A Review of Flotation Separation of Mg Carbonates (Dolomite and Magnesite)

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Abstract: It is well documented that flotation has high economic viability for the beneficiation of valuable minerals when their main ore bodies contain magnesium (Mg) carbonates such as dolomite and magnesite. Flotation separation of Mg carbonates from their associated valuable minerals (AVMs) presents several challenges, and Mg carbonates have high levels of adverse effects on separation efficiency. These complexities can be attributed to various reasons: Mg carbonates are naturally hydrophilic, soluble, and exhibit similar surface characteristics as their AVMs. This study presents a compilation of various parameters, including zeta potential, pH, particle size, reagents (collectors, depressant, and modifiers), and bio-flotation, which were examined in several investigations into separating Mg carbonates from their AVMs by froth flotation.

Keywords: dolomite; magnesite; flotation; bio-flotation

1. Introduction

Magnesium (Mg) carbonates (salt-type minerals) are typical gangue phases associated with several valuable minerals, and have complicated processing [1,2]. Dolomite ($CaMg(CO_3)_2$) and magnesite ($MgCO_3$) are the main Mg carbonates [3–8] that can be associated with other salt-type minerals, including phosphates (e.g., Apatite), sulfates (e.g., Barite), halides (e.g., Fluorite) and tungstates (e.g., Scheelite) [5,9], as well as sulfides [10], and other oxides [2].

The ease of separation of Mg carbonates from their associated valuable minerals (AVMs) is dependent on various processing conditions. To achieve adequate separation efficiency, different processing methods based on AVM properties have been used: magnetic separation [8], dense medium separation [1,8,11–13], electronic sorting techniques (when iron and titanium oxides are AVMs) [1,8], calcination [8,11] and froth flotation [1,8,10,11,13–15].

The first flotation separation for the rejection of magnesite was reported by Doerner and Dwigh (1930s) [12]. Flotation of Mg carbonates is typically carried out by using fatty acids, since these collectors give insoluble complexes with all divalent cations [5]. Determination of the appropriate depressing reagents for sinking valuable minerals in the presence of collectors for carbonates is a cardinal stage in obtaining an efficient separation in the direct flotation of Mg carbonate [7]. One of the essential challenges during flotation in the presence of Mg carbonate is the occurrence of slimes. The low hardness of carbonates leads to slime problems. Carbonate slimes can cover the surfaces of their AVMs, change their properties, and make their flotation complicated [11,16–18]. Moreover,

Mg carbonates are semi-soluble and hydrophilic in nature; the dissolved species of carbonates undergo reactions such as hydrolysis, complexation, adsorption, and bulk precipitations, which inhibit the selective interaction of flotation reagents with surfaces of minerals [2,12,19–22]. Therefore, rejection of Mg carbonates prior to processing of other minerals has been recommended.

Nevertheless, even with these rejections, selectivity is still a major challenge in achieving satisfactory separation [6,11], especially when the valuable mineral is also a salt-type mineral, and complexity increases [5,6,23] due to the similarities in crystal structure (crystalline and sedimentary minerals behave similarly, but the crystalline minerals have much lower surface areas and consume less collector than the sedimentary minerals) and physiochemical surface properties [17,18,24,25]. Thus, a literature review for flotation of Mg carbonates could be useful and suggest new directions for future investigations. The aim of this paper is to provide a robust review of various flotation conditions for Mg carbonates, with a focus on the collectors, depressant, modifiers, isoelectric point, particle size, and solubility of these minerals during flotation.

2. Particle Size Effect

Particle size and degree of mineral liberation are important factors for flotation separation [26]. Grinding of salt-type minerals to liberate them is quite challenging where their solubility is increased by reducing their sizes (ions of salt minerals in the pulp undergo various hydrolysis reactions, forming different complexes) [15]. It has been reported that coarse particles of Mg carbonates are relatively able to float, and separation of fine particles by flotation would have several difficulties [27]. Fine dolomite particles can cover the surface of other AVMs and change their surface properties [23]. Xi-mei et al. [2] reported that during the beneficiation of hematite, fine dolomites ($-45 + 18$ μm) significantly affected the final concentrate recovery. Fine carbonates (-45 μm) exhibit low selectivity in flotation systems [23]; floating these fines would require an immense increase in the collector concentration beyond economic viability. Furthermore, the entrainment effect of fine carbonates can significantly increase the losses of valuable minerals in the froth (reverse flotation) [22,28–30]. In general, coarse particle size favors the selective separation of Mg carbonates from oxides, while decreasing the particle size could be complicated for their separation from other salt-type minerals. It has been suggested that oil agglomeration could be effective in handling the quandaries related to fines [31]. The relationship between particle size and dolomite recovery is shown in Table 1.

Table 1. Relationship between size and flotation recovery of dolomite and its associated minerals.

