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Flocculation of Pyrite Fines in Aqueous Suspensions with Corn Starch to Eliminate Mechanical Entrainment in Flotation

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Abstract: The hydrophilic flocculation of pyrite fines in aqueous suspensions with corn starch was studied by measuring particle size distribution, microscopy observation and micro-flotation. Furthermore, the interaction of corn starch with pyrite was investigated by determining the adsorption density and based on zeta potential measurements and X-ray photoelectron spectrometer (XPS) analysis in this work. The results of the particle size distribution measurement show that corn starch can effectively aggregate pyrite fines, and the pyrite floccules (flocs) are sensitive to mechanical stirring. The micro-flotation results suggest that the mechanical entrainment of pyrite fines in flotation can be effectively eliminated through the formation of large-size flocs. The zeta potential of pyrite particles decreases with the addition of corn starch. The XPS results prove that carboxyl groups are generated on the digested corn starch, and both iron hydroxyl compounds and ferrous disulfide on the pyrite surface can chemically interact with the corn starch digested by sodium hydroxide.

Keywords: hydrophilic flocculation; pyrite fines; corn starch; mechanical entrainment; adsorption

1. Introduction

In froth flotation, mineral particles are floated through two methods: true flotation and mechanical entrainment. The former is a selective separation process, by which hydrophobic mineral particles are attached to bubbles and transferred into the froth product. The latter is a non-selective process, where both hydrophilic and hydrophobic particles can be carried into the froth product through water in the triangle zone among air bubbles [1,2]. The entrainment is the primary mechanism, by which liberated and dispersed gangue fines (minus 30 μm) enter the froth products [3], which leads to a poor concentrate in grade. It was reported that the formation of hydrophilic flocs of gangue mineral fines before the flotation was an effective method to eliminate the entrainment [4–7].

Pyrite is a common mineral impurity in sulfide mineral flotation. Many reports have investigated the depression of pyrite with particle size larger than 30 μm in flotation; they indicate that several depressants such as dextrin, carboxy methyl cellulose (CMC), starch and tannins can significantly depress pyrite in the corresponding conditions because hydrophilic surfaces form on the pyrite [8–14]. However, if the sulfide ore is finely disseminated (the grain size is smaller than 30 μm), the pyrite is easily recovered using mechanical entrainment. Thus, it is difficult to remove pyrite from other valuable sulfide minerals in flotation even under good depressing conditions. Few works report on reducing the entrainment of pyrite fines using hydrophilic flocculation.

In this work, the hydrophilic flocculation of pyrite fines in aqueous suspensions was studied with corn starch as a flocculant using flocculation tests, microscopy observation, and micro-flotation tests. The interaction of corn starch with pyrite was investigated in the adsorption test, zeta potential measurement and X-ray photoelectron spectrometer analysis. The objective is to better understand the flocculation behavior and the interaction mechanism between pyrite and corn starch, and to discover a potential method to avoid the mechanical entrainment of pyrite fines in sulfide mineral flotation.

2. Experimental

2.1. Materials

The pyrite sample used in this study was collected from Daye iron mine, Hubei province, China. It was analyzed with chemical analysis and X-ray diffraction and showed approximately 96% FeS_2 in purity. The sample was ground and sieved to obtain the minus 30 μm fraction, which was maintained in a sealed plastic bottle and stored in a refrigerator. Figure 1 illustrates the particle size distribution; the d50 (particle size at 50% cumulative undersize) is approximately 8.5 μm, and d80 (particle size at 80% cumulative undersize) is approximately 17.5 μm.

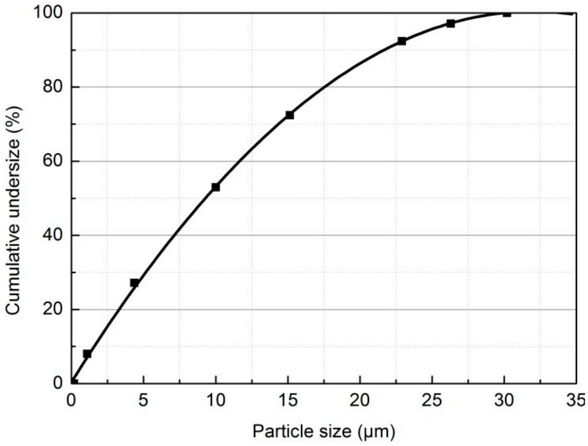

Figure 1. Size distribution of pyrite fines.

