

Surface Chemistry and Microflotation of Xenotime and Selected Gangue Minerals Using Octanohydroxamic Acid as the Collector

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Abstract This research study was designed to investigate the principles of surface chemistry and microflotation of xenotime and selected gangue minerals, and to achieve a better understanding of the factors affecting flotation performance and separation of xenotime from associated gangue minerals in an efficient way. A preconcentrated xenotime sample and four selected gangue minerals such as ilmenite, zircon, schorl, and staurolite were used in this study. Using octanohydroxamic acid as a collector, surface chemistry was investigated through surface area measurements, zeta potential tests, and adsorption density determinations. The zeta potential of xenotime was measured as 3.90 in this study. The results of adsorption studies showed a mechanism of chemisorption and correlated well with the results of microflotation tests conducted at room temperature in a Partridge–Smith cell. In this paper, the surface chemistry and microflotation behaviors are discussed based on both the lab observations and literature review, in the hope to shed light on further research and industrial flotation operation.

Keywords Xenotime · Surface chemistry · Microflotation

Introduction

Very few researchers have studied the surface chemistry of xenotime (YOP₄) in detail to date. The research findings have suggested that there are no problems with reagent adsorption and bubble adhesion during froth flotation operation. The feasibility and efficiency of this technique have been proven by industrial and engineering practices.

In 1993, Cheng et al. [1] investigated the surface chemistry and flotation behavior of xenotime using sodium oleate as the collector and a modified Hallimond tube. They found that the PZC of xenotime occurred at pH 3.0, and the maximum TREO recovery was found to be above 90 % at pH 7–8. Then, they concluded that the sodium oleate was chemisorbed on the surface of xenotime because the maximum recoveries were found in the pH range where the zeta potential remained negative. They also tried to explain the correlation between ionic species stability in the solid–liquid system and the flotation recovery of xenotime. They found that the more hydroxyl species present in the solution, the more xenotime was floated. This suggested the positive effect of dissociation of lattice ions on the mineral surface on the flotation behavior.

For the second time, in 1994, Cheng et al. [2] announced the results of their surface chemistry research of xenotime. They defined the effects of pH, flotation time, collector concentration, and temperature on the surface properties and flotation performance of xenotime. The maximum recovery using sodium oleate as the collector was found at a pH of 7–8. In addition, the chemical modeling of the speciation of xenotime showed that the distribution of the first hydroxyl rare-earth species, RE(OH)²⁺, had a good influence on the adsorption, bubble–particle adhesion strength, and flotation results. From a physical–chemical point of view, they concluded two important roles of pH in

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the adsorption and flotation processes: (1) In the acidic region, the pH decreased the solubility of oleic acid, stimulating aqueous or surface precipitation and resulting in poor flotation; (2) in the alkaline region, the precipitation of RE hydroxides became prevalent on the surface. Thus, there were no active spots on the mineral surface for oleate collector to adsorb resulting in poor flotation.

Later, in 1997, another research group, Pereira and Peres [3], announced their results of the microflotation of a xenotime concentrate by taking advantage of a modified Hallimond tube. Unlike Cheng, they used hydroxamate as the collector, and the depressants were lignin sulfonate, quebracho, conventional corn starch (RMB), amylopectin (SIGMA), and sodium metasilicate PA (weight ratio $\text{SiO}_2:\text{Na}_2\text{O} = 1:1$). The initial grade of the xenotime concentrate was relatively low at 9.2 %. The recovery of xenotime in the absence of a depressant was 98 % at a pH 10 ± 0.05 , whereas in the presence of oleic acid at 70 mg/l as a collector and sodium metasilicate at 65 mg/l as the depressant, it was 95.9 % at the pH range of 5 and 6. The PZC of xenotime was determined by microelectrophoresis as 2.3 and by the Mular and Roberts method as 3. In the presence of hydroxamate, the zeta potential was negative near and below the zero charge condition. This set of comparative experiments reflected the effects of hydroxamate and depressants on xenotime flotation.

Three years later, in 2000, Cheng [4] reported his further research on the chemical composition, zeta potential measurement, and IEP of xenotime, taking advantage of high-tech equipments. Results showed that the IEP for yttrium phosphate was around pH 7.0. In Cheng's summary, from 1993 to 2000, the reported PZCs of different xenotime samples varied from 2.3 to 5.0.

Some other summary reports about xenotime beneficiation were published during the 1990s and 2000s. Analyses of surface chemistry using hydroxamic acid as the collector have also been conducted on other rare-earth minerals, since Pradip [5] used hydroxamate in the lab to float bastnaesite gained from Molycorp out of barite and calcite. The results will be discussed later.

Materials and Methods

The preconcentrated xenotime sample used in this study was obtained from a Chinese rutile mining plant in Hainan Province, China. Xenotime as a byproduct of the beach placer deposit was separated and concentrated from rutile ores by physical methods like washing, shaking table processing, electric separation, and magnetic separation. MLA analysis determined that xenotime (YOP_4) was the major phase at 67.7 % wt%. An iron–titanium oxide called pseudo-rutile was present at 12 %, followed in abundance

by silicates-staurolite ($(\text{Fe}^{2+}, \text{Mg})_2\text{Al}_6(\text{Si}, \text{Al})_4\text{O}_{20}(\text{O}, \text{OH})_4$) at 6 %, zircon (ZrSiO_4) at 4 %, and schorl ($\text{NaFe}_3^{2+}\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4$) at 3 %. Since the pseudo-rutile is a weathering product of ilmenite ($\text{Fe}^{2+}\text{TiO}_3$), and a FeTiO-bearing mineral similar to ilmenite, the author finally chose ilmenite as one of the four major gangue minerals. The other three were zircon, schorl, and staurolite.