Particle Size Fraction (μm)	Flotation Type	Dolomite Recovery (%)	Associated Mineral Recovery (%)	Mineral Type	References
$-180 + 125$	Direct	~27	-	Single pure	[32]
-74	Direct	98.30	Calcite: 93.9	Single pure	[5]
$-100 + 65$	Reverse	~49	Quartz: 96.66	Single pure	[23]
$-212 + 150$	Reverse	11.37–8.91	Apatite: 86.86–91.86	Single pure	[7]
		4.45	Apatite: 87.10	Pure mixture	
$-74 + 38$	Reverse	31.37	Apatite: 64.89	Single pure	[33]
$-106 + 38$	Reverse	~10	Monazite: 37	Single pure	[34]
$-106 + 38$	Direct	66	Monazite: 29	Single pure	
$-212 + 150$	Reverse	18	Apatite: 87.7	Single pure	[14]
$-212 + 150$	Reverse	~20	Apatite: 80	Pure mixture	
$-106 + 38$	Direct	~90	Gold Bearing Chalcopyrite: ~20	Single pure	[10]
$-212 + 150$	Reverse	~10	Apatite: ~80	Single pure	[35]
$-212 + 150$	Reverse	37.60	Apatite: 53.3	Pure mixture	

Table 1. *Cont.*

Particle Size Fraction (µm)	Flotation Type	Dolomite Recovery (%)	Associated Mineral Recovery (%)	Mineral Type	References
−100 + 74	Reverse	~15	Apatite: ~85	Pure mixture	[27]
−500 + 100	Reverse	~20	Apatite: ~95	Pure mixture	
−100 + 74	Direct	80	~95	Single pure	[36]
−74	Reverse	12.57	Apatite: 87.20	Ore	[30]
−106 + 45	Direct	~80	~90	Single pure	[18]
−106	Reverse	~10	Apatite: 88	Pure mixture	[37]
−106	Reverse	~10	Apatite: 82	Ore	
−74	Reverse	9.80	Apatite: 86.01	Ore	[38]

3. Surface Properties

3.1. Electrical Charge

Zeta potential (ZP) can be used to describe and determine the relationship between the adsorption behavior of reagents (including bacteria) and the surface charge of mineral particles through flotation separation. ZP measurement can assess surface charges and determines the effect of attraction-repulsion forces [22,39,40]. ZP measurement, which is the determination of mineral surface charges at different pH values, is among the most important techniques used to understand the flotation characteristics of minerals with similar surface properties [35].

Various investigations have indicated that dolomite and magnesite seem to have similar surface electrical charge behaviors when they are conditioned at a constant pH [22,33,35,39]. Generally, the isoelectric points (IEPs) of pure magnesite and dolomite have been reported in the pH ranges of 6.5–6.8 and 5.5–7.6, respectively (Table 2). Mineral dissolution primarily activates the surface charge of salt-type minerals under the influence of water molecules (at various pHs); Mg carbonates are noted to be highly affected in acidic regions [12].

Table 2. The IEP of Mg carbonates in various conditions.

IEP (Pure Minerals)		IEP (Presence of Reagents)		Reagents	References
Associated Mineral	Carbonates	Associated Mineral	Carbonates		
Apatite: 5.5	Dolomite: 7	7.1	9.3	$Ca(NO_3)_2$	[3]
Apatite: 5.5	Dolomite: 7	7.2	8.4	$Mg(NO_3)_2$	
Magnesite: 6.8	Dolomite: 7.6	5.5	5.5	Sodium Silicate ($NaSiO_3$)	[12]
Apatite: 6.8	Dolomite: 8.5	6.8 (ZPC)	8.6 (ZPC)	Sodium Chloride (NaCl)	[37]
Apatite: 6.5	Dolomite: 4.4	6.4	3.6	B-naphthyl sulfonate formaldehyde condensate (NSFC)	[38]
Magnesite: 6.7	Dolomite: 6	9.8	9.1	Dodecylamine (DDA)	[23]
Monazite: 5	Dolomite: 5	5.5	4.2	Benzohydroxamic acid	[34]
Magnesite: 6.5	Dolomite: ~7	7	7	Sodium hexametaphosphate (SHMP)	[15]
Magnesite: 6.5	Dolomite: ~7	7	6.5	Carboxymethyl cellulose (CMC)	
Monazite: 5	Dolomite: 5	3.5	Negative ZP (pH 3–11)	Sodium oleate (NaOl)	[34]
Apatite: 4.2	Dolomite: 6.2	5.4	Negative ZP (pH 5.5–11)	Potassium Chloride (KCl) + Sodium Silicate (Na_2SiO_3)	[11]
Apatite: 5.3	Dolomite: 11	Negative ZP (pH 4–11)	5.5	Sodium Chloride (NaCl)	[14]
Calcite: 11	Dolomite: 11.5	Negative ZP (pH 6.5–11.5)	Negative ZP (pH 6.5–11.5)	Water Glass/ modify water glass (ferric silicate hydrosols)	[5]
Monazite: 5	Dolomite: 5	Negative ZP (pH 3–11)	Negative ZP (pH 3–11)	Flotinor 1682 (organic phosphoric acid)	[34]

