

The flotation of apatite and calcite using different reagents: A comparative study

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ABSTRACT

Apatite is the most important phosphate mineral and flotation serves as the primary method for separating it from its predominant gangue mineral, calcite (CaCO_3). In this study, the direct flotation of pure samples of apatite and calcite was studied using a micro flotation system. Fatty acid collectors were confirmed to be highly effective for the flotation of apatite and calcite minerals. The collectors Aero 825, Oleic acid, Potassium amyl xanthate (Z6), FS-2, Armac C, Hexa Decyl Amine, Sodium oleate, Corn oil, Armofelote 18, Dirol, Alke, and Atrac 1580 were applied in the experiments. Aero 825 at a concentration of 100 g/t for calcite and the Atrac at a concentration of 400 g/t for apatite provided the most optimal flotation conditions. Recoveries of calcite and apatite were 93% and 83%, respectively. After achieving the maximum recovery for each mineral, the depression capabilities of various depressants on both minerals were separately examined. Sodium hexametaphosphate (SHMP), Sodium silicate, Iron (II) sulfate, Sodium carbonate, Calcium chloride 2-hydrate, Carboxymethylcellulose (CMC), Sodium dodecyl sulfate (SDS), Aluminum sulfate 18-hydrate, Phosphoric acid, Sulfuric acid, Oxalic acid dihydrate, Tartaric acid, Lactic acid, Starch, Dextrin, Hydrochloric acid, and Sodium hydroxide were applied as depressants. SHMP for calcite and both Lactic acid and Oxalic acid dihydrate for apatite provided the best depression conditions. The recoveries of calcite and apatite were reduced to 10% and 25%, respectively. Calcite flotation kinetics is followed by the first-order kinetics model and apatite flotation kinetics is followed by the first-order with rectangular distribution and the second-order with rectangular distribution kinetics models.

Keywords: Flotation, Apatite, Calcite, Micro-flotation, Kinetics, Depressant.

1. Introduction

Phosphate is extensively utilized in fertilizer manufacturing and plays a crucial role in fostering the growth of the agricultural sector [1, 2]. Igneous and sedimentary rocks are among the most important natural resources. Apatite is categorized into various types, including hydroxyapatite, fluorapatite, and chlorapatite [3]. According to P_2O_5 grade, phosphate ores are divided into low-grade (12-16%), medium-grade (17-25%), and high-grade (25-35%) categories [4, 5]. The processing methods for phosphate ore rely on the specific phosphate structural type and the accompanying tailing minerals. Numerous phosphate deposits comprise sedimentary resources containing varying proportions of carbonates, such as calcite or dolomite, as well as silica and silicates [6]. Froth flotation is commonly incorporated into the upgrading process of such ores, particularly when distinguishing properties between the valuable mineral and its calcium-bearing impurities are lacking [7]. Flotation methods can vary between direct and reverse, contingent upon factors, such as ore composition, reagent costs, treatment capacity of the concentrator plant, and so forth [1, 8, 9]. It has been reported that more than 60% of the world's commercial phosphate is concentrated by the flotation process [2, 10]. Although more than half of the world's phosphate production is related to the flotation process, the flotation of apatite is complicated due to the similarity of surface properties of valuable minerals and associated tailings [8, 11]. The flotation of apatite is performed directly using anionic collectors at neutral pH [8, 12]. Fatty acids are commonly used

as an anionic collector for the flotation of apatite [13]. The higher recovery of apatite occurs at neutral pH with a low dosage of sodium oleate as a collector [14]. In research conducted by Jafari et al. (2018), fatty acids were applied as special collectors for the flotation of apatite from low-grade apatite ore. They concluded that a mixture of collectors was more effective than a single collector. The highest recovery was achieved by combining three anionic collectors of Dirol, Alke, and Atrac with concentrations of 364, 295.2, and 140.8 g/t, respectively. They stated that the highest grade and recovery were obtained by Dirol and Alke, respectively [15]. In 2017, a study by Liu et al. on the mechanism of phosphoric acid in the apatite and dolomite flotation system postulated that at 25 mg/l sodium oleate as a collector, 80% of apatite was recovered. Also, its recovery was reduced to approximately 25% using phosphoric acid as a depressant with an ideal selectivity at a concentration of 80 mg/l and pH=5.5 [16]. Souza et al. (2014) studied the effects of silicate and carbonate depressants in the direct flotation of phosphate ore. These depressants were sodium silicate, corn starch, cassava starch, modified starch 1 and 2, carboxymethylcellulose, and dextrin at concentrations of 100 to 600 g/t. The results showed that the recovery of P_2O_5 in the presence of all depressants was reduced (a 45% decrease in the presence of sodium silicate and dextrin) [17].

Calcite is one of the most common and important minerals in sedimentary rocks [18]. Although calcite is found naturally in association with other valuable minerals, it has the least value and must

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be separated from other minerals [19]. Calcite is one of the most abundant carbonate tailings in the flotation of smithsonite, fluorite, scheelite, apatite, and celestite [20-25]. The separation of calcite from valuable minerals is highly intricate due to the similarity in chemical composition and the influence of soluble ions on their floatability. Sodium oleate is the main collector used in the flotation of the abovementioned minerals, but its selectivity in the separation of these minerals from calcite is usually very low [26, 27]. The flotation of calcite has excessive importance in industries for the production of raw materials for fertilizer, cement, fillers, and other related materials. A wide range of collectors has been applied for calcite, including fatty acid chains and their alkaline salts, especially oleic acid and sodium oleate. The flotation efficiency depends on the experiment's condition, such as the pH, concentration of the collectors, among others. [28-30]. Using sodium oleate at pH < 8 results in low recovery rates of calcite [14]. Therefore, many efforts have been made to separate calcite in the flotation process using different collectors [31]. Some binary minerals have analogous surface characteristics, such as scheelite-fluorite, fluorite-calcite, apatite-calcite, and fluorite-barite which makes it challenging to separate them [12]. Liu et al. (2019) reached a 90% recovery of calcite and apatite using oleate as the collector at concentrations of 1.5×10^{-4} and 2×10^{-4} mol/l, respectively. In this research, the pH of the pulp was 8.5. 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) exhibited the selectivity for calcite depression in binary apatite and calcite flotation systems. The recovery of calcite was reduced to 10% at a concentration of 10 mg/L [32]. El-Mofty et al. (2015) conducted a study on calcite flotation in which 100% recovery was achieved using 5×10^{-5} M of potassium oleate as a collector. Subsequently, the recovery was reduced to 20% using 13×10^{-3} M of potassium dihydrogen phosphate as a depressant at pH=6.5 [33]. Chen et al. (2017) studied the flotation of calcite. They achieved 90% recovery using 1.5×10^{-4} mol/l of sodium oleate as a collector at pH=7. Afterwards, they reduced the recovery to 5% using 5×10^{-5} mol/l of DSS as a depressant at pH=7 [34]. In other research, Liu et al. (2016) conducted a study on the effect of depressants on the selective flotation of calcite in which the recovery reached up to 90% by applying oxidized paraffin soap as a collector at a concentration of 30 mg/l at pH=9. Based on the results, the recovery of calcite particles was reduced to 40% and 30% using tannin and SHMP at a concentration of 20 mg/l and pH=9, respectively [35]. Rahimi et al. (2017) studied the flotation of pyrolusite and calcite by two types of cationic collectors. By using dodecylamine (DDA) and dodecyl trimethyl ammonium chloride (DTAC) at pH=7.5, the recovery of calcite particles reached 60% and 35%, respectively. Subsequently, the recovery was reduced to 20% using sodium carbonate and calcium chloride depressants for both types of collector at pH=7.5 [36].

