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Chitosan as an Eco-Friendly Alternative for Silicate Depressant in Phosphate Flotation

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Abstract

The quest for environmentally friendly reagents in froth flotation processes has gained significant importance for minimizing ecological impacts. This research investigates the utilization of chitosan polymer as a green depressant for silicate minerals in the direct flotation of phosphate minerals. To understand the behaviour of the flotation feed, zeta potential measurements were conducted to assess the electrical properties of mineral surfaces in the presence and absence of chitosan polymer. Furthermore, the effects of chitosan dosage, pulp pH, and flotation time on the flotation recoveries and concentrate grade of phosphates were studied. Comparative analyses were performed by comparing the flotation recoveries of phosphate minerals achieved using chitosan polymer with those obtained when employing a commercial silicate dispersant, sodium silicate. The findings revealed that at a dosage of 300g/ton, the recovery of phosphate minerals reached approximately 70% when using chitosan polymer, whereas the recovery was only around 40% with the same dosage of sodium silicate dispersant. These outcomes demonstrate the potential of chitosan as an effective and sustainable silicate depressant in the phosphate flotation process under specific conditions.

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Introduction

In the phosphate ore plants, froth flotation is an essential process that is used to separate phosphate minerals from gangue minerals such as silicates and carbonates (El-Shall *et al.*, 2004; Moudgil and Vasudevan, 1988). This process is usually carried out by the double flotation process, either direct-reverse or reverse-direct flotation- as applies in International Minerals and Chemicals IMC Four Corners Mine in Florida (Kawatra, 2013; Wang and Miller, 2006). Conventional reagents are typically used to enhance the separation of phosphate minerals. For example, fatty acids are used as phosphate collectors, whereas starch can be used either as a dispersant or as a collector in direct and reverse floatation, respectively. Sodium silicate is frequently employed in the direct froth flotation technique to disperse silicate particles and prevent their flotation (Sis and Chander, 2003). Recent research has revealed that sodium silicate is harmful to both aquatic and terrestrial creatures, even though it has demonstrated excellent performance in reducing the flotation of silicate minerals (Alsafasfeh, 2020; Andersen, 2005; Bobby and Bennett, 1965). Additionally, it could irritate the skin and eyes (Andersen, 2005; Bobby and Bennett 1965). Therefore, using green reagents made from sustainable resources in its stead is interesting. Both synthetic and natural polymers have been extensively applied for decades in mineral flotation. Polyacrylamide-based polymers (PAMs), for example, have been utilized as collectors, depressants, activators, or modifiers due to their integrated functional groups (Alagha *et al.*, 2011; Alsafasfeh and Alagha, 2020; Alsafasfeh, 2020; Alsafasfeh *et al.*, 2018). In a recent investigation, single-batch flotation studies were performed on a phosphate ore sample containing >60% silicate minerals in the presence of a silicate depressant, polyacrylamide-grafted nanoparticle (Hy-PAM).

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For process optimization, variables such as pH, flotation duration, and polymer doses were investigated. The results showed that in the presence of 250g of Hy-PAM per ton of ore at natural pH, Hy-PAM outperformed sodium silicates in terms of phosphate concentrate recovery and grade (Alsafasfeh *et al.*, 2018; Alsafasfeh and Alagha, 2017). In recent studies, the biodegradable polymer, chitosan, has shown a promising depressing ability for ferrous sulfide minerals in the polymetallic sulfide flotation process. Chitosan is the most abundant polysaccharide after cellulose. It is a cationic, co-polymer of N-acetyl-D-Glucosamine(Hayat *et al.*, 2017). Chitosan is often synthesized by deacetylating chitin in hot alkali conditions (Huang, and Liu 2013). Because of its high adsorption capacity, it is most commonly used in flocculation-based solid-liquid separation processes for the removal of heavy metal ions (copper, zinc, and nickel) from water (Bassi and Simpson, 2000; Crini and Badot, 2008; Gerente *et al.*, 2007). Chitosan has been effectively evaluated as a green depressant in mineral flotation to replace sodium cyanide in complicated sulfide ore flotation (Hayat *et al.*, 2017). Recent investigations employing electrokinetic measurements on quartz samples in the presence of chitosan revealed that chitosan interacts with the quartz surface more strongly than the apatite surface (Feng *et al.*, 2017). Thus, chitosan has a high potential to be an efficient and environmentally friendly silicate mineral depressant in the direct flotation of phosphate ores.
Therefore, this research aimed at evaluating the performance of chitosan as a green depressant of silicates in the conventional flotation process of phosphate minerals. Influencing parameters such as chitosan dosage, pulp pH, and flotation time were tested for process optimization. X-ray diffraction (XRD) and mineral liberation analysis (MLA) were carried out to characterize the flotation feed. Furthermore, the electrostatic properties of mineral surfaces in the presence and absence of chitosan polymer were examined and compared using zeta potential measurements.

