

MAGNESITE BENEFICIATION METHODS: A REVIEW

Georgios-Michail Bimpilas, Georgios N. Anastassakis

National Technical University of Athens (NTUA), 9 Heron Polytechniou str., NTUA Campus, 15780 Zographou, Greece, ganastas@metal.ntua.gr

ABSTRACT. Magnesite is one of the most important mineral commodities mostly because of its technological and industrial applications. The most important commercial sources for its recovery are the corresponding ores. The deposits are characterised by the differences in reference to magnesite mineral crystallinity and gangue composition. For these reasons, the separation efficiency of magnesite from gangue varies from relatively easy to impossible. Another problem is the stocked waste, often of relatively high-grade in magnesite, derived from industrial processing, which may be viewed as future potential deposits. This paper contributes a detailed review on the methods applied to separate magnesite from gangue both on industrial and bench scale; potential processing methods for fine particle size are also reviewed.

Keywords: separation methods of magnesite, magnesite processing, magnesite flotation, serpentine

Introduction

Magnesium is the eighth most abundant element of the earth crust and the third one in the sea-water with average concentration of 20,900 ppm and 1,350 mg/l correspondingly (Mason and Moore, 1982; Theodorikas, 2014). Magnesium is encountered in many minerals, both siliceous and non-siliceous. In the non-siliceous minerals the following are included: the carbonate ones magnesite (MgCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), the hydroxylated form brucite $[\text{Mg}(\text{OH})_2]$, and the minerals of evaporate group carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) and brunerite, which is a solid solution of magnesium carbonate and iron carbonate, with its FeCO_3 content ranging between 5 and 30%. Among the siliceous minerals the most important are olivine $[(\text{MgFe})_2\text{SiO}_4]$, talc $[\text{H}_2\text{Mg}_3(\text{SiO}_3)_4]$ and serpentine $[\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9]$.

From the magnesite rock mined, only a small part is used to produce magnesium metal while the great majority is directed to industrial uses, with magnesite being the most important mineral from the commercial point of view. The most important magnesite products are raw magnesite, caustic calcined magnesia, dead-burnt magnesia and refractory mass. Magnesite is white coloured, chemically inert, soft enough and good absorbent. Because of these properties, it is used as primary raw material in a wide spectrum of industrial applications, such as: ceramics and refractories, steel production, magnesium metal and alloys production, cement industry, fertilizers and cattle feed, environmental depollution, pharmaceuticals, etc.

Magnesite ore deposits

Magnesite is encountered in two forms with different structure: microcrystalline and crystalline. Although crystalline magnesite deposits represent more than 90% of the global deposits, the microcrystalline ones are commercially more preferable due to their higher quality and advantages (Pohl, 1990).

The microcrystalline form is also referred to as cryptocrystalline or amorphous (Nasedkin et al., 2001), but these terms do not correspond to reality because magnesite grains do present crystallinity but their size is very small (between 1 and 5 μm). The small magnesite grains are aggregated to form a compact rock with conchoidal fracture, which is characterised by high MgCO_3 content (sometimes reaching up to 87 - 90% MgCO_3); in some cases, the aggregates

have porous structure, with pores' size between 20 and 80 μm , which provides them with higher specific surface and activity compared to the crystalline.

The genesis of microcrystalline magnesite is due to the alteration of ultramafic rocks of ophiolitic complexes (e.g. serpentine, peridotite); this form is encountered as variable size veins within the mass of the host rock. Due to its genesis, the gangue minerals are mostly composed of serpentine, various SiO_2 forms (quartz, opal, chalcedony), calcite and dolomite; minor gangue minerals are iron and aluminium oxides, talc $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]$, chlorite $[(\text{Al}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Li}, \text{Mg}, \text{Mn}, \text{Ni})_{5-6}(\text{Al}, \text{Fe}^{3+}, \text{Si})_4\text{O}_{10}(\text{OH})_8]$, etc. Microcrystalline magnesite may also be of sedimentary origin as layers intercalated with calcite, dolomite, or clayey layers (Davis, 1957).

