CARRIER MICROENCAPSULATION USING Si AND CATECHOL TO SUPPRESS PYRITE FLOTATION AND OXIDATION

Rani Kumari Thakur JHA
Candidate for the degree of master of engineering
Supervisor: Prof. Masami TSUNEKAWA
Division of Solid Waste, Resources and Geo-environmental Engineering

Introduction

In coal and metal sulfide mines, pyrite (FeS₂), a common gangue mineral, is rejected from valuable minerals by physical separation techniques such as flotation, and it is wasted into a tailing pond [Petruk (2000), Wills(1997)]. The waste contains huge amount (<1 to nearly 60%) of sulfide bearing minerals along with trace amounts of valuable minerals [Petruk (2000)]. Froth flotation is widely applied to remove the pyrite from coal and other valuable minerals; problem associated with this process is the entrapment of pyrite in the froth layer of valuable minerals during flotation process: this takes place due to the hydrophobic nature of pyrite, and results to the lowering of the separation efficiency. In order to produce high quality concentrate the pyrite entrapment in the froth layer should be suppressed.

The separated pyrite is then disposed as waste into tailing ponds or dams. The oxidation of such type of mine waste; sulfide bearing minerals especially pyrite in the dam generates the Acid Mine Drainage or AMD. AMD is polluted water flowing from the mining or processing sites characterized by a low pH: as low as 2, high sulfate content, and the presence of dissolved metals such as aluminum and iron. [Evengelou (1995)] AMD formation creates environmental risks of ground water contamination, [Lottermoser (2003)]. To prevent the AMD formation several methods have been proposed in the past; e.g. suppression of the catalyzing effect of bacteria by adding bactericides, prevention of the contact of oxygen and water to pyrite by physical covering and chemical coating on the pyrite surface. Physical coverings has lots of drawbacks; chemical coating techniques e.g. coating the pyrite surface with ferric phosphate, iron oxide,[ Evengelou (2001)] to prevent O₂ diffusion has been a promising technique against AMD formation.

The present study investigated carrier microencapsulation; a chemical coating method for the pyrite surface as a prevention method against pyrite oxidation and as a control for pyrite floatability. In the proposed method; the pyrite surface is coated by a Si thin oxide/hydroxide layer using water soluble organic carrier catechol combined with Si ions. The layer converts the hydrophobic pyrite surface into hydrophilic and suppresses the floatability; it also acts like a barrier against pyrite oxidation by interrupting the contact of oxygen and water to the pyrite.

Experimental

Sample and chemicals

A specimen grade pyrite sample from Peru was dry-ground with a ball mill and sieved to obtain + 106 - 150 µm fraction. The sample was washed with ethanol, 1 kmol m⁻³ nitric acid, distilled water and acetone; then dried for 24 hours inside a vacuum dryer. Catechol, benzene 1,2-diol (H₂Cat), and Na₂SiO₃.9H₂O are of reagent grade.

Carrier microencapsulation

For CME treatment, 1g of pyrite sample was shaken in 10 cm³ of 5 mol m⁻³ Si(Cat)₂²⁻ solution (prepared by dissolving 0.142 g of Na₂SiO₃.9H₂O and 0.165 g of benzene 1,2-diol or catechol, into 10 cm³ distilled water) inside a 50 cm³ Erlenmeyer flask at 25°C under aerobic conditions using a water bath shaker. The shaking amplitude of water bath shaker was 4 cm; and the frequency was 120 min⁻¹.

Bubble pick-up experiments

Bubble pick-up experiment was carried out using the electronic induction timer MCT-100 at constant amplitude of bubble pick up with various contact times [Yoon(1991)]. The pyrite sample and solution in the flask used for CME treatment were transferred...
to a rectangular optical glass cell to form a bed of pyrite particles. The air bubble was formed on the tip of a capillary tube inside the cell, and bubble was brought into contact with pyrite bed. The attachment of pyrite to bubble was observed with the help of a microscope connected to a computer display. The probability of attachment was counted by ten different measurements at different places of particle bed. The effects of contact time, pH, CME treatment time and the Si(Cat)$_3^{2-}$ concentration on the attachment probability were investigated.

**Flotation experiments**

Flotation experiments were conducted using a Hallimond tube. CME treatment of pyrite was initially performed for 60 minutes then the pyrite and Si-catechol complex mixture was transferred to a beaker containing 100 cm$^3$ distilled water. Potassium ethyl xanthate (1.1 cm$^3$ of 0.01 kmol m$^{-3}$) or 0.278 cm$^3$ of the kerosene-water emulsion (kerosene content, 625ppm) was added as collector and the mixture was stirred over a magnetic stirrer for 5 min. Then the mixture was transferred to the Hallimond tube. The air was supplied at a flow rate of 100 cm$^3$ min$^{-1}$ for 5 min. The froth and tailings were recovered by filtration the weights of the dried samples, the percentage recoveries of pyrite in the froth were calculated.

**Leaching experiment**

For leaching experiment CME treatment was performed on pyrite, after the treatment filtrate was thoroughly washed, vacuum dried and 2 g of pyrite was shaken in the presence of 20 ml. of distilled water under aerobic conditions. The shaking amplitude of water bath shaker was 4 cm, the temperature was 25$^\circ$C and the frequency was 120 min$^{-1}$. The supernatant was sampled and analyzed for the Si, Fe, and S content by ICP-AES. The pH was also measured.