Table 2. *Cont.*

IEP (Pure Minerals)		IEP (Presence of Reagents)		Reagents	References
Associated Mineral	Carbonates	Associated Mineral	Carbonates		
Magnesite: 6.5	Dolomite: ~7	Negative ZP (pH 7–12)	Negative ZP (pH 7.5–12)	Tetrasodium pyrophosphate (TSPP)	[15]
Apatite: 5.5	Dolomite: 10.3	-	-	-	[41]
Dolomite: 6.3	Magnesite: 6.7	-	-	-	[12]
Dolomite: 6.3	Magnesite: 6.8	-	-	-	[42]
Apatite: 4.5	Dolomite: 6.8	-	-	-	[11]

ZP measurements have revealed that cationic and anionic collectors have pronounced effects on the surface charge of Mg carbonate minerals (Table 2). It has been observed that cationic collector dodecylamine (DDA) shifts the IEP of Mg carbonates to basic pH 9, and exhibits negative ZP up to pH 12 [23]. On the other hand, with anionic collector sodium oleate (NaOl), Mg carbonates experience negative ZP from pH 3 to 11 [34]; it can also be noted that the ZP of Mg carbonates become negative with increased NaOl concentration [31].

In carbonate bio-flotation, high negative charges are generated on the bacteria surfaces over a wider pH range when they are introduced in pulp containing Mg^{2+} and Ca^{2+} ions [3,23,33] (Table 2); suggesting high adsorption of the bacteria on the dolomite [33]. Even though both these ions are adsorbed by the bacteria, Mg^{2+} is adsorbed to a greater extent than Ca^{2+} [33]. Moreover, this phenomenon could be due to the presence of teichoic acid in the surface of the bacteria, which can bind with these ions [43]. Hence, it is suggested that bacteria could be used in the selective separation of dolomite from AVMs.

3.2. Contact Angle

Contact angle measurement between mineral surfaces and air bubbles is an important characteristic and a typical method that can be used to quantify mineral hydrophobicity in the presence or absence of reagents (high contact angles translate to highly hydrophobic surfaces) [11,31,42,44]. In other words, higher contact angles indicate higher surface tension and adhesion between particles and bubbles [45]. It is well understood that the recovery of minerals during flotation decreases with a decrease in the surface tension [46]. Hydrophobic surfaces are characterized by high contact angles ranging from 40° to 110° [42].

Naturally, Mg carbonates exhibit small contact angles in distilled water (magnesite 10.4° and dolomite 6.6°), and with the addition of cationic collectors (such as Dodecyl-amine (DDA)), the hydrophobicity of magnesite remains virtually the same, while for dolomite it is increased. Contrary to cationic collectors, in the presence of anionic collectors such as sodium oleate, the contact angle of magnesite and dolomite increased to 79° and 39°, respectively [13,23,42]. These variations suggest that Mg carbonates can be separated from each other by flotation in different conditions. Zhou et al. [11] reported that in the flotation separation of apatite from dolomite using conventional air bubble in the presence of the collector (Fatty acids), the contact angles of apatite and dolomite were 72.5° and 67.0°, respectively. However, when oil bubbles were used instead of air bubbles, the contact angles for apatite and dolomite were reported as 83.0° and 5.7°, respectively. Moreover, their results showed that the presence of sodium silicate as a depressant can decrease the contact angle of dolomite from 105° to 5.7° and can facilitate its separation from its AVMs [11].

4. Solubility

Mg carbonates as a group of salt-type minerals show a relative solubility and their dissolved species (multivalent metal ions, Ca and Mg ions) can undergo reactions such as hydrolysis, complexation, and adsorption, which influence interactions between collectors and minerals [12,13,18,20–22]. Magnesite and dolomite in aqueous dispersions are slightly dissolved, and give ions of Ca and Mg [12,32,42]. The solubility of magnesite increases at acidic pH [42]. Dolomite is highly affected by the solubility of metal cations—Ca^{2+} and Mg^{2+} ions [34]. Parts of Ca^{2+} exist in the dolomite structure dissolve in solutions

at pH < 11 and precipitate at pH > 12 [12], while Mg^{2+} in both magnesite and dolomite is reported to predominantly dissolve in solutions at pH < 9 and precipitate at pH > ~10.5–11 [12,17]. Furthermore, both Mg^{2+} and Ca^{2+} in dolomite possess similar concentrations at all variations of pH in their soluble state in water (pH < 9) [18]. Gence and Ozbay [13] reported that soluble concentration of Mg increases below pH 8. The presence of these lattice ions in flotation pulp inhibits the flotation of AVMs [18], except for the flotation of apatite in the presence of Ca^{2+} [47]. Solubility constants (K_{sp}) of magnesite and dolomite were reported to be 4.9 and 16.7, respectively [24]. In other words, the dissolution rate of dolomite is much faster than magnesite in water solution [12]. Solubility of Mg carbonates is well known to decrease with an increase in the temperature [48].