1 Materials and Methods

1.1 Samples

A representative phosphate ore sample was provided from a phosphate production plant located in North America. All chemicals used in the flotation tests were purchased from Fisher Scientific Company, USA. That includes sodium oleate as a collector of phosphate minerals, chitosan as a depressant of silicate minerals, and methyl isobutyl carbinol (MIBC) as a frother. Sodium carbonate (Na_2CO_3) and hydrochloric acid (HCl) were used to adjust the pH of the flotation pulp. X-ray powder diffraction (XRD) and mineral liberation analysis (MLA) were used to analyze the flotation feed and products (tailings and concentrate). XRD can provide information about the relative amounts of different mineral phases in samples by measuring the intensities of diffraction patterns, whereas MLA was obtained using the XBSE method, which uses the acquired backscattered electron (BSE) image to differentiate the mineral phases.

1.1 Zeta Potential Measurements

To understand the behavior of the flotation feed, zeta potential measurements were utilized to analyze the electrical characteristics of mineral surfaces in the presence and absence of chitosan polymer. A Zetasizer Nano ZS device (Malvern Instruments, Inc., Westborough, MA, USA) was used to measure zeta potentials. A stock solution of 0.1 wt.% pure minerals (apatite and quartz) in 0.1M KCl was made. The zeta potential was measured at two distinct pH levels (natural pH and pH 9). In all zeta potential experiments, the pH was adjusted with either HCl or NaOH.

1.2 Flotation Experiments

Flotation experiments were carried out using a Denver D-12 flotation machine. Chitosan was evaluated as a silicate mineral depressant at four different dosages: 150, 200, 250, and 300g/ton. The flotation pulp's pH and flotation time were also changed. Other process parameters were established based on earlier research (Alsafasfeh and Alagha, 2017). These parameters include solid concentration, collector (sodium oleate) concentration, and rotor speed, which were fixed at 60 wt. %, 250g/ton, and 1,200rpm, respectively. The flotation feed was prepared and sieved based on the optimum size fraction between +35 and -125µm (Santana *et al.*, 2008). A typical flotation experiment began with agitating the pulp containing the ore sample in tap water for 4 minutes, followed by the addition of both NaOH and Na_2CO_3 to change the pH as needed. Following that, a preset dosage of chitosan was added. The pulp was stirred for 4 minutes after the addition of chitosan, and then MIBC was added. The concentrated products were collected at different flotation times, dried, and characterized. The recovery and grade of phosphate minerals in concentrate products were used to evaluate flotation performance.

2 Results and Discussion

2.1Characterization of flotation feed

Using XRD on the flotation feed, the mineral phases in phosphate ore samples were determined. Apatite and quartz were the two main minerals that were found, as can be seen in **Figure 1. Figure 2** shows a flotation feed illustration in an MLA picture. The two main phosphorus-containing phases were apatite and an apatite-fluorite mixture. In the flotation feed, apatite and the mixed apatite phase (apatite-fluorite mix) were found at 33.06% and 29.96%, respectively. Additionally, fluorite was 4.95%, mica (K-Al silicate) was 8.49%, and quartz was 17.81%. K-Feldspar was 4.24%.

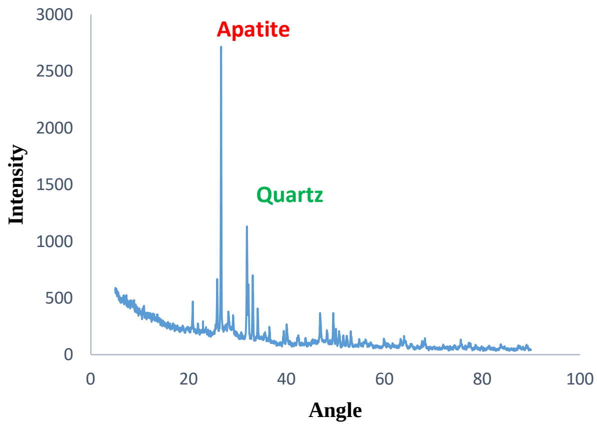

Fig. 1 XRD spectra of the flotation feed used in this study.