In this study, the effects of the type and concentration of chemical additives, such as collectors, frothers, and depressants on the flotation and depression behaviors of two pure apatite and calcite samples were studied in the micro flotation system. For this purpose, various anionic and cationic collectors (Aero 825, Oleic acid, Potassium amyl xanthate (Z6), FS-2, Armac C, HexaDecyl Amine, sodium oleate, corn oil, armofelote 18, dirol, alke and Atrac1580), frothers (pine oil, MIBC, and A65), and depressants (sodium hexametaphosphate (SHMP), sodium silicate, Iron(II) sulfate, Sodium carbonate, Calcium chloride 2-hydrate, Carboxymethylcellulose (CMC), Sodium dodecyl sulfate (SDS), Aluminum sulfate 18-hydrate, Phosphoric acid, Sulfuric acid, Oxalic acid dihydrate, Tartaric acid, Lactic acid, Starch, Dextrin, Hydrochloric acid, and Sodium hydroxide) were tested. Ultimately, after determining the optimal condition in both flotation and depression stages for pure apatite and calcite samples, flotation kinetics for these two samples were studied.

2. Methodology

2.1. Minerals & Characterization studies

Pure samples of apatite and calcite were prepared from the Esfordy region, the central part of Iran. The samples were crushed to -2 mm by jaw and roller crushers and then their particle size was reduced to -150

μm using a rod mill. The size fraction of -150+38 μm obtained by the wet sieving method was selected for micro flotation experiments. The particle size distribution of both samples is shown in Figure 1. According to the results, d_{25} , d_{50} , and d_{90} of the samples were determined as 50, 84, and 139 μm for apatite and 37, 75, and 135 μm for calcite, respectively. Also, the fine fraction (<38 μm) constituted 18.0% and 26.4% of the apatite and calcite samples.

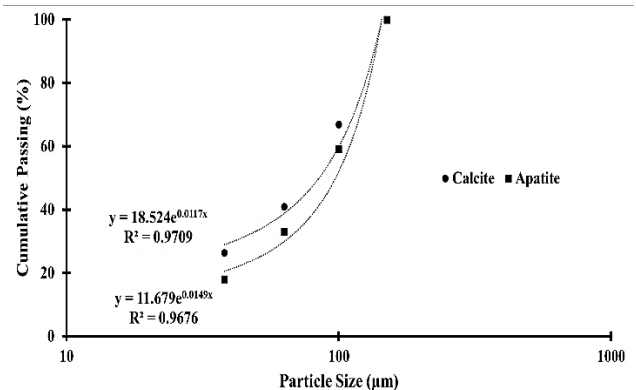


Figure 1. The particle size distribution of the samples after crushing and grinding stages, (A) apatite, and (B) calcite.

The analyses of X-ray diffraction (XRD, Bruker as D8-Advance) and X-ray fluorescence (XRF, Perkin Elmer Optima 4300 DV) were performed on both calcite and apatite samples, and their results are presented in Figure 2 and Table 1, respectively. The XRD graphs were presented with the standard cards of these pure minerals. The results of XRD and XRF analyses illustrated that the apatite and calcite samples had high purity. The major impurities of the apatite sample were Fe_2O_3 (2.85%) and SiO_2 (1.6%) as well as TiO_2 (0.21%) and MgO (0.13%). The impurity of the calcite sample was a low percentage of MgO (0.18%).

2.2. Reagents

The chemical additives for the micro flotation tests, including collectors, frothers, depressants, regulators, and their properties (role and chemical formula) are listed in Table 2. It is important to note that certain depressants may be utilized for both calcite and apatite minerals and could be classified under both categories. However, they are categorized separately for each mineral due to their significant consumption and reagent content.

2.3. Flotation tests

Micro flotation tests were performed in a Modified Hallimond tube as a micro flotation system [37]. The Modified Hallimond tube shown in Figure 3 is a laboratory tool that was used to study the flotation behavior of pure minerals. The volume of the cell was 150 ml and the rate of aeration can be changed. In this type of cell, the agitation mechanism was performed by the stirring magnet. The stirring speed was set to 360 rpm in all experiments. The pulp was prepared inside the cell and the pH was measured and adjusted with HCL and NaOH simultaneously by testing. The amount of sample used for each test was 5 g. In addition, deionized water was used in all experiments to avoid the impact of total dissolved solids (TDS) and electrical conductivity (EC). To reduce the error and its effect on the results, the experiments were repeated twice and the average of results was reported.

In order to study the flotation behavior of the minerals in the flotation test, initially, the micro flotation experiment was performed on the pure sample without any chemical additives. Then, the samples were floated using different collectors at different concentrations. Additionally, to determine the effect of frothers, the flotation tests were carried out separately using several frothers at different concentrations. Finally, the flotation behavior was investigated by the simultaneous usage of the

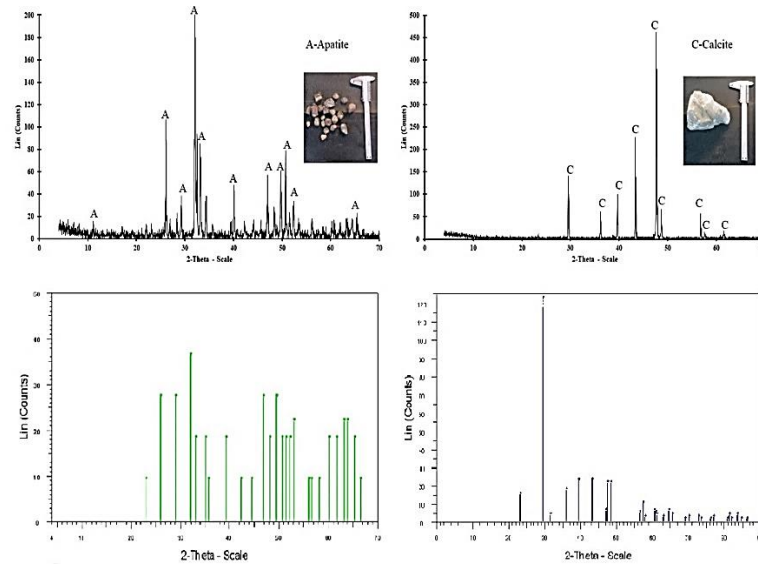


Figure 2. The results of the XRD analysis of the apatite and calcite samples with standard cards.