Corn starch used as a flocculant in this study was from Aladdin Industrial Co. (Shanghai, China). Its molecular weight of 150,000 was determined using the dynamic light scattering technique. Hydrochloric acid and sodium hydroxide, which were used to adjust the pH, were obtained from the Xinyang chemical reagent and Sinopharm Chemical Reagent Co. (Shanghai, China), respectively. All chemicals were of analytical purity.

The water in this work was produced using a Millipore Milli-Q Direct 8 water purification system (Millipore SAS, Molsheim, France) with the resistivity of 18.25 MΩ· cm.

The corn starch stock solution was prepared by mixing 20 mL of 2.5 mol/L NaOH solution with 0.1 g corn starch in 50 mL water and subsequently diluted to 100 mL.

2.2. Methods

2.2.1. Hydrophilic Flocculation Test

The hydrophilic flocculation of pyrite fines in aqueous suspensions was conducted in a stirring tank (Xing Rui experimental equipment business department, Nantong, China) of 42-mm inner diameter and 100-mm height with a blade impeller. First, 1 g of pyrite and 100 mL of water were mixed while HCl or NaOH solution was added for the pH adjustment. Then, the suspension was conditioned at a given stirring speed for a given time in the presence of corn starch.

2.2.2. Particle Size Analysis

A Malvern Mastersizer 2000 (Malvern Instruments, Worcestershire, UK) was used to determine the size distributions of the original and flocculated pyrite particles in this study. d50 (Mean floc size) was reported in this paper. A peristaltic pump was used to circulate the flocs through the size analyzer instead of the fan impellers to protect the flocs from breakage during the measurements. The speed of the peristaltic pump was fixed at 280 rev/min. Each test was performed in triplicate, and the error was within ±2.5 μm. The arithmetic average result of the three tests was reported in this paper.

2.2.3. Observation of Pyrite Flocs

Hydrophilic flocs were observed using a Leica DMLP optical microscope (Leica, Wetzlar, Germany), which was equipped with a digital camera. The sample was prepared by dropping the suspensions of pyrite flocs onto a glass plate. During the observation, the flocs were imaged.

2.2.4. Micro-Flotation Tests

Micro-flotation was performed in a Hallimond flotation tube (Xing Rui experimental equipment business department, Nantong, China) with nitrogen as the bubble source. A pyrite suspension was transferred into the tube and subsequently diluted to 100 mL. Then, flotation was performed for 4 min at a nitrogen gas flow rate of 15 mL/min. During the flotation, no collector or frother was used. The floated and non-floated products were dried. The recovery was obtained using the total weight of two products divided by the floated product weight. Each test was performed in triplicate. The arithmetic average result of the three tests was reported in this paper.

2.2.5. Adsorption Density Determination

The adsorption densities were determined using the batch depletion method, and the specific surface area of the 3.169 m^2/g pyrite sample was measured using a BET Monosorb unit (Gold Aipu Technology Co., Ltd, Beijing, China). 0.5 g of pyrite powder was taken to make 50 mL of solution by adding the desired amounts of 10^{-3} mol/L NaCl and corn starch solution of known concentration, and the pH was adjusted in 150-mL Erlenmeyer flasks. The suspensions were subsequently agitated for 2 h in a shaking bath at 25 °C. After equilibration, the solution pH was again recorded. The solution was subsequently centrifuged for 30 min at approximately 1720 g using a Thermo Scientific Sorvall ST 16 Centrifuge (Thermo Scientific, Waltham, MA, USA). Then, the supernatant liquid was analyzed to obtain the equilibrium concentration of corn starch that remained in the solution using a Thermo Scientific spectrometer (Thermo Scientific) with the phenol-sulfuric acid method [15]. Each test was performed in triplicate. The arithmetic average result of the three tests was reported in this paper.

2.2.6. Zeta Potential Measurements

Zeta potential measurements were conducted using a Malvern Zetasizer Zeta-Nano (Malvern Instruments). In the measurements, all solutions and reagents were prepared with stock solutions of 10^{-3} mol/L NaCl to maintain a constant ionic strength. 1 g of the pyrite fines was dispersed in 1 L NaCl solution. For each measurement, 10 mL of this solution was siphoned out and diluted to 100 mL; the pH adjustment and reagent additions were also performed. The conditioned sample was placed in the sample cell of ZetaPALS, and the zeta potentials of the suspended particles were recorded.

