The Surface Chemistry and Microflotation of Xenotime and Depression of Gangue Minerals

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The Surface Chemistry and Microflotation of Xenotime and Depression of Gangue Minerals

Mr. Yicheng Zhang  
Dr. Corby Anderson  
May 2, 2018

Beneficiation of Phosphates VIII  
Cape Town, South Africa
Colorado School of Mines

- Est. 1874
- Golden, Colorado
- 3 Colleges & 21 Technical Majors
- About 200 Faculty
- About 5500 Students

- “...has a unique mission in energy, mineral, and materials science and engineering...”
- “has the most stringent admission standards of any US public engineering school.”
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- “Ranked as #1 US Engineering school” by USA Today.
- “average starting salary of a BSc Mines graduate is $10 K more than an Ivy League graduate.”
The Kroll Institute for Extractive Metallurgy

Dr. Patrick R. Taylor, Director KIEM
George S. Ansell Department of Metallurgical & Materials Engineering
Colorado School of Mines
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Annual Short Course

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Annual Short Course

**June 26 - 28, 2018**
Golden, Colorado USA
https://csm-space.com/events/recycmetals/
What is xenotime?

- Yttrium Orthophosphate (YPO$_4$)
  - A source of yttrium
  - Impurities include uranium and thorium, radioactive
  - Located in Australia, Southern China and Malaysia
  - Sometimes associated with other metallic deposits
Why xenotime?

- Applications
  - Yttrium aluminum garnet laser (YAG)
  - Yttrium vanadate as host for europium in television and phosphor
  - YBCO high-temperature superconductor
  - Yttrium-stabilized zirconia (YSZ)
  - Yttrium iron garnet (YIG) microwave filter
  - Energy-efficient light bulbs
  - Additive to steel
  - ......
Why froth flotation?

- A fundamental method
  - Surface chemistry and beneficiation of rare-earth bearing minerals
  - Able to process a wide range of fine particle sizes
  - Can be tailored to the unique mineralogy of a given deposit

Mountain Pass Rare Earth Mine in USA
Bayan Obo Rare Earth Mine in China
Mount Weld Rare Earth Mine in Australia
Why this project critical?

Rare Earth Elements: World Production, Reserves and U.S. Imports

113TH CONGRESS
1ST SESSION

H. R. 761

IN THE SENATE OF THE UNITED STATES
SEPTEMBER 19, 2013
Received; read twice and referred to the Committee on Energy and Natural Resources

To require the Secretary of Agriculture to conduct a study of the availability of critical minerals and their sources and report to Congress.

246-178
Passed

COLORADO SCHOOL OF MINES
EARTH • ENERGY • ENVIRONMENT
Why this project critical?
Overview

- **Work done**
  - Literature research
  - MLA analysis
  - Zeta potential tests
  - Surface area measurement
  - Adsorption studies
  - Microflotation

- **Minerals**
  - Xenotime
  - Ilmenite
  - Zircon
  - Schorl
  - Staurolite

- **Materials**
  - Octano-hydroxamic acid
  - Sodium oleate

- **Sodium silicate**
- **Ammonium lignosulfonate**

- **Variables**
  - Temperature
  - pH
  - Concentration

### Sieve fraction mass distribution

<table>
<thead>
<tr>
<th>Sieve (US mesh)</th>
<th>Xenotime Con.</th>
</tr>
</thead>
<tbody>
<tr>
<td>+100</td>
<td>3.0</td>
</tr>
<tr>
<td>100 X 200</td>
<td>84.0</td>
</tr>
<tr>
<td>200 X 400</td>
<td>13.0</td>
</tr>
<tr>
<td>-400</td>
<td>--</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>
Mineral Introduction

China

Classifier MLA Image from the Xenotime Concentrate 100 X 200 Mesh Sieve Fraction. Particle inset units are in pixels and concentration palette values are in surface area percentage.
Mineral Introduction

Major Mineral Content

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Modal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenotime</td>
<td>YPO4</td>
<td>67.7</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>Fe₂Ti₃O₉</td>
<td>11.6</td>
</tr>
<tr>
<td>Zircon</td>
<td>ZrSiO₄</td>
<td>4.00</td>
</tr>
<tr>
<td>Schorl</td>
<td>NaFe₃Al₆(BO₃)₃Si₆O₁₈(OH)₄</td>
<td>3.05</td>
</tr>
<tr>
<td>Staurolite</td>
<td>Fe₂Al₉Si₄O₂₀(OH)₄</td>
<td>5.94</td>
</tr>
</tbody>
</table>
Mineral Introduction