Table 1. The results of the XRF analysis of the apatite and calcite samples.

Element	SiO ₂	Al ₂ O ₃	BaO	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SO ₃	TiO ₂	LOI
Unit	%	%	%	%	%	%	%	%	%	%	%	%	%
Apatite	1.60	<0.05	<0.05	49.35	2.85	<0.05	0.13	<0.05	<0.05	44.83	<0.05	0.21	0.43
Calcite	<0.05	<0.05	<0.05	55.90	<0.05	<0.05	0.18	<0.05	<0.05	<0.05	<0.05	<0.05	43.92

Table 2. The Characteristics of chemicals used in the micro flotation tests.

Chemical	Supplier	Role	Formula
Aero 825	Cytec	Calcite/Apatite Collector	-
Oleic acid	Sigma-Aldrich	Calcite/Apatite Collector	C ₁₈ H ₃₄ O ₂
Potassium amyl xanthate (Z6)	-	Calcite Collector	C ₅ H ₁₁ OCS ₂ K
FS-2	Clariant	Calcite/Apatite Collector	-
Armac C	Akzo Nobel	Calcite Collector	-
Hexa Decyl Amine	Merck	Calcite Collector	CH ₃ (CH ₂) ₁₅ NH ₂
Sodium oleate	BDH	Apatite Collector	C ₁₇ H ₃₃ COONa
Corn oil	-	Apatite Collector	-
Armofelote 18	Akzo Nobel	Apatite Collector	-
Dirol	I.C.C.	Apatite Collector	-
Alke	I.C.C.	Apatite Collector	-
Atrac 1580	Akzo Nobel	Apatite Collector	-
Pine oil	-	Calcite/Apatite Frother	-
Methyl isobutyl carbinol (MIBC)	-	Calcite/Apatite Frother	C ₆ H ₁₄ O
Polypropylene glycol (A65)	Cytec	Calcite/Apatite Frother	C ₃ H ₈ O ₂
Sodium hexametaphosphate (SHMP)	Scharlau	Calcite/Apatite Depressant	(NaPO ₃) ₆
Sodium silicate	Chem-Lab	Calcite/Apatite Depressant	Na ₂ SiO ₃
Iron (II) sulfate	Merck	Calcite Depressant	FeSO ₄ .7H ₂ O
Sodium carbonate	-	Calcite/Apatite Depressant	Na ₂ CO ₃
Calcium chloride 2-hydrate	Merck	Calcite Depressant	CaCl ₂ .2H ₂ O
Carboxymethylcellulose (CMC)	Sigma-Aldrich	Calcite/Apatite Depressant	C ₈ H ₁₆ O ₈
Sodium dodecyl sulfate (SDS)	Merck	Calcite Depressant	CH ₃ (CH ₂) ₁₁ SO ₄ Na
Aluminum sulfate 18-hydrate	Merck	Apatite Depressant	Al ₂ (SO ₄) ₃ .18H ₂ O
Phosphoric acid	Neutron	Apatite Depressant	H ₃ PO ₄
Sulfuric acid	Neutron	Apatite Depressant	H ₂ SO ₄
Oxalic acid dihydrate	Neutron	Apatite Depressant	C ₂ H ₂ O ₄ .2H ₂ O
Tartaric acid	BDH	Apatite Depressant	C ₄ H ₆ O ₆
Lactic acid	Panreac	Apatite Depressant	C ₃ H ₆ O ₃
Starch	Merck	Calcite/Apatite Depressant	(C ₆ H ₁₀ O ₅) _n
Dextrin	Merck	Apatite Depressant	(C ₆ H ₁₀ O ₅) _n .xH ₂ O
Hydrochloric acid	DRM	pH Modifier	HCl
Sodium hydroxide	Merck	pH Modifier	NaOH

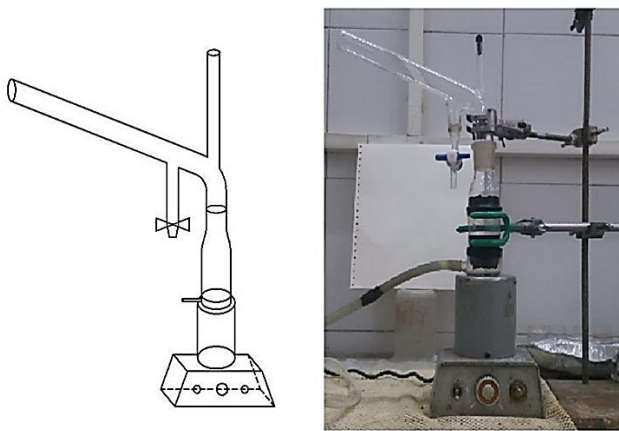


Figure 3. The schematic and real photos of the micro flotation system used in this study.

collector and frother. After determining the optimal type and concentration of the collector and frother, the experiments were carried out at different pHs to examine the effect of pH changes. In the next step, the effects of inorganic and organic depressants at different concentrations were studied under ideal flotation conditions to determine the depressants with the greatest ability to depress the apatite and calcite particles.

At the preparation stage in the flotation cell, pH was adjusted before starting the experiment. The sample was in contact with the depressant for 2 minutes. The collector was then added to the cell and stirred for 3 minutes. The frother conditioning time was also 1 minute. Ultimately, aerating and frothing were performed for 2 minutes. Due to the purity of the samples, after the end of the experiment, the floated sample was collected, filtered, and dried; consequently, the recovery was calculated from the weight of the mineral floated using Equation 1:

$$R = \frac{C}{F} \times 100 \quad (1)$$

Where R is the recovery in percentage, C is the mass of mineral or concentrates floated and F is the mass of raw material or feed.

2.4. Kinetic studies

Kinetics is defined as the alteration of a particular parameter over time; therefore, the flotation kinetics means the change in the flotation response parameter (recovery) over time. Up to the present time, more than 10 kinetic equations have been presented. Each of them was used

for specific situations, but the first-order model was very common and applicable [38]. In this study, we explored various flotation kinetics models to determine which best described the behavior of our experimental data. These models are detailed in Table 3.

