

Fundamental Studies on the Surface Chemistry of Ancylyte, Calcite, and Strontianite

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Abstract The fundamentals of the surface chemistry of ancylite, strontianite, and calcite in the presence of hydroxamic acid (HXY) were investigated based on their zeta potential, adsorption, infrared measurement, and microflotation. Zeta potential studies indicate that the isoelectric points of ancylite, strontianite, and calcite are around 5.46, 4.50, and 5.50, respectively. HXY is chemically adsorbed onto the surface of ancylite, which was confirmed by both zeta potential and infrared measurements. At room temperature, the monolayer coverage of HXY on ancylite is shown as $20 \mu\text{mol}/\text{m}^2$, which is much higher than the monolayer coverages for strontianite and calcite. In the comparison of adsorption densities of strontianite, calcite, and ancylite at both room temperature and 50°C , the results show that strontianite and calcite appear more sensitive to temperature than ancylite. Microflotation studies of pure minerals show that theoretically, calcite could be separated from strontianite and ancylite at pH 7.5 in the presence of 5×10^{-4} M HXY, and ancylite can be separated from strontianite in the presence of 2×10^{-4} M HXY when pH is around 9. However, as indicated from the zeta potential results, the dissolved species from minerals significantly change the flotation behavior of minerals' mixture. Thus, a successful flotation separation could not be achieved without any modifiers.

Keywords Ancylyte · Strontianite · Calcite · Hydroxamic acid · Zeta potential · Adsorption density · Microflotation · FTIR

Introduction

Bastnaesite, monazite, and xenotime are the major rare earth-bearing minerals, which are typically economically exploited. There have been numerous studies on separation of these three minerals. However, a limited discussion on other numerous minerals that contain rare earth has been published. For instance, ancylite, a group of strontium carbonate minerals enriched by cerium, lanthanum, and minor amounts of other rare earth [1], is rarely studied. It is a carbonate mineral chemical formula for which is $(\text{RE})_x(\text{Sr}, \text{Ca})_{2-x}(\text{CO}_3)_2(\text{OH})_x \cdot (2-x)\text{H}_2\text{O}$ [2]. Ancylyte-(Ce) and ancylite-(La) are common types which occur in some nepheline syenites and carbonates [3]. The composition of ancylite varies from place to place. It is distributed throughout the world including Canada, Russia, USA, Brazil, and Greenland [3]. Under the sunlight, the color of ancylite will possibly be pale yellow-orange, pink, yellowish brown to brown, and gray, and it will be colorless in transmitted light [3]. In the Bear Lodge deposit, ancylite is mainly associated with strontianite and calcite.

As the main gangue mineral that is associated with rare earth minerals, calcite has been extensively studied for several decades, including its PZC (point of zero charge), adsorption in hydroxamic acid (HXY) and fatty acid, performance in the presence of various depressants, and flotation behavior as a function of temperature. Different isoelectric points (IEPs) of calcite were reported in the literature. There is a considerable variance, ranging from 5 to 10.5 [4–7]. Compared with plenty of monographs on

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calcite, there is limited literature on strontianite, probably because strontianite production has limited commercialization. Martínez and Uribe reported that, from the viewpoint of thermodynamics, the isoelectric point (defined as the pH of equilibrium of salt-type mineral slurry) of strontianite aqueous suspension took place at pH 8 and the IEP (defined as the zeta potential at the plane of shear is zero) occurred at pH 7.4 [8].

Hydroxamic acids, the derivatives of both hydroxyl amines and carboxylic acids [9], are extensively used as the chelating collectors for the flotation of sulfide minerals, oxide minerals, and rare earths. They, represented by the general formula R–CO–NHOH, exist in two tautomeric forms shown in Fig. 1 [10]. HXY is widely employed in flotation, because of the formation of a metal complex as shown in Fig. 2. The chelation happens where a metal ion replaces hydrogen, using the carbonyl oxygen atom to create a ring closure [11].

Hydroxamic acid has been extensively used in a wide range of minerals flotation studies, including hematite, rhodonite, chrysocolla, pyrochlore, cassiterite, fluorite, barite, calcite, monazite, and bastnaesite. Lee et al. studied the flotations of mixed copper oxide and sulfide minerals in the presence of xanthate and hydroxamate collectors [12]. The success was obtained in terms of simultaneously recovering copper sulfides and oxides [12]. The hydroxamate is employed in the phosphate industry as well. Miller reported that the phosphate recovery of 95 % in a single-stage flotation was achieved with a concentrate grade of 31 % P₂O₅ in the presence of hydroxamate [13]. A study is made by Pradip and Fuerstenau to investigate the adsorptions of HXY on bastnaesite and semisoluble minerals as functions of concentration and pH, as well as temperature [10, 14]. They identified that HXYs were favorably specific to rare earth elements instead of alkaline earth elements, and the formation of a complex between rare earth and HXY was endothermic by calculating their free energies. Fuerstenau et al. compared flotations of iron oxide in the presence of hydroxamate and fatty acid, and found that the usage of hydroxamate was much lower than that of fatty acids, even though the adsorption mechanisms of fatty acids and hydroxamates were of chemisorption [15]. Guoxing et al. made a comparison of properties of carboxyl and hydroxyl oxime groups based on the effects of chelation and the energy of conjugated Pi bonding for active group of specific collectors [16]. The results showed that the hydroxyl oxime group ranked at the top in the energy of

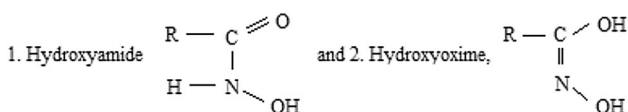


Fig. 1 Two tautomeric forms of HXY [10]

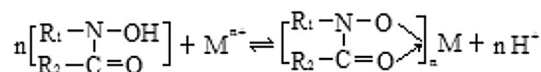


Fig. 2 The formation of a metal complex in addition of HXY [11]

conjugated Pi bonding, followed by carboxyl and carbonyl groups, which meant that the highest stability of the rare earth complex could be achieved by the hydroxyl oxime and carboxyl group that constituted the HXY [16]. Ren et al. showed that MOHA, a modified HXY, was a selective and an efficient collector for bastnaesite flotation with chemisorption accompanied by the nonhomogeneous and physical adsorption [17]. Jinqui et al. found 2-hydroxyl-1-naphthaldoxime as a new collector to efficiently float bastnaesite and monazite from silicate minerals in the presence of water glass as the depressant [18]. Pavez et al. suggested that the adsorption mechanism of HXY on monazite and bastnaesite was of chemisorption at pH 9 and 9.3, respectively, while physical adsorption of sodium oleate on monazite and bastnaesite occurred throughout the pH and chemisorption of sodium oleate on bastnaesite occurred at pH 3 [19]. Moreover, Pereira et al. reported that the recovery rates of xenotime in microflotation tests could reach 93.9 and 96.5 %, respectively, in the presence of HXY as the collector, and sodium silicate and starch as the depressants [20].

The purpose of this study was to investigate the fundamentals of surface chemistry for ancylite, strontianite, and calcite in order to delineate the flotation performance in the presence of HXY.

Materials and Methods

Minerals and Chemicals

Calcite was obtained through Ward’s Natural Science Establishment, New York, and ancylite and strontianite were obtained from Ebay. Strontianite and ancylite were hand-picked based on their physical characteristics. Semi-quantitative X-ray fluorescence spectroscopic analysis along with X-ray diffraction confirmed that the purities of calcite, strontianite, and ancylite are around 97, 95, and 84 %, respectively. The major impurity ions for ancylite are the calcium and silicon ions. Calcium and fluorine ions are the major impurity ions in strontianite and calcite, respectively. The minerals were ground to minus 325 mesh for zeta potential, adsorption, microflotation, and Fourier Transform Infrared Spectroscopy (FTIR) measurements. The BET nitrogen-specific surface areas of the minus 325 mesh fractions for ancylite, strontianite, and calcite were found to be 3.8025, 3.3602, and 5.0928 m²/g, respectively.

All the reagents used in the study are chemical reagents of analytic grade. OctanoHXY was purchased from Tokyo Chemical Industry Co., Ltd.

