Effect of gangues on flotation of valuable phosphate and silicate minerals: Characterization and modeling studies

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Effect of Particle Characteristics on Fatty Acid Flotation of Florida Phosphate Rock

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Phosphate minerals

82% - Fertilizer, 18% - industrial use

- Sedimentary phosphates (80% of global supply)
- Igneous phosphates (15-20 % of global supply)
- Biogenic phosphates (tiny fraction of global supply)

Source: UNIDO and IFDC 1998; Zapata and Roy 2004; Abouzeid 2008.

Beneficiation of Phosphate Ore edited by Kawatra, and Carlson, 2013, SME

Phosphate mining

Peak phosphate: 2033-2034??
- Conservative phosphate reserves – 15,000 million metric tons (mmt)
- Yearly production approaching 200 mmt

Cost of processing phosphate ore is continuously increasing
- Decreasing grade of the phosphate ore
  - Open pit mining - moving overburden, which is several times over the ore mined
  - More number of processing steps and expensive technology
  - Increased consumption of water and energy for separation

Amount of phosphate and other valuables lost in tailings
- 5-20 % of phosphate is lost during processing

Beneficiation of Phosphate Ore edited by Kawatra, and Carlson, 2013, SME

Phosphate rock composition

Francolite (mostly in sedimentary deposits)

- **$Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$**

Apatite (mostly in igneous deposits)

- **fluorapatite ($Ca_{10}(PO_4)_6F_2$)**
- **chlorapatite ($Ca_{10}(PO_4)_6(Cl)_2$)**
- **hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$)**

Beneficiation of Phosphate Ore edited by Kawatra, and Carlson, 2013, SME

Typical processing circuit

$$Ca_5(PO_4)_3F_{(s)} + 5H_2SO_{4(l)} + 10H_2O_{(l)} \rightarrow 5(CaSO_4 \cdot 2H_2O)_{(s)} + HF_{(aq)} + 3H_3PO_{4(aq)}$$