All the four gangue minerals were obtained as crystals from international dealers online. The XRF data are as follows:

Ilmenite contained 35.8 % Fe and 29.9 % Ti, major impurities include 2.2 % Si, 0.9 % Zn, 1.1 % Mg; staurolite contained 25.9 % Al, 11.5 % Si, 10.2 % Fe, and 1.7 % Mg, impurities include minor Li and Ca; zircon contained 45.2 % Zr and 16.3 % Si, impurities include minor Ca, Mg, and some REEs; and schorl contained 17.7 % Si, 16.2 % Fe, 14.2 % Al, 3.0 % B, and 2.1 % Na, impurities include minor Ca and Mg.

After collection, all the minerals were pulverized in an Angstrom TE250 Ring Pulverizer, respectively, to 200×400 US mesh. Liberation of the sample was excellent at above 95 % in the most prevalent size fraction. The materials were then washed and dried for experimental use.

Ferric perchlorate ($\text{Fe}(\text{ClO}_4)_3$) was used as a concentration indicator for the hydroxamate solution which was analyzed spectrophotometrically by the well-known ferric hydroxamate method [5], the method will be further described later. Hydrochloric acid (HCl) and potassium hydroxide (NaOH) were also used in this study as pH modifiers.

The two collectors used, sodium oleate ($\text{C}_{18}\text{H}_{33}\text{NaO}_2$) and octanohydroxamic acid ($\text{C}_8\text{H}_{17}\text{NO}_2$), were both supplied by Tokyo Chemicals Inc. One depressant, pentahydrate sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 10\text{H}_2\text{O}$) was obtained from an unknown supplier; the other depressant, ammonium lignosulfonate ($\text{C}_{20}\text{H}_{26}\text{O}_{10}\text{S}_2$ for lignin sulfonate), was supplied by HBC Chem Inc.

Octanohydroxamic acid was used in the zeta potential tests, adsorption tests, and microflotation tests; sodium oleate was used as an alternative collector. Sodium silicate and ammonium lignosulfonate were used as the depressants in the microflotation tests for comparison with octanohydroxamic acid. Those four reagents were already available in the lab.

The BELSORP-mini instrument manufactured by Microtrac was used to measure the surface area of the minerals, and the nitrogen gas was used as the absorbent. This equipment can measure the specific surface area/pore size distributions by the volumetric gas adsorption technique. Microtrac's unique dead volume evaluation method (AFSM) makes highly accurate and reproducible measurements free of environmental change. In each test, a 0.5 g sample of 200×400 mesh fraction mineral was prepared.

The Stabino, also manufactured by Microtrac, was used for the zeta potential measurement. Before performing Stabino testing, the equilibrium time of samples in solution was determined first through the adsorption tests. Then, the samples for Stabino tests were prepared as follows: the samples for zeta potential measurements were first ground in a pulverizer to 200×400 mesh and then, 0.02 g of each mineral was added in 40 ml of distilled water or an octanohydroxamic acid solution and then shaken for 24 h. The solution utilized contained 0.0005 M hydroxamic acid to check the effect of this reagent on the zeta potential. The pH was adjusted as required with NaOH and HCl.

Adsorption tests were performed under different reagent concentrations, testing temperatures, and values of pH. These analyses were performed with a UV–Vis spectrometer.

For the adsorption testing, a calibration curve was first created. So, 4 ml of 2.94 g/l ferric perchlorate solution was added to 2 ml of hydroxamic acid solution with known concentrations ranging from 5×10^{-4} to 2.0×10^{-3} M. This was because if the concentration was above 2.0×10^{-3} M, the calibration curve would be no longer linear. The curve is shown in Fig. 1. The sensitivity of this method is 1×10^{-4} M, below which the absorbance at 498 nm cannot be determined.

By using the trendline equation, the absorbance readout was converted to a correlated concentration. For the tests conducted at room temperature, 0.05 g of a mineral was conditioned each time in a 10-ml solution of octanohydroxamic acid, having a concentration of 1.0×10^{-3} M for a certain period of time before the spectrometric measurement, in order to determine the equilibrium time for adsorption. Then, conditioning using different concentrations of the solution ranging from 5×10^{-4} to 2.0×10^{-3} M at different pHs ranging from 3 to 11 was conducted for 20 h. After 20-h conditioning, the sample was centrifuged for 20 min. Then, 2 ml of the supernatant was collected and mixed with 4 ml of 2.94 g/l ferric perchlorate solution. The concentration of hydroxamic acid remained in the supernatant was measured by the method described above.

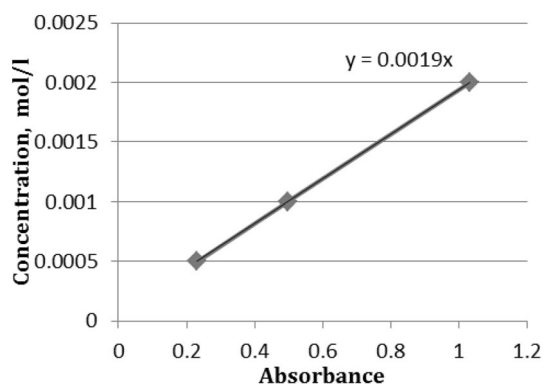


Fig. 1 Calibration curve for adsorption tests

Because the initial concentration was already known, the amount of hydroxamic acid absorbed by the mineral could be figured out by difference. For the tests conducted at 80 °C, the sample was heated during conditioning.