On the contrary, crystalline magnesite is composed of sparry grains, with their size usually ranging between 0.5 and 20 mm, and, in some cases, even so large as 5 to 6 cm (Nasedkin et al., 2001). The major gangue minerals are dolomite and calcite; the minor ones are serpentine, talc, chlorite, quartz, hematite, diopside ($\text{CaMgSi}_2\text{O}_6$), tremolite $[\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2]$, etc.

Due to the huge demand for magnesite products and high quality refractory materials, it is a necessity to remove the impurities from the host rock by mineral processing methods. The increased levels of miscellaneous impurities (e.g., CaO , SiO_2 , Fe_2O_3 , Al_2O_3) have a detrimental impact on the efficiency of the process and the properties of the refractories. The depletion of the high-grade and high-purity magnesite deposits along with the continuously increasing demand for magnesite products lead to the urgent need to focus on the processing of lower grade deposits.

The chemical composition of raw magnesite, after mining or beneficiation, determines its suitability for the various uses and the quality of products after calcination. It must be pointed out that there are no certain limits for the determination of the product quality, because quality is not determined solely by MgO content but from the content of the impurities as well; the presence of impurities (such as CaO , SiO_2 , Fe_2O_3 and Al_2O_3) in magnesite products usually render difficult the processing and adversely affect refractoriness. From quality point of view, the commercial specifications of magnesite are not standard. Magnesite for caustic calcined magnesia, which is the main feedstock for refractories, is considered commercial for MgO content higher than 40% (corresponding to 84.0% MgCO_3). Internationally, the specifications of commercial magnesite for

refractories range between: MgO 40-47% (or MgCO₃ 84.0-99.0), CaO 0-3.5%, SiO₂ 0-7%, Fe₂O₃ + Al₂O₃ 0-3% (Minerals and Refractories, 2020).

Due to the diversity of gangue minerals, their similar properties with magnesite and the high commercial importance of magnesite, extensive scientific work has been carried out on magnesite beneficiation. The target of the current paper is to critically overview the processing methods related to magnesite separation both at industrial and laboratory scale.

Magnesite Processing Methods

A. Industrial scale

At industrial level, the separation method to be applied depends on gangue minerals, product specifications and processing cost. The industrial separation schemes for magnesite usually include the following methods:

- *Optical (or visual) sorting.* This is a common practice to separate magnesite (white) from coloured gangue minerals (e.g. serpentine). This principle has been applied in the past as hand-sorting for coarse particles or, currently, as digital sorting with laser beam or camera for particle size 4-10 mm (GRECIAN MAGNESITE 2020).

- *Magnetic separation,* which has been used to remove magnetic gangue. Dry high-intensity magnetic separators with superconducting magnets have also been used (GRECIAN MAGNESITE 2020).

- *Gravity heavy media separation* has been used to remove silicate minerals and dolomite (light product) from magnesite (Rau, 1985; GRECIAN MAGNESITE, 2020). Due to the slight difference between their specific gravity, this procedure is not always efficient; hence, further processing by magnetic separation or visual sorting is often required to improve the results (Frangiskos et al., 1981).

- *Flotation* has relatively limited industrial application to separate gangue from magnesite (Rau, 1985). In general, magnesite can be effectively separated by flotation from silicate gangue minerals but not from carbonates. The flotation scheme to be used depends on the nature of the minerals involved. In case the ore has increased percentage in silicates, reverse flotation can be used in the presence of cationic collectors' mixture. By this process, high quality product is produced, suitable for dead burned magnesite production. This practice has been industrially applied, developed and patented at Mantoudi (Euboea, Greece) magnesite mineral processing plant (Gambopoulos and Nestoridis, 1976).

B. Laboratory scale

The need for high purity MgO has increased in the last few years; as a result it is vital to apply more efficient methods to separate magnesite from gangue minerals targeting products of higher purity. The methods that meet these requirements are gravity methods for coarse particles (> 1 mm) and flotation for fine particles, especially if high-grade product is required.