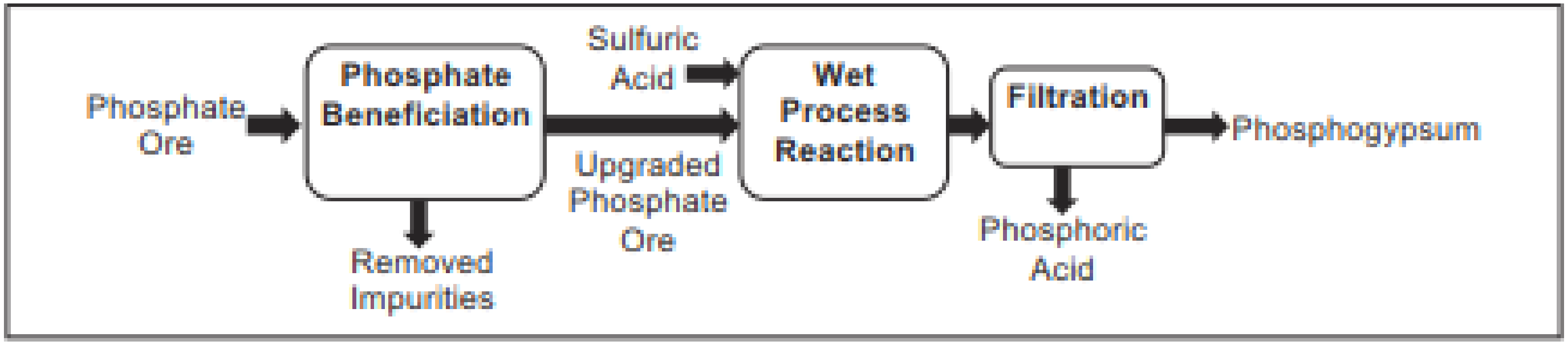


Figure 1.1 Simplified process flow diagram for production of phosphoric acid

Beneficiation of Phosphate Ore edited by Kawatra, and Carlson, 2013, SME

Nature of gangue minerals

Siliceous vs. Calcareous, dolomitic phosphate rocks

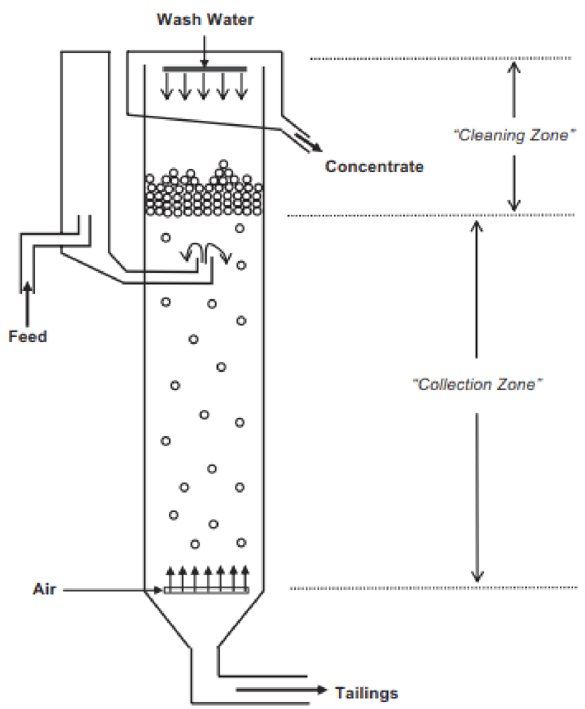
Siliceous impurities

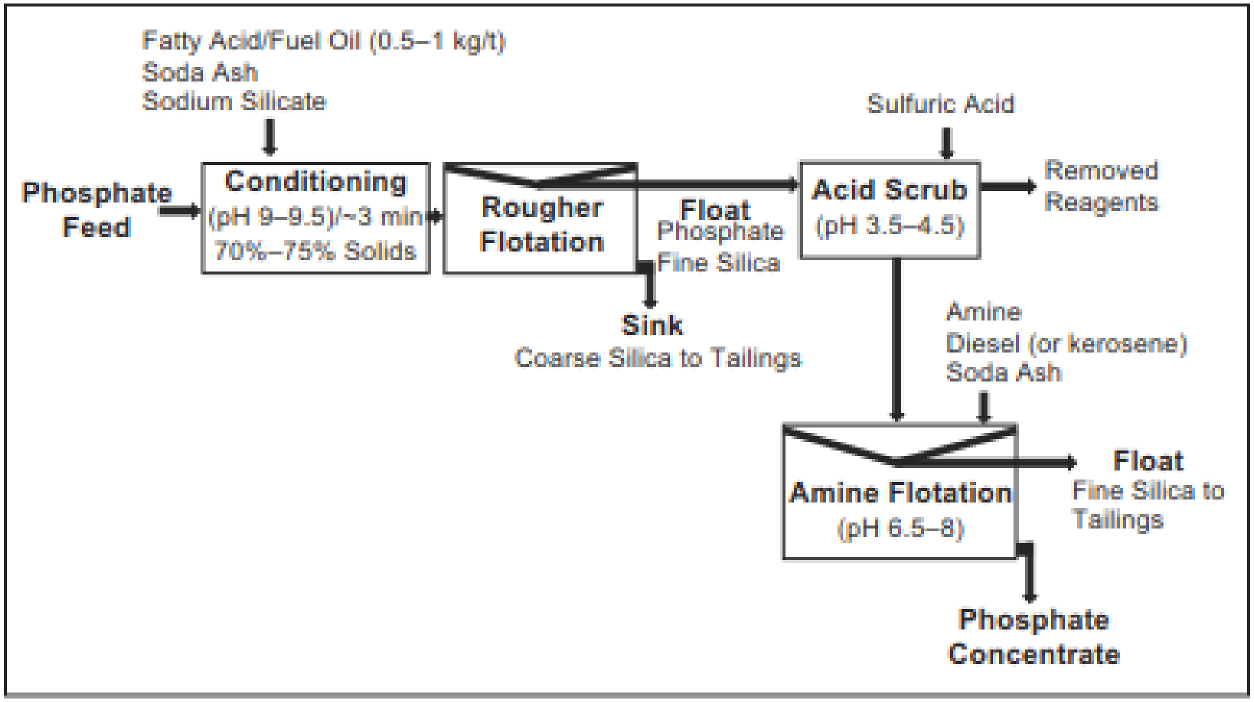
- Clays (montmorillonite ($Si_8Al_{3.5}Mg_{0.5}O_{20}(OH)_4$), palygorskite ($(Mg,Al)_2Si_4O_{10}(OH) \cdot 4(H_2O)$), and kaolinite ($Al_4(Si_4O_{10})(OH)_8$))
  - Interferes in flotation through slime formation
  - Removed by washer screens and hydrocyclones
- Quartz
  - Increases the volume of transport and erosion of equipment
  - Removed by 2-stage froth flotation