Microflotation tests were conducted using a Partridge–Smith microflotation cell. In practice, 0.5 g of mineral sample (or a mixed sample of xenotime and gangue minerals) was stirred with 40 ml of collector solution with the concentration ranging from 0.0005 to 0.002 M. This was done in a 100-ml beaker for 15 min at specific pH values. Then the sample was transferred to the cell and 10 ml of the collector with the concentration and pH was used to wash down any residual material in the beaker to the cell.

The pH was measured with a pH meter before conditioning and then modified with NaOH and HCl.

Then the pulp was transferred to the cell and stirred with a magnetic bar at 600 rpm. The compressed air flow rate was maintained at 30 cc/min. After 2 min of flotation, the concentrate and tailings were filtered and dried for weighing. Then, the dried concentrate was prepared for XRF analysis.

Zeta Potential

By using the Microtrac’s Stabino instrument, zeta potentials of xenotime and gangue minerals were measured both in distilled water and 0.0005 M octanohydroxamic acid solution. As shown in Fig. 2, in the absence of a collector, the PZC of xenotime was observed to be at pH 3.90. This value was between 2.3 and 5, which is within the range summarized by Cheng in [4] when considering all of the measured PZCs of xenotime. The PZC of ilmenite was 4.20, lower than 5.4 or 5.6 which were the PZC’s of ilmenite published by Song et al. in [7] and Irannajad et al. in [6]. The PZC of zircon was 3.95, slightly lower than the one measured by Pereira in 1997 [3], which was at 4.0. The PZC of schorl was 4.70, larger than the one measured by Lameiras in [8], which was at 4.0. The PZC of staurolite was 4.4, with no comparison available in the literature. The differences between the values of the pH corresponding to PZCs determined in this study and previously are hard to explain. They might arise from several variables such as impurities or the specific experimental method.

For these semi-soluble minerals, the predominant species in the solid–liquid system can be classified into cations and anions. The cations (basically metal ions) and anions (basically PO_4^{3-} , TiO_3^{2-} , or SiO_4^{4-}) are transferred from the mineral surface into water to form hydroxylated ion species. Thus, the remaining ion species on the surface determine the zeta potential.

For xenotime, the PZC was measured as 3.90, which means that at pH 3.90, the electrokinetic charge density at the diffusion layer of xenotime surface was zero. At a pH

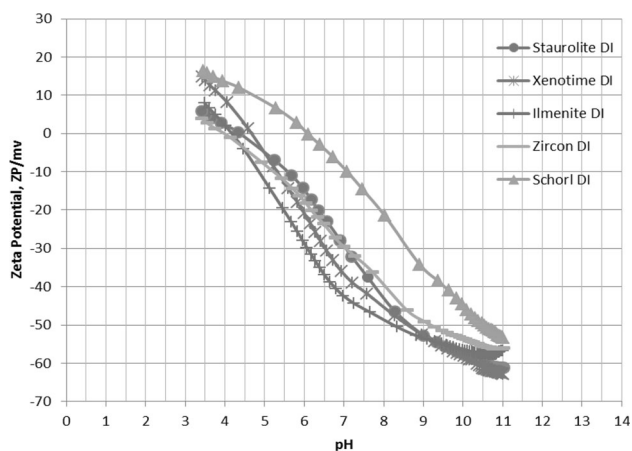


Fig. 2 Zeta potential of xenotime and gangue minerals in distilled water

lower than 3.90, the zeta potential of xenotime was positive. For physical adsorption, an anionic collector will be favored and thus good recovery should be observed. At a pH higher than 3.90, the zeta potential was negative, and a cationic collector will be favored, and thus, a good recovery should also be observed. However, in this study, the maximum adsorption and recovery when using anionic collector were all observed in alkaline conditions, which suggests that chemisorption likely happened on the surface of xenotime.

To understand better the relation between the zeta potential of xenotime and the mechanism of chemisorption of the anionic collector on the surface of xenotime, we need to determine what was happening in the xenotime–water system. As Anderson in [9] modeled, the stability diagrams of the two predominant species are presented in Figs. 3 and 4.

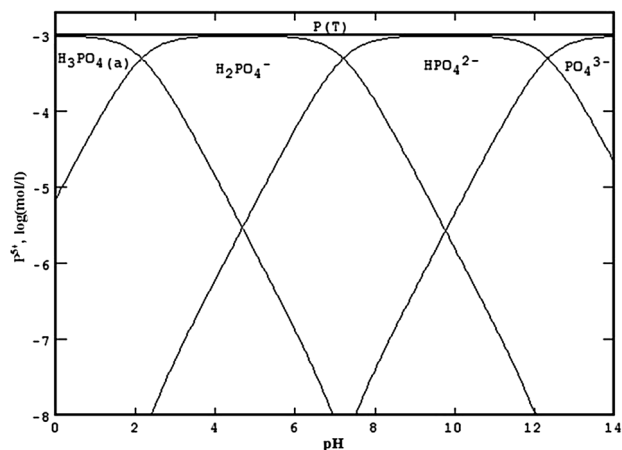


Fig. 3 Solubility diagram of phosphate species (0.001 M total solution concentration) [9]

