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$MgCO_3$ obtaining from wastewaters generated during the acidic leaching of zinc concentrates

ANDRZEJ JAROSIŃSKI[1] and LUCYNA MADEJSKA[2]

Katedra Technologii Nieorganicznej i Biotechnologii Środowiska, Politechnika Krakowska,
ul. Warszawska 24, PL-31-155 Kraków, Polska
[1]ajar@chemia.pk.edu.pl; [2]mad@chemia.pk.edu.pl

Abstract

Leachates formed in the process of zinc concentrates leaching by means of HCl solutions were utilized for the magnesite obtaining. Earlier defined process parameters were adjusted to precipitation of magnesium carbonate. Leachate impurities, such as iron, calcium and other ions were removed by the precipitation, adjusting pH level. Optionally the ion exchange process was used to achieve a best quality of magnesium solution. Crystalline $MgCO_3$ was precipitated using Na_2CO_3 solution. The product contained 28.7 % of MgO with 98.5 % purity of the final product.

Key words: wastewaters, zinc contentrates, acidic leaching, $MgCO_3$

Introduction

Synthesis of required materials with controlled size and morphology is often driven by the industry requirements in the diverse areas. Magnesium carbonate is mainly used to produce magnesium metal and basic refractory materials. The other applications combine flooring, fireproofing, cosmetics (toothpastes, face powders, etc.), pharmaceuticals (antacids, laxatives, cardiac regulators), food additives, paints, pigments, rubbers, lithographing inks, and the use as precursors to prepare other magnesium-based chemicals. Although magnesium carbonate is well known in the form of the anhydrous salt called *magnesite* ($MgCO_3$), several hydrated and basic minerals also exist: di-, tri- and pentahydrates are known as *barringtonite* ($MgCO_3 \cdot 2H_2O$), *nesquehonite* ($MgCO_3 \cdot 3H_2O$) and *lansfordite* ($MgCO_3 \cdot 5H_2O$), respectively. Some basic forms such as *artinite* ($MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$), *hydromagnesite* ($4\ MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$) and *dypingite* ($4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$) also occur as minerals.

There are many possibilities of the magnesium carbonate obtaining, but the interesting one proposed below is based on the leachates generated during the processing of the Zn, Pb concentrates. Magnesium carbonates have been studied for both their preparation and properties (Kloprogge, 2003; Min, 2010; Deelman, 2003; Sheila, 1989), but many questions still remain opened concerning the formation of the magnesium carbonates in both natural and artificial systems, due to the presence of different forms of hydrated or basic carbonates (Wang, 2008).

Characterization of investigated problem

During processing of zinc concentrates the leachates are generated, containing magnesium, calcium and other metals depending on the raw ore content. Purification processes, adapted to the zinc concentrate quality improvement, use different kinds of mineral acids, in order to remove magnesium from the final product. Among these leaching agents the sulphuric, phosphoric and hydrochloric acids were tested, and the results were described (Jarosiński, 2009; Jarosiński, 2010).

In this study the solution formed during hydrochloric acid leaching is investigated, in order to precipitate magnesium carbonate by the reaction:

$$MgCl_2 \cdot Na_2CO_3 + nH_2O \Rightarrow MgCO_3 \cdot nH_2O + 2\ NaCl$$

The parameters of precipitation, as well as possibilities of different forms of magnesium carbonate obtaining were studied.

The aim of the present work is to select proper conditions and target precipitates with the adequate crystallographic characteristics for extracting magnesium from the brine, and prepare magnesium carbonate hydrates with the high purity.

Experimental part

Materials

Leachates were prepared in the laboratory as the model chlorine solution, containing the following concentrations [mg/dm^3]: 0.115 Mg; 0.235 Ca; 0.020 Fe; 0.030 Zn; 0.055 Pb. The above chemical content was adapted from the experiments with post flotation wastewaters, obtained during the zinc concentrates extraction with the hydrochloric acid (Jarosiński, 2009).

All chemical reagents used for leachate preparation (Na_2CO_3, KOH) had were analytical grade without further purification.