Due to solubility of Mg carbonates, after immersion, their surfaces are rough and present several hydrolysis holes, either when the alkaline-earth ions or Mg and Ca ions have left the surface [13]. Surface precipitation occurs when the reagent interacts with these rough surfaces while bulk precipitation of the metal reagent salts follows when the dissolved lattice ions form an insoluble compound with collectors away from the surface of the minerals [34]. The extent of bulk versus surface precipitation would essentially depend upon the mineral solubility and the dissolution kinetics; high solubility and fast kinetics would promote bulk precipitation. Therefore, collectors needed for flotation are consumed by bulk precipitation, rendering the collector unavailable for surface precipitation; hence, bulk precipitation is detrimental for flotation of Mg carbonates [15]. In general, based on the relative solubility of Mg carbonates in the acidic region, their flotation in the basic region can be recommended, where their solubility decreases with increasing solution pH.

5. Flotation

5.1. Direct Flotation

The flotation separation of Mg carbonates from non-salt type minerals (hematite, gold-bearing sulfides, and monazite) is typically less difficult as compared to their separation from other salt-type minerals (phosphate) [8,10,14,17,18,34,49]. As they are the major gangue minerals of phosphate ore, an effective method of separating them from phosphate minerals is direct flotation of Mg carbonates [50,51].

5.1.1. Collectors

Direct flotation of dolomite can be achieved by using different collectors (Table 3) [12,32,41]. Sodium oleate as an anionic collector is the most popular collector used for floating dolomite; however, its selectivity is low, and it is highly sensitive to water hardness and flotation temperature [37,38]. As a result, in the absence of depressants or pH modifiers, the recovery of dolomite is in roughly equal proportion to its associated minerals [10,38,41], and the overall flotation is not selectively efficient.

Due to the relatively low selectivity of anionic fatty acids and their derivatives, cationic collectors are also used in the flotation of Mg carbonates with modification of parameters, and the use of modifiers/depressants. Single mineral flotation by cationic collectors was demonstrated to be encouraging for Mg carbonates. It was observed that DTAB (Dodecyltrimethyl ammonium bromide) can satisfactorily float dolomite, exhibiting an intermediate collecting strength (recovery) in the absence of modifiers [5]. Increasing the chain length of cationic collectors enhances dolomite recovery considerably, but selectivity is relatively decreased with increasing collector concentrations in the pulp [34,36,52].

Table 3. Various anionic and cationic collectors for direct flotation of Mg carbonate.

Collector	Carbonate Recovery (%)	Reference
Sodium Oleate (NaOl)	90	[32]
	95	[41]
	~70	[34]
	~90	[10]
	~80	[18]
	~80	[38]

Table 3. *Cont.*

Collector	Carbonate Recovery (%)	Reference
Flotinor 1682 (organic phosphoric acid)	~70	[34]
Saponified Gutter Oil Fatty Acid (GOFA)	12.57	[30]
5-propylsalicylaldoxime	~50	[52]
Dodecyltrimethyl ammonium bromide (DTAB)	~60	[5]
Dodecylamine (DDA)	~49	[23]
Dodecyl phosphate	98 80	[12] [53]
Dodecylamine hydrochloride (DDA-HC1)	37.60 18.50	[35] [14]
Dodecylamine hydrochloride (DDA-HC1)	10	[35]
Octadecylamine-kerosene Emulsion (1:3)	~15	[36]
Dodecyl-*N*-carboxyethyl-*N*-hydroxyethyl-imidazoline	~98	[37]

In general, cationic flotation is more sensitive toward desliming the flotation feed, while the anionic route is more sensitive toward the ionic composition of the pulp [2,3,7,17,32–34]. Therefore, to achieve selective separation, it is crucial to develop selective collectors [51,54,55]. It has been reported that a new kind of collector, "Saponified gutter oil fatty acid" (GOFA), which is an environmentally friendly, cost-effective, and selective collector, exhibits excellent selectivity towards adsorption on dolomite owing to the considerably high magnesium content of dolomite and the lack of magnesium in apatite during reverse flotation of apatite in collophanite ore [30]. Moreover, recovery of Mg carbonates was high when dodecyl phosphate was used as a collector, which indicates effective adsorption capabilities on both magnesite and dolomite [12]. Since Mg carbonate flotation is so sensitive to pH, it is possible to selectively float dolomite from monazite ((REE)PO$_4$) using sodium oleate at pH 4 or by using flotinor 1682 (organic phosphoric acid) at pH 4 or 7; however, depressants and activators are necessary for a more effective separation [34]. Various investigations indicated that Mg carbonate recovery is pH dependent, and separation is effective in acidic regions as well as at alkaline pH. However, as a result of lattice dissolution of dolomite in acidic conditions, there would be increased collector adsorption density to satisfy both value and gangue minerals [34,41]. Therefore, flotation in the acidic region may not be encouraged. Generally, several studies have shown that various collectors produce high recoveries of Mg carbonates; furthermore, efficiency and selectivity can be improved by the use and modification of several other parameters and the use of depressants.