Experimental Procedures

Zeta Potential Measurements

Zeta potential measurements were conducted on a Microtrac Stabino[®] instrument distributed by Microreac Europe GmbH. The suspension was made at 0.5 g/l solid: liquid ratio in 50-ml polyethylene bottles with predetermined conditioning times. Various reagents with different concentrations were employed to identify the determining ion depending on a certain mineral composition. The pH adjustment was achieved using 0.1 N HCl and KOH solution. A series of investigations were conducted in mineral supernatants as well as in water to confirm the effect of dissolved species in ancylite–strontianite and ancylite–calcite systems. The supernatant was prepared by shaking the minerals with distilled water for 24 h followed by centrifugation. The supernatant obtained was used for predetermined time conditioning of the desired mineral prior to zeta potential measurements.

Adsorption Measurements

The adsorption of octanoHXY as functions of concentration, time, and pH was performed by determining difference in the concentrations of the collectors in solution before and after the addition of mineral powders. The experiments at room temperature (21 °C) were carried out in 15-ml polyethylene bottles at a solid:liquid ratio of 8 g/l for pure calcite, strontianite, and ancylite. Conditioning time was determined from adsorption kinetics experiments. The suspension was agitated using a shaker at 650 rpm. After equilibration, the slurry was centrifuged in a VWR clinical 100 centrifuge for 20 min at 6500 rpm in order to separate solid from liquid. The concentration of HXY was measured using a Shimadzu UV160U spectrometer with the well-known ferric hydroxamate method, mentioned in Pradip's thesis [21]. The theory is that the purple-colored ferric hydroxamate complex has the unique peak at 510 nm measured by UV–Visible spectrometer [21]. The ferric hydroxamate was made by mixing HXY with ferric perchlorate at a volume ratio of 1:2. At 50 °C, adsorption experiments were performed in 7-ml tubes that are made by special materials, and conditioning was carried out in a Benchmark multitherm shaker at 900 rpm. The separation of solid from liquid and the measurement of the concentration of HXY were performed in the same ways as those at room temperature. The slurry pH values were recorded before and after adsorption. KOH and HCl solutions were

used as the pH adjustment reagents. The adsorption density of minerals is expressed by Eq. 1.

$$\delta = \Delta C \cdot V / (A \cdot S) \quad (1)$$

where ΔC is the change of concentration of surfactant, V is the original volume of solution, A is the specific area of the mineral measured by BET, and S is the mass of solids.

Microflotation

Floatability studies were performed using a Partridge-Smith cell, shown in Fig. 3. Octanohydroxamic acid was used as a collector. For the pure mineral flotation tests, 0.4 g of minus 325 mesh pure mineral samples were pulped to 52 ml with the collector and conditioned with the chosen reagents at a desired pH for 15 min using a magnetic stirrer at 600 rpm. Then the sample was transferred to the Partridge-Smith cell and agitated by another magnetic stirrer at 800 rpm. A two-minute flotation was performed by passing air gas at the rate of 39.7 cm³/min. The concentration range of octanohydroxamic acid was from 5×10^{-4} to 2×10^{-3} M, and the pH range was from 5.5 to 11.5. After flotation, the concentrate and the tailing fractions were separately filtered, dried, and weighed. The recoveries for pure minerals were expressed on a weight basis.

FTIR Measurement

Spectra were recorded using Nicolet iSTM50 FT-IR spectrometer procured from Thermo Fisher Scientific Inc. Typical measurements were carried out at a resolution of 4 cm⁻¹. After 15-min adsorption in the presence of 1×10^{-3} M HXY, solids were washed three times with



Fig. 3 The Partridge-Smith cell set-up

deionized water (18 MΩ cm) and allowed to be air-dried at room temperature overnight. The pure minerals both before and after adsorption were measured by FTIR-ATR. Atmospheric water was considered in the determination.

Results and Discussion

Zeta Potential Measurements

The experimental results shown in Fig. 4 were obtained by initially equilibrating ancylite, strontianite, and calcite in distilled water. IEPs of ancylite, strontianite, and calcite are around 5.46, 4.50 and 5.50, respectively. As expected, the electrokinetic behavior of ancylite in an aqueous solution reveals that pH plays a significant role. At pH below 5.46, the zeta potential of ancylite becomes positive, while zeta potential is more negative as pH increases.

The effects of CO_3^{2-} , HCO_3^- , and Sr^{2+} on the electrokinetic behavior of ancylite were also investigated, and it was found that Sr^{2+} , CO_3^{2-} , and HCO_3^- are the potential-determining ions. To be specific, Fig. 5 indicates that the additions of CO_3^{2-} and HCO_3^- considerably shift the IEP of ancylite in the acidic direction, whereas the addition of Sr^{2+} contributes to an increase of zeta potential compared with ancylite in water. This could be explained by a fact that the strontium ion, one of the lattice ions in the ancylite crystal, could undergo hydrolysis to form a strontium hydroxyl complex. Due to limited knowledge of the solubility product of ancylite, it is difficult to thermodynamically calculate the solid-aqueous solution equilibria for the ancylite- H_2O system. However, investigations on calcite- H_2O and strontianite- H_2O solution equilibria were conducted in several studies of the literature. In an aqueous suspension of strontianite and calcite particles, both cations

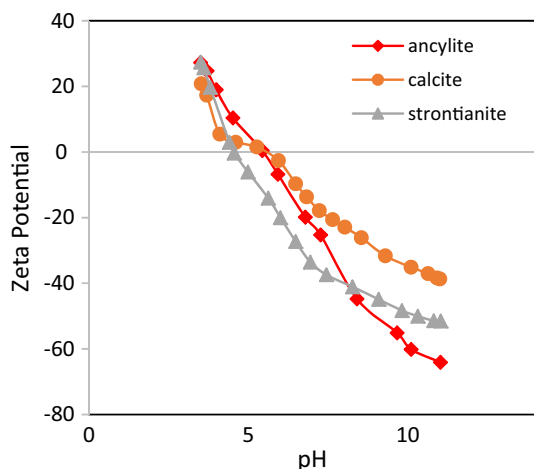


Fig. 4 Zeta potentials of calcite, ancylite, and strontianite in distilled water

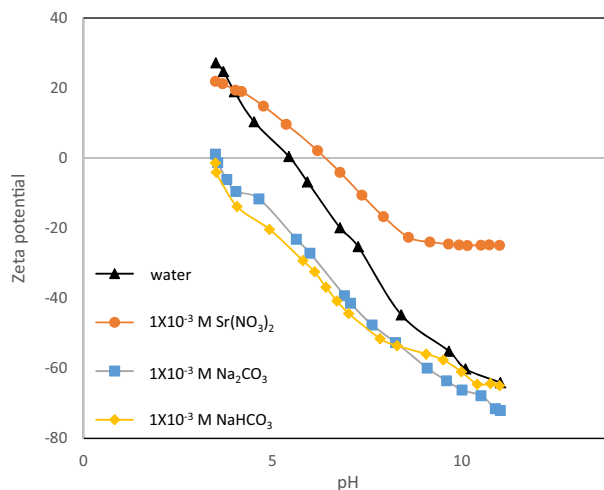


Fig. 5 Zeta potentials of ancylite in different electrolytes

and anions from the mineral lattice will dissolve and interact with the ions of the water based on the following reactions at room temperature [8].

Reactions	pK	Equations
$\text{SrCO}_3(\text{s}) = \text{Sr}^{2+} + \text{CO}_3^{2-}$	9.15	2
$\text{CO}_2(\text{g}) + 2\text{OH}^- = \text{CO}_3^{2-} + \text{H}_2\text{O}$	-9.87	3
$\text{CO}_3^{2-} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{OH}^-$	3.67	4
$\text{CO}_3^{2-} + 2\text{H}_2\text{O} = \text{H}_2\text{CO}_3(\text{aq}) + 2\text{OH}^-$	11.30	5
$\text{Sr}^{2+} + \text{OH}^- = \text{Sr}(\text{OH})^+$	-0.82	6
$\text{Sr}^{2+} + 2\text{OH}^- = \text{Sr}(\text{OH})_2(\text{s})$	0.43	7
$\text{CaCO}_3(\text{s}) = \text{CaCO}_3(\text{aq})$	5.15	8
$\text{CaCO}_3(\text{aq}) = \text{Ca}^{2+} + \text{COCO}_3^{2-}$	3.20	9
$\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaHCO}_3^+$	-0.87	10
$\text{Ca}^{2+} + \text{OH}^- = \text{Ca}(\text{OH})^+$	-1.30	11

The inconsistencies in the IEPs for calcite and strontianite could be attributed to several factors, such as different sources, incorporation of different cations into the mineral crystal, and various methodologies of electrokinetic measurements. The varied IEPs or the points of zero charge (PZC) in the previous studies are shown in Table 1.