Due to the wide spectrum of applications and the required high quality standards of magnesite products, extensive research has been carried out at lab-scale to solve practical problems that prevent the complete separation of magnesite from gangue minerals, especially carbonates. To meet the target, various physical and physicochemical methods or combination of methods have been tested, with most of them being devoted to separation by flotation.

Physical Separation Methods

Back in 1970s, a separation method that includes calcination of magnesite ore at 600 - 800°C and subsequent gravity separation of the calcined product on a Berry air-separator was developed in the laboratories of the former Skalistiri group (Euboea, Greece) and successfully applied, (Frangiskos and Kontopoulos, 1976). The separation scheme provides very good results in the case of serpentine and other silicate gangue minerals, due to the significant enhancement of specific gravity difference between magnesite ore and gangue minerals after calcination.

Similar scheme was applied in another magnesite processing plant in Greece, located at Vavdos, Chalkidiki; in this case, it must be pointed out that, after calcination, gravity heavy media separation was applied instead of air-separation (Frangiskos, 1995). In addition to the industrial schemes, lab-scale tests including calcination and multi gravity separation (MGS) achieved encouraging results in terms of MgO content but with relatively low recovery (Gence, 2001). Through this process, a concentrate containing 78,14 MgO, 1,51% CaO and 0,55% SiO₂ was obtained, but the recovery in MgO was only 57,21%, while the feed content was 44.87% MgO, 3.1% CaO and 0,5% SiO₂.

Suslikov et al. (1966) attempted to separate magnesite from dolomite by exclusively applying heavy media (gravity) separation. According to the results, the concentrate of magnesite was of high purity, with 82-84% weight recovery, while a high purity dolomite product was obtained as well.

Other researchers combined calcination with subsequent high intensity dry magnetic separator testing on magnesite ore of fine particle size and intimate association of magnesite grains with gangue constituents. The separation yielded encouraging results but further improvement is necessary for industrial application (Potapenko et al., 1981). The same methodology was applied to middling product derived from magnesite processing. The results of the research showed that it is possible to produce a marketable product with 89.5% MgO content and low content in harmful constituents (Bentli et al., 2017). A similar procedure (calcination and magnetic separation) was tested on magnesite ore with high impurities content from Slovakia, which resulted in a product with 82,77% weight yield, 81,91% MgO content and 89,19% MgO recovery (Hredzak et al., 2014).

Contrary to magnetic, Cao et al. (2016) applied electrostatic separation to raw magnesite ore of very fine particle size (< 20 µm) without particular success with regard to the removal of gangue minerals (quartz, dolomite, calcite, chlorite and talc). On the other hand, researchers from the former Soviet Union applied photometric and radiometric separation to magnesite deposits with dolomite, calcite, chlorite and quartz as gangue minerals, with particle size 8-150 mm (Rogozina et al., 1989, 1990). The tests lead to particularly satisfactory results, as the concentrate produced was of high MgO content (90-92% MgO). Other researchers (Aksel'rod et al., 2016) applied X-ray separation that resulted in a product with SiO₂ and CaO content less than 1,1 and 2,1% respectively.

Due to the difficulty of separating magnesite from gangue minerals, especially carbonates, a significant portion of magnesite is lost to the tailings and middlings, which are deposited as piles for potential future exploitation. It should be noted, however, that the removal of calcareous impurities is much more difficult, even impossible, than that of silicate impurities. At present, large tonnage of such magnesite-containing material has been deposited onto piles as gangue,

because it can't be processed at low cost; however, it is a potential magnesite source, when an economically viable processing scheme is invented. As a result, a considerable part of the research efforts has been devoted to the recovery of magnesite from middlings and tailings, regardless of the separation schemes applied.