3. Results and Discussion

3.1. Calcite

3.1.1. Flotation

To determine the exact flotation behavior of the calcite, a micro flotation experiment was performed on the pure calcite sample without applying any chemical additives. The results revealed that the recovery of calcite without chemicals was only 18%. Six types of collectors, including Aero 825, Oleic acid, Potassium amyl xanthate (Z6), FS-2, Armac C, and Hexa Decyl Amine at six concentration levels of 5, 25, 50, 100, 200, and 400 g/t were applied and their recoveries were measured (Figure 4). It should be noted that in the experiments with Aero 825, Oleic acid, Potassium amyl xanthate (Z6), and FS-2 the pH value was 8, whereas, in the experiments with Armac C and Hexa Decyl Amine, the pH was 11. In all experiments, the collector conditioning time was 3 minutes and the frothing time was 2 minutes. As can be seen in Figure 4, more than 80% of the sample was recovered by collectors Aero 825 and Armac C at lower concentrations (50 g/t) and also FS-2 at higher concentrations (400 g/t).

The collector oleic acid recovered above 50% of the calcite, but higher concentrations might be needed to reach higher recoveries, which may not be economically feasible. Other collectors did not provide adequate floatability for calcite and had a maximum recovery of 20%, indicating that these collectors were not appropriate for the calcite flotation process. The variation in recovery rates of calcite with different collectors can be attributed to the specific chemical interactions between the collectors and the calcite surface, as well as the pH conditions during the flotation process [39, 40]. Collectors, such as Aero 825 and Armac C, which showed high recovery at lower concentrations, also have a strong affinity for the calcite surface, forming a hydrophobic layer that enhances floatability.

Armac C, a cationic collector, particularly benefits from the higher pH of 11, where it interacts effectively with the negatively charged calcite surface, leading to increased hydrophobicity and improved recovery. In contrast, oleic acid, a fatty acid collector known for its effectiveness in oxide and carbonate mineral flotation, exhibited moderate recovery [41]. This suggests that while oleic acid can be effective, it may require higher concentrations to achieve optimal adsorption on the calcite surface, which could be economically impractical.

Table 3. The kinetic models of discontinuous flotation operation.

No.	Model Name	Model	Description
1	Classical first-order model	$R = R_{\infty} [1 - e^{-kt}]$	This model has been reported to forecast the best value when the recovery is especially low.
2	First-order model with rectangular distribution of floatabilities	$R = R_{\infty} \left\{ 1 - \frac{1}{kt} [\ln(1 + kt)] \right\}$	This model has been reported to be the best of all models tested to fit experimental data, because the rectangular distribution of floatabilities gives an added flexibility.
3	Fully mixed reactor model	$R = R_{\infty} \left(1 - \frac{1}{1 + \frac{t}{k}} \right)$	This model assumes that flotation components are exponentially distributed, which gives an added flexibility over the classical first-order model and enables it to fit the observed values very well.
4	Improved gas/solid adsorption model	$R = R_{\infty} \left(\frac{kt}{1 + kt} \right)$	This mathematical form of model 4 is similar to model 3, which can be derived from model 3 by assuming $k_3 = 1/k_4$
5	Second-order kinetic model	$R = \left(\frac{R_{\infty}^2 kt}{1 + R_{\infty} kt} \right)$	This model can be derived from the first-order model by assuming $N = 2$, which is a two-parameter expression that describes the flotation of a monodisperse feed with particles having a constant floatability
6	Second-order model with rectangular distribution of floatabilities	$R = R_{\infty} \left\{ 1 - \frac{1}{kt} [\ln(1 + kt)] \right\}$	Similar to model 2, this model assumes that flotation components are rectangularly distributed.

The pH of the flotation environment plays a critical role in the effectiveness of these collectors. For example, the alkaline conditions used with Armac C and Hexa Decyl Amine enhance the collectors' ability to adsorb onto the mineral surface by neutralizing surface charges, leading to better recovery rates. Additionally, the molecular structure of collectors, such as FS-2, which requires higher concentrations to achieve significant recovery may influence the kinetics of adsorption or the number of surface sites required. This suggests that while some collectors can achieve high recovery rates, their economic feasibility at higher concentrations must be considered when selecting the most appropriate collector for industrial applications.

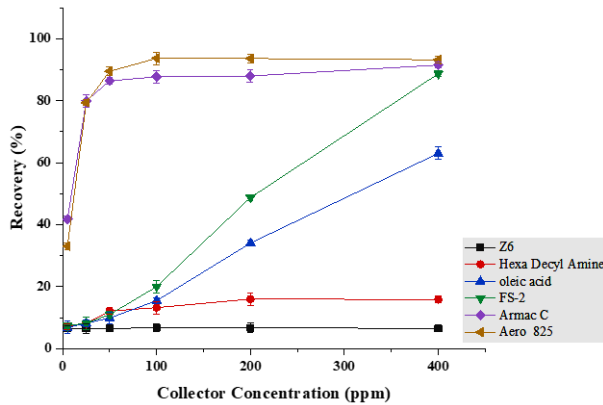


Figure 4. The effect of type and concentration of collector on calcite flotation (collector conditioning time=3 min, frothing time=2 min, and pH = 8 for Aero 825, Oleic acid, Z6 and FS-2 and pH=11 for Hexa Decyl Amine and Armac C).

The effect of different frothers including pine oil, methyl isobutyl carbinol (MIBC), and polypropylene glycol (A65) on the flotation of calcite at four different concentration levels of 5, 10, 20, and 40 g/t was examined. The results of the experiments are shown in Figure 5 (A). In all experiments, the pH was set at 8, the conditioning time of the frother was 1 minute and the time of frothing was 2 minutes. From the results of these experiments, it can be concluded that pine oil's capability of floating the calcite particles is superior in comparison with the other two frothers and also results in higher recovery at a lower concentration. For this reason, pine oil was selected to evaluate the simultaneous usage of collector and frother. For a more precise evaluation, pine oil was applied at the optimal concentration (100 g/t) of each collector to determine its effect on the recovery. Also, MIBC was used for these experiments to compare the behavior of the frothers in flotation efficiency. The results of these experiments are presented in Figure 5 (B). In all experiments, the conditioning times of the collector and frother were 3 and 1 minutes, respectively. Also, the time of frothing was 2 minutes. As can be seen in this figure, the usage of frothers had a slight effect on the flotation of calcite in the presence of some collectors such as Aero 825 and Armac C. In contrast, in the presence of some other collectors, such as Oleic acid and FS-2, the frothers' effect was significant. Since collectors also had frothing properties, frothers had not shown much effect in this process.