5.1.2. Depressants and Modifiers

As mentioned earlier, carbonates are typically gangues for their AVMs, and they are most often depressed; however, in some cases they are floated, and their associated valuable minerals are depressed (reverse flotation when AVM are the target). As has been reported, fine particles have interactive effects on each other that could depress another mineral [56]; fine particles of Mg carbonates can coat the surface of their associated minerals and depress them [17,18,23,57].

In addition to the depressing effect of fine Mg carbonates, in the separation by reverse flotation, their associated valuable minerals are typically depressed using various depressants based on their types (Figure 1). These depressants partially affect Mg carbonate flotation by changing pH value. pH, collector, and depressant concentrations are the main parameters for a selective Mg carbonate separation. For instance, it has been reported that thioglycollic acid and citric acid selectively depressed pyrite between pH 9.0 and 10, but could not depress dolomite during flotation by NaOI (Table 4) [10].

It is well understood that the main uses of modifiers in flotation are their great capability for dispersion, modification of froth properties, control of pH, precipitation of metallic ions, and modification of collector action [15]. In the flotation of salt-type minerals which have similar surface properties, efficient separation

can be achieved customarily by the application of modifiers [15,32,34]. They act either as depressant agents or activators [32]. It has been reported that sodium silicate has a slight activation on magnesite but depresses dolomite strongly at pH less than 9.0 (sodium silicate activated apatite flotation in the presence of oleate as collector but depressed silicates) [32].
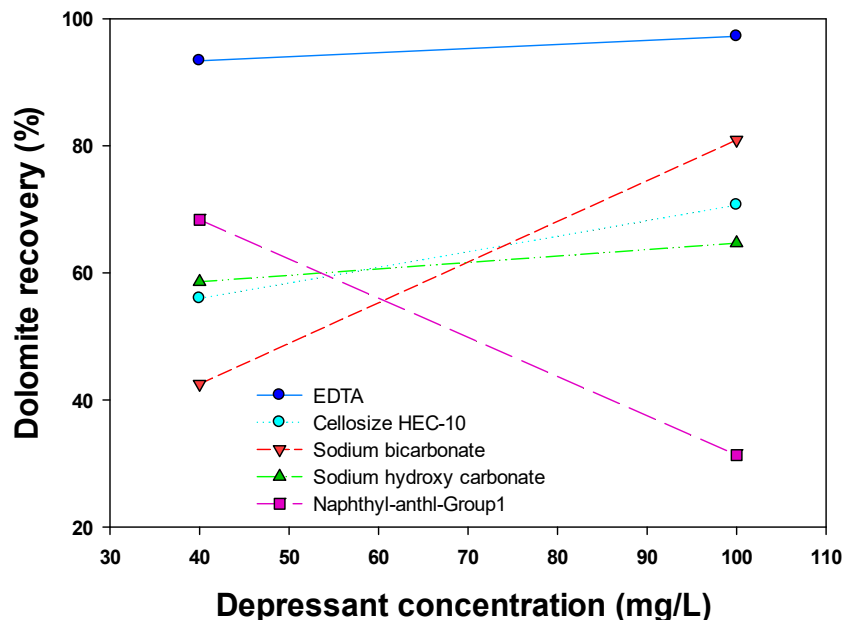
Figure 1. Effect of typical depressants on Mg carbonate flotation in the presence of 60 mg/L NaOI as a collector.

Table 4. Effect of depressants on associated minerals of Mg carbonates through flotation separation (in all conditions, dolomite recovery was around 90%).