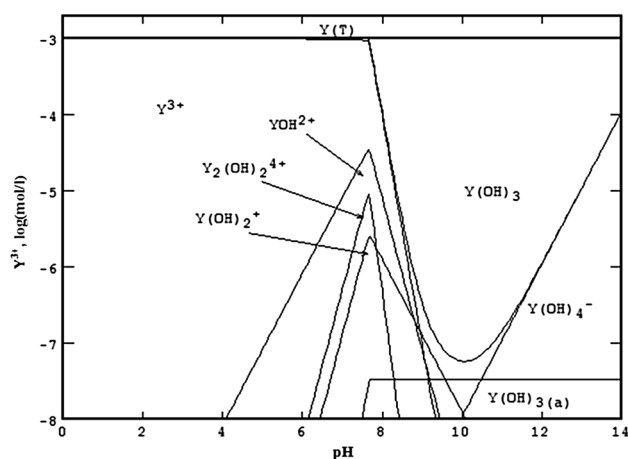


Fig. 4 Solubility diagram of Y^{3+} species (0.001 M total solution concentration) [9]

As shown in Fig. 3, at a pH below 3.90, the predominant species are H_3PO_4 and $H_2PO_4^-$, and at pH above 3.90, HPO_4^{2-} and PO_4^{3-} become dominant. This means as the solution goes from acidic to alkaline, more H_3PO_4 will be hydrolyzed into PO_4^{3-} . According to Fig. 4, at a pH below 3.90, the predominant species is Y^{3+} , and at a pH above 3.90, $Y(OH)^{2+}$, $Y(OH)_2^+$, and $Y(OH)_3$ become prevalent. This means as the solution goes from acidic to alkaline, more Y^{3+} will be hydrolyzed to $Y(OH)_3$. It is reasonable to hypothesize that at a relatively low pH, less active areas on the surface of xenotime would be available as more Y^{3+} is dissolved from the xenotime surface. At a relatively high pH, more hydroxyl ions would be there competing with anionic collector ions for the area on the xenotime surface.

This hypothesis corresponds well with both the adsorption and microflotation results. When the pH went below 5 or above 9, sharp drops were observed both with the adsorption of octanohydroxamic acid on the surface of xenotime and with the recovery of xenotime when using octanohydroxamic acid as the collector. Pradip in [5] also observed similar drops in the adsorption curves of hydroxamate on the surface of bastnaesite.

The theory of a predominant species could also be applied to the selected gangue minerals. For ilmenite, the two predominant species were Fe^{2+} and TiO_3^{2-} , and for zircon, the two predominant species were Zr^{4+} and SiO_4^{4-} . The change of the predominant species as a function of pH could also influence the zeta potential. In addition, an extreme pH could also decrease the chemisorption density of the anionic collector and the recoveries of xenotime when using anionic collectors.

Comparisons were made between the zeta potential curves in the presence and absence of octanohydroxamic acid, as shown in Fig. 5. According to the comparisons, it