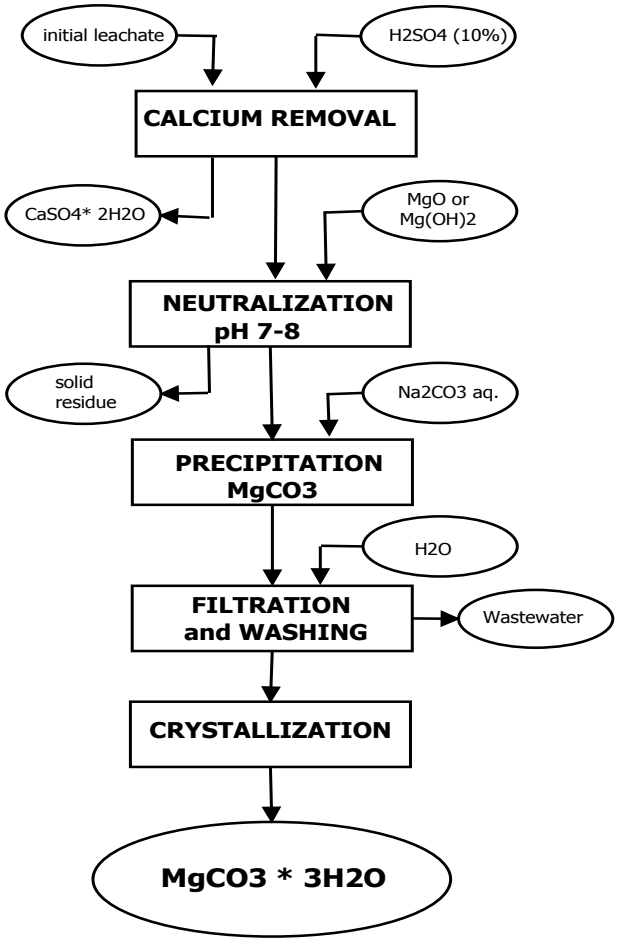

Fig. 1. Simplified flowsheet of the experimental procedure.

Experimental procedures

The experiments were performed in a 1-liter double--jacketed glass reactor, connected with a water circulator. Reaction mixture was agitated at a rate 300 r.p.m. and then filtered under vacuum in a Buchner-type filter. The experimental procedure is presented in Fig. 1 in the form of the simplified flowsheet.

Purification of $MgCl_2$ solution

Calcium ions, the major dissolved impurity of the leachate, were precipitated as sulphates, using sulphuric acid solution (Jarosiński, 2009). The other dissolved impurities like iron, zinc and lead were removed by the precipitation at pH 7 – 8 for 15 minutes at 45 °C by the addition of magnesium oxide or hydroxide.

$MgCO_3$ precipitation

Purified solution of magnesium chloride (0.5 mol/dm^3) was mixed with the sodium carbonate solution (0.5 mol/dm^3) in the glass reactor. The experiments were carried out within the temperature range 20 – 45 °C, using different time of reaction (up to 240 minutes). At the end of each experimental cycle, the slurry was settled till the next day and then washed with distilled water for 5 minutes, to remove any possible ionic remnants. Finally, each sample was dried in a drier at 50 °C for 10 hours.

Product characterization

The structure and morphology of the synthesized samples were examined using the X-ray powder diffraction and scanning electron microscopy. X-ray powder diffraction (XRD, Philips model with X´Pert system) patterns were recorded on a diffractometer (using CuKα radiation). A diffractometer scanning rate was applied to record the patterns in the 2Θ angle range from 10° to 60°. The morphology of the samples was examined by a scanning electron microscopy (FEI E-SEM XL30 with X EDAX GEMINI 4000 dispersion spectrometer).

The concentration of magnesium ions in the solution was determined by the titration method using standard EDTA solution. The concentration of the other ions was determined using ICP – MS spectrometer (Perkin Elmer model).

The density of the product was tested using standard procedure with the glass densitometer.

The results and discussion

XRD observations

It is generally recognized that the properties of crystals are profoundly influenced by the temperature during their preparation and the time of the reaction. Fig. 2 displays the typical XRD pattern of the $MgCO_3 \cdot 3H_2O$ sample. The diffraction peaks confirm a high purity of the carbonate sample.

SEM images

Fig. 3 provides a typical SEM image corresponding to the magnesium carbonate hydrates prepared at 40 °C. The presented sample exhibits good morphology and the surface is covered by many small grain-like crystals. The main particles are needle-like with different sizes, as shown in Fig. 3. The length of crystals is in the range 5 – 53 μm with the axis diameter in the range of 2 – 8 μm. The needle-like particles exhibit smooth surfaces.

The other precipitates (magnesium carbonate hydrates), which synthesized at lower temperatures and shorter reaction time (25 °C, several minutes), were poor crystalline or even amorphous products.