Associated Mineral	Collector (mg/L)	Depressant (mg/L)	pH	Recovery (%)	Reference
Hematite	NaOI (120)	-	9–12.5	75.25	[2]
Hematite	NaOI (120)	CaCl$_2$ (15)	9	15	[2]
Hematite	NaOI (120)	CaCl$_2$ (50 & 100)	9.5–12.5	0	[2]
Pyrite	NaOI (60.8)	-	10	80	[10]
Pyrite	NaOI (91.2)	Thioglycollic acid (9.2)	9–10.5	12.5	[10]
Pyrite	NaOI (91.2)	Citric acid (19.2)	10	8.53	[10]

Sodium silicate hydrolyzed in aqueous solutions forms many products, such as poly silicic acid and colloidal silica in high concentrations, and depolymerization products in dilution, which can modify the process [32]. In the presence of fatty acid collector, sodium hexametaphosphate (SHMP) and carboxymethylcellulose (CMC) were used as modifiers in the flotation of magnesite [32]. Moreover, water glass and its modified version, ferric silicate hydrosol, not only enhance recovery of dolomite, but also reduce the amount of DTAB used as a cationic collector for the flotation process [5]. EDTA, a chelating reagent which can typically be used as a depressant, activates the surface of dolomite, produces soluble complexes, and clean dolomite surfaces for oleate adsorption [7]. The concentration of modifiers may play an essential role, in controlling the alkalinity or acidity of the pulp for an optimum flotation, where in some cases, by increasing the concentration of modifiers dolomite may depress and its recovery decreases (Figure 2). Since flotation of Mg carbonate is dependent on the pH of the solution, some modifiers are used as pH regulators. Changes in pH may change several parameters such as zeta potentials, which could affect the flotation results.
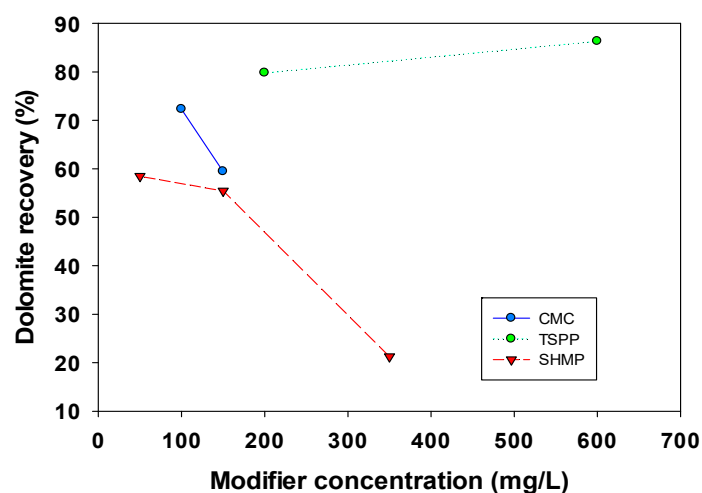
Figure 2. Effect of various modifiers on Mg carbonate flotation in different conditions.

5.2. Depression of Mg Carbonates

Various investigations have indicated that flotation of Mg carbonates poses several difficulties where the fatty acids and their derivatives, which are used as collectors, have a poor selectivity for carbonates and phosphate minerals [47]. On the other hand, Mg carbonates cause adverse effects on the flotation of their associated valuable minerals; therefore, their depression is a growing procedure in the mineral processing industry. Owing to the significant content of cations (Ca^{2+} and Mg^{2+}), organic and inorganic depressants can adsorb on the surface of dolomite [13]. Kerosene as a modifier in the presence of amine collector depresses dolomite [11,27]; however, conventional depressants for dolomite are sodium silicates [7,11] and sodium hydroxide (both can be used as pH regulators) [7].

Moudgil and Ince [35] indicated that apatite can efficiently be separated from its mixture with dolomite at pH 6.3 with DDA in the presence of NaCl, which reduces the rate of collector adsorption on the surface of dolomite by compressing the electrical double layer. Dolomite can be significantly depressed by CMC as well as with citric acid and naphthylanthyl sulfonates. CMC not only depresses MgO as gangue, it also improves the efficiency of process by increasing the concentrate grade (especially during separation of carbonates from copper and niobium minerals). CMC is not pH dependent, and its depression impacts can be attributed to many functional carboxylate groups, or the large molecular volume adsorbing on the dolomite surface which is obstructing the dolomite-collector adsorption mechanism. In the case of citric acid, depression occurs as a result of the capability of carboxylate groups to bind with the cations (Ca^{2+} and Mg^{2+}), forming insoluble citrate on dolomite surfaces. CMC, citric acid, and naphthylanthyl sulfonates depress dolomite, but do not have an effect on apatite, due to its structural characteristics, thus indicating that Mg carbonates are considerably depressed by appropriate depressants while apatite remains for froth flotation [7].
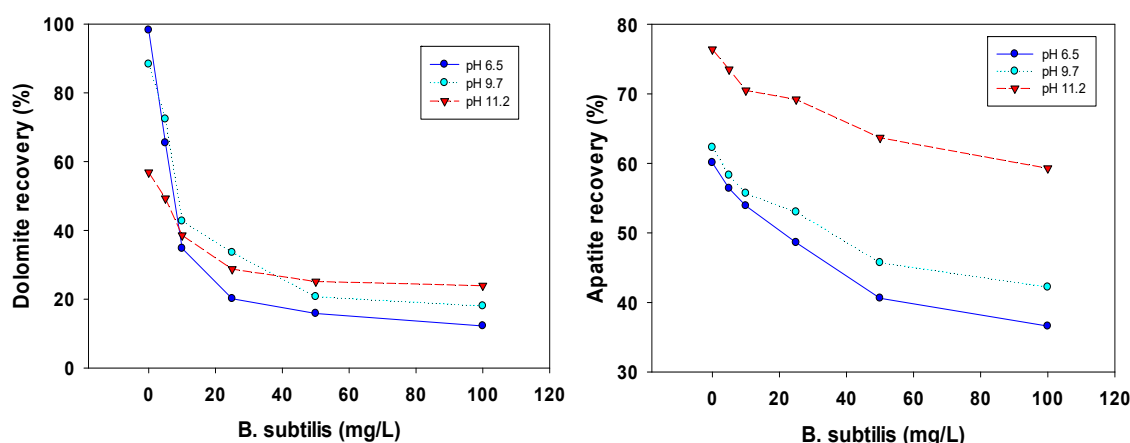
Bio Depression