The determining ions for calcite and strontianite are also shown in Figs. 6 and 7, and it is found that CO_3^{2-} and HCO_3^- are the determining ions for both calcite and strontianite, while Sr^{2+} plays more important role for strontianite compared with the effect of Ca^{2+} for calcite.

A series of investigations were conducted in mineral supernatants as well as in water in order to confirm the effects of dissolved species in the ancylite-strontianite and ancylite-calcite systems. The supernatant was prepared by

shaking the mineral with distilled water for 24 h followed by centrifugation. The supernatant obtained was used for the predetermined time conditioning of the desired mineral prior to zeta potential measurements. It is observed from Fig. 8 that the ancylite surface is more negatively charged in both strontianite and calcite supernatants than in water. It is also observed that the isoelectric point of ancylite in strontianite supernatant has shifted from around 5.46 in water to 4.26.

Similarly, the zeta potentials of calcite and strontianite in ancylite supernatant were measured as well. Figure 9 shows that the zeta potential of strontianite in the ancylite supernatant behaves in the same way as that in water, except that the IEP of strontianite in ancylite supernatant is slightly lower than that in water. However, Fig. 10 indicates that the IEP of calcite is only slightly affected by the ancylite supernatant. This scenario is in agreement with previous studies by Amankonah et al. [25] and Somasundaran et al. [26]. In mixed mineral systems, the interfacial behavior of minerals is quite different from that of individual minerals due to the dissolved species present in the supernatants. The following microflotation of the mixed minerals also shows different results using the same condition as that for individual minerals.

The electrokinetic behaviors of ancylite, strontianite, and calcite in the presence of HXY were investigated to delineate the adsorption mechanism of HXY on the surface of minerals. Figure 11 shows that as the concentration of HXY increases, the IEP of ancylite decreases, and the zeta potential in the entire pH range becomes narrow compared to that in distilled water. The effect of HXY addition on strontianite, shown in Fig. 12, is the same as that of ancylite. However, Fig. 13 illustrates that the addition of HXY has a slight effect on calcite, compared with strontianite and ancylite, which could be explained by the fact that HXY is more preferably adsorbed onto the surfaces of strontianite and ancylite. The change of zeta potential in the entire pH range, especially above the IEP, can be attributed to a conclusion that the adsorption mechanism of HXY on these three minerals is chemisorption, which is

Table 1 Summary of PZC for calcite and strontianite

Mineral	PZC	Measurement	Reference
Calcite	9.5	Streaming potential	[22]
	8.2	Streaming potential	[7]
	11	Electrophoretic mobility	[23]
	10.5 (IEP)	Streaming potential	[6]
	10	Electrophoretic mobility	[21]
	5.5	Streaming potential	[24]
	8.2	Electrophoretic mobility	[8]
Strontianite	8.0	Electrophoretic mobility	[8]

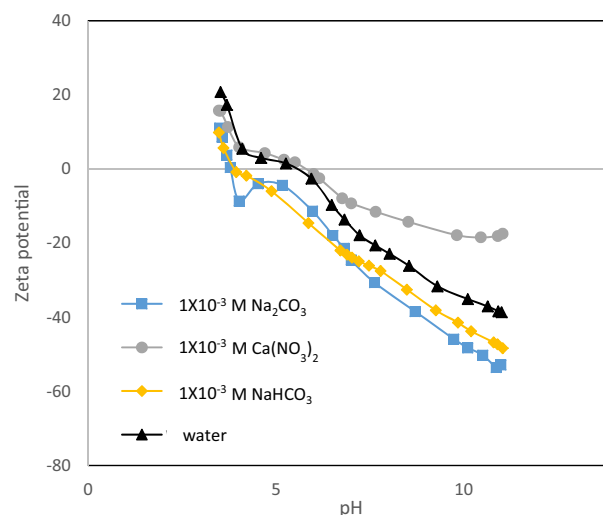


Fig. 6 Zeta potentials of calcite in different electrolytes

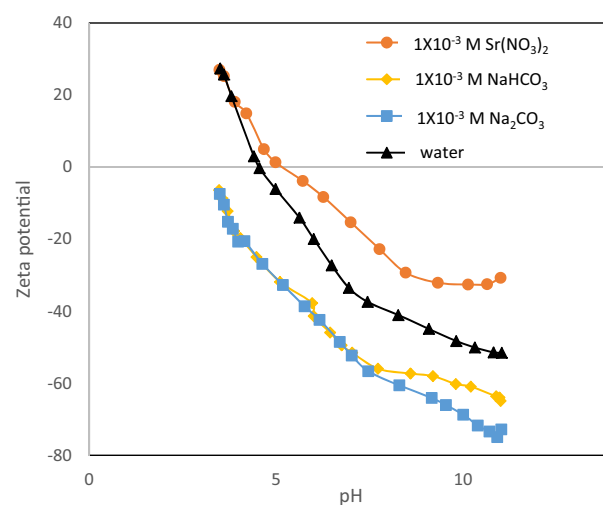


Fig. 7 Zeta potentials of strontianite in different electrolytes

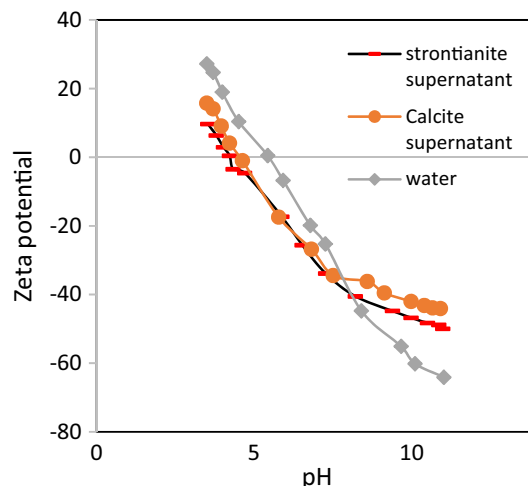


Fig. 8 Effects of calcite and strontianite supernatants on the zeta potential of ancylite

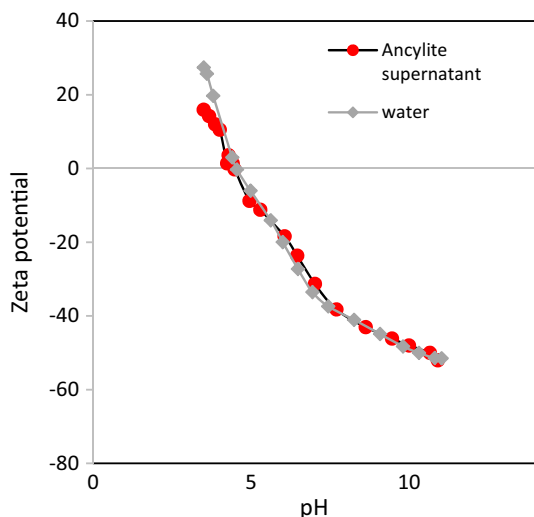


Fig. 9 Effect of ancylite supernatant on the zeta potential of strontianite

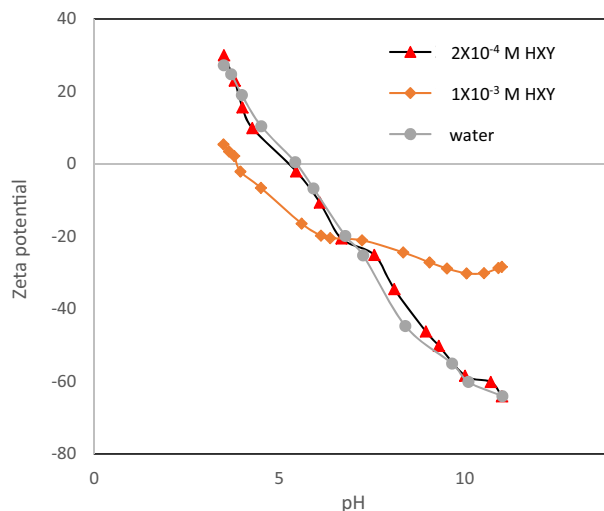


Fig. 11 Zeta potentials of ancylite in the presence of 1×10^{-3} and 2×10^{-4} M HXY

