

## Depressing effect of hydroxamic polyacrylamide on pyrite<sup>①</sup>

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**Abstract:** The performance of hydroxamic polyacrylamide (HPAM) in mineral flotation was tested on the samples of calcite, diaspore and pyrite. It is found that HPAM expresses intensive depression on pyrite and can be used as effective depressants for pyrite. The depression mechanism of HPAM to pyrite was investigated by the determination of contact angle, zeta potential, adsorptive capacity for collectors and infrared spectrum. A lower contact angle, more negative zeta potential, less xanthate adsorptive capacity, and the formation of chemical bonding were determined, which reveals that the strong chemical interactions exist between HPAM and pyrite surface. The group electronegativity of HPAM was calculated to explain the differences of interaction between reagent and minerals.

**Key words:** hydroxamic; polyacrylamide; depressant; pyrite

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### 1 INTRODUCTION

Natural and synthetic polymers have been widely used in industrial and environmental processes such as oil recovery, paint manufacturing, papermaking, mineral separation, medical formulation, food processing, water treatment, and soil remediation. Polyacrylamide (PAM) and its derivatives are among the most widely used commercial polymers, particularly in water treatment and mineral processing<sup>[1, 2]</sup>.

Polyacrylamide possesses the chemical characteristic as common acidamide does, such as hydrolysis, alcoholysis and aminolysis, which may result in PAM derivatives by modifications. Generally, PAM can be modified in two ways. One is the transformation into ionic polymers, which can enhance its hydrophilicity and solubility such as hydrolysis and sulfonation<sup>[3, 4]</sup>, and the other is the synthesis of graft copolymers with other macromolecules such as carboxyl methyl cellulose (CMC), starch, amylase and amylopectin<sup>[5, 6]</sup>. It has been found that the graft copolymers of polyacrylamide with polysaccharides exhibit much better flocculation performance than the conventional polysaccharide and synthetic polymer-based flocculants<sup>[7]</sup>.

During mineral processing, PAM and modified PAM can be used as flocculants to flocculate fine particle minerals<sup>[8, 9]</sup> and as depressants for sulfide minerals and non-sulfide minerals<sup>[10, 11]</sup>. Nagaraj<sup>[12]</sup> found that PAM with different functional groups

exhibited depressing ability for ferrous-containing sulfide. Boulton et al<sup>[11]</sup> used PAM with low relative molecular mass to separate copper-activated sphalerite from pyrite in the presence of isobutyl xanthate. The effects of carboxyl, sulfonate, and hydroxyl or thiourea functional groups attached to the polymers on the flotation recoveries of sphalerite and pyrite were studied as a function of polymer concentration and order of reagent addition. It has been shown that all the PAM demonstrated obvious depression on pyrite but unobvious depression on sphalerite.

Our previous study<sup>[13]</sup> presented a new kind of hydrophilic and soluble polyacrylamide derivative, hydroxamic polyacrylamide (HPAM), which was prepared from PAM and hydroxylamine hydrochloride in KOH/alcohol solution with 5.78% of substitution degree. In this paper, the performance of HPAM in mineral flotation on three types of minerals involving calcite, pyrite and diaspore was investigated, in which the former two minerals are the common gangue existing in oxidized and sulfide minerals while diaspore is to be depressed in inverse-flotation of bauxite.

### 2 EXPERIMENTAL

#### 2.1 Materials

Polyacrylamide (PAM), with relative molecular mass of 2 500 000, analytically pure, was purchased from Beijing Chemical Factory in China. Hydroxamic polyacrylamide (HPAM) with substitution degree of 5.78% was prepared and purified according to Ref.

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[ 13] . Hydroxylamine hydrochloride, KOH, and alcohol are analytical reagents. The other chemicals are all of analytical or chemical grade. The minerals were obtained from different deposits in China as shown in Table 1. Lumps of minerals were crushed, ground in porcelain mill and dry screened. The fractions of the particle size of 37 - 74 μm were used for flotation and adsorption tests.