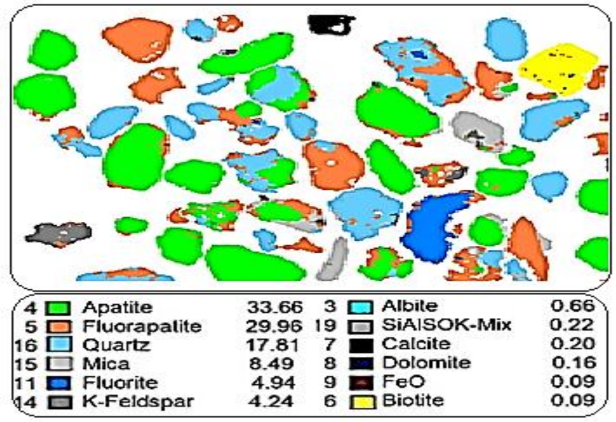

Fig. 2 Classified MLA image of flotation feed (200 X 400 mesh). Particle inset units are in pixels and concentration.

2.2 Zeta Potential Measurements

Pure minerals were used to evaluate the zeta potential of apatite and quartz at two pH levels: natural pH (7) and pH 9. Zeta potential measurements may be used to investigate and compare the surface properties and electrical properties of mineral suspensions, as well as to determine the interaction model between the mineral and other chemicals. The zeta potential of apatite and quartz under different conditions is shown in **Figure 3**. As shown, the magnitude of the change in zeta potential following chitosan addition was greater for quartz at both pH levels examined. As an example, At pH 9, which is thought to be the optimal pulp pH in large-scale phosphate flotation operations, (Alsafasfeh and Alagha, 2017), the magnitude of the zeta potential (Δζ) shift after the addition of 250ppm chitosan polymer to quartz was +30.2mV against +0.3mV for apatite. Because of the difference in electrical properties at pH 9, it is possible to selectively alter the surface properties of quartz by adding chitosan to suppress the flotation of silicate minerals and therefore improve the flotation efficiency of apatite.

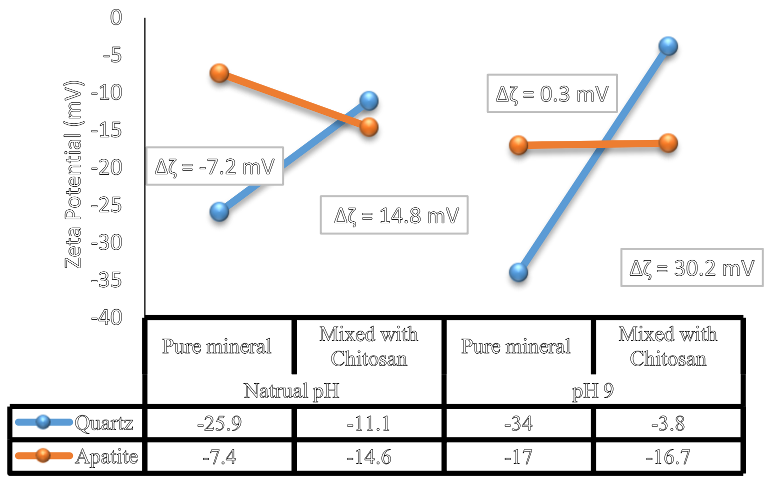

Fig. 3 Zeta potential of apatite and quartz at different pH values.