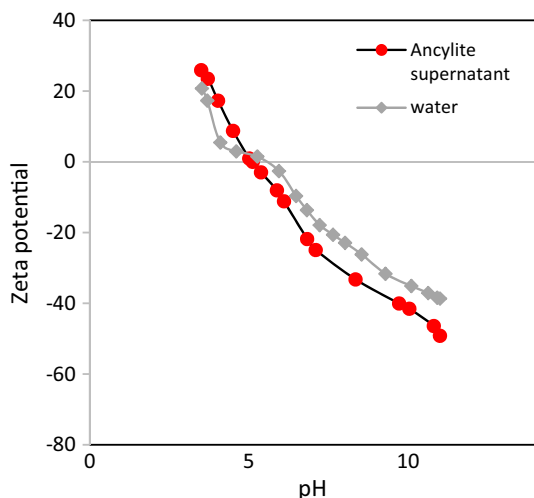


Fig. 10 Effect of ancylite supernatant on the zeta potential of calcite

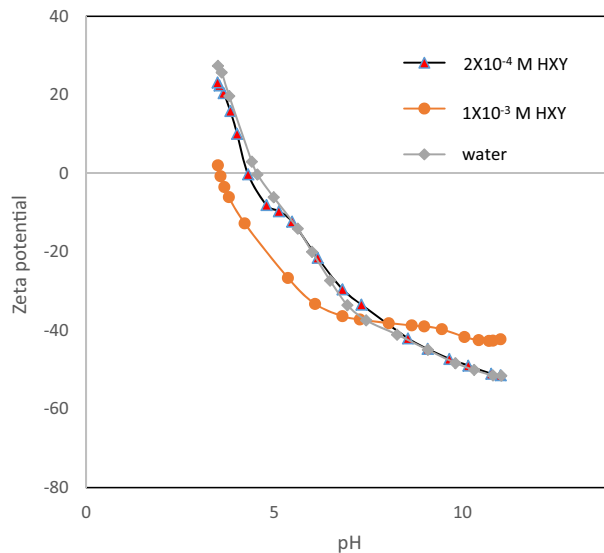


Fig. 12 Zeta potentials of strontianite in the presence of 1×10^{-3} and 2×10^{-4} M HXY

also confirmed by the following adsorption studies and FTIR results.

Adsorption Measurements

Figure 14 shows the results of uptake of octanohydroxamic acid on ancylite, calcite, and strontianite as a function of time with the initial concentration of 1×10^{-3} M at room temperature. Clearly, calcite reaches the equilibrium in about 2 h with the lowest adsorption. Strontianite takes as long as 48 h to reach equilibrium, while ancylite takes 29 h to reach equilibrium to get the highest adsorption among the three minerals. The reason that calcite can reach equilibrium quickly with low adsorption is probably that

calcite is more soluble in comparison with strontianite and ancylite.

The uptake of octanohydroxamic acid by ancylite at $\text{pH } 9 \pm 0.3$ is presented in Fig. 15. The adsorption isotherm curve is characterized by three well-defined regions: (a) at low collector concentrations, the adsorption displays a marked dependence on the HXY concentration; (b) the adsorption remains relatively constant; and (c) the adsorption increases with the increasing concentration of HXY. The adsorption density of HXY on ancylite is $20 \mu\text{mol}/\text{m}^2$, assuming that a surface area of the HXY head group is 20.5 \AA [10]. According to calculation, it is found that the ratio of the rare earth cation to hydroxamate ion is

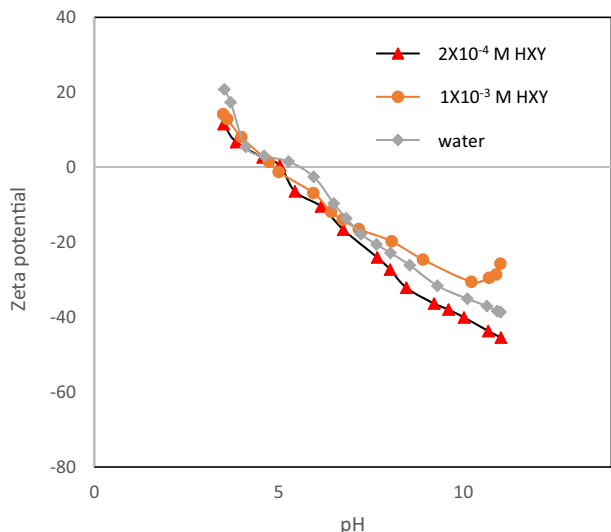


Fig. 13 Zeta potentials of calcite in the presence of 1×10^{-3} and 2×10^{-4} M HXY

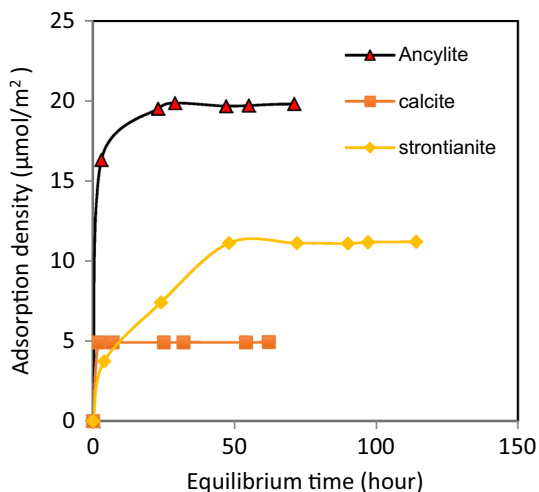


Fig. 14 Adsorption density of calcite, strontianite, and ancylite as a function of time at concentration HXY of 1×10^{-3} M

approximately 1:2.5, which could be in concordance with theoretical expectation in terms of the composition of ancylite. Because the lattice of ancylite contains both rare earth ions and strontium ions, which contributes to a fact that the ratio of the cationic ion to hydroxamate should be theoretically in the range of 1:3–1:2. At higher concentrations, however, there seems to be another plateau where the amount of HXY absorbed is far more than that required for the formation of a close-packed vertically oriented monolayer. It could be due to a scenario that a multilayer adsorption occurs, which is probably due to the physical adsorption by hydrogen bonding after the surface chelation (Eqs. 12, 13), as mentioned by Raghavan and Fuerstenau [9]. The adsorption of HXY on rare earth minerals, such as bastnaesite, has been ascribed to the formation of a rare

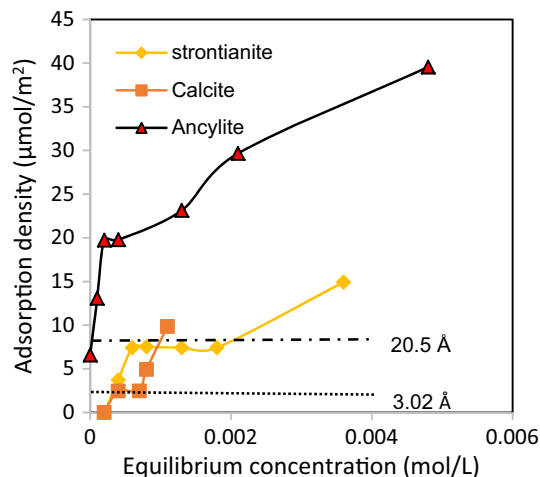
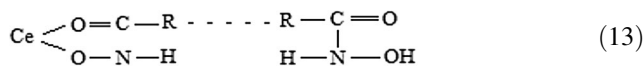
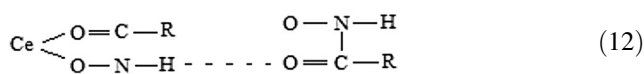


Fig. 15 Adsorption densities of calcite, strontianite, and ancylite as a function of concentration HXY

earth–hydroxamate complex on the mineral surface, and a similar mechanism might be applicable in the present system [10, 17, 19].



The adsorption isotherms of calcite and strontianite at $\text{pH } 9 \pm 0.3$ (Fig. 15) display a typical S-type shape as well; however, the adsorption densities are significantly lower than that of ancylite. The adsorption density plateau of calcite obtained is far less than that needed for the formation of a close-packed monolayer where all the molecules are horizontally oriented, attaining an adsorption density of $3.02 \mu\text{mol}/\text{m}^2$.

