conditions, the majority of toxic species (As, Pb, Zn, Cr, Cu, Ti, Mn, Co and Ni) hardly dissolve and their concentration values remained under regulatory limits (Chimenos et al., 2012).

The buffering pH range is controlled by the solubility of the magnesium hydroxide. In this respect, an alternative to the natural spontaneous process for obtaining LG-Mg(OH)<sub>2</sub> was assessed by the authors using different hydration agents (del Valle-Zermeño et al., 2012). The results reported by the authors showed that much shorter hydration times are possible and therefore, an industrial alternative to the spontaneous process could satisfy an increasing demand for magnesium hydroxide.

Low-grade magnesium (hydr)oxides have also been found to be suitable and economically feasible for use in remediation and/or wastewater treatment. Thereby, permeable reactive barriers using MgO as a filler were tested for removing heavy metals from contaminated ground (Cortina et al., 2003; Navarro et al., 2006; Rötting et al., 2006). Moreover, magnesium oxide as a source of magnesium has been used as a reagent to remove and recover ammonium and/or phosphates from wastewater; these precipitate in the form of struvite (MgNH<sub>4</sub>PO<sub>4</sub> · 6H<sub>2</sub>O), bobierite (Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · 8H<sub>2</sub>O) or newberyite (MgHPO<sub>4</sub> · 3H<sub>2</sub>O) in the presence of magnesium (Chimenos et al., 2003, 2006). On the other hand, chemically bonded phosphate ceramics (CBPCs) are well suited for hazardous waste encapsulation because solidification occurs at low temperatures and within a wide pH range

(Rao et al., 2000). CBPCs are mainly fabricated from an acid–base reaction between calcined MgO and monopotassium phosphate (KH<sub>2</sub>PO<sub>4</sub>) in solution to form a hard and dense magnesium potassium phosphate hydrate (MgKPO<sub>4</sub> · 6H<sub>2</sub>O) ceramic. The use of a highly pure MgO requires prior calcination at 1300 °C (Jeong and Wagh, 2003). This significantly increases the cost of the raw materials, complicating its potential use as a substitute for ordinary Portland cement for encapsulation. However, the use of MgO-containing by-products as raw materials for CBPC formulation could reduce production costs while improving mechanical properties (Formosa et al., 2012).

### 1.2. Reuse of MgO by-products as stabilizing agents

The effectiveness of LG-MgO as a stabilizing agent in heavily polluted soils or as a reagent in wastewater treatment, as well as other potential environmental applications, is a function of its reactivity and, mainly, its behaviour across the whole pH range (Ho et al., 2012). The reactivity of MgO is usually measured using the citric acid test, in which the time needed for the magnesium sample to neutralize the citric acid solution is measured (Strydom et al., 2005). It is also directly related to its specific surface area and particle size distribution (Demir et al., 2006). The acid–base properties of solid wastes have been found to considerably influence the leaching of solid wastes by changing the pH environment (González-Núñez et al., 2012; Yan et al., 2000). The pH environment of the system can be defined by the buffering capacity, which is usually measured by means of the acid neutralization capacity (ANC) test (CEN 14997). This standardized test determines the ability of any material to maintain a stable pH range as acid is added. The ANC test is a measure of the acidity of a solution and it is almost linearly related to alkalinity and non-linearly related to pH (Förstner and Haase, 1998; Neal et al., 1999).

Against the above background, the main objective of this study was to characterize the main by-products obtained from the calcination of natural magnesite in order to determine the boundaries of reutilization in the environmental field taking into consideration the materials' heterogeneity. For this purpose, their chemical and mineralogical composition as well as various physical properties were characterized. Likewise, the ANC test was used as a tool to predict their effectiveness as neutralization agents in acid effluents and their buffering capacity in, for example, the amendment of highly contaminated soils or the stabilization of solid wastes, as this can give sufficient information about the release of metals in certain pH conditions. Moreover, this capacity factor is significant for predicting the potentially reactive amount of waste in neutralizing reactions (Cappuyens et al., 2004; Yan et al., 2000). The experimental results were further compared to geochemical modelling predictions using Visual MINTEQ, which is based on the code originally built for MINTEQA2 (Allison and Brown, 1991). This geochemical modelling software allows the assessment of the transport and precipitation of heavy metals as well as adsorption equilibria (Shi et al., 2013; Wagner and Kaupenjohann, 2014; Yu et al., 2014). It is also used for leaching predictions and for calculating the composition of the leachates in equilibrium with potential solubility-controlling minerals (Houben et al., 2012; Jung et al., 2012; Meima and Comans, 1997, 1999; Sjöstedt et al., 2013). Thus the mineral phases controlling the leaching in the pH range of interest for each by-product were identified by comparing theoretical modelling with experimental data.

The use of these by-products addresses two issues: on one hand, it becomes possible to reuse a by-product that follows the path towards sustainability and on the other hand, an environmental solution is attained by means of an environmentally friendly agent.

## 2. Materials and methods

Three by-products were considered, differing mainly in their particle size and Mg/Ca content. Selected samples of around 25 kg each were supplied by Magnesitas Navarras S.A., located in Navarra (Spain).

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