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Specific Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenotime</td>
<td>YPO4</td>
<td>4.27</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>Fe₂Ti₃O₉</td>
<td>4.7</td>
</tr>
<tr>
<td>Zircon</td>
<td>ZrSiO₄</td>
<td>4.7</td>
</tr>
<tr>
<td>Schorl</td>
<td>NaFe₃Al₆(BO₃)₃Si₆O₁₈(OH)₄</td>
<td>3.15</td>
</tr>
<tr>
<td>Staurolite</td>
<td>Fe₂Al₉Si₄O₂₀(OH)₄</td>
<td>3.71</td>
</tr>
</tbody>
</table>

Concentration Criterion (CC)

\[ CC = \frac{D_h - D_f}{D_i - D_f} \]

Where:  
\( D_h \) = Sp. Gr. of heavy particle  
\( D_i \) = Sp. Gr. of light particle  
\( D_f \) = Sp. Gr. of fluid medium (usually water, \( D_f = 1 \))

If CC > 2.5, the separation is considered relatively easy;  
if 2.5 > CC > 1.25, the separation is considered difficult or possible; and  
if CC < 1.25, the separation is considered impossible except for heavy liquids.

If water is used as the fluid medium, the CC for separating xenotime against each gangue mineral is 1.13, 1.13, 1.21, and 1.52, respectively, indicating that it is difficult or even impossible to separate these gangue minerals from xenotime by gravity separation.
Mineral Introduction

Magnetic Response and Electrostatic Response at Room Temperature

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Magnetic Response</th>
<th>Electrostatic Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenotime</td>
<td>YPO4</td>
<td>Para</td>
<td>Electrostatic</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>Fe2Ti3O9</td>
<td>Para</td>
<td>no</td>
</tr>
<tr>
<td>Zircon</td>
<td>ZrSiO4</td>
<td>None para</td>
<td>no</td>
</tr>
<tr>
<td>Schorl</td>
<td>NaFe3Al6(BO3)3Si6O18(OH)4</td>
<td>Para</td>
<td>no</td>
</tr>
<tr>
<td>Staurolite</td>
<td>Fe2Al9Si4O20(OH)4</td>
<td>Para</td>
<td>no</td>
</tr>
</tbody>
</table>
Flotation literature research

- **Cheng et al. in 1992**
  - Using sodium oleate as the collector and a modified Hallimond tube;
  - PZC of xenotime occurred at pH 3.0;
  - Maximum recovery was above 90% at pH 7-8;
  - Chemisorption;
  - More hydroxyl species, higher the recovery.

- **Cheng et al. in 1994**
  - Maximum recovery using sodium oleate as the collector occurred at pH 7-8;
  - RE(OH)$_2^+$ had a positive effect on adsorption and flotation results;
  - In the acidic region, pH decreased the solubility of oleic acid, stimulating surface precipitation;
  - In the alkaline region, the precipitation of RE hydroxides became prevalent on the surface, less active spots on the surface.

- **Pereira and Peres in 1997**
  - Using hydroxamate as the collector, several depressants and a modified Hallimond tube;
  - Maximum recovery was above 98% at pH 10±0.5;
  - PZC of xenotime occurred at 2.3 and 3;
  - Chemisorption.

- **Cheng in 1999**
  - IEP of xenotime occurred at pH 7;
  - PZCs of different xenotime samples had varied from 2.3 to 5.0.
Electrical Double Layer

Schematic Expression of the Electric Double Layer and the Potential Drop through the Double Layer at A Mineral/Water Interface. The potential at the Stern plane, $\Psi_0$, is approximated by the measured electrokinetic potential, $\zeta$, zeta potential.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>PZC</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenotime</td>
<td>2.3-5.0</td>
<td>Cheng, 1999</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>5.4</td>
<td>Mehdi et al, 2014</td>
</tr>
<tr>
<td>Zircon</td>
<td>4.0</td>
<td>Pereira et al, 1997</td>
</tr>
<tr>
<td>Schorl</td>
<td>4.0</td>
<td>Lameiras et al, 2008</td>
</tr>
<tr>
<td>Staurolite</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>
Zeta Potential Measurement

- Octano-hydroxamic acid (HXM)
- Hydrophobic
- Active head

- 200X400 mesh;
- 0.0005M hydroxamic solution;
- 0.02g added into 40 ml solution or distilled water;
- 24 hours.
Zeta Potential Measurement

- PZC of xenotime = 3.90;
- PZC of ilmenite = 4.20;
- PZC of zircon = 3.95;
- PZC of Schorl = 4.70;
- PZC of Staurolite = 4.4.
As the solution goes from acidic to alkaline, more $\text{H}_3\text{PO}_4$ is going to be hydrolyzed into $\text{PO}_4^{3-}$ and more $\text{Y}^{3+}$ is going to be hydrolyzed to $\text{Y(OH)}_3$.