**Result and discussions**

Catechol makes a tris-complexes with Si$^{4+}$ i.e. Si(Cat)$_3^{2-}$, which is stable, and water soluble. [Caulfield et.al.(2001), Kansal et.al.1994].In the present study, triscatecholato silicate complex ion Si(Cat)$_3^{2-}$, prepared from catechol and sodium meta silicate, is selected for CME to form SiO$_2$ or Si(OH)$_4$ coating on pyrite surface.

After the CME treatment, the bubble pick up experiment were carried out; Fig. 2 shows the effect of concentration of additives on probability of attachment of the pyrite particles to air bubble. The attachment probability decreased with increasing the concentration of Si(Cat)$_3^{2-}$, but the values were over 0.3 even in the presence of the highest concentration of each additive. On the other hand, the attachment probabilities for pyrite treated with Si(cat)$_3^{2-}$ were zero at the concentrations above 0.5 mol m$^{-3}$. This confirms that Si(cat)$_3^{2-}$ is most effective for suppressing pyrite hydrophobicity.

Fig. 3 shows the effect of pH on the probability of attachment of pyrite particle to air bubble The attachment probability was over 0.6 for the pyrite treated with distilled water while the pyrite treated with Si(cat)$_3^{2-}$ did not attach to air bubble over the wide initial pH range of 4 to 10, and the attachment was observed only at very acidic region (pH 2).

**Fig.2.** Effect of concentration on probability of attachment of pyrite particle to air bubble in dynamic bubble pick up experiments. CME treatment time was 1 hr. The pH values were 5~7 for H$_2$Cat, 10~11 for Na$_2$SiO$_3$ and 7~9 for Si (cat)$_3$.  

**Fig.3.** Effect of pH on probability of attachment of pyrite particle to the air bubble in dynamic bubble pick up experiments CME treatment time was 24 h. The pH was adjusted by adding NaOH and H$_2$SO$_4$. Contact time was 1 second.
In all of the above experiments the CME treatment time was 1 hour; however, in real flotation plant the conditioning time is limited. Considering this, the effect of CME treatment with shorter treatment time on the attachment probability of pyrite particle to the air bubble was investigated. Fig. 4 shows the result of effect of shorter treatment time on the attachment probability. The Si(Cat)3 treated pyrite had almost no attachment even the treatment time was less than 3 min, while the pyrite without treatment remained hydrophobic and the attachment probability was 0.9 to 1.0 throughout the experiment. This result indicates that CME treatment is effective to suppress pyrite floatability even with short treatment time.

Fig. 4. Effect of shorter treatment time (in minutes) on the probability of attachment of pyrite particle to air bubble in the dynamic bubble pick up experiment. The pH value was 5.93 for control and 6.62 for Si (Cat)3.

Fig. 5 shows the effect of CME treatment on pyrite floatation with or without typical collectors used for metal ore flotation (xanthate) and coal flotation (kerosene). Without CME treatment the pyrite recovery in the forth was 21% without additives, and 87.0% with xanthate and 72% with kerosene. CME treatment made the pyrite hydrophilic and reduces the pyrite recovery in the froth: the recovery of pyrite in forth was recorded only 0.6% without collector, 2.5% with xanthate and 8.12% with kerosene.

All the results shown in Figure 2 to figure 5 indicate that CME treatment using Si(Cat)3 2- is effective for suppressing pyrite floatability. This is assumed to be due to SiO2 or Si(OH)4 layer formed on pyrite surface by CME treatment. To confirm the presence of Si on pyrite surface, SEM-EDX analysis of the pyrite treated with 100 kmol m-3 Si(Cat)3 solution for 1 h was performed. As shown in Fig 5, EDX spectra peaks corresponding to Si and SEM mapping it was confirmed that Si is present on most of pyrite surface.

The bubble pick up and flotation experiment results proved the suppressing effect of CME in pyrite floatation; the effect of CME in suppression of pyrite oxidation was analyzed next. To analyze this, leaching experiment was carried out under atmospheric conditions; the Figures 7, 8, 9 and 10 shows the pH trend, Fe, Si and S content in the supernatant of the leaching experiment respectively.
The pH of the CME treated pyrite dropped to 3 after the 30 days leaching even with for pyrite treated with the lower concentration of 1 mM Si(Cat)₃ solution, while the pH of the pyrite treated with distilled water continued to decrease with the time and after 30 days it was recorded 1.8. The Fe, Si and S content in the leachate of raw pyrite is very high in comparison of that of CME treated pyrite leachate. The Fe content in the leachate of control pyrite was recorded 12 ppm in the other hand the CME treated pyrite leachate gave the value around 6 even with the lowest concentration. The Sulfur content in the leachate of pyrite treated with distilled water is very high but the CME treated pyrite has very low content of leached sulfur, it was around 0.5 for the CME treated pyrite leachate. The Si trend was also the same as the sulfur trend; in the leachate of raw pyrite very high amount of Si leached while in the CME treated pyrite gave very less value of leached Si in the leachate which was recorded 2 ppm. The result shows that the leaching of Fe and S is successfully suppressed by the carrier microencapsulation.

Conclusions

The effects of carrier microencapsulation (CME) treatment using silicon-catechol complex on pyrite wettability was investigated by bubble pick up experiments and Hallimond tube flotation experiments. CME treatment changed the hydrophobic pyrite surface to hydrophilic and suppresses the floatability of pyrite particle. The addition of collectors in flotation cell has no significant effect on CME. The leaching test confirmed that the CME is very effective in suppression of pyrite oxidation under atmospheric conditions.

References