Processing of Magnesite Rich Flotation Waste Deposited on a Heap

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http://doi.org/10.29227/IM-2018-01-20

Abstract

Reverse froth flotation processing was used for beneficiation of magnesite rich material – tailings from processing of primary talc ore. This possible secondary magnesite ore, which contains over 40% MgO and 45,5% loss on ignition (LOI) is stored on a heap. Because of high content of impurities it cannot be directly used. Utilizable magnesite concentrate with 46% MgO, 49,4% LOI (1000°C) and content of SiO_2 *below 1,5% was prepared in single stage flotation at selected conditions. Yield of magnesite concentrate exceeding 69% could mean significant reduction in amount of stored material.*

Keywords: reverse froth flotation, secondary raw material, magnesite, refractory magnesia

Introduction

Although enrichment of ores is known to men for millennia and it was used in times of ancient Egypt, Greece and other cultures, importance of beneficiation to remove as much gangue minerals as possible as a means of improving economics of smelting was not fully realized until medieval times (Habashi, 2006). It was not until 16th century when first summarized scientific work on mineral processing "De re metallica" was published by Georgius Agricola in 1556. Methods used at those times involved sorting, roasting, crushing, grinding and washing using launders and washing tables. Use of machines improved overall characteristics of beneficiation in terms of concentrate grade and recovery, but even though only high grade ores could be used and large portions of valuable minerals were lost in tailings. Thanks to relatively small scale mining operations coupled with abundance of high grade ore deposits this was not a big issue. Although industrialization brought further improvements and development of new, more efficient types of beneficiation machines, gravity concentration remained the only method used in mineral processing for entire centuries. New developments in machine design and further mechanization allowed for processing of medium grade ores, but the main drawback of physical separation techniques remained – limit in fine particle separation. At the times of rapid industrial expansion in mid-19th century the demand for raw materials could not be fully met by only using high grade ore deposits. At these times, first attempts were made to use novel techniques, which would allow processing of lower grade ores and fine grained ores. Flotation as a separation technique based on physico-chemical properties of particles was a very promising method. However, economics of early stage flotation process using large quantities of oils was not satisfactory. A "giant leap" in mineral processing was made in early 20th century, when froth flotation was introduced (Lynch et al., 2007). In froth flotation, particles of valuable minerals are collected using air bubbles and consumption of oils was lowered to a fraction, lowering the overall cost of the process. In following decades, further developments were made in flotation machine design and flotation reagents usage. Introduction of different groups of reagents allowed achieving selectivity of the separation process and further increased importance of this beneficiation method. Many materials previously considered wastes could now be considered raw materials. Froth flotation not only allowed economical separation of fine grained ores, but also significantly increased recoveries and concentrate grades. This paper confirms the potential of using froth flotation as a method for preparing tradable concentrate from material currently deposited on a heap.

Analysis

Sample used in this study was collected from flotation tailings heap Hnúšťa-Mútnik, Slovakia. Although the talc-magnesite ore contains significant amounts of magnesite, only talc is being recovered. Talc deposits in the Veporic area of the West Carpathians are formed at the margin of magnesite lenses, which are usually rimmed with clinochlore-talcose schists against the wall rock – the chlorite-sericite schist (Kužvart, 1984). Hnúšťa-Mútnik deposit consist of several talc-magnesite lenses. Talc as a valuable mineral is accompanied by magnesite, dolomite and calcite, with chlorite at margins and amphibolite host rock. Pyrite, tremolite, phlogopite, clinozoisite and zoisite were also identified on this deposit (Kodera and Radvanec, 2002). Talc as a naturally hydrophobic mineral is floated from primary talc ore using only polyethylene glycol (PEG-600) frother. Natural floatability of talc and hydrophilicity of carbonate minerals allows recovery of talc ranging from 60 to 80% in flotation processing with one cleaning and one scavenging stage. Cell product with about 5–10% talc and high magnesite content is then deposited on a heap. This tailing cumulates on a heap because of high content of impurities, such as SiO_2, FeO, CaO and Al_2O_3. Further froth flotation processing could be used to prepare tradable magnesite concentrates and this waste could be considered secondary magnesite ore.

Although processing of talc-magnesite ores (Hojamberdiev et al., 2010) or talc-carbonate ores (Yehia and Al-Wakeel, 2000) and even magnesite ores with chemical composition similar to composition of the material (Santana and Peres, 2001; Aslani et al., 2009) was previously investigated, all of the works were using primary ores. We have no knowledge of any research work being published where the investigated material was flotation waste, deposited on a heap. Long time exposure of powdered material to open atmosphere, coupled with rainfall, snow and significant changes in temperatures through the year can cause significant changes to surface of mineral particles present in the ore. Although these changes can affect results of froth flotation processing of secondary ore, we have tried using the same approaches found in literature for primary ores.