Dolomite and calcite impurities

- Increased H_2SO_4 consumption and increased suspension viscosity
- Difficult to separate economically – still a open problem

Froth flotation – separation of phosphate from gangues

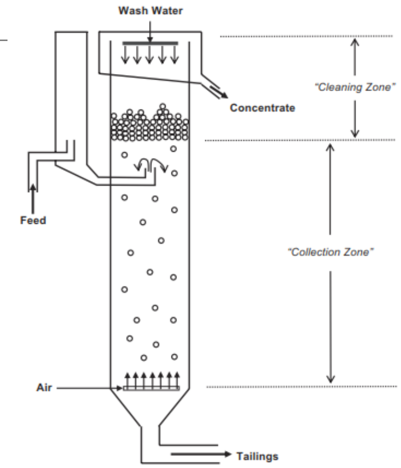




Source: Adapted from Guan 2009b.

Beneficiation of Phosphate Ore edited by Kawatra, and Carlson, 2013, SME

Florida phosphate rock separation issues



Variation in feed quality

Beneficiation of Phosphate Ore edited by Kawatra, and Carlson, 2013, SME
World Phosphate Rock Reserves and Resources, IFDC, 2010
Effect of Particle Characteristics on Fatty Acid Flotation of Florida Phosphate Rock, Florida Institute of Phosphate Research, 2010

Samples from different ore deposits from Florida

Table 1. Flotation Results of Received Samples.

Sample	Feed BPL (%)	Concentrate BPL (%)	Recovery (%)	Flotation Characteristics
CF East Pit	12.15	46.19	96.7	Good
CF West Pit	9.88	43.62	96.6	Good
CF Combined	16.94	52.42	96.3	Good
SFM	14.44	49.88	95.2	Good
3057 Split 2	12.88	64.62	86.4	Good
464 Split 1	27.65	36.79	76.5	Bad*
464 Split 2	31.93	57.69	61.0	Bad
1862 Split 2	26.72	48.72	25.6	Bad
1862 Split 2	26.67	46.33	66.6	Bad

* The flotation behavior is classified as bad if the recovery is below 80%.