Table 1 Purity and specific area of mineral samples

Sample	Source	Purity / %	Specific area/ (m <sup>2</sup> ·g <sup>-1</sup> )
Calcite	Fangsan, Beijing	99.1	2.70
Diaspore	Xiaoguang Henan Province	90.0	1.42
Pyrite	Dongpo, Hunan Province	98.3	0.78

2.2 Flotation test

Flotation tests were conducted in a 50 mL laboratory microflotation cell with materials of 2 g at a stirring rate of 1 650 r/min by the following procedure: stirring 2 min for HPAM addition, another 2 min for collectors, adjusting pH value with NaOH and HCl, and collecting the frothing part for 3 min. The collectors for calcite, diaspore and pyrite are sodium oleate of 1.0 × 10<sup>-4</sup> mol/L, lauryl ammonium acetate of 1.0 × 10<sup>-4</sup> mol/L, and butyl xanthate of 1.0 × 10<sup>-4</sup> mol/L, respectively.

2.3 Contact angle measurement

The sessile drop technique was used for contact angle measurements with a goniometer. The polished lump samples treated in collector solution and dried in vacuum were placed in a rectangular glass chamber and a water drop was introduced onto the substrate through a microsyringe. The needle was maintained in contact with the drop. Special care was taken in these measurements to avoid vibrations of the needle and to avoid distortion of drop shape by the needle. The advancing contact angles were measured for different liquid drops with 3 - 4 mm drop base diameter at room temperature.

2.4 Zeta potential measurements

Zeta potential was determined on a Zeta plus analyzer (Brookhaven Corporation, USA). The mineral samples were ground to less than 5 μm in an agate mortar. The suspensions containing 0.05 % (mass fraction) solids were dispersed in a beaker for 15 min and the pH value was measured. 1 mmol/L KNO<sub>3</sub> was used as a supporting electrolyte. The measurement error was found to be within ± 5 mV after at least three measurements in all cases.

2.5 HPAM adsorption measurement

The suspensions containing 1 g minerals of the fraction of with size 38 - 74 μm in 50 mL hydroxamic polyacrylamide(HPAM) solutions at a given pH value were stirred in a 150 mL beaker at room temperature for 30 min. A sample of suspension was taken and centrifuged at 3 000 r/min for 15 min. The residual concentration of HPAM in the separated supernatant was determined using a UV 3000 (Shimadu Corporation). The difference of the initial and equilibrium HPAM concentrations was considered as the amount of the HPAM adsorbed on the mineral sample.

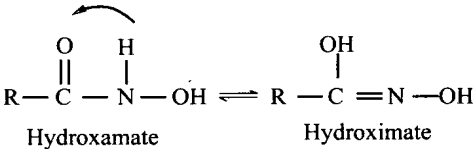
2.6 Fourier-transform-infrared spectra

Fourier-transform-infrared(FT-IR) spectra were obtained with a Perkin Elmer Corporation Instrument System 2000 FT-IR. The diffuse reflectance infrared (DRI) spectra were measured using the DRI accessory on air-dried which is less than 5 μm power after dealing with HPAM solution.

3 RESULTS AND DISCUSSION

3.1 Depression ability of PAM and HPAM

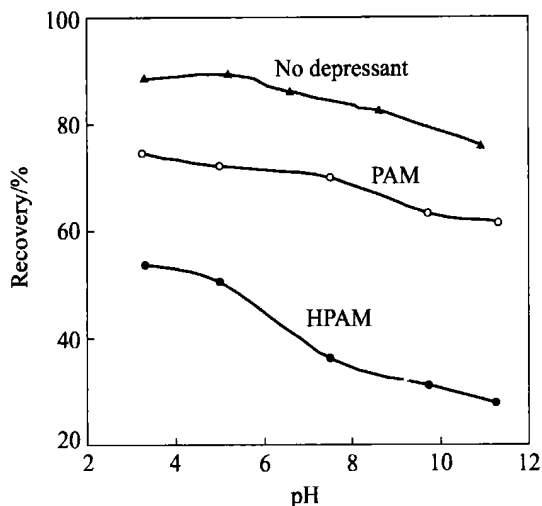
PAM is generally believed to be a soluble polymer with many polar amido groups on its long hydrophilic chains. HPAM is tested to be more soluble and hydrophilic by the formation of hydroxamate group with larger polarity. There are two isomers for HPAM as follows:



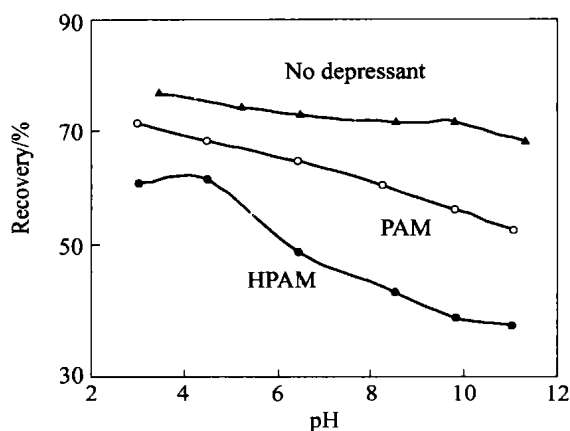
The hydroximate type can be easily formed for electronic conjugation of hydroxyl group to C = N bond, leading to an intramolecular hydrogen bond. It is obvious that hydroximate of HPAM can be easier to dissociate in solutions for a larger acidity.

The flotation recovery as a function of pH value for pyrite, diaspore and calcite in the presence of 40 mg/L PAM and HPAM are shown in Figs. 1 - 3. It can be seen that PAM shows slight depressing effect while HPAM exhibits much stronger depression on the three minerals.

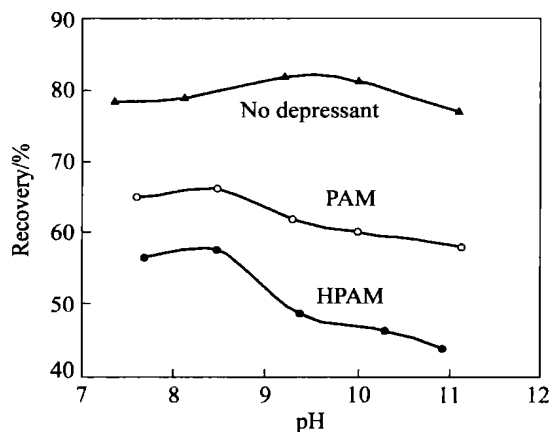
It is notable that the depressing ability of HPAM increases gradually with the rise of flotation pH value, and this may be explained by the great dissociation of HPAM in alkaline solutions leading to intensive interaction between HPAM and the mineral surface. Our previous study revealed that the substitution degree of modified PAM, ie HPAM, was only 5.78%, but the small parts of introduced hydroxamic group may greatly improve its performance. When the content of HPAM increases



**Fig. 1** Flotation recovery of pyrite vs pH value in presence and absence of depressants



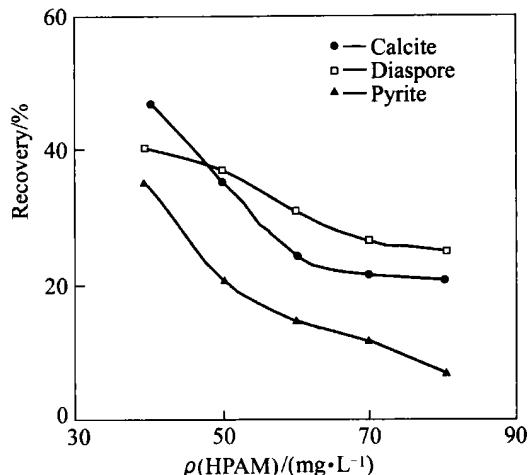
**Fig. 2** Flotation recovery of diaspoire vs pH value in presence and absence of depressants



**Fig. 3** Flotation recovery of calcite vs pH value in presence and absence of depressants

to 80 mg/L at pH 9.7, the recoveries of the three minerals decrease to 20.7%, 25.0% and 6.8%, respectively, as shown in Fig. 4. The results show

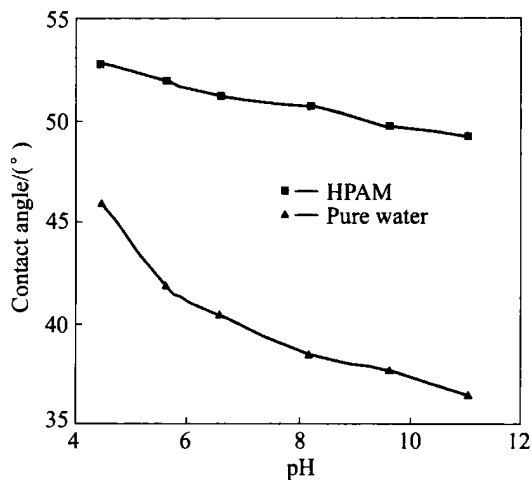
that HPAM performs effective depression on pyrite and certain extent of depression on diaspoire and calcite.