2.3 Flotation Experiments

As previously mentioned, a series of flotation experiments were carried out to evaluate the effects of chitosan on phosphate mineral flotation efficiency under different conditions (i.e., pH, flotation time, and chitosan dose). The feed slurries were treated with sodium oleate (collector), chitosan, and MIBC (frother) in the order stated in the methods section. Figure 4 shows the average recovery and grade of phosphate concentrates collected after 4 and 10 minutes at natural pH (pH7) and pH 9 respectively. As previously stated, increasing the flotation time improved the flotation performance of phosphate minerals. After 10 minutes of flotation time, the highest recovery and grade of phosphate concentrates recovered were 66% and 25%, respectively, compared to 55% and 23% after 4 minutes of flotation time. The flotation performance of phosphate minerals was enhanced when the pulp pH changed to 9 at both 4 and 10 minutes of flotation time. For example, at pH 9 and 10 minutes of flotation time, the recovery and grade of phosphate concentrate were 67% and 25%, respectively, compared to 54.1% and 21.6% at natural pH. These findings back with the zeta potential tests, which showed that interactions between quartz and chitosan were greater at higher pH. Furthermore, increasing the dose of chitosan enhanced the flotation recovery of phosphate minerals at both pH levels evaluated, regardless of flotation time. For example, in the presence of 300g/ton chitosan polymer, phosphate mineral recovery was 68% compared to 62% at 250g/ton. Overall, the findings showed that 300g/ton of chitosan, pH 9, and 10 minutes of flotation time are the optimal conditions for phosphate flotation and simultaneously depression of silicates in the presence of chitosan polymer. When commercial silicate dispersants were present, the overall recovery of phosphate minerals was 40%, as compared to 70% under these optimal conditions (Alsafasfeh and Alagha, 2017).

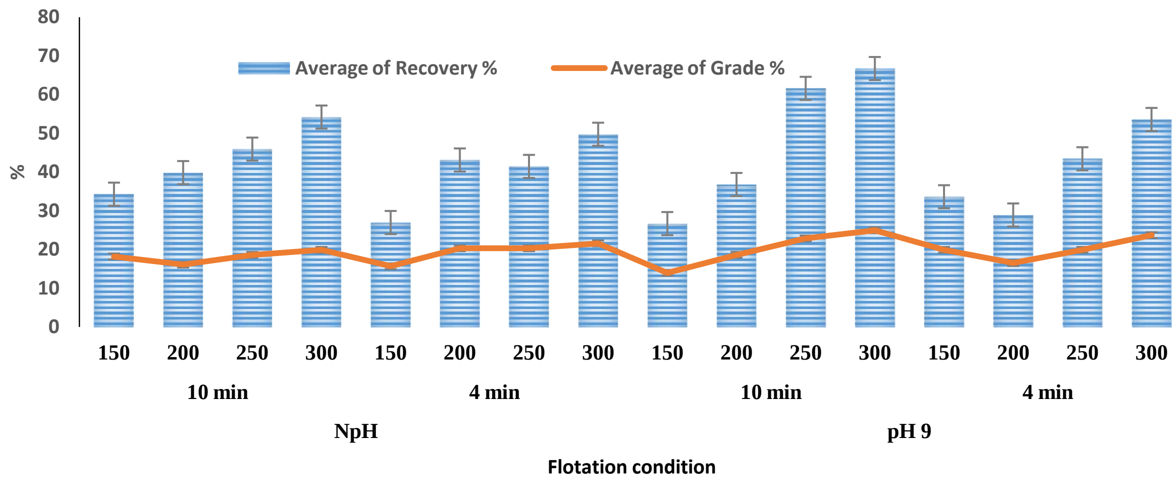

Fig. 4 Flotation performance of phosphate minerals in the presence of chitosan polymer at different experimental conditions.

Conclusions

The objective of this study was to assess chitosan's potential as a green depressant in the direct flotation of phosphate ore containing a significant amount of silicate minerals. To better understand the behaviour of the flotation feed, zeta potential measurements on apatite (a model phosphate mineral) and quartz (a model silicate mineral) were carried out before flotation experiments. These measurements evaluated the electrical characteristics of mineral surfaces in the presence and absence of chitosan polymer. According to the findings, the quartz surface and chitosan interacted more strongly at pH 9 than they did with apatite. The dose of chitosan, the pH of the pulp, and the flotation period were all varied in bench-scale flotation studies of phosphate ore with chitosan polymer. The recovery and grade of phosphate concentrates were 70% and 25%, respectively, in the presence of 300g/ton of chitosan polymer. These findings showed that, under certain conditions, chitosan might be employed as a green and sustainable depressant of silicate minerals in the phosphate flotation process.

Nomenclature

Δζ	=Zeta potential magnitude of the	[mV]
NpH	=Natural pH	[-]
ZS	=Zita sizer	[-]

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