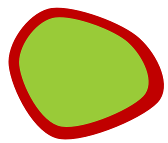
Florida phosphate rock recovery issues

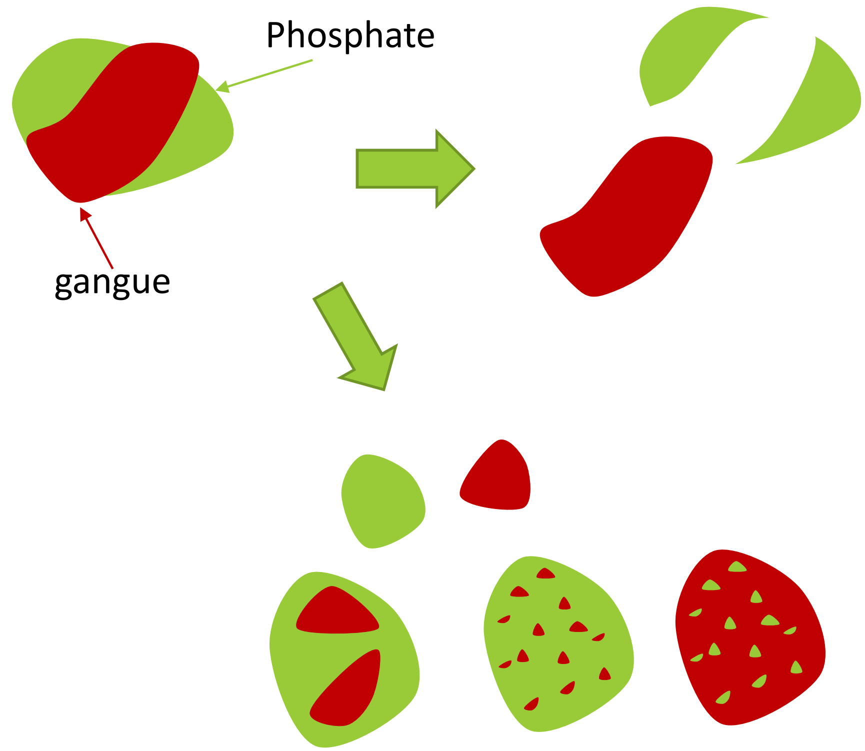
Liberation

Surface contamination

Size

Morphology

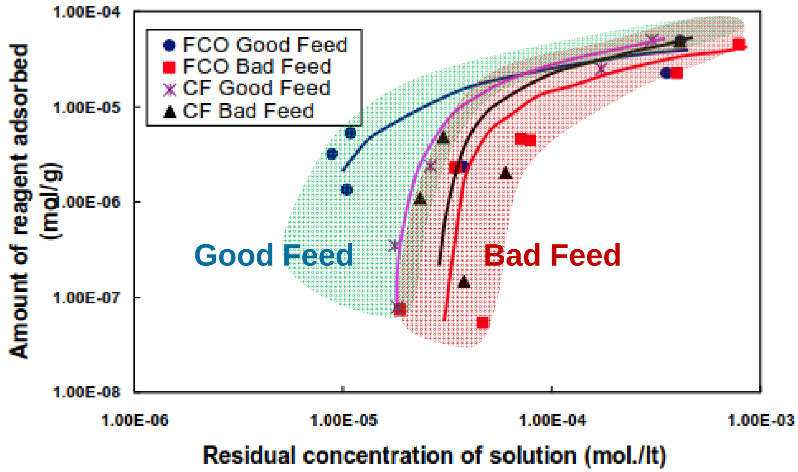




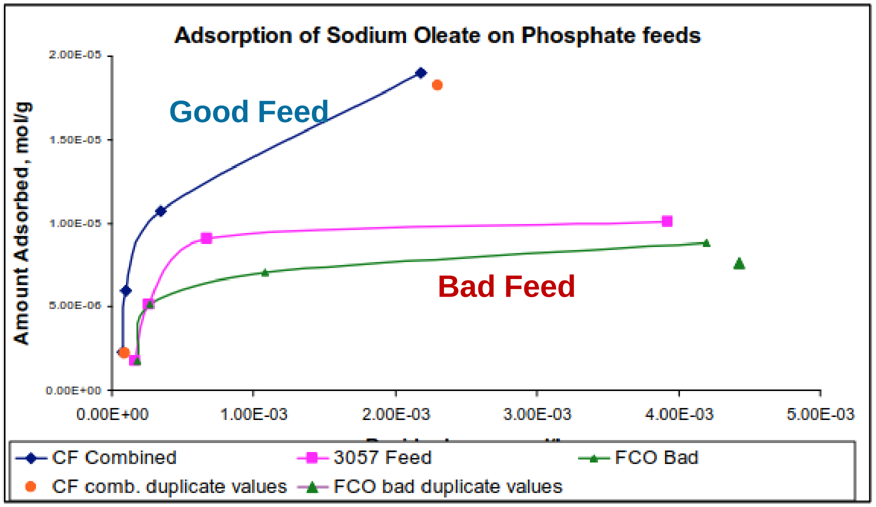
Effect of Particle Characteristics on Fatty Acid Flotation of Florida Phosphate Rock,
Florida Institute of Phosphate Research, 2010

Surface modification?