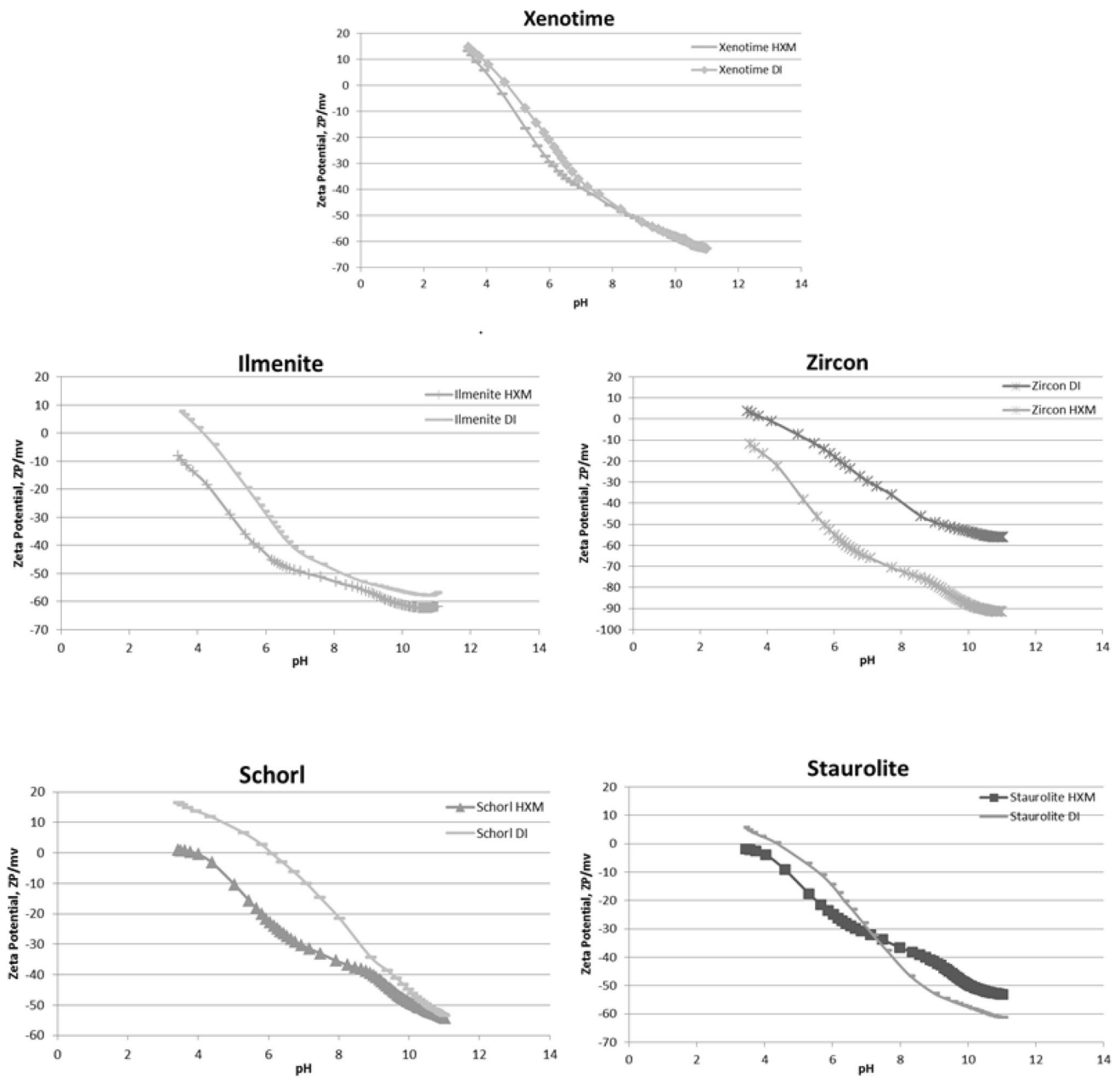


Fig. 5 Zeta potential curves of xenotime and gangue minerals in distilled water and hydroxamate acid

seems that the anionic collector significantly shifted all the curves to the left. The results in this case are most likely caused by the fact that the addition of anionic octanohydroxamic ions increased the availability of the anionic ions that could be adsorbed on the surface of minerals. This resulted in the zeta potentials remaining negative at the original PZCs. To what extent the addition of octanohydroxamic acid could shift the curves to the left could probably be determined by the properties of surfaces (contact angle) and the adsorption kinetics (chemical adsorption).

Adsorption Studies

According to the literature, it is well known that the selectivity of a reagent is achieved through its selective adsorption onto desired minerals. To understand better the underlying mechanism of the octanohydroxamic acid interactions, the effects of temperature and pH, and systematic adsorption tests were conducted on both the xenotime and selected gangue minerals.

The surface area must be evaluated first to calculate the adsorption density. The surface areas of the mineral

samples were measured by the BET method using a Microtrac's BELSORP-Mini BET instrument. The values are shown in Table 1. The relative surface area appears in the order of:

Staurolite > xenotime > schorl > ilmenite > zircon.

In addition, the surface area of hydroxamate reported in the literature [5, 9, 10] is 21 \AA^2 when considering vertically oriented adsorption, and 55 \AA^2 when considering horizontally oriented adsorption.

Adsorption Equilibrium

Hydroxamate adsorption on the mineral surface is chemical in nature, and it is well known that metal ions will chelate complexes with hydroxamate anions [10–14]. Because the surface area of semi-soluble minerals is given, the adsorption of reagent will approach equilibrium after a given time. Figure 6 shows the results of the adsorption of octanohydroxamic acid on xenotime, ilmenite, zircon, schorl, and staurolite as a function of time at room temperature and 80°C . The initial concentration of the octanohydroxamic acid used was 0.001 M in all of these tests.

As the above results show, at room temperature, except for schorl, which did not really approach equilibrium after 20 h, the equilibrium time of xenotime, ilmenite, zircon, and staurolite was 20 h. For future experiments, 20 h was

set to be the conditioning time for valid and repeatable adsorption density evaluations.

At 80°C , however, the equilibrium curves of the five minerals were totally different. First, high temperature enhanced the adsorption of hydroxamic acid on the surfaces of the minerals. Second, 20 h was not enough for equilibrium of ilmenite, the equilibrium of adsorption reached a new and higher level after 50 h. This was likely because of the oxidation of F^{2+} ions and formation of Fe^{3+} ions on ilmenite surfaces in the solution at high temperature, allowing more anionic hydroxamic ions to adsorb on. This result corresponded well with the conclusion carried out by Irannajad et al. [6] that the conversion of F^{2+} to F^{3+} improved floatability of ilmenite in their microflotation tests. The effect of temperature on the adsorption of hydroxamic acid will be discussed later in the manuscript.

Adsorption Isotherm

Adsorption isotherm tests were carried out in a pH range from 3 to 11 and both at room temperature and 80°C . The adsorption isotherms of the xenotime sample and the gangue minerals at different conditions are shown in Fig. 7.

Figure 7 illustrates that at room temperature, xenotime, ilmenite, and zircon reached equilibrium with a concentration of octanohydroxamic acid at around 0.001 M in the pH range from 3 to 11. However, for schorl and staurolite, at room temperature, the adsorption did not reach equilibrium at all, and the adsorption increased with the concentration of hydroxamic acid. At 80°C , the overall adsorption of each mineral was higher than the adsorption at room temperature. All the minerals did not reach equilibrium at 80°C , but they increased with the concentration of hydroxamic acid in the entire pH scale tested.