The adsorption density of strontianite increases sharply at lower HXY concentration, but it is constant at around $7 \mu\text{mol}/\text{m}^2$ in the concentration range from 6×10^{-4} to 1.8×10^{-3} M. Then a linear increase in the uptake of HXY on the strontianite is obtained at higher concentration. The reason that the plateaus for uptake of HXY on calcite and strontianite are much lower than that of ancylite is that Sr^{2+} and Ca^{2+} are divalent ions; in comparison, the rare earth ions are trivalent ions, which suggests that the formation of the metal–hydroxamate complex for rare earth ions consumes more hydroxamate than that for divalent ions.

The adsorptions of HXY on three minerals at various pH values are presented in Figs. 16, 17, and 18. The experiments were conducted at the collector concentrations of both 1×10^{-3} and 5×10^{-4} M. Among these three figures, there is a common characterization that at pH below 7, the adsorption density in the presence of 1×10^{-3} M

HXY increases abruptly as pH decreases. It might be attributed to the presence of CO₂. Several literature studies reported that the presence of such species as CaHCO₃⁺ and CaOH⁺ could increase the flotation recovery of calcite, which is attributed to an increase of electrostatic attraction by carbonation inducing a positive charge on the calcite interface through the adsorptions of CaHCO₃⁺ and CaOH⁺ [21, 27].

Figure 16 indicates that adsorption of strontianite has a slight decrease in the range of pH 6.5–9 at 10⁻³ M HXY, followed by a sharp increase above pH 9. A minimum adsorption density is obtained where the pH is around 7.4 at the collector concentration of 5 × 10⁻⁴ M. There is a drop happening above pH 11, which is probably due to the formation of strontium carbonate precipitated on the surface of strontianite to prevent the adsorption of HXY.

Calcite (Fig. 17) behaves similarly to strontianite, except that there is a relatively constant adsorption density ranging from pH 7 to 9 in the presence of 1 × 10⁻³ M HXY. However, the drop in adsorption density at around pH 7.5 in the presence of 5 × 10⁻⁴ M HXY could not be easily explained. Perhaps some other strontium and calcium species are formed and are responsible for HXY uptake.

The adsorption of HXY on ancyllite as a function of pH is presented in Fig. 18. It is apparent that the adsorption density of the collector on ancyllite is relatively independent of pH variation in the range of 7–10 compared to those for calcite and strontianite. At 10⁻³ M concentration, the predominant ion species that might be responsible for the plateau are MOH²⁺, M³⁺, M(OH)₂⁺, and M(OH)₃(aq) (Fig. 19), in which M represents rare earth metal. Pradip et al. also observed this plateau in their bastnaesite flotation study [10]. In an alkaline environment, especially above

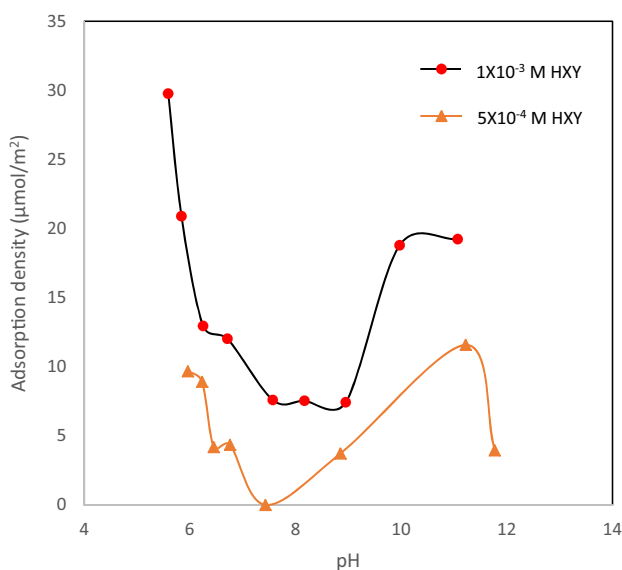


Fig. 16 Adsorption density of strontianite as a function of pH values

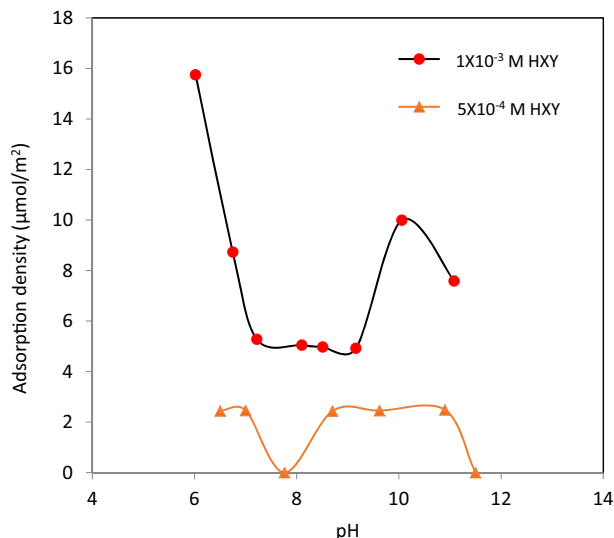


Fig. 17 Adsorption density of calcite as a function of pH values

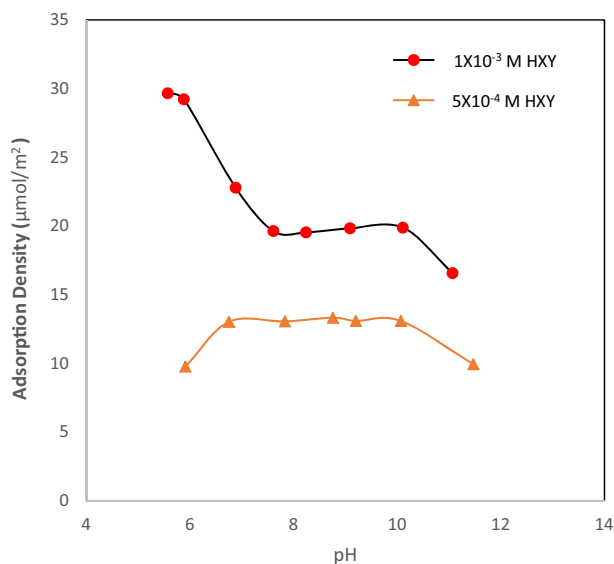


Fig. 18 Adsorption density of ancyllite as a function of pH values

pH 10, there is a drop of adsorption density, which could be attributed to formation of M(OH)₃ and M(OH)₄⁻ that precipitate on the surface of mineral particles.

Since the uptake of HXY on minerals indicates the interaction between HXY and minerals, some adsorption experiments on 50 °C were also carried out to investigate the effect of temperature, and a series of thermodynamic calculations were also made to theoretically illustrate the mechanism of adsorption of HXY on minerals. From the results given in Fig. 20, it can be seen that the time required to attain equilibrium at high temperature is much longer than that at room temperature, and the amount of HXY adsorbed increases with the increasing temperature. It might be attributed to the higher solubility of three minerals at elevated temperature and the endothermic

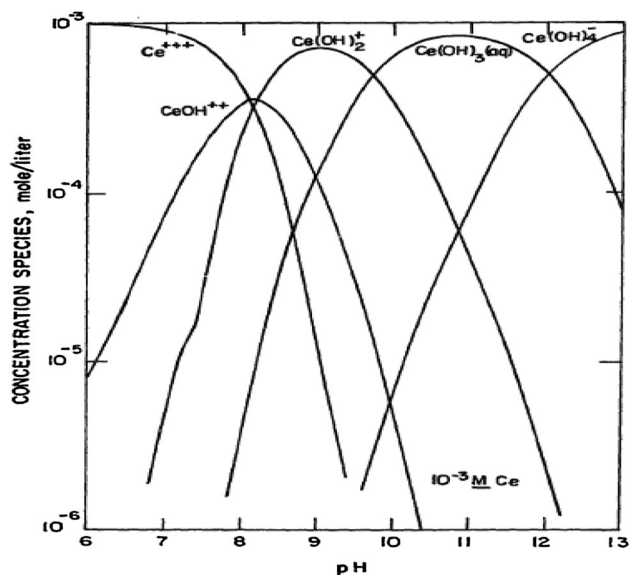


Fig. 19 Aqueous solution equilibria for cerium at 1×10^{-3} M total concentration [21]

reactions for the adsorption of hydroxamate on these minerals. Figure 21 seems to indicate that the high temperature plays a more important role in adsorption for strontianite than that for ancyllite. Interestingly, there are two plateaus to be observed in the adsorption isotherm plots for calcite, ancyllite, and strontianite. Adsorption isotherm of calcite has the two plateaus which take place at 7.31 and 14.76 $\mu\text{mol}/\text{m}^2$, respectively. Ancyllite has the same trend as calcite does, and the two plateaus happen at 22.5 and 39.05 $\mu\text{mol}/\text{m}^2$, respectively, which could be attributed to the fact that a lower plateau corresponds to the horizontal monolayer of hydroxamic ion. The second plateau occurs when hydroxamic ion vertically adsorbs onto the mineral surface area.