2.2.7. X-Ray Photoelectron Spectrometer (XPS) Studies

The XPS analyses were performed using a VG Multilab 2000 X-ray photoelectron spectrometer (Thermo Scientific) and an Al Kα X-ray source with a solution of 0.47 eV. The sample of pyrite, which was treated with corn starch, was prepared by mixing 0.5 g of pyrite with 100 mL of 50 mg/L corn starch solution at pH 7.3. The treated pyrite sample was filtered and washed with deionized water after stirring with a magnetic bar at 25 °C. All samples were dried in a vacuum desiccator.

3. Results and Discussion

3.1. Flocculation of Pyrite Fines

Figure 2 shows the effect of pH on the size of the pyrite flocs with corn starch. As observed, the flocs size significantly increases with the presence of corn starch. The size of the pyrite flocs increases with the increase in pH: at pH 3.6, the size is approximately 40 μm, which is nearly five times larger than the original particle size (d50 = 8 μm), and it increases to approximately 60 μm at pH 11.3. The results suggest that corn starch is an effective flocculant for pyrite fines in the tested pH range in aqueous suspensions, and the alkaline pulp is favorable for the formation of pyrite flocs.

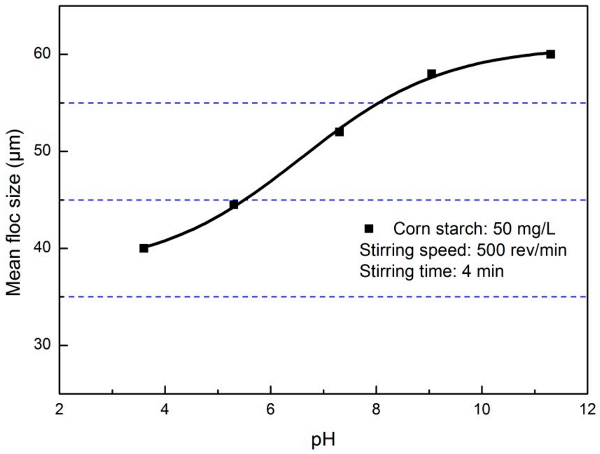

Figure 2. Effect of pH on the mean size of pyrite flocs in the presence of corn starch.

The effect of the stirring speed on the size of pyrite flocs was studied, and the results are illustrated in Figure 3. Figure 3 shows that the stirring strength strongly affects the size in the presence of corn starch. The sizes increase with the increase in stirring speed until a maximum value is reached and subsequently decrease. The critical stirring speed is 400 rev/min for corn starch. At high stirring speeds, the decrease in floc sizes may be attributed to the destruction of the pyrite flocs. This result suggests that the flocculated flocs with the polymers are much weaker than the hydrophobic agglomeration in terms of strength [16].

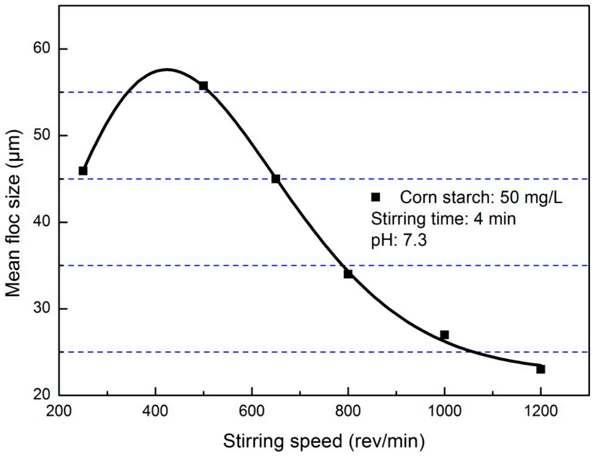

Figure 3. Effect of the stirring speed on the size of pyrite flocs with corn starch.

The size of the pyrite flocs as a function of stirring time at the speed of 500 rev/min is shown in Figure 4. Pyrite fines are quickly flocculated by corn starch, and the size of the pyrite flocs is approximately 70 µm with 1 min of stirring. With the increase in stirring time, the size rapidly decreases to approximately 40 µm in 8 min; then it slightly decreases from 40 µm to approximately 35 µm in 12 min. This result indicates that the hydrophilic flocculation with corn starch is sensitive to mechanical agitation, and the larger flocs are more likely damaged than smaller ones.