In Greece, the research was focused on the exploitation of the material of particle size -40 mm that had been deposited onto piles as tailings from previous separation (Dimopoulos, 2012, Dimopoulos and Anastassakis, 2013). The methods examined were hand-sorting on belt, heavy-liquid separation and magnetic separation. Hand-sorting, which was applied to particle size $-40+10$ mm and $-10+4,75$ mm, provided concentrates with recovery and content in MgCO_3 both higher than 90%. Heavy-liquid separation, which was applied to particle size $-10+4,75$ mm, provided with concentrate of 95% MgCO_3 with 72% recovery. As regards magnetic separation, the size fractions used were $-10+4,75$ mm, $-4,75+2,36$ mm and $-2,36$ mm. The grade of the concentrates ranged between 80 and 87% MgCO_3 while the recovery was of the order 90%, except the fraction $-2,36$ mm, whose recovery was about 60%.

Physicochemical Separation Methods

Since magnesite paragenesis involves minerals with similar physical properties and gangue separation is not always easy, especially in fine particles, a great share of the research on lab-scale has been focused on flotation. As mentioned before, the major gangue minerals are silicates (mainly talc, serpentine, quartz) and carbonates (dolomite and calcite). The type of impurities and their proportion in the ore directly affect the flotation results. From the aforementioned gangue minerals, silicates, quartz and iron oxides present different physicochemical behaviour during flotation in comparison to that of magnesite and, therefore, their separation is relatively easy. On the contrary, dolomite and calcite have similar physicochemical properties and behaviour to magnesite; consequently, their separation by flotation is difficult even with the use of regulatory reagents.

The efforts to separate the aforementioned minerals by flotation have been undertaken upon the depletion of the high-grade magnesite deposits. Based on their experimental results, Doerner and Harris (1938) suggested that magnesite can be separated from silicate gangue minerals by flotation at neutral pH, in the presence of sodium alkyl sulphonate collector and caustic soda depressant.

In the United States, other researchers have tried to separate magnesite from gangue minerals that accompany it (dolomite, calcite, silicates) by applying one or two flotation stages with proper collectors and regulatory reagents on a case by case basis. These methods have been patented (Doerner and Harris, 1940; Fahrenwald, 1942; Hellmann, 1950; Jepsen, 1972). Lefforge (1945) also used flotation to separate magnesite from serpentine, chromite and anthophyllite ($< 100 \mu\text{m}$) with oleic acid collector.

In the case of silicate minerals as major gangue, they are easily separated by reverse flotation. This method has been applied on industrial scale and, as previously mentioned, has been patented by Greek researchers with international patent (Gambopoulos and Nestoridis, 1976). Laboratory tests have also shown that it is possible to separate magnesite with anionic collectors (Rau, 1985).

Reverse flotation is usually used when a high-grade magnesite concentrate is required; in this case, cationic

collectors are used to remove silicate minerals. The most common collector used on a lab-scale is dodecylamine, while low cost amine mixtures are used on industrial scale. Also, several novel cationic collectors have been used to separate quartz from magnesite (Brezani et al., 2017; Liu et al., 2019), with satisfactory results on lab-scale but not tested in practice.

On lab-scale, Karantzavelos (1984) has also applied two flotation stages to low-grade magnesite deposits with silicate gangue. The first stage includes flotation with primary amine collector to produce rough magnesite concentrate, which contains silicate minerals. Subsequently, the rough concentrate is subjected to a second flotation stage with quaternary amine collector aiming at floating of the harmful impurities. The results showed that it is possible to obtain a cleaner concentrate of high-grade in magnesite and low in impurities (0,99 – 0,20% SiO_2 and 2,84 – 0,46% CaO). By adjusting the parameters that control the flotation effect, it is possible to achieve $\text{CaO}:\text{SiO}_2$ ratio between 0,32 and 5,79, which are the acceptable limits to produce dead-burned magnesia.