**Fig. 4** Flotation recovery of minerals vs content of HPAM

### 3.2 Wettability of pyrite by HPAM

The contact angles of pyrite in the absence and presence of HPAM as a function of pH value are shown in Fig. 5. It can be seen that the contact angles of pyrite can be obviously changed in the presence of HPAM. The contact angle of pyrite can be up to 45° in pure water, and lower to 35° at pH > 10 in the presence of 40 mg/L HPAM, which indicates that HPAM is adsorbed on the mineral surface and its hydrophilicity is increased.

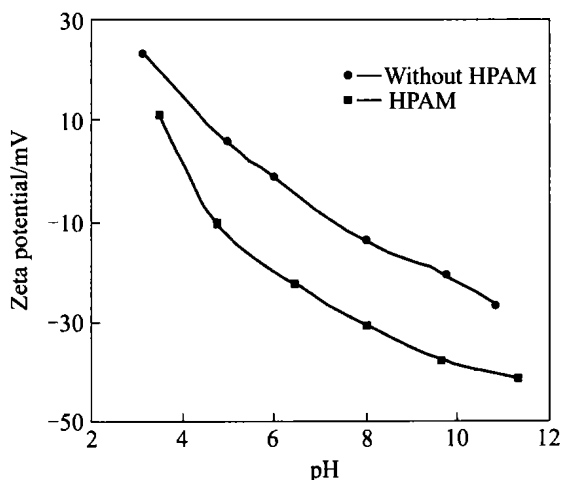


**Fig. 5** Effect of HPAM on contact angle of pyrite

### 3.3 Adsorption of HPAM on pyrite

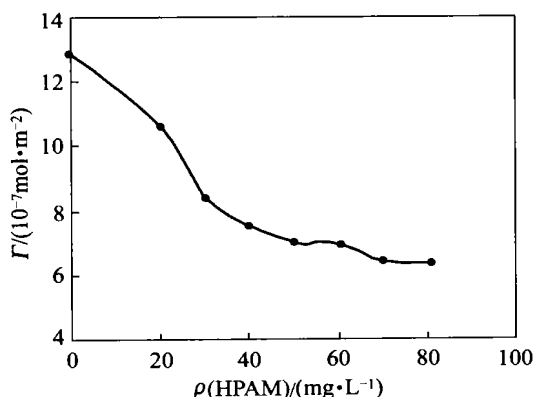
Macromolecular depressant can interact with mineral surface in three bridging ways: electrostatic force, hydrogen-bond force, and chemical adsorption force. HPAM contains two kinds of ionic groups: hydroxamic and hydroximic groups. They can be easily dissociated in alkaline solution, especially the latter, which may lead to chemical interactions with

mineral surface. This is proved by the results of Zeta potential as a function of pH value in the presence of HPAM, as shown in Fig. 6. It can be seen that, even in the alkaline condition, where HPAM is of ionic state, the negative Zeta potential of pyrite still increases with the increase of pH value.



**Fig. 6** Effect of HPAM on Zeta-potential of pyrite surface

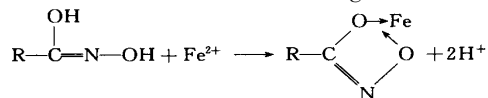
It may be deduced that there exists chemical adsorption force between the reagent and mineral surface. Fig. 7 shows the variation of adsorptive capacity for collectors on mineral surface. It indicates that the xanthate adsorptive capacity on pyrite is decreased with the increase of HPAM dosage due to the depressing effect of HPAM on xanthate flotation to pyrite.