Adsorption and zeta potential experiments



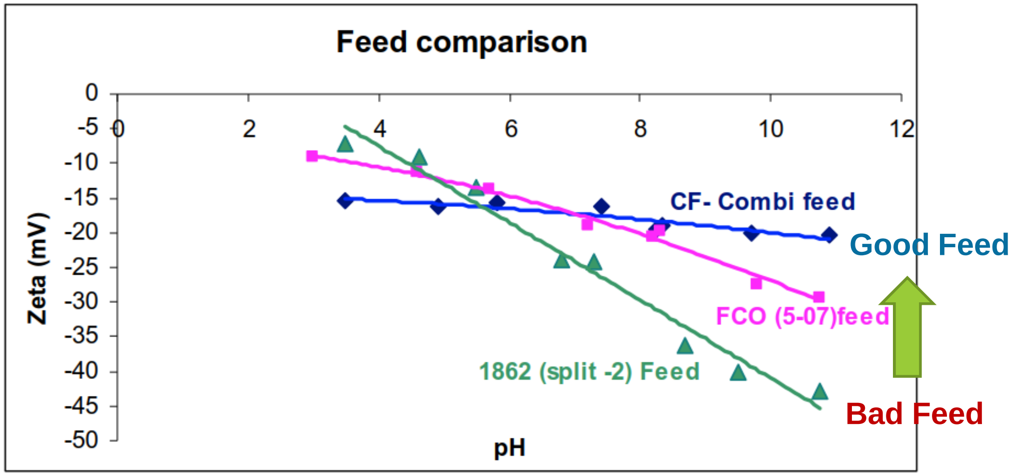
Adsorption Density of Sodium Oleate on Both Good and Bad Feed Samples of FCO, CF Rock Phosphate Sources at Natural pH.



Adsorption Density of Sodium Oleate on Both Good (CF Combined) and Bad (3057 and FCO Bad) Feed Samples at pH 9.2.

- Reason for relatively poorer adsorption of oleate on Bad-feeds:
  - Unliberated of fine phosphates from quartz gangues?
  - Coating of clay slimes on phosphate surfaces
  - Coating of gypsum and/or interference of calcium in surfactant adsorption

Electrokinetics: Zeta potentials



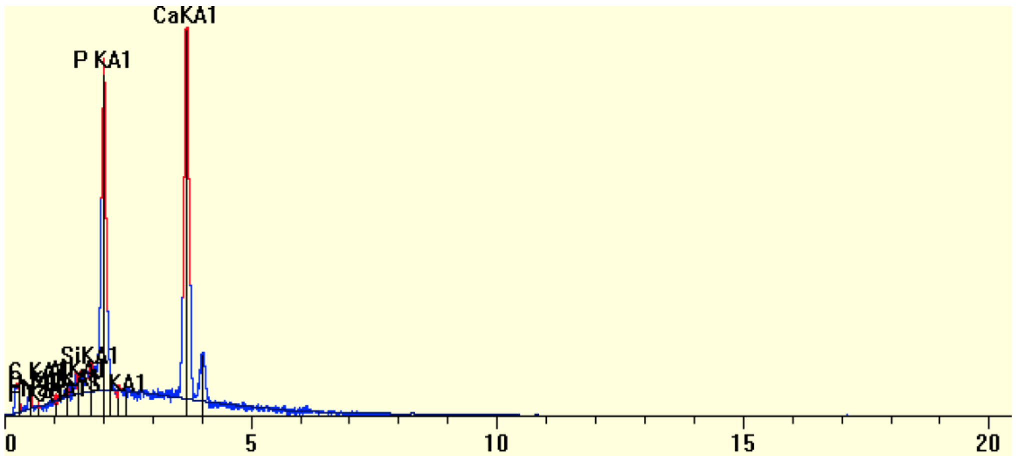
Zeta Potential of Phosphate Samples (FCO 5-07, 1862-S2 and CF Combined Feed).

Bad-feed: surface presence of quartz or siliceous minerals (either as inclusions or as slimes)

Quartz vs. Clays: EDS-Analysis

Which impurity is associated with the rejection of phosphates in the tailings of Good- or Bad-feeds?