Solubility Diagram of Phosphate and $\text{Y}^{3+}$ Species (0.001 M total solution concentration)
Zeta Potential Measurement

- With HXM adsorption, the zeta potentials became negative than the original DI PZCs.
Adsorption Studies

Octano-hydroxamic acid

Hydrophobic

Active head

The Mechanism of Collector Attachment

Chemisorption

van der Waals forces

The Mechanism of Micelle Attachment

The Mechanism of Micelle Attachment
# Physical Adsorption vs. Chemisorption

<table>
<thead>
<tr>
<th>Physical Adsorption</th>
<th>Chemical Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>- The forces operating in this case are weak Vander Waal’s forces.</td>
<td>- The forces operating are chemical bonds (ionic or covalent bond).</td>
</tr>
<tr>
<td>- The heat of adsorption is low at about 20-40 Kj mol(^{-1}).</td>
<td>- The heat of adsorption are high at about 40-400 Kj mol(^{-1}).</td>
</tr>
<tr>
<td>- The process is reversible. Desorption can occur by increasing temperature or decreasing pressure.</td>
<td>- The process is irreversible. Efforts to reverse the adsorption give different compounds.</td>
</tr>
<tr>
<td>- It does not require any activation energy.</td>
<td>- It requires an activation energy.</td>
</tr>
<tr>
<td>- It takes place at low temperature and decreases with an increase in the temperature.</td>
<td>- Adsorption increases with an increase in temperature</td>
</tr>
<tr>
<td>- Adsorption increases with the increase in the surface area of the adsorbent.</td>
<td>- Adsorption increases with an increase in the surface area of adsorbent.</td>
</tr>
<tr>
<td>- It forms a multi-molecular layer.</td>
<td>- It forms a unimolecular layer.</td>
</tr>
</tbody>
</table>

- Parkins et al in 1975;
Adsorption Studies

- Calibration
  - 4ml of 2.94 g/l ferric perchlorate solution;
  - 2ml of hydroxamic acid solution.
  - Concentration ranged from 0.0005M to 0.002M.
  - Sensitivity is 0.0001M.

- Equilibrium time determination
  - 0.05g of a mineral;
  - 10ml 0.001M concentration;

- Adsorption density measurement
  - 0.05g of a mineral;
  - Concentration ranging from 0.0005M to 0.002M;
  - 20 hours’ conditioning;
  - 20 minutes’ centrifuge;
  - 2 ml of the supernatant was mixed with 4 ml 2.94 g/l ferric perchlorate solution;
  - At room temperature and 80°C;
  - pH ranging from 3 to 11.
BET Tests

Surface Areas of Xenotime and Gangue Minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenotime</td>
<td>2.9471</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>0.8630</td>
</tr>
<tr>
<td>Staurolite</td>
<td>4.7698</td>
</tr>
<tr>
<td>Schorl</td>
<td>1.7263</td>
</tr>
<tr>
<td>Zircon</td>
<td>0.6558</td>
</tr>
</tbody>
</table>
Adsorption Tests With Temperature

- Equilibrium time were 20 hours;
- At 80 °C, 20 hours was not enough for ilmenite to reach equilibrium;
- High temperature enhanced the adsorption of hydroxamic acid on the surfaces of the minerals;
- The conversion of Fe$^{2+}$ to Fe$^{3+}$ improved the floatability of ilmenite in their microflotation tests (Irannajad et al in 2014)
Adsorption Tests With pH

- Overall adsorption density at 80 °C was higher than that at room temperature;
- the minerals did not reach equilibrium at 80 °C;
- High temperatures enhanced the adsorption;

- At room temperature, flotation results indicated the recoveries of ilmenite and schorl were lower than that of xenotime at pH's of 5 to 9.
  - Density of ilmenite is larger than that of xenotime;
  - Aggregation of schorl particles might happen in the solution;
  - Xenotime reached equilibrium but ilmenite and schorl did not.
Effect of Temperature and Concentration

- High temperature enhanced the free energy in the solid-liquid system;
- More active areas;
- Higher temperature amplified the differences of adsorption density at varying pHs.
- pH 9 was the optimum.
Effect of pH

- Adsorption results were more or less symmetric but less sharp than the results of flotation recoveries;
- 20 hours vs. 15 minutes;
- A sharp peak in the range of pH 5-9;
- Hydrolysis of the mineral surfaces;
- Xenotime had the best floatability but worst adsorption results.
Microflotation

- Collectors
  - Octano-hydroxamic acid (used in Bayan Obo rare earth deposit processing bastnaesite);
  - Sodium oleate (used in Mountain Pass deposit processing bastnaesite).