Karanika (1992) dealt with the separation of cryptocrystalline magnesite deposit, with serpentine as major and hematite/ calcite as minor gangue minerals, by flotation or combination of methods that include flotation. The target was to utilise the tailings (with particle size -2 mm) of the magnesite processing plant located at Paraskevorema Mantoudi (Euboea). The conclusions of the research are summarised to the following:

- The direct flotation of magnesite with cationic collectors (Armac C and Armac T) and various modifiers (sodium silicate, phosphates) were not successful, because of the high content of the concentrate in impurities.
- The combination of direct flotation (magnesite flotation) using anionic collectors (fatty acids) and reverse flotation using cationic collectors (amines), provided with concentrates of acceptable content in impurities.
- The combination of pre-concentration with high-intensity dry magnetic separation and subsequent reverse flotation (serpentine flotation) using cationic collectors (amines) produced concentrates with acceptable content in SiO_2 and Fe_2O_3 but not in CaO . However, it should be pointed out that, in cases where flotation was applied, the reagents consumption was high.

Gence and Ozdag (1995) studied the surface properties of magnesite and serpentine in the presence of various collectors (oleic acid, sodium oleate and Armoflote 14) and sodium silicate, which was used as serpentine depressant during anionic flotation of magnesite. Tests on mineral mixture with 90% magnesite showed a slight improvement of the concentrate (1 to 2 points) compared to the original content, but with 70-80% magnesite recovery.

Also, Santana and Perez (2000) were involved in the production of high purity magnesite concentrate (SiO_2 content less than 0.20%) and magnesite recovery by weight greater than 84%. These researchers applied reverse flotation (silicates flotation) using amine collector and corn starch as magnesite depressant with satisfactory results. They achieved high purity magnesite concentrate, with quartz and other silicate content of 0,17%, and weight recovery of approximately 92%.

Similarly, Aslani et al. (2010) applied reverse cationic flotation to magnesite deposits in eastern Iran to remove silicates using sodium silicate as magnesite depressant. According to the results, it seems feasible to remove silicates

and produce magnesite concentrate suitable for use in the magnesium refractory brick industry.

Chinese researchers (Li and Liu, 2015) carried out experimental work on deposit, in the province of Liaoning, with high content in silicates and low in magnesite, applying reverse flotation for the silicates and direct flotation for the magnesite; the separation scheme included one stage of rough flotation and two cleaning stages to remove silicates. The second cleaner concentrate had the following content: 47,48% MgO, 0,21% SiO₂ and 0,76% CaO while magnesite recovery was 65,46%.

Other Chinese researchers (Wei et al., 2012) carried out tests on low-grade magnesite deposit with finely disseminated quartz as major gangue mineral. After very fine grinding (92,6% was -0,074 mm), they applied reverse flotation of quartz with lauric amine 350 g/t and, subsequently, direct flotation of magnesite with sodium oleate (1500 g/t) and sodium silicate (3500 g/t) as depressant of the remaining silicates. This treatment resulted in concentrate with 46.85% MgO and 1,21% SiO₂.

Chen and Dai (2016) tested reverse flotation on magnesite deposit with relatively low content in gangue minerals (mainly talc and dolomite). By using amine collector and hexametaphosphate or sodium silicate as magnesite depressants, they achieved slight improvement of the initial MgO content.

Reverse flotation has been used to remove silicates from magnesite with dodecylamine collector, after prior treatment with bacteria (Teng et al., 2018). For comparison, tests were also performed without pre-treatment with bacteria. The results showed that without pre-treatment with bacteria the concentrate content was 4,61% SiO₂, while after treatment the content in SiO₂ was reduced to 2,56%.

In the case of carbonate gangue minerals, such as calcite and dolomite, separation becomes more difficult to impossible; the difficulty increases with the content in the aforementioned mineral. In such a case, anionic flotation with fatty acid collectors can be used along with modifiers to depress the gangue. Due to this, a lot of lab-scale effort has been devoted to the selective separation of magnesite from carbonates for a long time. In most cases, the tests were performed on pure minerals or artificial mineral mixtures.

Komlev and Potapenko (1972) separated magnesite from dolomite and calcite by using fatty acids/synthetic aliphatic alcohols mixture as magnesite collector. Sodium carbonate, used as pH regulator, proved to have depressing effect on dolomite, with optimum results obtained in the pH range between 9,5 and 10,5. Sodium hexametaphosphate and NaH₂PO₄ had depressing effect on dolomite as well.