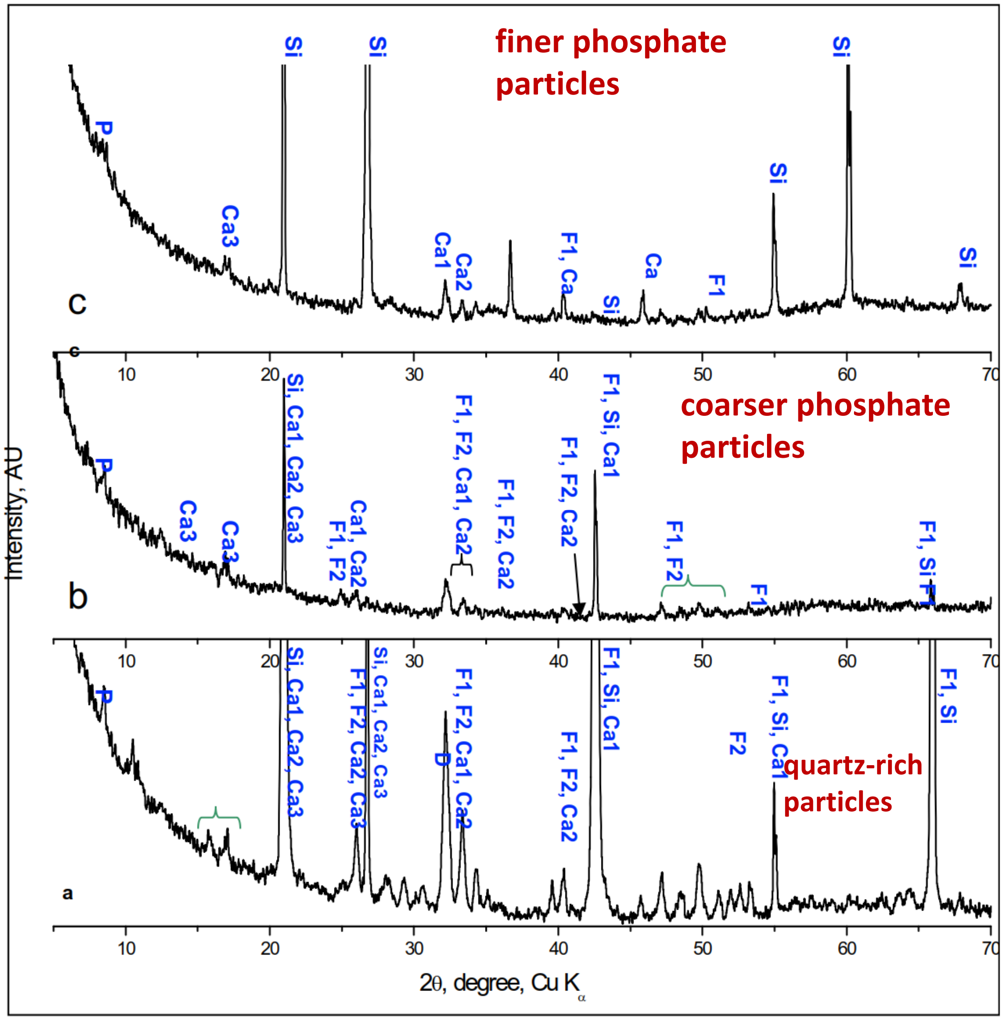
EDS analysis of phosphate rich particles in Bad-feeds



Element	Line	keV	KRatio	Wt%	At%	At Prop	ChiSquared
C	KA1	0.277	0.0639	31.29	53.57	0.0	4.35
Al	KA1	1.487	0.0092	1.27	0.97	0.0	6.26
Si	KA1	1.740	0.0135	1.62	1.18	0.0	6.26
Ca	KA1	3.691	0.3111	35.45	18.19	0.0	14.89
Mg	KA1	1.254	0.0019	0.31	0.26	0.0	6.26
O	KA1	0.523	0.0126	9.42	12.10	0.0	4.35
P	KA1	2.013	0.1722	20.56	13.65	0.0	6.26
Na	KA1	1.041	0.0004	0.08	0.07	0.0	6.26
F	KA1	0.677	0.0000	0.01	0.02	0.0	4.35
S	KA1	2.307	0.0000	0.00	0.00	0.0	
Total			0.5848	100.00	100.00	0.0	8.18