- Depressants
  - Sodium silicate (Bayan Obo);
  - Ammonium lignosulfonate (Mountain Pass).

Without addition of a depressant
- 0.5g of mineral sample (or mixed sample);
- 40 ml of collector solution;
- Concentration ranged from 0.0005M to 0.002M;
- 15 minutes of conditioning;
- 10 ml of collector solution to wash down residual;
- 600 rpm stirring speed and 30cc air flow rate;
- 2 minutes of flotation.

With addition of a depressant
- 0.5g;
- Conditioning with 25ml 0.001M depressant for 5 minutes;
- 15 minutes more after the addition of 15ml collector solution with concentration ranging from 0.001M to 0.004M;
- 10 ml of the same collector solution used to wash down residual;

- pH modifier: NaOH and HCl.
Microflotation

- Maximum recovery was observed in the range of pH 5 to 9;
- Sharp drops at extreme pH conditions;

pH 9 was more favorable for separation using hydroxamic acid as the collector.

Microflotation recoveries of xenotime with different concentration of octano-hydroxamic acid as a function of pH at room temperature

Microflotation recoveries of xenotime and gangue minerals with 0.0005M octano-hydroxamic acid as a function of pH at room temperature
Microflotation

- Selectivity expressed;
- The lower the initial grade, the more xenotime was selectively collected.

Recoveries and ΔGrade of mixed samples (weight ratio of xenotime and gangue minerals=1:4 and 1:1) with 0.0005HXM at pH9 at room temperature

- Maximum recovery of xenotime occurred in the range of pH 7 to 9;
- Zircon had a wider range.

Microflotation recoveries of xenotime and gangue minerals with 0.0005M sodium oleate as a function of pH at room temperature
Comparisons between effects of octano-hydroxamic acid and sodium oleate on xenotime flotation as a function of pH

- HXM possessed a wider range;
- Temperature might have a negative influence on the flotation of xenotime using sodium oleate at certain pH values;
- pH 9 was chosen for further comparative tests.
Microflotation

- Original grade of xenotime was 33.85%.
- Sodium oleate was more selective!
- Pavez in 1996.

Recoveries and ∆Grades of xenotime with 0.0005M HXM vs. 0.0005M SOT at pH 9 at room temperature
Comparisons between effects of sodium silicate and ammonium lignosulfonate before the addition of octano-hydroxamic or sodium oleate at pH 9 and room temperature.

- Sodium silicates were slightly better;
- No depressant expressed depressing power when used with octano-hydroxamic acid;
- The testing of depressants using sodium oleate as the collector had mixed success.
Comparisons between effects of sodium silicate and ammonium lignosulfonate before the addition of octano-hydroxamic or sodium oleate at pH 9 and room temperature

- Sodium silicates were slightly better;
- No depressant expressed depressing power when with octano-hydroxamic acid.
Effect of Temperature

- High temperature enhanced the free energy;

According to lab observations, bubbles were more stable in a sodium oleate solution at higher temperature;

When in a solution of HXM, bubbles were generated faster at higher temperature.

Effect of temperature on recoveries and Δgrades in the presence of sodium oleate and ammonium lignosulfonate at room temperature and 80°C, at pH 9.
Conclusions

- The zeta potential of xenotime was measured at pH 3.90 in this project.
- Chemisorption likely occurred on the surface of xenotime using either octano-hydroxamic acid or sodium oleate as the collector.
- At elevated temperatures, xenotime reached equilibrium adsorption but ilmenite did not. This suggests a mechanism of separation based on hydrophilic area on the surface of ilmenite limiting their floatability.
- Octano-hydroxamic acid is efficient as a collector in the flotation of xenotime. The optimum pH to separate xenotime from the selected gangue minerals is pH 9.
- Sodium oleate expresses stronger selectivity than octano-hydroxamic acid in the flotation of xenotime from selected gangue minerals.
- The depressants, sodium silicate and ammonium lignosulfonate are efficient in the presence of sodium oleate to depress all the gangue minerals at room temperature.
- The stability of bubbles is a significant factor in the performance of flotation. However, it’s hard to quantify the advantage of higher bubble stability. It does seem to reduce the selectivity of octano-hydroxamic acid.
- Ammonium lignosulfonate is better than sodium silicate when used to depress ilmenite in the presence of sodium oleate.
- While temperature appears to decreases the bubble stability when using sodium oleate alone, temperature enhances the performance of ammonium lignosulfonate in the presence of sodium oleate.
Acknowledgement

The Critical Materials Institute, the sponsor of this project, and Prof. Patrick Zhang from FIPR in Florida, is gratefully acknowledged.


Questions?
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May 2, 2018

Beneficiation of Phosphates VIII
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