In mineral processing, there is a growing interest in using microorganisms as flocculants for fine particles or as flotation reagents [3]. Bacteria adhere to mineral surfaces with strains, modifying mineral surfaces, and aiding in the selective recovery of valuable minerals in flotation or flocculation processes [3,33,58]. Microorganisms boost the selectivity of conventional flotation processes where they are interchanged with chemical reagents to separate minerals with similar surface properties [11]. Depression by bacteria is achieved by oxidizing (in the case of sulfide ores) or modifying the mineral surface to less hydrophobicity and preventing collector adsorption [3,10,44]. Bacteria bind to the surface of particles due to characteristics of the soluble fraction in teichoic acid and peptidoglycan in their cell wall. On the other hand, adhesion of bacteria to solid substrates has been postulated

due to electrical, bridging, and London–van der Waals forces [3,59]. Bacteria compete with the collector on the mineral surface, reducing collector adsorption on the mineral and thereby causing a depressing effect [3]. After the initial approach and attachment to solid surfaces, bacteria increase their secretion of polysaccharides, which stabilizes colonization and leads to the formation of biofilms on the solid surfaces [3].

It has been reported that bacteria adsorb onto the surface of dolomite, binding dolomite contents more than apatite [3,43]. Bacteria create a capsule on the dolomite, making sure that when the collector is introduced into the pulp, it will have limited interaction with the dolomite surface [3,40]. Conditioning is significant to the recovery process when using bacteria. Appreciable recovery can be achieved when the bacteria is conditioned over a longer time, reducing MgO < 1%. In other words, increased conditioning time for the microorganism favors lower collector dosage and selective depression of dolomite [40]. Various investigations have examined different microorganisms (*Bacillus subtilis* (BS), *Pseudomonas aeruginosa* (PA), *Corynebacterium diphtheriae intermedius* (CDI) *and Mycobacterium phlei* (MP)) and indicated that BS and PA can selectively depress dolomite. *B. subtilis* in the presence of oleate as an anionic collector depressed dolomite in a mixture with apatite (Figure 3) [3]. Meanwhile, PA, with the same performance, was used in the presence of a cationic collector (dodecyl-*N*-carboxyethyl-*N*-hyroxyethyl-imidazoline) [40]. These bacteria exhibit depression characteristics on dolomite under basic pH conditions [3,40]. Zheng et al. [4] claimed that bacterial species tend to compete with an anionic collector to a greater extent on the surface of the Mg-containing minerals in comparison with minerals with no Mg, and function as a better depressant for the Mg-containing minerals. Consequently, appropriate use of bacteria with anionic or cationic collector proves to be selective in separating dolomite from value ores (apatite).

Figure 3. Effect of *B. subtilis* on dolomite (depression) and apatite in the presence of 10 mg/L sodium oleate as a collector

5.3. Flotation Separation of Dolomite from Magnesite

Surface characterizations of dolomite and magnesite indicate that their separation from each other is quite complicated; however, separation can be achieved using flotation at optimum conditions aided by using modifiers along with collectors. pH and mineral dissolution are cardinal for their selective separation, and using dissolve air flotation can enhance the separation efficiency when slime is apparent [12,15,53,60,61]. In the absence of modifiers, dolomite and magnesite recoveries were around 80% and 45%, respectively. The presence of modifiers enhanced particle dispersion in the pulp and depressed the target mineral. The results (Table 5) indicate the optimum conditions for a selective separation of Mg carbonates.

Table 5. Various conditions for flotation separation of dolomite from magnesite.