- In tailings
  - phosphate particles have alumonisilicate inclusions rather than quartz
  - quartz fine particles have minor inclusions of phosphate

XRD of Bad samples - Fine vs. coarse tailing particles



F1 = Francolite $CaF(Ca,C)_4[(P,C)(O,OH,F)_4]_3$ JCPDS 02-0833
F2 = Carbonatehydroxyapatite $Ca_{10}(PO_4)_3(CO_3)(OH)_2$ JCPDS 19-0272 or Calcium Carbonate Hydrate JCPDS 83-1923
P = Palygorskite $MgAlSi_4O_{10}(OH).4H_2O$ JCPDS 29-0855; 31-0783
C = Cordierite $Mg5(Si,Al)8O_20(OH)_2.8H_2O$ JCPDS 86-1550; 85-1722
Ca1 = Calcium Aluminum Silicate Hydrate $CaAl_2Si_2O_8.4H_2O$ JCPDS 20-0452
Ca2 = Calcium Aluminum Silicate Hydrate $CaAl_2Si_2O_8.4H_2O$ JCPDS 39-1373
Ca3 = Calcium Aluminum Silicate Hydrate $CaAl_2Si_2O_8.4H_2O$ JCPDS 13-0495
Si = Quartz
D = Dolomite $CaMg(CO_3)_2$ JCPDS 79-1346

Phosphate phases: mostly Francolite and some carbonate hydroxyapatite

Quartz bulk inclusion in finer particles

Aluminosilicate bulk inclusions dominate coarser phosphate particles

Some phosphate lost in quartz particles

Somasundaran et. al., Similarities and dissimilarities in Florida phosphate ore types, IMPC, 2010

Vibrational Spectroscopy - concentrates

Stretching bands of PO_4^{3-} tetrahedra: ~ 1030 cm^{-1} and ~970 cm^{-1} satellite

- **signature of polytypes of apatite**
- **stoichiometry and crystallinity of apatite → position and width of this band**