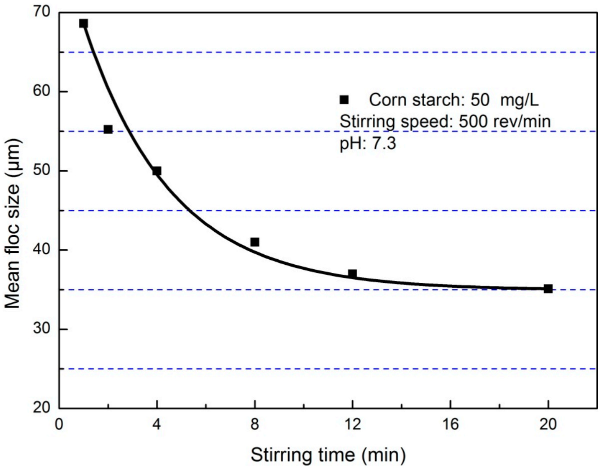

Figure 4. Effect of the stirring time on the size of pyrite flocs with corn starch.

Figure 5 illustrates the effect of the flocculant addition on the size of pyrite flocs. Corn starch effectively flocculates the pyrite fines even at a low addition of approximately 10 mg/L. The maximum size is approximately 56 µm at 40 mg/L corn starch. However, the size begins to decrease when the concentration of corn starch is over 40 mg/L. The decrease in size at high addition can be attributed to the steric effect of adsorbed flocculants on the pyrite surfaces. This result shows that an appropriate addition of corn starch is beneficial to the pyrite flocculation.

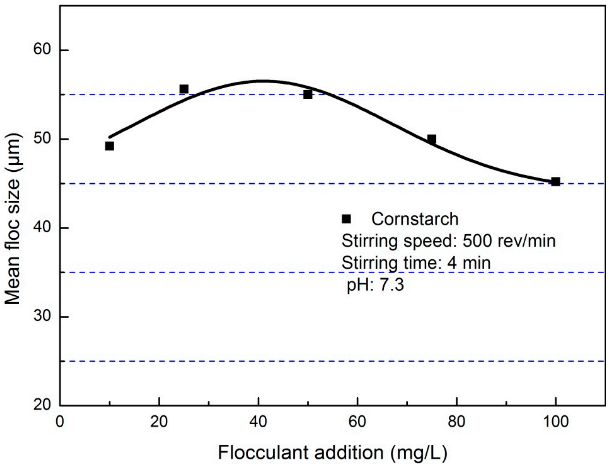

Figure 5. Effect of the flocculant addition on the size of pyrite flocs with corn starch.

3.2. Morphology of Pyrite Flocs

The optical microscopy image of pyrite flocs with the addition of 50 mg/L corn starch at pH 7.3 is shown in Figure 6. It is observed that the pyrite fines indeed form flocs in the presence of corn starch, and the floc size is larger than 100 µm. However, the floc has a loose porous structure and high sensibility to the stirring time and stirring speed, as shown in Figure 6.

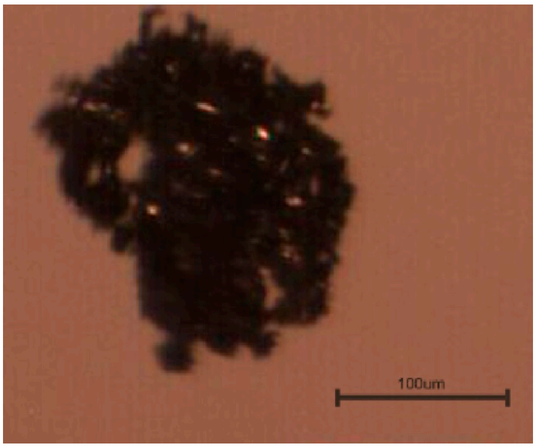

Figure 6. Optical microscopy image of pyrite flocs in the presence of corn starch.