At room temperature, even though the adsorption densities of hydroxamic acid on the surfaces of ilmenite and

Table 1 Surface areas of xenotime and gangue minerals unit: m^2/g

Minerals	Surface areas
Xenotime	2.9471
Ilmenite	0.8630
Staurolite	4.7698
Schorl	1.7263
Zircon	0.6558

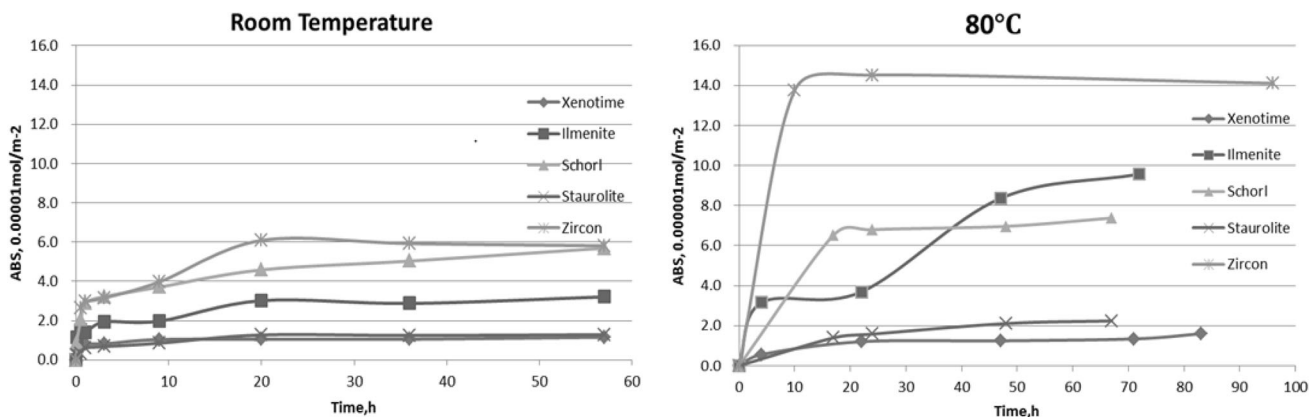


Fig. 6 Adsorption equilibrium at room temperature and at 80°C

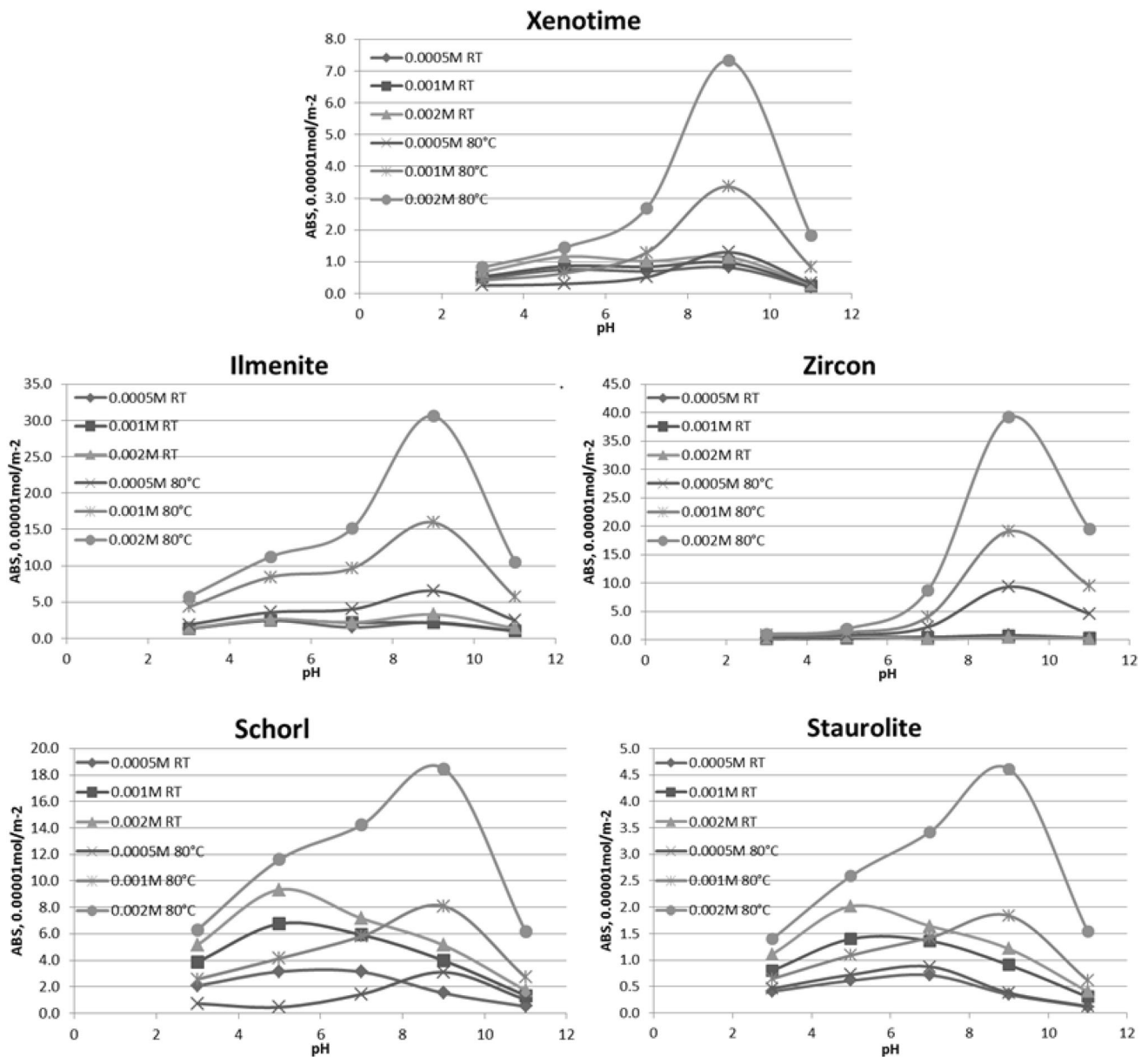


Fig. 7 Adsorption densities of xenotime and gangue minerals as a function of pH with different concentrations of hydroxamate solution at room temperature and 80 °C

schorl were much higher than that of xenotime, the flotation results showed that the recoveries of ilmenite and schorl were lower than that of xenotime at pH 5, 7, and 9. This discrepancy was because xenotime has the biggest surface area than ilmenite and schorl, as shown in Table 1; accordingly, even when using the same concentration of collector, the adsorption density of xenotime was supposed to be lower. Further, in the flotation tests with 0.0005 M octanohydroxamic acid, which is likely, xenotime reached an equilibrium adsorption but ilmenite and schorl did not. Hence, the hydrophilic areas on the surface of ilmenite and schorl resulted in lower recoveries. Also, it expressed the selectivity of the collector against the two gangue minerals.