Gallios (1987) studied the anionic flotation using pure magnesite and dolomite minerals and sodium oleate collector; he investigated the effect of the key process parameters, such as conditioning time, flotation time, collector concentration, pH, and water hardness effect. The effect of various modifiers on the flotation of pure minerals as a function of pH was also examined. The reagents tested were sodium pyrophosphate, sodium hexametaphosphate, sodium silicate (Na₂O·xSiO₂), sodium fluorosilicate (Na₂SiF₆), carboxymethylcellulose (CMC), Calgon and 1- (2-hydroxy-1-naphthylazo)-2-naphthol-4-sulphonate (C₂₀H₁₃N₂NaO₅S). The results showed that these reagents have different effect on the above minerals. All the aforementioned reagents, more or less, depress dolomite flotation in the basic pH range (pH = 7-12), unless sodium silicate that depresses dolomite for pH < 9. Regarding magnesite: a) sodium fluoride, pyrophosphate and hexametaphosphate adversely affect its

floatability, with the effect of sodium fluoride being strong while of the others slight. b) Carboxymethylcellulose and Calgon practically do not affect magnesite. c) Sodium silicate has little activating effect on magnesite. In general, in all cases, the action of the above depressants is stronger on dolomite than on magnesite. Tests on artificial mixtures, in various ratios, have shown that the separation is incomplete due to the interaction of the minerals, despite the encouraging results achieved with pure minerals (Gallios, 1987; Matis and Gallios, 1989).

Chen and Tao (2005) used dodecyl phosphate collector to separate magnesite from dolomite by reverse flotation in the presence of sodium silicate as magnesite depressant. After previous study of the minerals chemistry and its effect on the minerals flotation mechanism, they concluded that the separation is more efficient for 4,5 < pH < 7,5, because in this region sodium silicate selectively precipitates magnesite (Chen and Tao, 2004).

Gence (2006) used pure magnesite and dolomite minerals to study the effect of various depressants on mineral contact angle; the collector used was sodium oleate, alone or along with various depressants such as quebracco, carboxymethylcellulose, or sodium silicate. According to the results, selective flotation of magnesite can be achieved with sodium oleate collector and sodium silicate as dolomite depressant; no further investigation of the minerals floatability was carried out, even on artificial mineral mixtures.

Finely disseminated dolomite is the major gangue of many magnesite deposits in Liaoning Province of China. After very fine grinding of the material (90% less than 0.074mm), Wang and Yang (2010) applied flotation scheme with one rougher and two scavenger stages using SHX collector and sodium hexametaphosphate as a regulator in the neutral pH range. According to the results, they obtained concentrate with yield 72,15% of the initial feed and content 0,71% CaO and 47,1% MgO.

In addition to the traditional anionic collectors used to float carbonates, the microorganism *Rhodococcus opacus* has been tested and evaluated as bio-collector of magnesite and calcite on bench scale (Casas Botero et al., 2007). The results showed higher affinity of the collector with magnesite, better absorption and higher floatability of magnesite in all tests.

Significant research has been carried out to separate magnesite from silicate and carbonate minerals. A lot of effort has been devoted by Chinese researchers, because of the huge but low-grade magnesite deposits located in Liaoning Province and the necessity to separate these minerals from magnesite.

Li et al. (2010) tried successive flotation stages to separate: a) magnesite from quartz with dodecylamine collector and LM1 (trade name) as a regulator, b) magnesite from dolomite, calcite and quartz with sodium oleate collector for magnesite along with LM2 (trade name) and sodium hexametaphosphate depressants for dolomite and quartz. Sodium carbonate was used as a pH regulator. After investigating the effect of particle size, collectors and modifying reagents, tests were performed at optimum experimental conditions. The results showed that the content of the concentrate in MgO increased from 32,36% to 42,25% while the corresponding in CaO and SiO₂ decreased from 1,08% and 17,7% to 0.19% and 6,73%, respectively; in any case, the recovery of magnesite was not satisfactory.