3.3. Flotation of Pyrite Flocs

The recovery of pyrite in froth flotation with and without corn starch as a function of pH is illustrated in Figure 7. As observed, the recovery of pyrite with size of −74 + 48 μm without corn starch is less than 3% in the tested pH range. However, the recovery of pyrite fines with the size of −20 μm is approximately 40%. This result suggests that the mechanical entrainment leads to the high recovery of pyrite fines without corn starch. The recovery of pyrite fines is strongly depressed in the presence of corn starch at 50 mg/L. It decreases from 40% to 5% at pH 7.5. The decrease becomes sharper with the increase in pH, which corresponds to the increase in floc size, as shown in Figure 2. Clearly, the mechanical entrainment of pyrite fines in flotation can be weakened or eliminated using the formation of hydrophilic flocs. Larger flocs have lower recovery. The flotation results suggest that selectively hydrophilic flocculation is an effective method to reduce the entrainment of pyrite fines in the separation of galena from pyrite, if galena cannot be depressed by the digested corn starch.

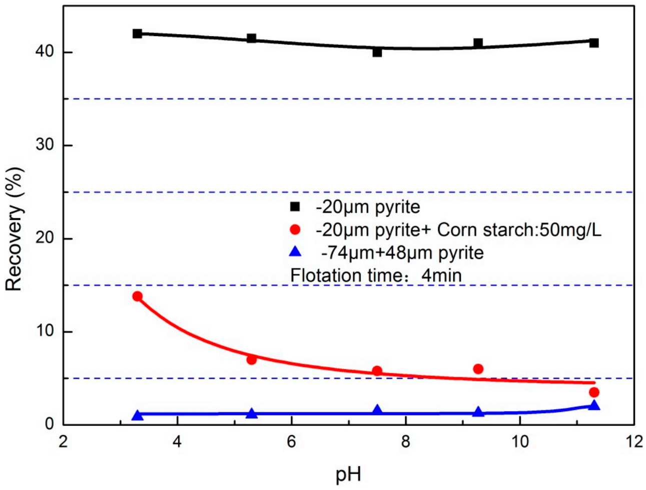

Figure 7. Effect of pH on the recovery of pyrite fines in froth flotation with and without the flocculant.

3.4. Adsorption Isotherm

The adsorption isotherm of corn starch onto pyrite at pH 7.5 is shown in Figure 8. The adsorbed amount of corn starch exhibits a slow continual increase with the increase in flocculant concentration and does not reach the maximum adsorbed amount in the tested concentration. However, as shown in Figure 9, in the tested concentration range, the isotherm complies with Langmuir equation when we plotted the reciprocal of the adsorbed amount *versus* the reciprocal of the equilibrium concentration with R^2 (correlation coefficient) of 0.992. The isotherm may follow Langmuirian behavior according to the Giles classification [17]. The calculated q_m (saturated adsorption amount on a monolayer) and b (adsorption equilibrium constant) values were 16.7 mg/m^2 and 0.0042 L/mg, respectively.

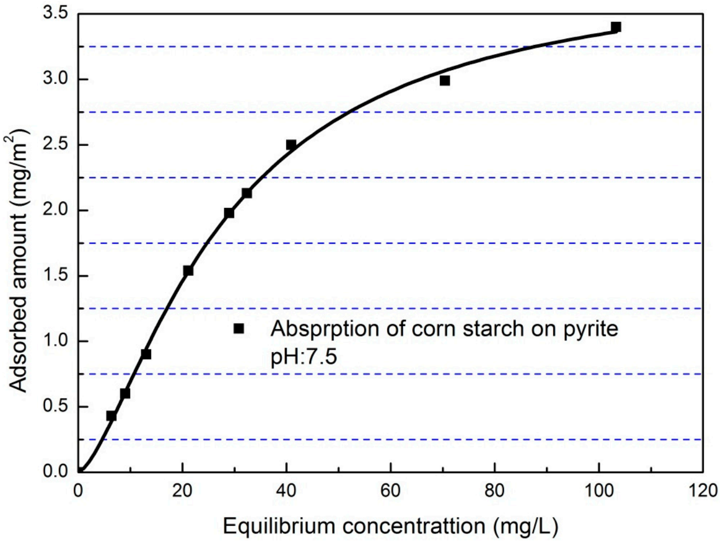

Figure 8. Adsorption isotherm of corn starch onto pyrite.