To examine the effect of pH on the recovery of the sample using anionic and cationic collectors, Aero 825 and Armac C, four different pHs of 4, 6, and 8 for Aero 825, and 10, and five different pHs of 8, 10, 11, 12, and 13 for Armac C were selected and tested. The concentration of collectors was 100 g/t. To decrease and increase the pH in the flotation environment, HCl and NaOH were added, respectively. The results are shown in Figure 6. By examining the effect of pH and considering the reported zeta potential for the calcite sample, it was found that the Aero 825 at pH=8 and the Armac C at pH=11 resulted in the highest recovery. A slight portion of the calcite dissolved in acidic conditions; therefore, at low pHs, the amount of floated calcite and the recovery slightly decreased. Also, the decrease in recovery can be due to different modes of absorption of various anionic and cationic collectors. For the calcite

sample, the ZPC was located at pH=7.8, which can be reduced to pH=5.5 in the presence of a depressant [33]. The result of another research indicated that the ZPC of the calcite lies at pH=8.5 [35]. Overall, the ZPC of the calcite was reported in the range of pH= 7.7-9.9 [37, 42, 43].

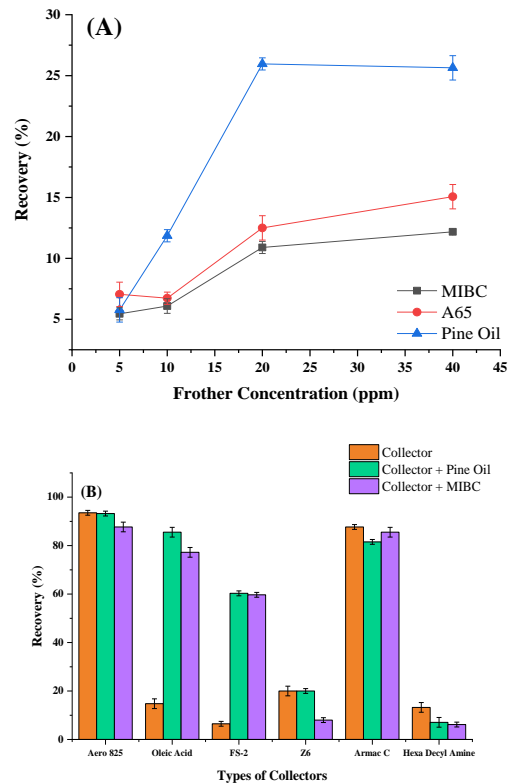


Figure 5. (A) The effect of the type and concentration of frothers on calcite flotation at 5, 10, 20, and 40 g/t (frother conditioning time=1 min, frothing time=2 min, and pH=8), and (B) The simultaneous usages of collector and frother on calcite flotation at 100 g/t of collector and 10 g/t of frother (collector conditioning time=3 min, frother conditioning time=1 min, frothing time=2 min and pH=8 for Aero 825, Oleic acid, Z6 and FS-2 and pH=11 for Hexa Decyl Amine and Armac C).

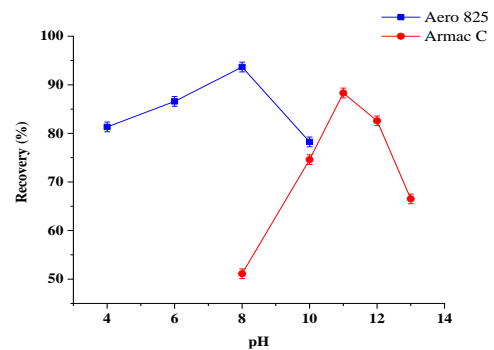


Figure 6. The effect of pH on calcite flotation with collector concentration of 100 g/t (collector conditioning time=3 min and frothing time =2 min).

3.1. Depression

After performing various experiments and considering the optimal condition, Aero 825 was selected as the best collector for the rest of the experiments; it provides the highest recovery at the lowest concentration at pH=8 and does not require pH adjustment with extra chemicals. In the depression stages, Aero 825 with a concentration of 100 g/t was added. In all experiments, the pH was adjusted to 8 and the

collector and depressant conditioning times were 3 and 2 minutes, respectively. Also, the frothing time was 2 minutes. To examine the depressing capability of floated particles, seven specific calcite depressants, including sodium hexametaphosphate (SHMP), sodium silicate, starch, iron (II) sulfate, sodium carbonate, calcium chloride 2-hydrate, and carboxymethylcellulose (CMC) were tested. Each depressant was tested at five different concentrations of 5, 10, 20, 40, and 80 g/t. It is worth mentioning that the depressant was added before the collector. As shown in Figure 7 (A), the SHMP and CMC exhibited the highest depressing capability and reduced the recovery from 93% to 10%. Besides, these depressants were capable of depressing calcite particles at a very low concentration. The SHMP has a strong complex effect on calcium ions. Taking into account this interaction between SHMP and calcium ions, the depression mechanism of minerals containing SHMP with calcium is probably due to the formation of Ca(II) complexes by SHMP. Calcium significantly dissolves from the calcite surface in the SHMP-bearing solution. The results showed that other depressants had an inconsiderable ability to depress the floated particles, which had also occurred at high concentrations. In the presence of sodium carbonate, it can be noted that CO_3^{2-} ions form a barrier for the absorption of other elements on the calcite surface and lead to ion-exchange reactions between them [38].

In order to examine the interaction of apatite specific depressants on the flotation behavior of calcite samples, several depressants were also tested. For these experiments, six apatite specific depressants, including Dextrin, Aluminum sulfate 18-hydrate, Tartaric acid, Lactic acid, Phosphoric acid, and Oxalic acid were used at five dosages of 5, 10, 20, 40, and 80 g/t. The results of these experiments are shown in Figure 7 (B). It can be seen that most apatite depressants had insignificant effects on the depression of floated calcite particles. They exhibited a maximum of 10% depression at higher concentrations. But Dextrin had a higher ability to depress calcite particles at lower concentrations.