Han et al. (2013) conducted flotation tests on primary ore from the same region containing magnesite, hematite, calcite, quartz and chlorite with 95,53% MgO, 0,85% SiO₂ and 0,82% Fe₂O₃ content. They used sodium silicate and sodium

hexametaphosphate as depressants and a LKD reagent (amine mixture) as collector; they produced concentrate with improved quality as follows: 0,17% SiO₂, 0,69% Fe₂O₃, and 97,31% MgO while MgO recovery was 78,86%.

Zhu et al. (2014) investigated the possibility to separate silicate minerals and calcite from low-grade magnesite deposit (but with high content of impurities) from Liaoning Province by flotation. The procedure composed of two flotation stages: a) reverse flotation with the novel BK428 anionic collector to remove silica and b) flotation with BK420 cationic collector to remove calcite. This treatment resulted in concentrate production with 47,02% MgO (compare to 43,52% MgO in feed) and 71,64% MgO recovery. Also, the content in impurities was significantly reduced from 3,74% to 0,29% for SiO₂ and from 2,63% to 0,93% for CaO.

Tan et al. (2015) studied the separation of magnesite deposit from another site of the same province of low-grade in magnesite but high-grade in silicates and dolomite (45,85% MgO, 2,40% SiO₂ and 0,87% CaO) by flotation. The applied flotation circuit aimed at the removal of the gangue minerals (silicates, dolomite) in two stages: a) reverse flotation at pH=7, using waterglass as modifying reagent and the anionic collector BK428 (trade name) and b) second flotation stage for further removal of the gangue using sodium hexametaphosphate as a modifier and BK419B cationic collector. This process produced a concentrate with slightly better MgO content but significantly lower in harmful impurities (46,81% MgO, 0,54% SiO₂ and 0,69% CaO) while magnesite recovery was 80,78%.

Also, Sun et al. (2017) dealt with the removal of silicate and calciferous gangues applying two stages of flotation on finely ground-ore (70% < -0.074 mm). In the first stage, a mixture of amine collectors of 150g/t dose was used. The second stage was performed in the basic pH range (adjusted with 800 g/t sodium carbonate) using waterglass and sodium hexametaphosphate mixture with 4:1 ratio (aggregate consumption 600 g/t) and sodium oleate collector (consumption 1200 g/t). Each flotation stage was successively repeated. The content of the concentrate was 46,87% MgO, 0,41% SiO₂ and 0,91% CaO (compare to 41,78% MgO, 4,21% SiO₂ and 3,15% CaO in feed) and the magnesite recovery was 68,21%.

Separation of Fine Particles

In many cases, magnesite and gangue minerals (quartz, dolomite) are encountered in microcrystalline form within the deposits; consequently, grinding to fine particle size is required for their liberation. Also, fine particles are generated during grinding, even if the raw material is liberated in coarse size. The fine particles have a multiple adverse effect on the separation by flotation in terms both of value recovery and of selectivity.

Matis et al. (1988) carried out selective separation tests by flotation on magnesite and dolomite of very fine size (-45+15 µm). Initially, pure minerals were tested with fatty acids mixture as collector, while the effect of various modifiers such as carboxymethylcellulose (CMC), sodium hexametaphosphate and sodium pyrophosphate was also examined. Subsequently, tests on synthetic mineral mixtures were performed, with encouraging results, especially during the reverse flotation of magnesite.

Yao et al. (2016) investigated the effect of fine magnesite and dolomite particles on quartz removal through reverse flotation. The size of the quartz was relatively coarse (-100 +65 µm), compared to the size of the other minerals. Artificial mixtures, were used as flotation feed throughout the study. The

results of the research, on binary mixtures of quartz – magnesite and quartz – dolomite, showed that, at pH = 9 and with dodecylamine collector, the recovery of quartz in the froth was drastically reduced (from 96.66% to 37,15%) for very fine magnesite particle size (-5 µm). Correspondingly, the recovery of quartz (coarser than magnesite) is significantly reduced (from 91,2 % to 75.08%), when the percentage of fine (-5 µm) dolomite particle increases from 2,5% to 20%.