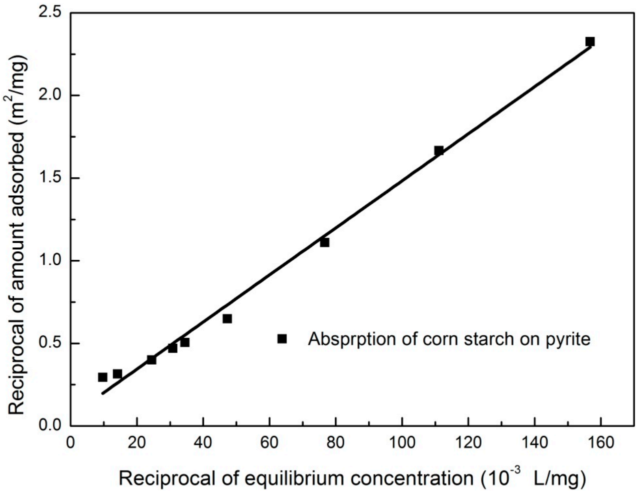

Figure 9. Plot of the reciprocal of adsorption density *versus* reciprocal of equilibrium concentration.

3.5. Effect of Corn Starch on the Zeta Potential of Pyrite

The zeta potential of pyrite as a function of pH without and with corn starch is shown in Figure 10. Pyrite shows an isoelectric point at approximately pH 3, and the addition of corn starch does not significantly change its isoelectric point, which may be attributed to the caustic digested corn starch with an isoelectric point at approximately pH 3 [18]. The addition of corn starch at 20 mg/L dramatically decreases the zeta potential of pyrite in alkaline condition, which is favorable for the flocculation of pyrite fines by the decrease in electrical repulsion force.

The effect of corn starch addition on the zeta potential of pyrite is shown in Figure 11. Corn starch can significantly decrease the pyrite zeta potential from approximately −19 to approximately −6 mV with its concentration less than 1 mg/L. Above 2 mg/L, the zeta potential of pyrite remains stable. The decrease in zeta potential of pyrite may result from the compression effect of the electric double layer for high ion concentration from the preparation of the starch solution.

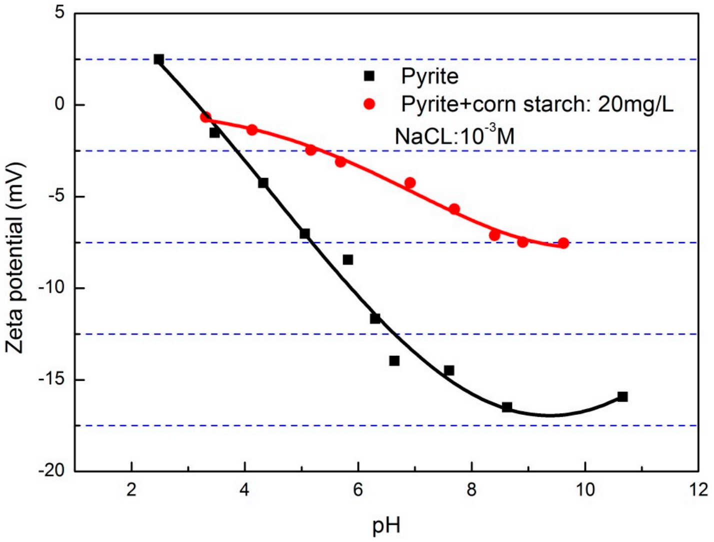

Figure 10. Zeta potential of pyrite as a function of pH without and with corn starch.

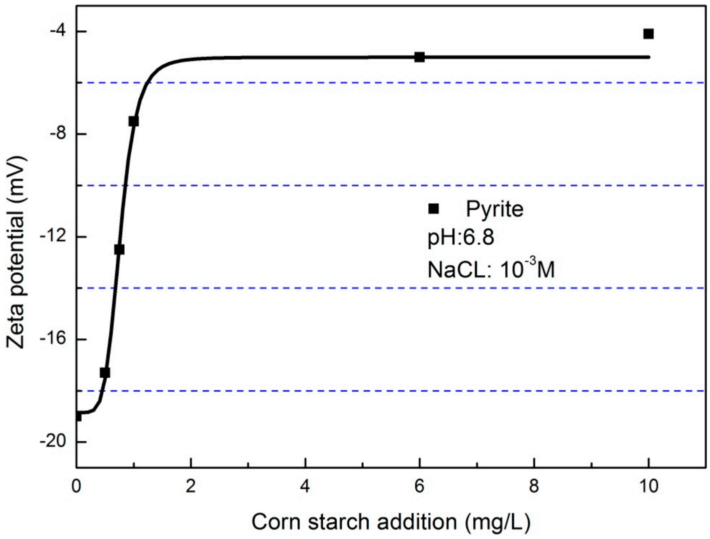

Figure 11. Effect of the corn starch addition on the zeta potential of pyrite.