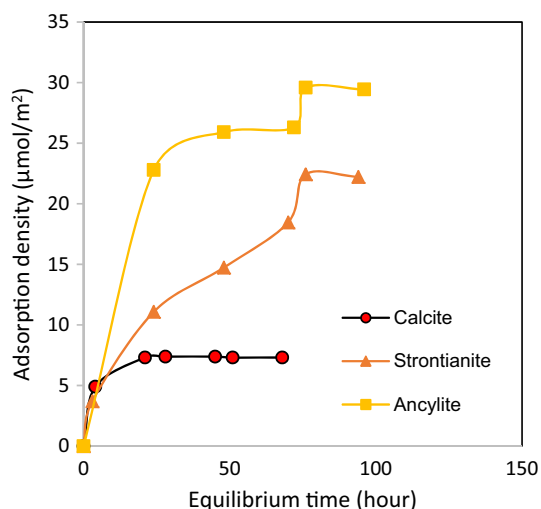


Fig. 20 Adsorption densities of calcite, strontianite, and ancyllite as a function of time at 50 °C

The free energies of adsorption for HXY on ancyllite, calcite, and strontianite were calculated using the Stern–Grahame equation shown in Eq. 14.

$$T_{\delta} = 2 \cdot r \cdot C \cdot \exp(-\Delta G_{\text{ads}}^{\circ}/R \cdot T) \quad (14)$$

where T_{δ} is the adsorption density in the stern plane, and r is the effective radius of the adsorbed ion, C is the equilibrium concentration, and $\Delta G_{\text{ads}}^{\circ}$ is the standard adsorption free energy.

The free energies of adsorption for HXY were found to be -6.15 , -4.93 , and -5.58 kcal/mol for ancyllite, calcite, and strontianite, respectively. The values of free energies are in agreement with the experimental results that HXY has the strongest affinity with ancyllite, followed by strontianite, whereas calcite hydroxamate complex has the weakest affinity.

Based on the adsorption density results at two different temperatures, the enthalpies ($\Delta H_{\text{ads}}^{\circ}$) and entropies ($\Delta S_{\text{ads}}^{\circ}$) for the adsorption of three minerals were estimated by Eqs. 16 and 17.

For any adsorption process, the standard free energy change is given by

$$\Delta G_{\text{ads}}^{\circ} = \Delta H_{\text{ads}}^{\circ} - T \cdot \Delta S_{\text{ads}}^{\circ} \quad (15)$$

assuming that enthalpy and entropy are independent of temperature in this study. Thus,

$$\Delta H_{\text{ads}}^{\circ} = [(\Delta G_1^{\circ}/T_1) - (\Delta G_2^{\circ}/T_2)]/(1/T_1 - 1/T_2) \quad (16)$$

$$\Delta S_{\text{ads}}^{\circ} = (\Delta G_1^{\circ} - \Delta G_2^{\circ})/(T_2 - T_1) \quad (17)$$

where ΔG_1° and ΔG_2° are the standard free energies of adsorption at two different temperatures, T_1 and T_2 , respectively. The standard free energies of the adsorptions of three minerals with different temperatures are plotted in Fig. 22, and the thermodynamic parameters are shown in

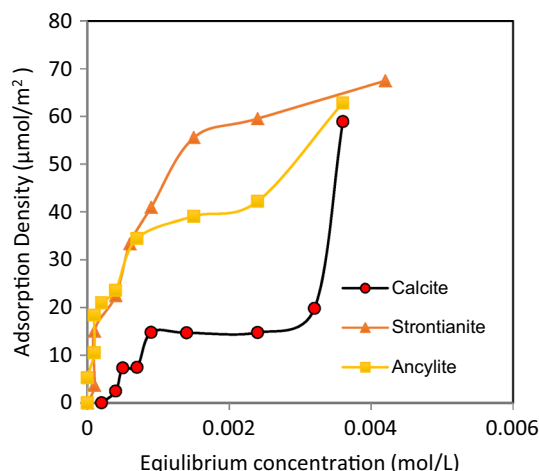


Fig. 21 Adsorption densities of calcite, ancyllite, and strontianite as a function of concentration of HXY at 50 °C

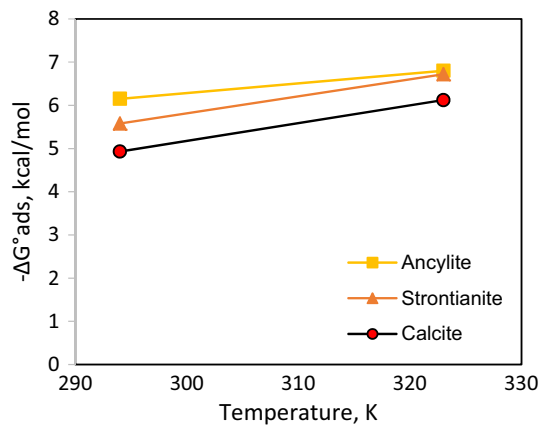


Fig. 22 The standard free energies of adsorption for calcite, ancylite, and strontianite at two temperatures

Table 2 Thermodynamic parameters for adsorption of HXY on minerals

Minerals	Enthalpy (kcal/mol)	Entropy [cal/(mol K)]
Ancylite	0.44	22.41
Strontianite	5.98	39.30
Calcite	7.13	40.00

Table 2. The enthalpy of ancylite is the lowest among the three minerals, which could explain why the adsorption density of ancylite has the smallest increase in comparison with the other minerals. Furthermore, a conclusion could be drawn that the adsorptions of HXY on the surface of these minerals are endothermic.

FTIR Measurement

IR spectra of the pure ancylite and ancylite–hydroxamate are shown in Fig. 23. There is a difference, shown in Fig. 23, between pure ancylite before and after adsorption. This indicates that chemisorption happens when hydroxamate adsorbs onto the surface of ancylite particles. However, in this case, the IR spectra cannot represent the true adsorbed formation of ancylite–hydroxamate complex. Chemisorptions of hydroxamate on strontianite and calcite are also identified from Figs. 24 and 25, respectively, which is in agreement with both electrokinetic measurements and adsorption experiments.

Microflotation of Pure Minerals

As is clear from the result given in Fig. 26, the recovery of pure ancylite is very sensitive to various concentrations of HXY. Particularly, at a low concentration from 3×10^{-4} to 5×10^{-4} M, there is a sharp increase from the recovery range of 8 to 94 %. Nevertheless, the recovery of strontianite is around 85 % at pH 9.5 in the presence of 2×10^{-4} M HXY, compared with the ancylite’s recovery of 5.15 %. Relatively, the maximum calcite recovery of 95 % is obtained at around 2×10^{-3} M, which is in agreement with adsorption studies showing that calcite has the lowest adsorption density among the three minerals studied.