**Fig. 7** Effect of HPAM on adsorptive capacity of xanthate on pyrite

The infrared spectra of pyrite, HPAM and pyrite treated by HPAM are shown in Fig. 8. The specific adsorptive bands of hydroxamic acid at 1 530, 1 640 and 1 116 cm<sup>-1</sup> with a weaker peak compared with the corresponding peak of HPAM can be found. The difference spectrum of pyrite adsorbed by HPAM

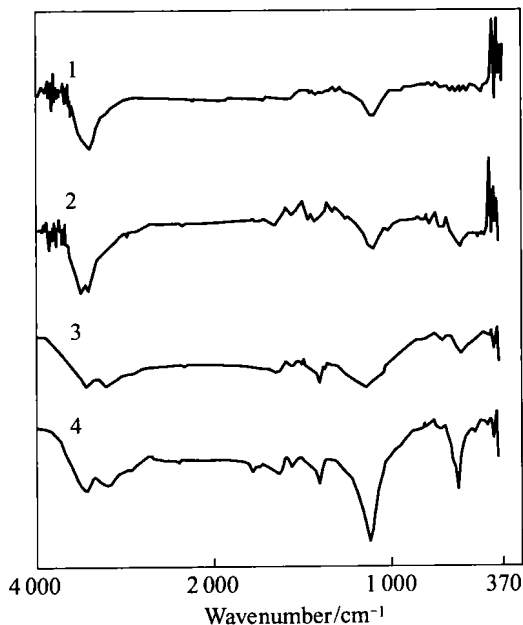
and pyrite is similar to that of HPAM. From the above discussion, it can be deduced that the intensive depression of HPAM on pyrite results from the strong chemical adsorption. It is suggested that a chelation might be generated between the two species as described in the following reaction because of Fe<sup>2+</sup> vacant 3d orbit to accommodate electrons and its large ionic radius to form stable five-ring chelation.



### 3. 4 Structure property of HPAM polar group

Based on the structure theory of flotation reagents, the group electronegativity ( $x_g$ ) of a polar group is a key index to evaluate the performance of flotation reagent. It was ever pointed out that the difference of electronegativity ( $\Delta x$ ) between the reagent polar group and mineral metal atom determined the interaction type and intensity of the bond between them, and the smaller the  $\Delta x$ , the greater the covalent interaction between the polar group and metal ion. The functional group of HPAM is either  $-\text{C}(\text{O})\text{NHOH}$  or  $-\text{C}(\text{OH})=\text{NOH}$ , and the  $x_g$  was determined according to Ref.[ 14 ].

The differences of electronegativity ( $\Delta x$ ) between HPAM and Ca, Al, Fe are listed in Table 2. Compared with group  $-\text{C}(\text{O})\text{NHOH}$ , group  $-\text{C}(\text{OH})=\text{NOH}$  has a smaller  $x_g$ . It has stronger



**Fig. 8** Infrared spectra of pyrite, HPAM and pyrite treated by HPAM  
1—Pyrite; 2—Pyrite treated by HPAM;  
3—Differential infrared spectrum of pyrite treated by HPAM and pyrite;  
4—HPAM

covalent bonding ability than the —C(O)NHOH, which is consonant with the chelating model above. On the other hand, the difference of electronegativity between the polar group and Fe, Al, Ca is in the order of  $\Delta x(\text{Fe}) < \Delta x(\text{Al}) < \Delta x(\text{Ca})$ . The polar group may have stronger covalent bonding ability for Fe element than Al or Ca elements owing to the depressing order on the three mine-rals.

**Table 2** Group electronegativity of HPAM ( $x_g$ ) and its difference ( $\Delta x$ ) with atoms of Ca, Al and Fe

Functional group	$x_g$	$\Delta x$		
		Ca	Al	Fe
—C(O)NHOH	3.85	2.85	2.35	2.05
—C(OH)=NOH	3.79	2.79	2.29	1.99

Note: Electronegativity of Ca, Al and Fe is 1.0, 1.5 and 1.8, respectively.

4 CONCLUSIONS

- 1) HPAM exhibits intensive depression to pyrite but certain extent of depression to diaspor and calcite.
- 2) Determinations of contact angle, Zeta potential, adsorptive capacity for collectors, and IR spectrum demonstrate that there exist strong chemical interactions between HPAM and pyrite surface.

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