Santana and Peres (2001) prefer reverse cationic flotation of magnesite ore as an alternative to direct anionic flotation. Suitability of reverse flotation process for beneficiation of magnesite ore was also confirmed by Aslani et al. (2009). Results of investigation confirmed that reverse flotation process can reduce the amount of siliceous inclusions to levels acceptable, so that this type of the processed magnesia is suitable for utilization in the refractory industries. Reverse flotation was also preferred for investigated secondary ore. Not only because of presence of naturally floatable talc particles and hydrophilic nature of magnesite surface, but also because in case of direct flotation, yield of the froth product would be very high and entrainment effect could negatively affect quality of prepared concentrate (Neethling and Cilliers, 2009).

Current practice in mineral processing plants proves, that selective flotation of talc from talc-carbonate ore is possible also without collectors, using only frothers such as PEG or MIBC (Methyl Isobutyl Carbinol) as the only reagents. For flotation of silicates, such as chlorite, it is however advisable to use cationic collectors and adjust the pH of flotation pulp. Although natural floatability of magnesite is due to hydrophilic character of its surface relatively low, further depression of magnesite floatability is possible using starch (Santana and Peres, 2001).

Results presented in this article are selected from a number of flotation test carried out in order to evaluate the effect of two cationic collectors – DDA and NDPCl (N-Dodecyl pyridiniumchlorid). Both single and mixed collectors systems were evaluated as mixed collector system were previously found to be advisable in some cases (Rao and Forssberg, 1997). Soluble starch was used in some of the test to evaluate its effect as magnesite depressor. PEG and a PEG/petroleum mixture was used as frother.

Methods

Ore

Raw material used in this study was collected from flotation tailings heap in Hnúšťa-Mútnik, Slovakia. Two different locations were chosen, both consisting of multiple sampling points. Top layer of material was removed and material from depth of 10 to 30 cm was used. Multiple samples from one location were mixed on site. Chemical analysis of these two samples and average chemical composition of secondary magnesite ore prepared by mixing the two samples 1:1 is shown in Table 1.

Phase composition characterization of finely powdered samples was done using RTG diffraction analysis on D8 Bruker 2 theta/2 theta diffractometer using CuKα radiation. JCPDS PDF 2 database was used for interpretation of measured spectra.

Laboratory sieve analysis revealed, that there was a relatively large portion of coarse particles, with about 50% wt. retained on 200 μm sieve. Ore was therefore grinded prior to flotation tests in closed circuit ball mill with resulting d80 value of about 100 μm.

Flotation tests

Flotation test were carried out in 3 l laboratory flotation cell. Flotation slurry was filled to about 1 cm below the overflow line resulting in slurry volume of 2.85 l. Slurry contained 20% wt. solids. Slurry temperature was kept at 22°C. Weighted amount of ore was mixed with part of needed water and transferred to agitated flotation cell. Agitation speed was set to 1600 revolutions per minute. pH was then adjusted to 6.5 using 0.1 M HCl solution. After achieving desired pH, collector (or two collectors) was then added and agitated with

Tab. 1. Chemical analysis of secondary magnesite ore (SMO) sampled from two different places of the heap (Sample I and II)

Tab. 1. Analiza chemiczna próbek wtórnej rudy magnezytu (SMO) pobranych z różnych punktów hałdy (próbka I i II)

Component / wt. %	Analyzed ore sample		
	Sample I	Sample II	SMO
LOI (1000 °C)	43.7	45.3	44.5
MgO	40.5	41.1	40.8
SiO_2	7.3	6.5	6.9
Fe_2O_3	2.7	2.7	2.7
Al_2O_3	1.6	1.3	1.4
CaO	0.8	0.6	0.7
S	0.3	0.3	0.3
Cu	0.05	0.06	0.05