Effect of Temperature

It is well known that an increase in temperature enhances the adsorption of the collector in chemisorbing types of flotation systems [5]. This is perhaps due to enhanced free energy in the solid–liquid system; therefore, more active areas on the mineral surface would be available for hydroxamate ions to adsorb on. Experiments were conducted at elevated temperatures to investigate the role of temperature in the adsorption of the five minerals. Adsorption studies of hydroxamate at both room temperature and 80 °C were conducted and the results are shown in Fig. 7.

As shown in Fig. 7, the adsorption density for each mineral was much higher at 80 °C than those performed at room temperature. Similar phenomena were also observed by Pradip in [5], Cheng et al. in [2], Zhang in [15], and Caelen in [9]. As calculated in the literature, the monolayer adsorption density of octanohydroxamic acid at room temperature was found to be $8.1 \times 10^{-6} \text{ mol m}^{-2}$. These results indicate that at room temperature, octanohydroxamic acid was monolayer-adsorbed on the surface of xenotime in a wide pH range from 5 to 9 and for others, relatively low adsorption densities were also observed. However, the adsorption density of octanohydroxamic acid for each mineral increased at 80 °C. This suggests that multiple layers of hydroxamic acid were adsorbed on the mineral surface. Cheng in [2] suggested that at elevated temperature, horizontal monolayers could appear. This density was calculated by Anderson in [9] as $3.0 \times 10^{-6} \text{ mol m}^{-2}$. Then, the number of layers of hydroxamic acid adsorbed on the surface was increased.

In addition, after thermodynamic calculation, the comparison of free energies of adsorption of octanohydroxamic acid on the surfaces of the minerals at room temperature and 80 °C also suggested that the mechanism of adsorption using this collector was chemisorption (Fig 8).

However, it is important to note that, for multiple layer adsorption, the van der Waals force is a predominant bonding collector ion onto the previously adsorbed monolayer. This suggests the physical adsorption [16]. Therefore, the adsorption of octanohydroxamic acid at increased concentration or with elevated temperature may be a combination of both chemisorption and physical adsorption. It is also obvious that higher temperature amplified the differences of adsorption density at varying pHs. The effect of pH is discussed in the following subsection.

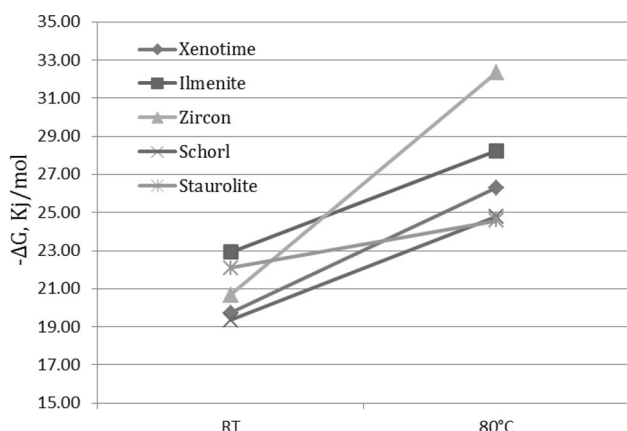


Fig. 8 Comparison of free energies of adsorption of octanohydroxamic acid at room temperature and 80 °C

Effect of pH

Figure 7 also shows the effect of pH on the adsorption density. Except for schorl, there was a distinct peak at pH 9 in the adsorption curve and a change in pH on either side of this peak resulting in a decrease in adsorption. This was very similar to the flotation behavior of the minerals in the presence of hydroxamic acid. The drop in adsorption density (both as % of initial concentration or in terms of adsorbed hydroxamic acid at the surface) was more or less symmetric but less sharp than the results of flotation recovery determined at 2 min. There were sharp drops in the adsorption density seen at pH 3 and pH 11. However, at room temperature, the adsorption densities of schorl at pH 7 were the highest, and they decreased as the pH increased. It is striking to find a pronounced one-to-one correspondence between the adsorption and flotation results here. The results on xenotime, ilmenite, and schorl typically illustrate this correlation. The adsorption curves of these three minerals were consistent with the curves of the weight recoveries determined in the same ranges of pH.

Figure 9 illustrates the observed trends in adsorption corresponding to the flotation recovery trends for xenotime, ilmenite, and schorl. Sharp peaks at pH 9 are directly correlated with the maximum in flotation recoveries for both xenotime and ilmenite. A sharp peak in the range of pH 5–9 is also directly correlated with the maximum in flotation recoveries of schorl.

The effect of pH could also be explained by hydrolysis of the mineral surface, as discussed before (see Figs. 3, 4). Within a pH range of 5–9, more hydrolyzed Y species and phosphate species were available in the solid–liquid system. This means that more active area on the mineral surface was available and more collector ions could be adsorbed.