Collector	Dosage (mg/L)	pH	Depressants	Dosage (mg/L)	Recovery Dolomite (%)	Recovery Magnesite (%)	Reference
NaOl	20	8.5	-	-	~90	~20	[32]
NaOl	20	7	Sodium silicate	240	~25	~70	
NaOl	30	10.5–11.5	Calcon	30	~30	~75	
Acintol FA-1 tall oil fatty acid	300	9.5	Sodium hexametaphosphate	100	~60	~20	[15]
Acintol FA-1 tall oil fatty acid	40	7.1	Tetrasodium pyrophosphate	600	~75	~20	
Acintol FA-1 tall oil fatty acid	30	9.5	CMC	100	~60	~30	
Acintol FA-1 tall oil fatty acid	40	9.5	CMC	100	~66	~38	
Dodecyl phosphate	100	6.5	Sodium silicate	75	~80	~10	[53]
Dodecyl phosphate	100	5.5	Sodium silicate	75	~76.64	~23.36	
Dodecyl phosphate	100	5.5	Sodium silicate	100	~82.97	~17.03	
DDA	159.57	9.2–9.5	-	-	~49	~5	[23]
Dodecyl phosphate	100 mg/L	9	-	-	98%	95%	[12]

It has been reported that in the presence of dodecyl phosphate (100 ppm) as a collector and sodium silicate (75 ppm) as a depressant at pH 5–6, 80%–98% of dolomite and 12%–28% of magnesite can be recovered (a selective depressant for magnesite in its reverse flotation from dolomite) [53]. Under flotation conditions using anionic fatty acid (Acintol FA-1 tall oil) with varying modifiers—SHMP, tetrasodium pyrophosphate (TSPP), and CMC in neutral to alkalinic region (pH 6–12) float dolomite and sink magnesite—Matis et al. 1988 suggested that selective separation can be further improved in several flotation stages [15]. Floatability of magnesite and depression of dolomite were examined by anionic sodium oleate (3044.5 mg/L) at pH 10.2 in the presence of sodium silicate (12.206 mg/L), and the results indicate that in this condition the contact angle of dolomite was 19°, where for magnesite it was 89° [42]. Moreover, Matis and Gallios [32] reported that the presence of sodium silicate provided an activating effect on magnesite in the pulp. These results specified that at various pHs, modifiers such as sodium silicate in carbonate flotation may play different roles (as activator or depressant).

6. Summary

The froth flotation technique can be considered one the most effective methods for beneficiation of carbonate salt-type minerals. While the flotation separation of Mg carbonates from non-salt-type minerals is relatively efficient, the beneficiation process is significantly more difficult when salt-type minerals are associated. This difficulty is due to their having similar crystal structures, surface characteristics and physicochemical properties to the carbonates. Therefore, several parameters (particle size, surface properties, solubility, collector type and concentration, modifier types and their concentrations, etc.) have to be adequately optimized to achieve an efficient flotation separation. Particle size is one of the main issues, where solubility of carbonates increases by decreasing their particles size, which in turn affects the separation. Mg carbonates dissolve (dolomite is more soluble than magnesite) in the pulp, affecting collector-mineral interactions, consuming reagents and influencing flotation results. While bubbles might be unable to carry very coarse particles, dissolution of fine particles and their recrystallization poses various challenges. Therefore, oil agglomeration can be introduced into flotation systems where fines are apparent. Moreover, short collector conditioning time can recommend for decreasing the slime generation and collector consumption during flotation.

Mg carbonate flotation is pH dependent. The flotation separation is effective at both acidic and alkaline pH; however, flotation is not recommended at acidic pH due to the high consumption of collectors used by the lattice dissolution of dolomite. The isoelectric point of pure magnesite and dolomite were reported in the pH ranges of 6.5–6.8 and 5.5–7.6, respectively. Several reagents are capable of changing the hydrophobicity of Mg carbonates and facilitating their selective flotation. Anionic fatty acids and their sodium derivatives are efficient collectors for floating Mg carbonates where their products have insoluble formation with divalent ions. However, due to their low selectivity, sensitivity to water hardness, and flotation temperature, they are invariably used with modifiers to obtain efficient flotation results. In other words, the concentration of modifiers has a significant effect on Mg carbonates flotation and can be detrimental for the selectivity in the process. In addition to selectivity, modifiers used in Mg carbonate flotation may reduce the amount of collector consumption. The negative surface charge by bacteria (such as *Bacillus subtilis* and *Pseudomonas aeruginosa*) confirms their abilities to selectively adsorb onto dolomite surfaces, compete with the collector, depress it and increase selective separation. Selective depression of dolomite is most effective under basic pH conditions.

These outcomes suggested that further investigations are demanded to better understand the impacts of particle size and application agglomeration to decrease problems of fine Mg carbonates. Exploring temperature effects on flotation of Mg carbonates is one of the areas that requires a detailed examination. Moreover, study and development of collectors that can selectively absorb on Mg carbonate at basic pH could be essential to increasing Mg carbonate flotation efficiency.

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