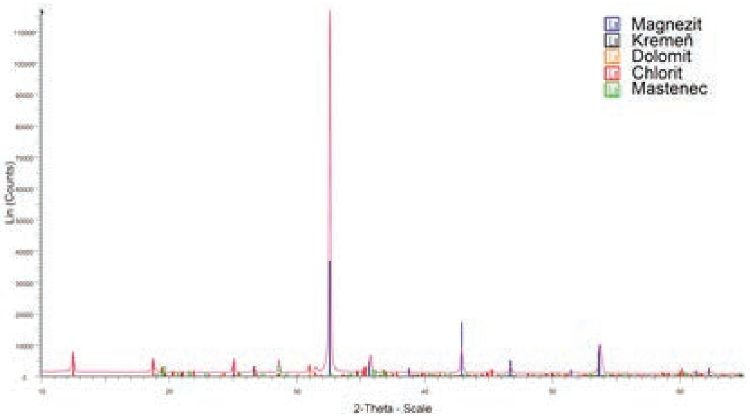

Fig. 1. RTG diffraction analysis of secondary magnesite ore

Rys. 1. Dyfrakcja RTG wtórnej rudy magnezytowej

slurry for 15 min. In case of using also depressor, this was added prior to collector and agitated for 5 min. Frother was added 1 min. prior to introduction of air, which was electronically regulated to 4 l.min-1 (Jg = 0.43 cm.s-1). Flotation time was limited to 20 min in which two froth products were collected – Froth I (first 10 min.) and Froth II (10–20 min.). Water had to be added during batch flotation tests to keep slurry/froth interface at constant level. 0.1 M HCl solution was used to keep constant pH of the pulp. At the end of each flotation test, froth products and cell product were filtered and dried at 60°C. Dry products were homogenized, weighted and representative samples were taken for grade analysis.

Results

Phase composition characterization shown in Figure 1 confirmed, that sample is mainly composed of magnesite, with minor content of talc, chlorite group minerals and dolomite. Same conclusions can be also drawn from chemical analysis of ore shown in Table 1. High content of carbonate minerals causes high LOI (45.5% wt. at 1000°C) as a result of their thermal decomposition. Relatively low CaO content (0.7% wt.) and high MgO content (40.8 % wt.) suggests that dolomite and calcite constitute only a fraction of carbonates and magnesite is highly dominant. High SiO2 content (6.9% wt.) is caused by presence of phyllosilicate minerals – talc ($Mg_3Si_4O_{10}(OH)_2$) and chlorite group minerals ($(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \bullet (Mg,Fe)_3(OH)_6$). Talc recoveries up to 80% can be achieved in flotation of primary talc ore using PEG frother as the only reagent. This leads to 5–10% content of talc in flotation tailings – secondary magnesite ore (SMO). Rest of the SiO_2 contamination and major part of Al_2O_3 and Fe_2O_3 can be attributed to presence of chlorite group minerals. These minerals have very low natural floatability and they cannot be effectively recovered to froth product without using a suitable collector. Presence of Sulphur in chemical compositions suggests trace amount of sulphide minerals such as pyrite and chalcopyrite. Froth flotation should be aimed at recovery of phyllosilicate minerals to froth product in order to lower the content of SiO_2, Fe_2O_3 and Al_2O_3 impurities to acceptable levels.

Research behind this paper consisted of number of planned flotation experiments where various effects were investigated: DDA as single collector, NDPCl as single collector, mixed collector systems, soluble starch (SS) as depressor for carbonate minerals, dosage of PEG frother and use of petroleum as a partial replacement of other reagents.

Tab. 2. Results of flotation in Regime 1

Tab 2. Wyniki flotacji (warunki 1)

Product	Yield / % wt.	Assay / % wt.			Recovery / % wt.	
		LOI	SiO_2	MgO	SiO_2	MgO
Froth I	36.8	37.1	11.1	38.9	80.6	33.5
Froth II	1.1	39.2	9.4	40.7	2.0	1.0
Cell	62.1	49.8	1.4	45.2	17.4	65.5

Tab. 3. Results of flotation in Regime 2

Tab. 3. Wyniki flotacji (warunki 2)

Product	Yield / % wt.	Content / % wt.			Recovery / % wt.	
		LOI	SiO_2	MgO	SiO_2	MgO
Froth I	30.8	36.6	17.3	32.3	84.5	23.8
Cell	69.2	49.4	1.4	46.0	15.5	76.2

Based on the PZC/IEP of individual minerals present in investigated ore, adjustment of slurry pH to 6.5 was chosen to be sufficient for selective separation phyllosilicates from magnesite, their attachment to rising air bubbles and formation of silicate rich froth. Cell product should thus be cleaned of SiO_2, Fe_2O_3 and Al_2O_3 impurities and primarily consist of particles of valuable mineral.

Statistical analysis confirmed expected results: collectors (NDPCl and DDA) had negative effect on yield of magnesite concentrate, while positively affecting its grade. Statistically significant increase in LOI as well as decrease in content of SiO_2 impurities were linked to increased collector dosages. Effect of the other three reagents was of minor statistical importance. These tests will not be discussed in full. Rather, two reagent regimes with best results in terms of magnesite grade and recovery will be discussed in more detail.

Regime 1

In this quite simple reagent regime, where only two reagents were used (except HCl used for pH adjustment): 400 $g.t^{-1}$ DDA in role of collector and 50 $g.t^{-1}$ PEG frother, acceptable results in terms of cell product grade were achieved. Results of this test are summarized in Table 2.