Figure 27 shows that at higher collector concentration of HXY (above 5×10^{-4} M), the recovery of ancylite is relatively independent of pH variation and has the same trend as the collector concentration increases. In comparison with trends at high concentration, there is a difference

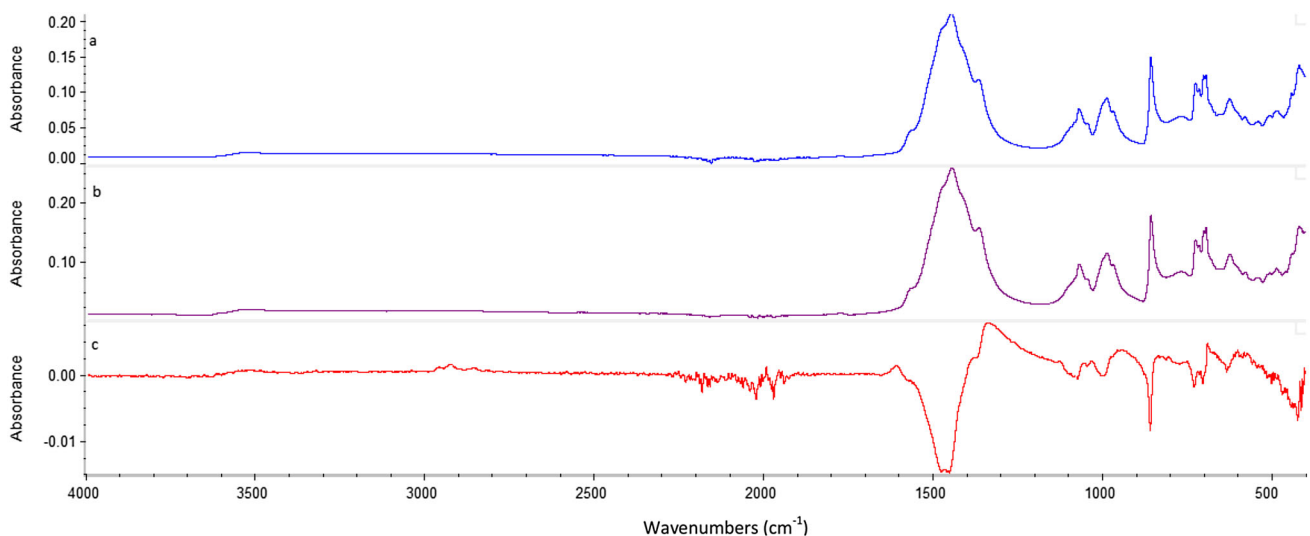


Fig. 23 IR spectra of ancylite. **a** Ancylite before adsorption. **b** Ancylite after adsorption. **c** Difference between ancylites, after and before adsorption

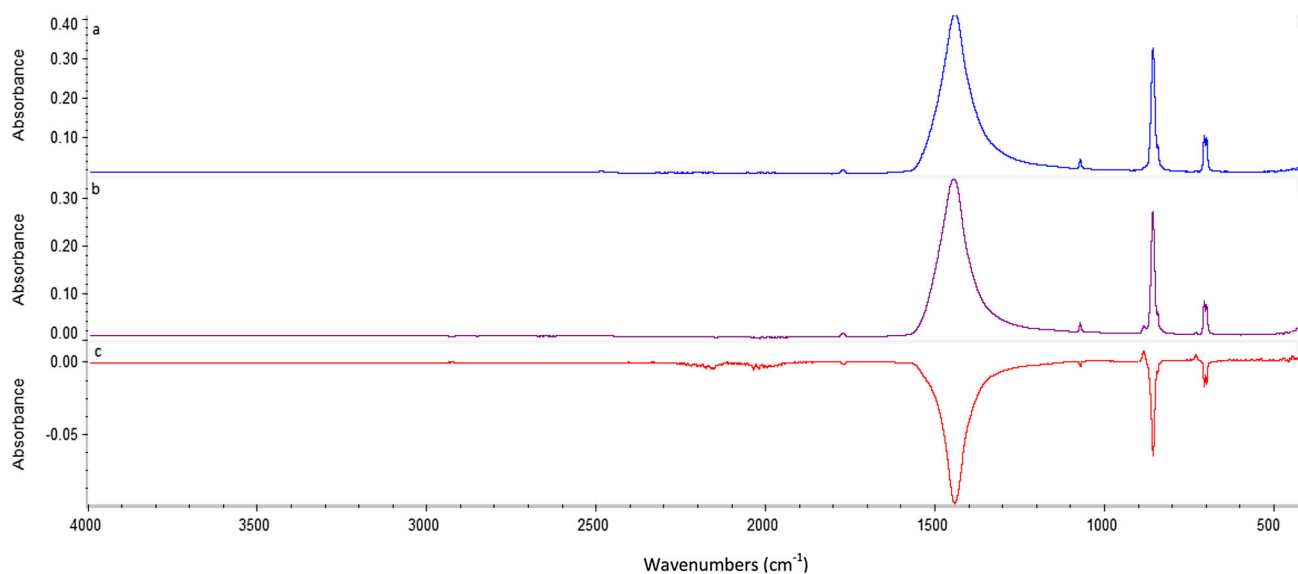


Fig. 24 IR spectra of strontianite. **a** Strontianite before adsorption. **b** Strontianite after adsorption. **c** Difference between strontianites, after and before adsorption

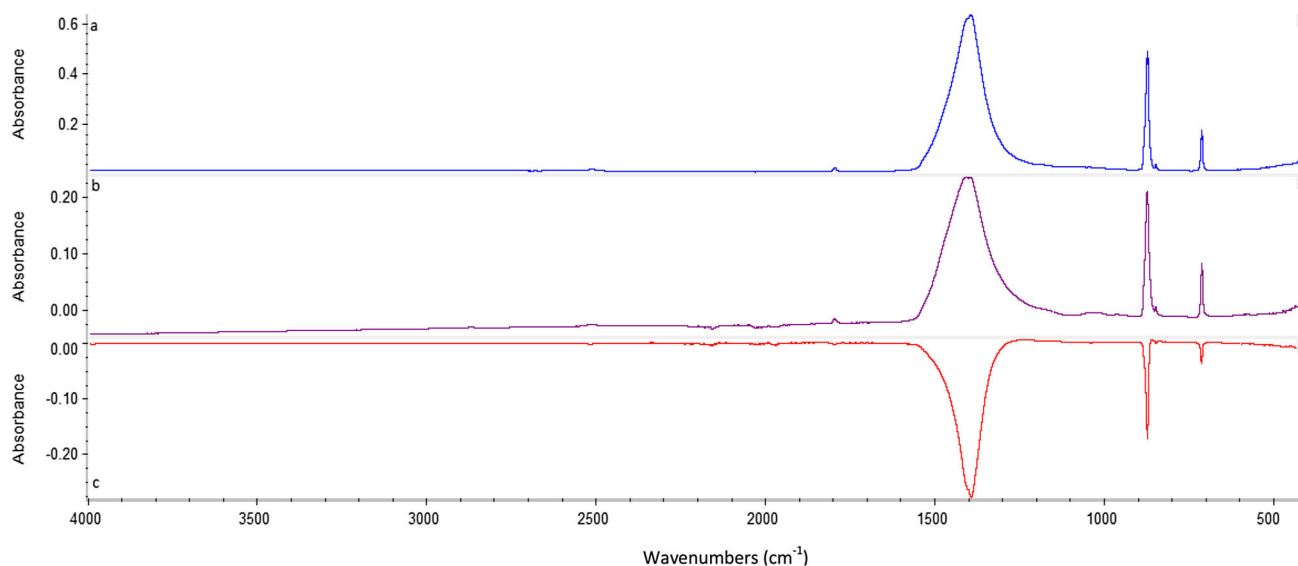


Fig. 25 IR spectra of calcite. **a** Calcite before adsorption. **b** Calcite after adsorption. **c** Difference between calcites, after and before adsorption

occurring at low collector concentration when pH increases. A drop recovery is found from pH 7 to 8.5, which also could be found in previous adsorption density studies. It is attributed to the fact that carbon dioxide plays a more significant role in activation of flotation at lower collector concentration than that at higher concentration.

The resemblance of recovery vs. pH trends for strontianite in the presence of varied collector concentrations of HXY is found in Fig. 28. The relatively low recovery of strontianite is obtained, even though the recovery is still above 60 %. However, the calcite recovery is extremely dependent on pH at all range concentrations (Fig. 29). Less

than 20 % recovery takes place when the pH value is below 7.5.