3.6. Interaction Mechanism between Pyrite and Digested Corn Starch

XPS analysis was used to examine the pyrite surface before and after the corn starch treatment. The surface species were identified based on deconvoluted peaks of the photoelectron binding energy spectra. Comparing the XPS spectra of pyrite before and after the treatment with corn starch, any obvious binding energy shifts (more than 0.1 eV) can be used to infer the chemical interactions between pyrite and corn starch.

Figure 12 shows the C 1s binding energy spectrum of corn starch after adsorption on pyrite, and the peak fitting results are shown in Table 1. The C 1s spectrum consists of six binding energy peaks at 283.91, 284.61, 285.23, 286.11, 287.51 and 288.7 0 eV. The peaks at 284.61, 286.11, 287.51 eV were assigned to C–C, C–H, C–O (alcohol) and O–C–O (acetal), respectively [19]. The presence of a 288.70 eV XPS signal was assigned to O=C–O (carboxyl and ester functions), which is not contained in natural corn starch. This peak indicates that the carboxyl was indeed generated in corn starch because of the treatment of the sodium hydroxide solution, which is consistent with the previous study [15]. The peaks at 283.91 and 285.23 eV are unknown because the structural change of corn starch that was digested with sodium hydroxide is not clear.

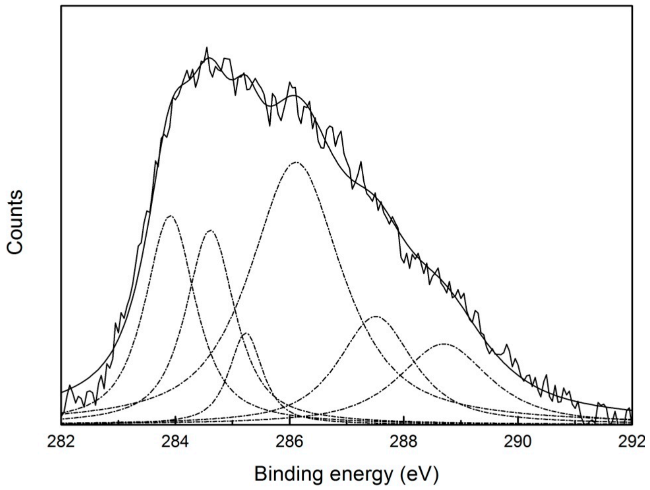

Figure 12. C 1s spectrum of corn starch after adsorption on the pyrite surface.

Table 1. X-ray photoelectron spectrometer (XPS) C 1s peak fitting for corn starch after adsorption on the pyrite surface.

Chemical State	**C**					
	C–C/C–H	**C–O**	**O=C–O**	**O–C–O**	**Unknown**	**Unknown**
BE (eV)	284.61	286.11	288.70	287.51	293.91	285.23

The Fe 2p3/2 spectrum of pyrite before and after the corn starch treatment is shown in Figure 13, and the peak fitting results are listed in Table 2. As observed in Table 2, the peak at 707.30 eV was assigned to FeS_2. The peaks at 708.73, 710.15, 711.80 and 713.88 eV belong to ferrous oxide, iron oxide, iron hydroxide, and ferric sulfate, respectively [20], which originate from the partial oxidation of the pyrite surface. After the treatment of pyrite by corn starch, the binding energies of three peaks obviously decrease. The shifts of 0.61, 0.2 and 0.19 eV for iron disulfide, ferrous hydroxide, and ferric sulfate, respectively, attest their chemical interactions with corn starch. Iron oxide and ferrous oxide on the surface of pyrite may not have participated in the chemical interaction with corn starch because their change in binding energy is less than 0.1 eV.