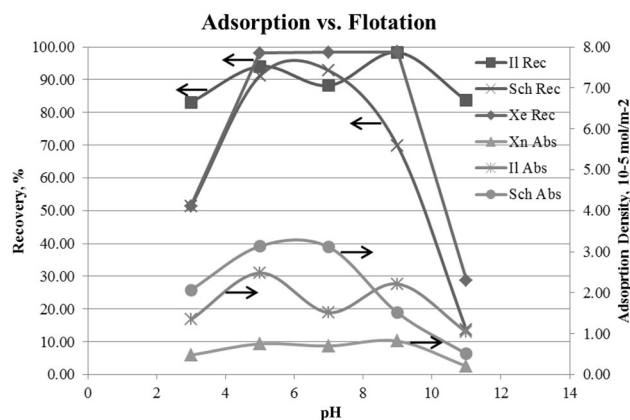


Fig. 9 Comparison of adsorption densities with flotation recoveries for xenotime, ilmenite, and schorl

Moreover, even though the adsorption densities of the two major gangue minerals were twice or more that of xenotime, the flotation recovery of xenotime was slightly higher than that for these minerals. This corresponds with the noted increases in concentration when floating mixed mineral samples with hydroxamate as a collector.

Accordingly, we can predict that effective separation will be achieved around pH 9. However, depressants are needed at elevated temperature to achieve effective separation. This is because the adsorption lines are so close and the collector consumption of some minerals such as schorl was much higher than that of xenotime.

Conclusions

In the surface chemistry and microflotation tests of xenotime and the selected gangue minerals such as ilmenite, zircon, schorl, and staurolite, several conclusions are made based on the results:

- (1) The zeta potential of xenotime was measured at pH 3.90.
- (2) The results of adsorption and microflotation tests when using octanohydroxamic acid as the collector show that the optimal pH is pH 9.
- (3) The maximum adsorption and recoveries using octanohydroxamic acid as the collector were observed in alkaline atmospheres where the zeta potential remains negative. This suggests that chemisorption happened on the surface of xenotime. Further calculation of free energies of adsorption also proved this mechanism.
- (4) At a pH below 3.90, the predominant specie is Y^{3+} , and at a pH above 3.90, $Y(OH)^{2+}$, $Y(OH)_2^+$, and $Y(OH)_3$ become prevalent. This suggests that as the solution goes from acidic to alkaline, more Y^{3+} is going to be hydrolyzed into $Y(OH)_3$. It is reasonable to hypothesis that at a relatively low pH, less active areas on the surface of xenotime would be available because more Y^{3+} ions are dissolved from xenotime surface. At a relatively high pH, more hydroxyl ions are competing with anionic collector ions for the xenotime surface. This hypothesis corresponds well with both the adsorption and microflotation results. Further work will be focused on competitive mechanism of adsorption to achieve better performance.
- (5) At elevated temperatures, xenotime reached equilibrium but ilmenite and schorl did not. This suggests

the mechanism of separation that the hydrophilic parts on the surface of ilmenite and schorl limit the flotation recovery. Temperature amplifies the differences of adsorption of collectors on the five mineral surfaces. Thus, better separation performance can be expected.

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References

1. Cheng TW, Holtham PN, Tran T (1993) Froth flotation of monazite and xenotime. *Miner Eng* 6(4):341–351
2. Cheng TW, Partridge AC, Tran T, Wong PL (1994) The surface properties and flotation behaviour of xenotime. *Miner Eng* 7(9):1085–1098
3. Pereira CA, Peres AEC (1997) Flotation concentration of a xenotime pre-concentrate. *Miner Eng* 10(11):1291–1295
4. Cheng TW (2000) The point of zero charge of monazite and xenotime. *Miner Eng* 13(1):105–109
5. Pradip (1981) The surface properties and flotation of rare-earth minerals. Dissertation, University of California, Berkeley
6. Irannajad M, Mehdilo A, Nuri OS (2014) Influence of microwave irradiation on ilmenite flotation behavior in the presence of different gangue minerals. *Sep Purif Technol* 132:401–412
7. Song Q, Tsai SC (1989) Flotation of ilmenite using benzyl arsonic acid and acidified sodium silicate. *Int J Miner Process* 26(1):111–121
8. Lameiras FS, Nunes EHM, Leal JM (2008) Backgrounds for the industrial use of black tourmaline based on its crystal structure characteristics. *Ferroelectrics* 377(1):107–119
9. Anderson CD (2015) Improved understanding of rare earth surface chemistry and its application to froth flotation. Dissertation, Colorado School of Mines
10. Houot R, Cuif JP, Mottot Y, Samama JC (1991) Recovery of rare earth minerals, with emphasis on flotation process. *Mater Sci Forum* 70
11. Pavez O, Brandao PRG, Peres AEC (1996) Adsorption of oleate and octano-hydroxamate on to rare-earths minerals. *Miner Eng* 9(3):357–366
12. Hu Y, Wang D, Xu Z (1997) A study of interactions and flotation of wolframite with octano hydroxamate. *Miner Eng* 10(6):623–633
13. Fuerstenau MC, Harper RW, Miller JD (1970) Hydroxamate vs fatty-acid flotation of iron oxide. *Trans Soc Min Eng Aime* 247(1):69–73
14. Zhou F, Yan C, Wang H, Sun Q, Wang Q, Alshameri A (2015) Flotation behavior of four C18 hydroxamic acids as collectors of rhodochrosite. *Miner Eng* 78:15–20
15. Zhang X (2014) Surface chemistry aspects of fluorite and bastnaesite flotation systems. Dissertation, The University of Utah
16. Taylor P (2011) Surface chemistry of flotation. CSM class lecture