Tests were also performed on pure quartz and magnesite minerals to investigate the loss of fine magnesite particles in the tailings of the reverse flotation, with amine as quartz collector (Wang and Sun 2008). The factors studied were the particle size of magnesite and the effect of the regulators KD-1 (trade name of calcium compounds) and of starch. The results showed that size reduction causes a drastic increase in the flotation rate, indicating that magnesite flotation caused by mechanical carry-over. Regarding the effect of the aforementioned reagents, they both cause reduction of magnesite fine particles in the froth for different reasons. KD-1 inhibits magnesite from floating due to viscosity reduction, while starch has a depressing effect on magnesite.

Özkan (2002) studied the effect of ultrasounds on the separation of very fine particles, with size -38µm, from magnesite primary raw ore containing calcite and ferrous clays as gangue. He carried out tests under the following conditions: conventional tests with direct magnesite flotation, ultrasound pre-treatment of the ore prior to flotation, and ultrasound flotation. The reagents used were sodium oleate collector and sodium silicate as depressant. The results showed a slight improvement in MgO content of the concentrate and reduction in harmful ingredients. The more efficient process proved the ultrasonic pre-treatment before flotation.

For very fine particles (-75 +25 µm), Anastasakis (1999) investigated the possibility to separate magnesite from serpentine by selective magnetic coating of the gangue with very fine magnetite particles (-5 µm). From tests on pure minerals, it was concluded that selective coating of serpentine with fine magnetite particles is possible in the pH range 6 < pH < 11, while magnesite is weakly coated for pH > 9. Tests were performed on artificial mixture of minerals, 50% of each, and optimal results were achieved for pH between 6 and 8. Almost all serpentine particles (over 99,5%) acquired magnetic coating and were removed in the magnetic product; the yield of the non-magnetic product (magnesite concentrate) was about 46%, its content in magnesite was higher than 99,5% and magnesite recovery was 92% to 93%. The same researcher studied the possibility of separating fine magnesite particles from quartz by selective magnetic coating of quartz using pure samples of minerals and magnetite as coating medium (Anastassakis 2002). The results showed that it was possible to separate fine magnesite particles from quartz in the pH range 6 < pH < 11, in the presence of dodecylamine and kerosene. Optimum results were obtained at pH = 8, with the non-magnetic product having a weight recovery of 50,9%, magnesite content 94,1% and magnesite recovery 95,4%.

Greek researchers (Bimpilas and Anastassakis, 2016) investigated the possibility to separate magnetic gangue minerals (serpentine, ilmenite, and olivine) from magnesite by co-agglomerating all the gangue components and subsequent magnetic separation of the agglomerates. In this respect, hydrophobic agglomeration tests were initially carried out on single minerals, which had been picked-up from the raw ore by hand sorting, to specify the favourable conditions to ensure

selectivity; the most favourable separation was achieved with amine in the basic pH region. Also, the use of non-polar oil improved the results. The results on single minerals were subsequently confirmed by tests on artificial mineral mixtures, as gangue minerals were removed and non-magnetic magnesite concentrates of commercial grade (magnesite content 95% approximately) and of high yield were obtained. Also, Bimpilas (2020) applied the same process to separate magnesite from gangue using primary raw ore. Although the material to be separated had some differences from the single minerals and their artificial mixtures, the results were very promising.

Conclusions

Magnesite ores are of high importance, as they are the major commercial sources of the corresponding commodity, which is used in many industrial and technological applications (e.g. refractories, magnesium metal and alloys production, etc.).

The deposits present differences, sometimes considerable, in regard to magnesite mineral crystallinity and gangue composition, which render magnesite separation difficult or impossible in some cases. Even if separation is relatively easy on industrial scale, a great portion of tailings are stocked on piles. These stocks are of relatively high-grade in magnesite, and may be considered as future potential deposits.

The target of the current paper is to review in details the methods applied to separate magnesite from gangue both on industrial and bench scale. Potential processing methods to separate magnesite from gangue minerals of fine particle size are also provided.

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