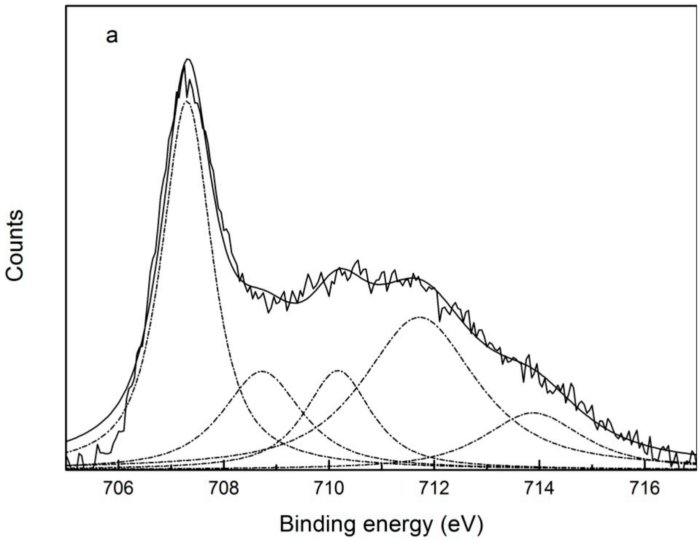

Figure 13. *Cont.*

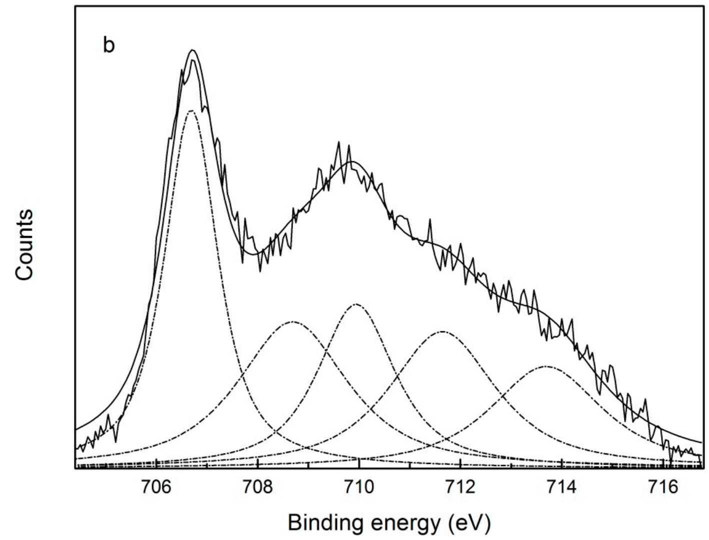

Figure 13. Fe 2p3/2 spectra of pyrite before (**a**) and after (**b**) the adsorption of corn starch.

Table 2. XPS Fe 2p3/2 peak fitting for pyrite before and after the treatment with corn starch.

Species	**Fe**				
	FeS_2	**FeO**	**Fe_2O_3**	**FeOOH**	**$Fe_2(SO_4)_3$**
BE (eV) [a]	707.30	708.73	710.15	711.8	713.88
BE (eV) [b]	706.69	708.69	710.09	711.6	713.69
Shift (eV)	0.61	0.04	0.06	0.2	0.19

([a]: pyrite; [b]: pyrite treated by corn starch).

In the interaction mechanism of polysaccharides on the pyrite surface, polysaccharides interact with hydroxylated metallic sites on the mineral surface [11,21]. According to this mechanism, the interaction mechanism of the adsorption of corn starch on the pyrite surface may be the interaction of hydroxyl or carboxyl groups on the corn starch with the iron hydroxyl species that form on the pyrite surface. In addition, iron atoms in iron disulfide and ferric sulfate interact with the corn starch.

4. Conclusions

(1) The mechanical entrainment of pyrite fines in flotation can be effectively eliminated by adding an appropriate amount of corn starch, which may be attributed to the formation of hydrophilic flocs of fines bridged by corn starch molecules. The flocculation is notably sensitive to mechanical stirring.

(2) The XPS studies provided good evidence of the presence of carboxyl groups on pyrite surfaces, which suggests a chemical interaction between pyrite and corn starch digested with sodium hydroxide (or chemical adsorption of corn starch on pyrite), which is also supported by the zeta potential results.

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Author Contributions: Hongqiang Li, Shaoxian Song and Wei Ge conceived and designed the experiments. Wei Ge, Yanzeng Ren and Feiyu Zhao prepared the samples and performed the experiments. Hongqiang Li and Wei Ge analyzed the data. Wei Ge, Hongqiang Li and Shaoxian Song contributed to the writing and revising of the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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