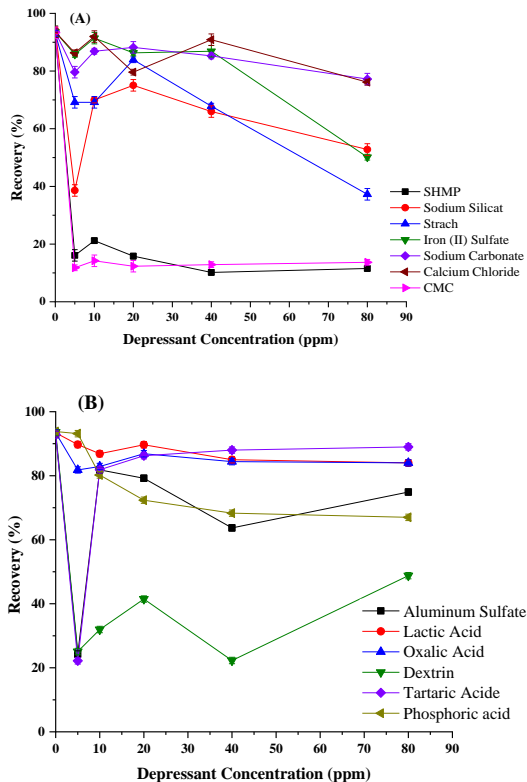


Figure 7. (A) The effect of the type and concentration of calcite depressants as a collector (100 g/t of Aero 825 collector, conditioning time=3 min, depressant conditioning time=2 min, frothing time = 2 min and pH=8) and (B) Effect of type and concentration of apatite depressants on calcite depression (100 g/t of Aero 825 collector, conditioning time=3 min, depressant conditioning time=2 minutes, frothing time=2 minutes, pH=8).

3.2. Calcite flotation kinetics

In order to study the kinetics of the performed experiments, the optimal flotation condition was selected to be studied at 0, 15, 30, 60, 90, and 120 seconds. The cumulative recovery was calculated and fitted to each of the previously mentioned kinetic models to select the best-fitting model. After performing the experiments and fitting the data, the results of the flotation rate constants, infinite recovery, and correlation coefficients were calculated and the results are presented in Table 4. To demonstrate the data, the kinetic curve of the floated particle is also shown in Figure 8.

As can be seen in Table 4 and Figure 8, all models fit acceptably to the flotation experiments data. The first-order model had the highest correlation coefficient with a kinetic constant value of 0.0305 and an infinite recovery of 93.34%.

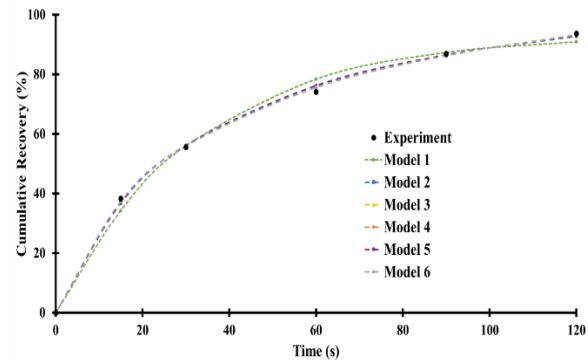


Figure 8. The kinetics of calcite flotation in the presence of collector Aero 825 at 100 g/t.

In the study of calcite flotation kinetics, various kinetic models were applied to evaluate the cumulative recovery over time under optimal flotation conditions. Among these models, Model 1 was identified as the best-fitting model, characterized by the highest correlation coefficient and specific kinetic parameters. Model 1 corresponds to a first-order kinetic model, which is commonly used to describe the flotation process of minerals.

The first-order kinetic model assumes that the rate of flotation is directly proportional to the concentration of floatable particles remaining in the pulp. Mathematically, this can be expressed as:

$$R = 1 - e^{-kt} \quad (2)$$

Equation (2) represents the exponential change of recovery over time; given that the negative exponential functions approach zero, the equation of kinetics of a single flotation demonstrates that under operating conditions (initial times), the concentration of particles never reaches zero. In this case, recovery tends to a maximum value, which is called infinite recovery (R_∞). Consequently, the first-order recovery equation can be modified as Equation 5:

$$R = R_\infty(1 - e^{-kt}) \quad (3)$$

The significance of Model 1 fitting well with the experimental data suggests that the flotation process for calcite under the studied conditions behaves in a manner consistent with first-order kinetics. This implies that the rate of particle recovery decreases exponentially over time, as fewer floatable particles remain in the pulp to be recovered. The kinetic constant k of 0.0305 and an infinite recovery R_∞ of 93.34% indicate a relatively fast flotation process with a high potential recovery under the given conditions.

This model is particularly useful in understanding the efficiency of the flotation process and in optimizing operational parameters to maximize recovery. By fitting the data to a first-order kinetic model, researchers can predict the behavior of the system under different conditions, aiding in the design and scaling-up of flotation operations.

Table 4. The results of kinetic models fitted to calcite flotation.

Time (s)	Experiment	Model 1	Model 2	Model 3	Model 4	Model 5	Model 6
	CR _{Exp} (%)	CR _{Cal} (%)	CR _{Cal} (%)	CR _{Cal} (%)	CR _{Cal} (%)	CR _{Cal} (%)	CR _{Cal} (%)
0	0	0	0	0	0	0	0
15	38.38	34.30	37.37	36.78	36.78	36.78	37.37
30	55.69	56.00	55.98	56.14	56.14	56.14	55.98
60	74.13	78.40	75.65	76.20	76.20	76.20	75.65
90	86.93	87.36	86.35	86.50	86.50	86.50	86.35
120	93.70	90.95	93.24	92.77	92.77	92.77	93.24
	R _∞ (%)	93.34	100.00	100.00	100.00	100.00	100.00
	k (1/s)	0.0305	0.0584	33.3439	0.0300	0.0003	0.0584
	DEVSQ	42.7303	3.9716	8.0905	8.0905	8.0905	3.9716
	R ²	0.9876	0.9209	0.9098	0.9098	0.9098	0.9209

3.3. Apatite

3.2.1. Flotation

To determine the flotation behavior of apatite, a micro flotation experiment was carried out on a pure apatite sample without adding any chemicals. The results showed that the recovery of apatite without chemical additives was only 7.2%. Nine types of collectors, including FS-2, sodium oleate, Dirol, Alke, Atrac, corn oil, Aero 825, Armofelote 18, and oleic acid at four concentrations of 25, 100, 400, and 600 g/t were tested and their results are shown in Figure 9. It should be noted that due to the nature of the chemicals in all the tests, the pH value was 8. In all experiments, the collector preparation and frothing times were 3 and 2 minutes, respectively. As can be seen from Figure 9, the Atrac recovered more than 80% of apatite at a concentration of 400 g/t. Aero 825, Armofelote 18, and Alke recovered more than 50% of apatite at a concentration of 400 g/t. However, the recovery did not increase with increasing the collector dosage. Dirol also has an effect in increasing apatite recovery, but it did not reach over 50% using this collector. Other collectors did not provide adequate floatability for apatite and had a maximum recovery of 20%, indicating that these collectors are not appropriate for the apatite flotation process.