Thus, it is clear to see (Fig. 30) that there is a potential methodology that could separate calcite from strontianite and ancyllite. The method could be illustrated that at pH 7.5, where calcite separation (Fig. 30) can be theoretically achieved in the presence of 5×10^{-4} M HXY, and then strontianite can be separated from ancyllite in the presence of 2×10^{-4} M HXY at pH 9.5, as shown in Fig. 31. However, a microflotation for a mixture of ancyllite and strontianite at the ratio 1:1 was conducted on the basis of the condition mentioned above. The result shows that

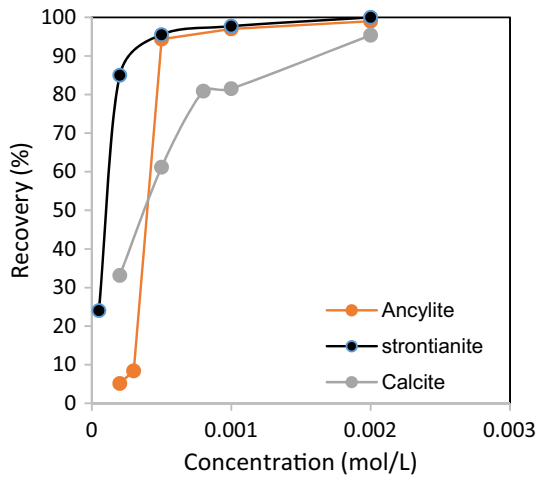


Fig. 26 Recovery versus collector concentration at pH 9.5

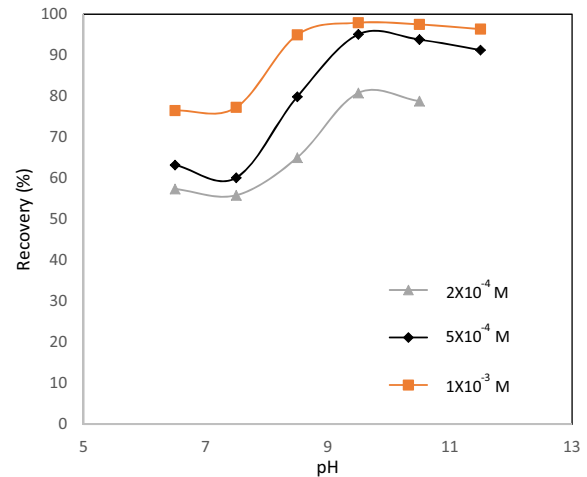


Fig. 28 Strontianite recoveries versus pH at 2×10^{-4} , 5×10^{-4} , and 1×10^{-3} M octanohydroxamic acid

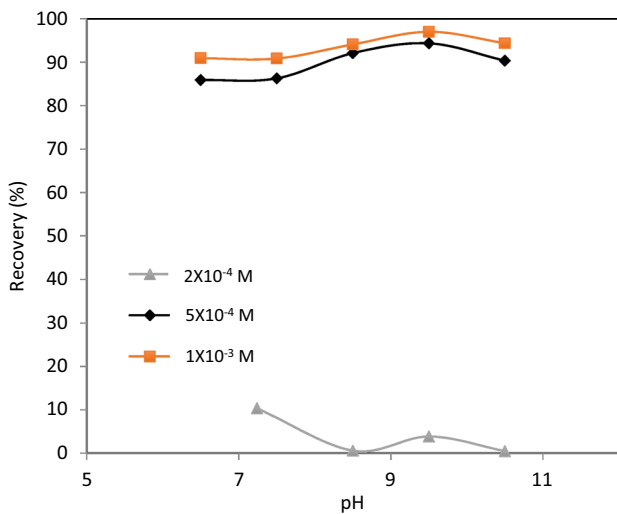


Fig. 27 Ancykite recoveries versus pH at 2×10^{-4} , 5×10^{-4} and 1×10^{-3} M octanohydroxamic acid

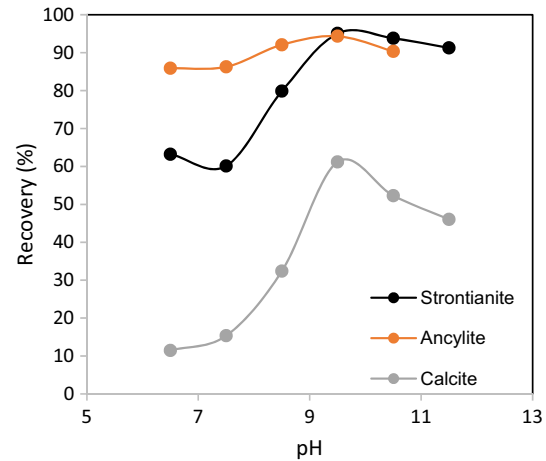


Fig. 30 Recoveries of calcite, ancykite, and strontianite at 5×10^{-4} M octanohydroxamic acid with varying pH values

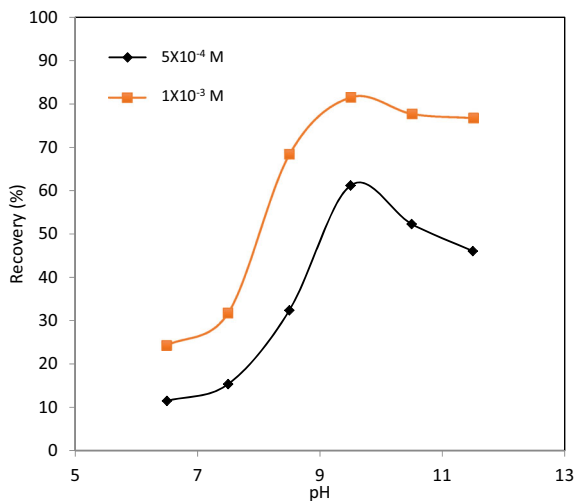


Fig. 29 Calcite recoveries versus pH at 5×10^{-4} and 1×10^{-3} M octanohydroxamic acid

strontianite cannot successfully be separated from ancykite. Also, another microflotation experiment using a mixture of calcite, ancykite, and strontianite also confirms that calcite separation is not successful as single mineral flotation. The zeta potential tests also show that the isoelectric point of the each mineral is altered by the supernatant of the other mineral. The discrepancies between the single mineral and the mixed minerals could result from the existence of dissolved species, since the solubility of semisoluble minerals is drastically higher than those in other systems. Amankonah et al. observed that the shifts in the isoelectric points of calcite and apatite in the supernatants of each other were the result of many complex surface reactions [25]. Somasundaran et al. investigated that calcite might reprecipitate under certain pH conditions to convert the

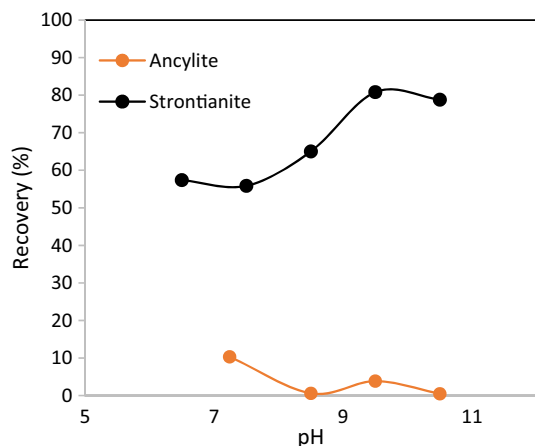


Fig. 31 Recoveries of strontianite and ancyllite at 2×10^{-4} M octanohydroxamic acid with varying pH values

surface of apatite to calcite, when apatite is accommodated in the supernatant of calcite [26].

Conclusion

The IEPs of ancyllite, strontianite, and calcite in water are 5.46, 4.50, and 5.50, respectively. The lattice ions of ancyllite play a significant role in determining the surface charge of ancyllite. A series of electrokinetic studies were conducted in mineral supernatants to develop an understanding on the effect of dissolved species. The results show that calcite and strontianite alter the surface charge of ancyllite, which could explain the difference in the flotation behaviors between the individual pure minerals and the mixture of minerals. The adsorptions of octanohydroxamic acid onto ancyllite, strontianite, and calcite have been investigated through adsorption measurements at room temperature and 50 °C, FTIR, and thermodynamic calculations. From the thermodynamic calculation, the most negative standard free energy of adsorption tends to confirm that HXY preferably adsorbs onto the surface of ancyllite, which is in accordance with results from the adsorption density tests. Temperature and pH values play relatively important roles on adsorptions of strontianite and calcite, compared with ancyllite. From both the electrokinetic measurements and FTIR, it can be concluded that the uptake of HXY on ancyllite is chemisorption, and the separations of ancyllite from strontianite and calcite could not be possible within a pH range of 5–8.0 in the absence of other modifiers.

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