Yield of individual products suggests, that there is no need for longer flotation time than 10 min. While 36.8% material was collected in first 10 min., only another 1.1% was collected in next 10 min. Such a small yield does not have any significant positive effect on final grade of cell product – magnesite concentrate and on the other side this would have negative effect on economics of the process. Same assumption can be made when considering SiO_2 recovery: 80.6% is recovered in first 10 min. while another 10 min. of flotation raises SiO_2 recovery to froth product only by another 2%. Prepared cell product in case of 10 min. flotation time would have 49.6% LOI, 45.1% MgO content and about 1.5% of SiO_2 impurities. If calcined at 1000°C, this would produce magnesia with about 89.5% MgO and content of SiO_2 impurities below 3%. Relatively high MgO content can be partially attributed to its presence in composition of talc and chlorites, but SiO_2/MgO ratio in froth product suggests, that there are also another mechanisms of MgO recovery. The most probable interpretation is overlapping of two mechanism – natural floatability of magnesite particles and entrainment effect. Because of high concentration of magnesite particles in slurry they have greater tendency to report to froth product due to entrainment. Relatively high content of magnesite in froth product causes also high LOI of froth product, close to 40%. For the comparison, LOI of pure magnesite is 52.2%, that of pure talc about 4.5% and that of chlorite group minerals in range of 10–15%.

Regime 2

Reagent regime 2 was aimed at lowering the recovery of magnesite to froth product. To achieve this goal, 500 $g.t^{-1}$ of soluble starch was used as magnesite depressor. 50 $g.t^{-1}$ PEG was used in role of frother, 300 $g.t^{-1}$ of DDA and 100 $g.t^{-1}$ of Petroleum was used as mixed collector for phyllosilicate minerals. Partial replacement of more expensive flotation collectors with cheaper oil based reagents such as Petroleum is common practice in flotation plants used to lower the overall costs of the process. Results of this test are summarized in Table 3.

In such conditions all the froth was created in first 10 min. and Froth II product could thus not be collected. Use of starch decreased overall amount of froth product to 30.8%, leaving 69.2% of cell product – magnesite concentrate. Decrease of yield can be attributed to lower recovery of magnesite due to its natural floatability by further surface hydrophobization. This resulted in lower LOI of froth product when compared to results without depressor. 36.6% LOI is still high suggesting strong entrainment effect. At pH 6.5 starch adsorbed predominantly on magnesite surface because of its lower PZC value when compared to dolomite. This allowed some separation and resulted in higher MgO and lower CaO content in magnesite concentrate. Calcination of this product at 1000°C would result in production of magnesia with 90.9% MgO and about 2.8% SiO_2. Such product would be applicable in production of refractory materials. Implementation of reverse magnesite flotation would lead to almost 70% reduction in amount of produced tailings. Further reduction could be achieved by reducing entrainment of magnesite particles.

Both presented results summarized in Table 2 and Table 3 were achieved in single stage flotation. Better results in terms of concentrate grade and recovery could be achieved by adding cleaning and scavenging stages. Lowering the entrainment effect is essential for maximizing magnesite recovery and minimizing tailings production. This could be achieved e.g. using higher froth height to allow better draining and/or by froth washing and/or by slurry recirculation. All of these mechanism are used in column flotation, which is expected to produce better results in single stage when compared to presented results achieved in flotation cell. Higher product grade can also be achieved by acid leaching of calcined product (Raschman et al., 2010).

Conclusions

Flotation concentrates with acceptable magnesite content were produced in single stage reverse froth flotation process from secondary magnesite ore deposited on a heap. This would lead to significant reduction in amount of produced tailings. Use of amine collectors is sufficient to achieve adequate results in terms of concentrate grade and yield when pH is adjusted. Use of soluble starch can further increase yield of magnesite concentrate as well as decrease content of impurities. Both presented reagent regimes resulted in production of magnesite concentrate, calcination of which would lead to production of magnesia utilizable in refractory industries.

Acknowledgements

This work was supported by the research grant project VEGA, no. 1/0843/15, and APVV 0423-11.

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Wzbogacanie odpadów bogatych w magnezyt zdeponowanych na składowisku

W procesie wzbogacania materiału bogatego w magnezyt wykorzystano odpady flotacyjne z wzboga-caniu talku zdeponowane na składowisku. Materiał magnezytowy będący materiałem wtórnym po wzbogacaniu talku zawierał ponad 40% MgO i 45,5% strat prażenia (LOI).

Z powodu dużej zawartości zanieczyszczeń nie można go wykorzystać bezpośrednio. Koncentrat ma-gnezytowy powinien charakteryzować się zawartością magnezu 46% MgO, stratami prażenia 49,4% LOI (1000°C) i zawartością SiO_2 poniżej 1,5% . Wzbogacanie odpadów przeprowadzono metodą flotacji odwrotnej, jednoetapowo. Otrzymano uzysk koncentratu magnezytu przekraczający 69% co może oznaczać możliwość znacznego zmniejszenie ilości deponowanego materiału.

Słowa kluczowe: flotacja odwrotna, surowiec wtórny, magnezyt, magnezyt ogniotrwały