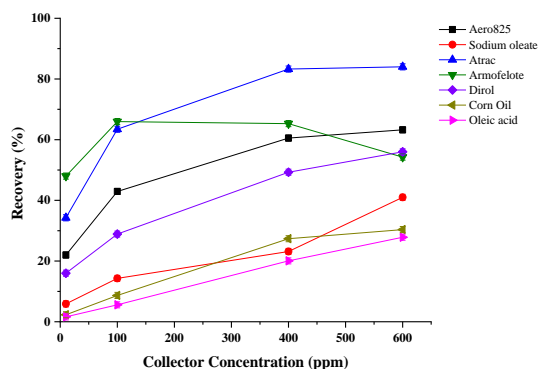


Figure 9. The effect of collector's type and concentration on apatite flotation behavior at 25, 100, 400, and 600 g/t (collector conditioning time=3 min, frothing time=2 min, pH=8).

To examine the effect of frothers on the flotation behavior of apatite more precisely, three frothers, including pine oil, methyl isobutyl carbinol (MIBC), and polypropylene glycol (A65) at different concentrations of 5, 10, and 20 g/t were applied. The results of the experiments are presented in Figure 10 (A). In all experiments, the pH was set at 8, the conditioning time of the frother was 1 minute, and the time of frothing was 2 minutes. The results of these experiments verified that none of the frothers could float the apatite sample properly, but the results for A65 were better than the other two frothers. Consequently, A65 was selected for the following experiments to investigate the simultaneous usage of collector and frother. For a more accurate examination, the frother A65 which provided a better recovery was

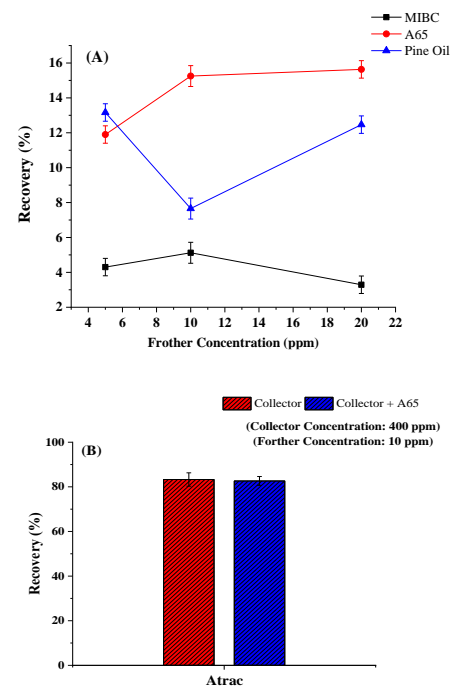


Figure 10. (A) The effect of frothers' type and concentration on apatite flotation at 5, 10, and 20 g/t (frother conditioning time=1 min, frothing time=2 min, pH=8) and (B) Simultaneous effect of collector and frother on apatite flotation at 400 g/t collector and 10 g/t frother (collector conditioning time=3 min, frother conditioning time=1 min, frothing time=2 min and pH=8).

tested at the optimal concentration (10 g/t) alongside Atrac as a collector. The results of these experiments are presented in Figure 10 (B). In all experiments, the conditioning time of the collector was 3 minutes. As can be seen, the frother has a negligible effect on the flotation of apatite.

To examine the effect of pH on the recovery of the apatite using the collector Atrac with the highest recovery, four different pHs of 4, 6, 8, and 10 were selected and tested. The concentration of the collector was 400 g/t. To decrease and increase the pH, HCl and NaOH were used, respectively. The results are presented in Figure 11. The isoelectric point (IEP) of apatite particles occurred at pH=6.5. Due to the negative charge of the apatite surface at pHs higher than this value, the possibility of adsorption of cationic collectors, such as amines is higher. Depending on the mineral composition, apatite exhibits different electrokinetic behaviors. The results have revealed that apatite and calcite show similar behavior at pH>6 [44]. In another research, the IEP of apatite was located at pH= 6.1. The presence of H₃PO₄ causes the zeta potential of apatite at different pHs to alter toward the negative direction, indicating that H₃PO₄ is strongly adsorbed on the apatite surface. Moreover, the zero point of charge (ZPC) of the apatite sample was located at pH=6 in

the research conducted by Liu et al. (2017) [16]. By examining the effect of pH and the reported ZPC for the apatite sample, it was found that the collector Atrac resulted in the highest recovery at pH=8.

3.2.2. Depression

Through performing various experiments and evaluating the optimal conditions, choosing Atrac as the collector seems to be more logical for the reason that it has the highest recovery and performs at pH 8 without the need for additional chemicals to adjust the pH. The effect of apatite depressants was examined by adding 400 g/t of each depressant. In all experiments, the pH was set to 8 and the conditioning times for the collector and depressant were 3 and 2 minutes, respectively. Also, the frothing time was 2 minutes.

Seven apatite specific depressants, including inorganic and organic reagents (Dextrin, Aluminum sulfate 18-hydrate, Tartaric acid, Lactic acid, Oxalic acid, Phosphoric acid, and Sulfuric acid) were applied to examine the depression ability on floated particles. Each depressant was tested at five different concentrations of 5, 25, 50, 200, and 300 g/t. The results of these experiments are illustrated in Figure 12 (A). As can be seen, lactic acid and oxalic acid dihydrate provided the highest depression potential, and the recovery reduced from 83% to 25%. However, other depressants were not able to depress the floated apatite particles at low concentrations. They were more effective at higher concentrations. This phenomenon can be observed in depressants, such as lactic acid and oxalic acid dihydrate.

In order to examine the interactions of specific calcite depressants on the floated apatite particles, several specific calcite depressants were also tested on the apatite depression behavior. For these experiments, seven specific calcite depressants, including sodium hexametaphosphate (SHMP), sodium silicate, starch, iron (II) sulfate, sodium carbonate, calcium chloride 2-hydrate, and carboxymethylcellulose (CMC) at five concentrations of 5, 25, 50, 100, and 200 g/t were applied. The results of these experiments are shown in Figure 12 (B). Based on the results, most calcite depressants are capable of reducing the recovery of floated apatite particles by up to about 40-50%. However, iron (II) sulfate resulted in a high depression rate, since at higher concentrations it reduced the recovery from 83% to 20%.

3.2.3. Apatite flotation kinetics

In order to study the kinetics of the performed experiments, the optimal flotation condition was selected to be studied at 0, 15, 30, 60, 90, and 120 seconds. The cumulative recovery was calculated and fitted to each of the previously mentioned kinetic models to select the most appropriate model. After testing and fitting the data, the results of the flotation rate constants, infinite recovery, and correlation coefficients were calculated (Table 5). To demonstrate the data, the kinetic curves of the floated particle are shown in Figure 13.