Purity of $MgCO_3 \cdot 3H_2O$

A certain amount of $MgCO_3 \cdot 3H_2O$ sample was dissolved in a slightly excessive hydrochloric acid of low concentration. The concentration of magnesium ions in the solution was determined by the titration method using standard EDTA solution. The Mg content in the tested

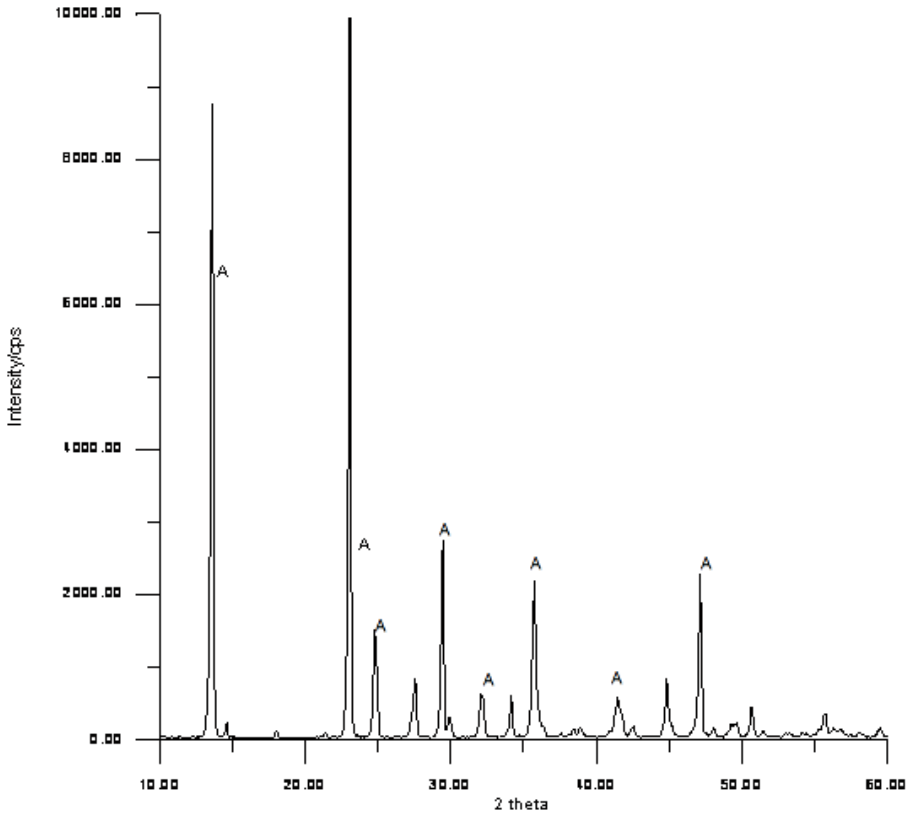

Fig. 2. XRD pattern of precipitated sample, A- $MgCO_3 \cdot 3H_2O$.

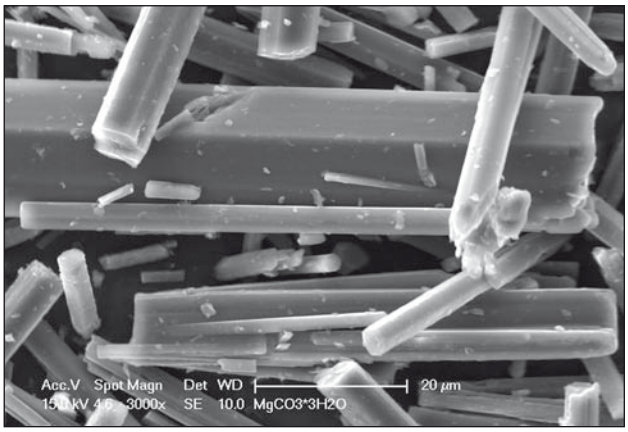

Fig. 3. SEM morphology for the particles of $MgCO_3 \cdot 3H_2O$.

samples was in the range 14.5 – 17.3 % that corresponded to 82.5 – 98.5 % purity of the products. The other impurities bounded into the structure of the magnesium carbonate hydrates did not exceed the level of 0.38 % that was determined by ICP analysis.

Conclusions

Purification process of the wastewaters, obtained during zinc concentrate processing, was examined in this study. As a result of purification the solution containing mainly magnesium ions was obtained. Magnesium carbonate trihydrate was prepared using homogeneous precipitation process at different reaction temperatures and times. In the temperature range 25 – 45 °C pure nesquehonite $MgCO_3 \cdot 3H_2O$ was obtained, but only at 40 °C needle-like crystals were identified. The morphology of the magnesium carbonate trihydrate changed from needle-like to amorphous, in dependence on the precipitation parameters. The uptake of the ionic impurities (Zn, Pb, Fe) in the magnesium carbonate hydrates could be neglected, because its amount does not exceed 0.38 %.

It seems that the purification method proposed for magnesium carbonate production from waste leachate is the appropriate way of its utilization. By the method applied in this study magnesium can be effectively separated from the leachate and using sodium carbonate (or the other water soluble carbonates) magnesium carbonate hydrates with the high purity can be produced.

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