As can be seen from Table 5 and Figure 13, the majority of the tested kinetic models did not align well with the experimental data. However, two models, Model 2 (the first-order model with rectangular distribution of floatabilities), described by Equation $R = R_{\infty} \left\{ 1 - \frac{1}{kt} [\ln(1 + kt)] \right\}$ and Model 6 (the second-order model with rectangular distribution of floatabilities), described by Equation $R = R_{\infty} \left\{ 1 - \frac{1}{kt} [\ln(1 + kt)] \right\}$, provided the best fit with the highest correlation coefficients and accuracy. Both models demonstrated a kinetic constant of 0.1382 and an infinite recovery R_{∞} of 84.68%. This suggests that the apatite flotation process involves a range of floatabilities among particles, and the second-order kinetics framework offers a more accurate description of the process.

The high correlation coefficients and similar infinite recoveries of these models highlight their effectiveness in capturing the complex behavior of apatite flotation compared to other models. These two models (Models 2 and 6) were able to accurately describe the flotation kinetics of apatite under the tested conditions, indicating that the process involves a range of floatabilities among particles.

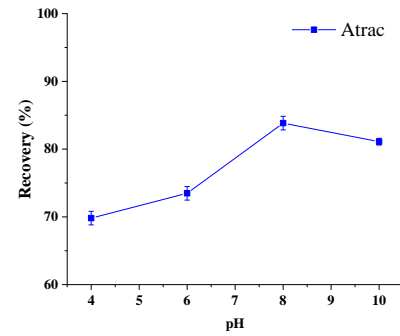


Figure 11. The effect of pH on apatite flotation with collector concentration of 400 g/t (collector conditioning time=3 min, frothing time=2 min).

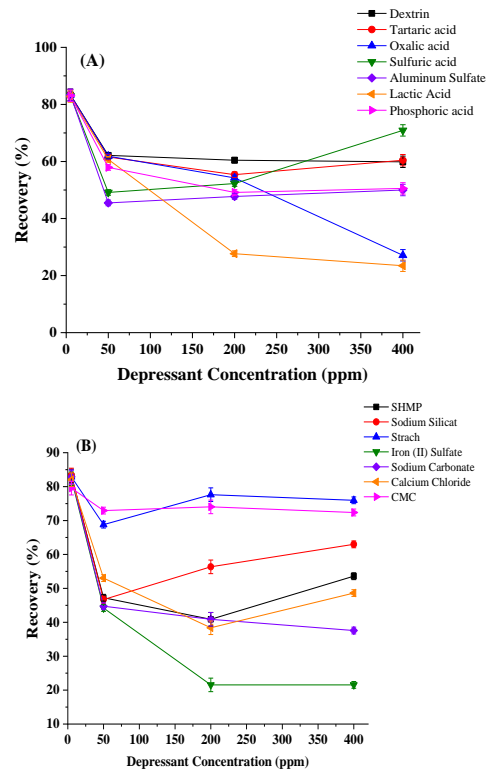


Figure 12. (A) The effect of type and concentration of apatite depressants at 5, 25, 50, 200, and 300 g/t and 400 g/t collector Atrac (collector conditioning time=3 min, depressant conditioning time=3 min, frothing time=2 min and pH=8) and (B) Effect of type and concentration of calcite specific depressants on apatite depression at 5, 50, 200 g/t and 400 g/t collector Atrac (collector conditioning time=3 min, depressant conditioning time=3 min, frothing time=2 minutes, pH=8).

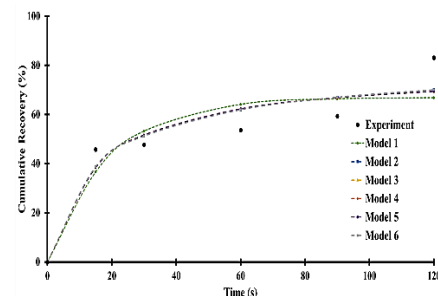


Figure 13. The kinetics flotation of apatite in the presence of Atrac, as collector at 400 g/t (collector conditioning time=3 min, frothing time=2 min, pH=8).

Table 5. The results of kinetic models fitted to apatite flotation.

Time (s)	Experiment	Model 1	Model 2	Model 3	Model 4	Model 5	Model 6
	CR _{Exp} (%)	CR _{Cal} (%)	CR _{Cal} (%)	CR _{Cal} (%)	CR _{Cal} (%)	CR _{Cal} (%)	CR _{Cal} (%)
0	0	0	0	0	0	0	0
15	45.77	36.67	38.82	38.51	38.51	38.51	38.82
30	47.80	53.26	51.22	51.66	51.66	51.66	51.22
60	53.73	64.17	61.91	62.29	62.29	62.29	61.91
90	59.38	66.40	66.99	66.88	66.88	66.88	66.99
120	83.20	66.85	70.04	69.44	69.44	69.44	70.04
R _∞ (%)		66.9715	84.6789	78.4392	78.4394	72.4790	84.6789
k (1/s)		0.0529	0.1382	15.5500	0.0643	0.0010	0.1382
DEVSQ		537.8691	358.0453	386.4758	386.4758	386.4758	358.0453
R ²		0.9266	0.9929	0.9860	0.9860	0.9860	0.9929

4. Conclusions

The findings of this research study revealed that Aero 825 served as an effective collector for floating calcite, yielding a remarkable 93% recovery at pH=8, while the impact of frother on calcite flotation was negligible. Moreover, the SHMP emerges as the optimal depressant for calcite particles, drastically reducing recovery from 93% to 10% with dextrin demonstrating a capacity to decrease calcite recovery by up to 20%. The first-order flotation kinetic model proved suitable for describing calcite flotation behavior. Similarly, Atrac, as a collector at pH=8 achieved the highest apatite recovery of 83%, with frother exhibiting minimal influence. Lactic acid and oxalic acid dihydrate emerged as the most effective depressants for apatite, reducing recovery from 83% to 25%, while iron (II) sulfate stood out among specific calcite depressants, reducing recovery from 83% to 20%. Apatite flotation kinetics aligned with first-order with rectangular distribution and second-order with rectangular distribution kinetics models, as evidenced by experimental data.

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Credit author statement

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Hadi Abdollahi: Conceptualization, Methodology, Supervision, Project administration, Funding acquisition, Validation, Resources.

Mahdi Gharabaghi: Conceptualization, Methodology, Validation, Supervision.

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Ehsan Ebrahimi: Software, Validation, Data curation, Writing – original draft, Writing – review & editing, Visualization.

Declaration of Competing Interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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