Isomorphically substituted carbonate bands: 1456, 1425, and 865 cm^{-1}

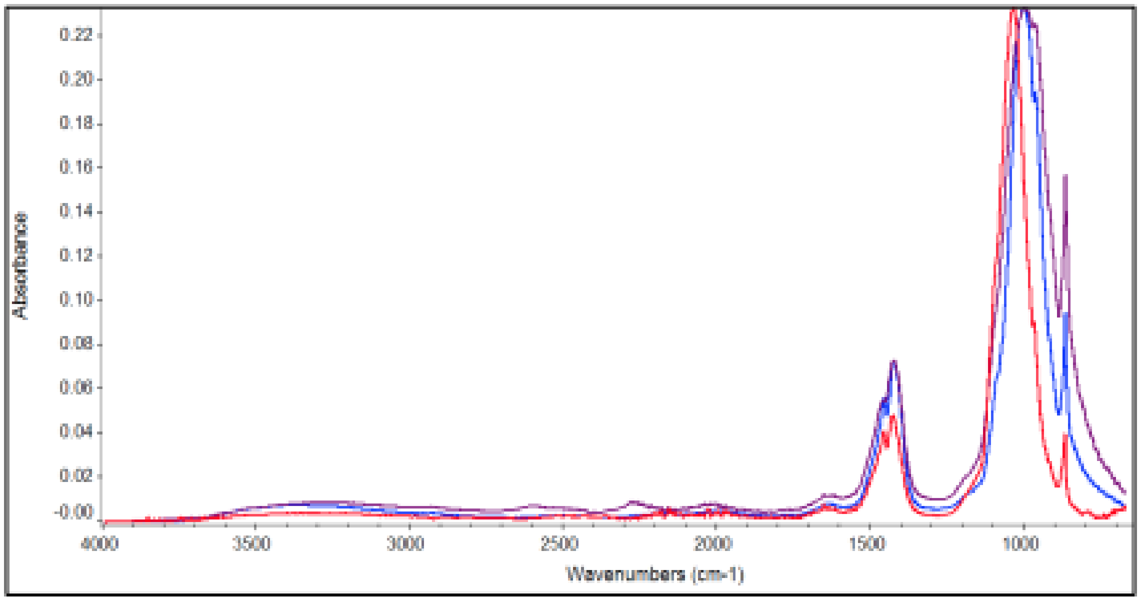


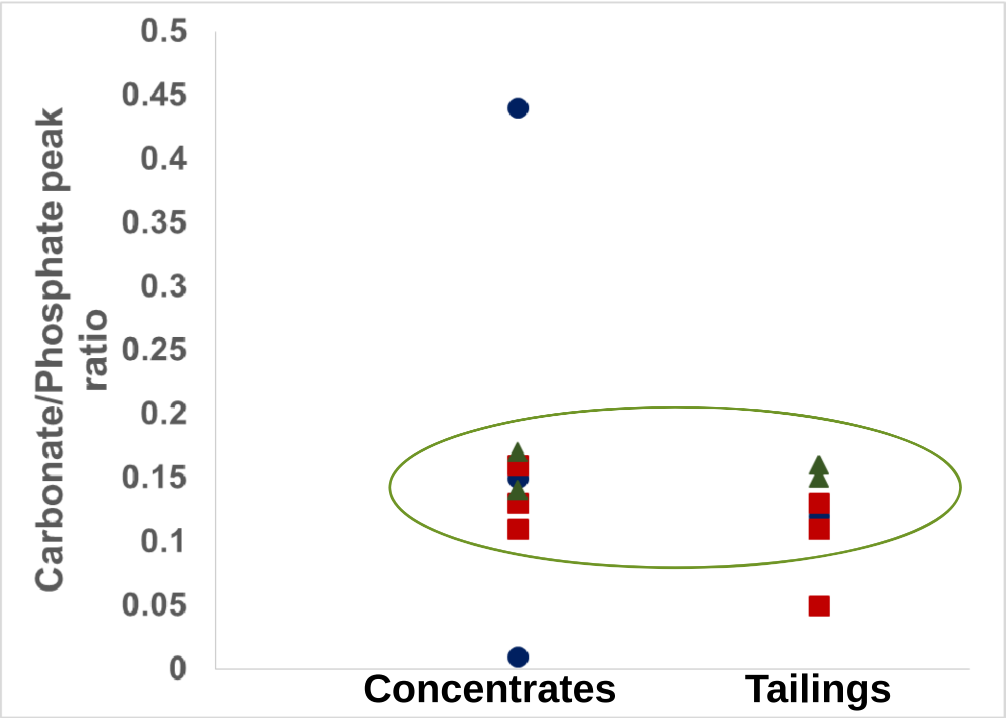
Figure 26. ATR Spectra of Three Coarse Black Particles Picked from the Concentrate of CF East Sample. Insert shows enlarged region due to stretching vibrations of the OH groups.

Table 2. Major Components of the PO_4^{3-} Band (Pleshko and others 1991).

Band Position, cm^{-1}	Assignment
960	$\nu_1 PO_4^{3-}$
996	PO_4^{3-} in apatitic environment
1020	Persistence of vacancies; nonstoichiometric apatites containing HPO_4^{2-} and/or CO_3
1032	PO_4^{3-} in stoichiometric apatites
1034	Type B carbonate apatites; hydroxyapatite
1056	Bands corresponding to the T_2 vibrational modes of apatite
1075	Bands corresponding to the T_2 vibrational modes of apatite
1092	Stoichiometric apatites
1109	Poorly crystalline apatites
1123	HPO_4^{2-}
1143	Apatites containing HPO_4^{2-}

Somasundaran et. al., Similarities and dissimilarities in Florida phosphate ore types, IMPC, 2010

Comparison of Good and Bad feed (Conc vs. tailings)



Carbonate substitution ruled out as reason for poor flotation performance

- **Carbonate substitution: no difference between conc. & tailings**
- **No systematic difference in width and position of PO_4^{-3} band**

Somasundaran et. al., Similarities and dissimilarities in Florida phosphate ore types, IMPC, 2010

Analysis of non-phosphate bands

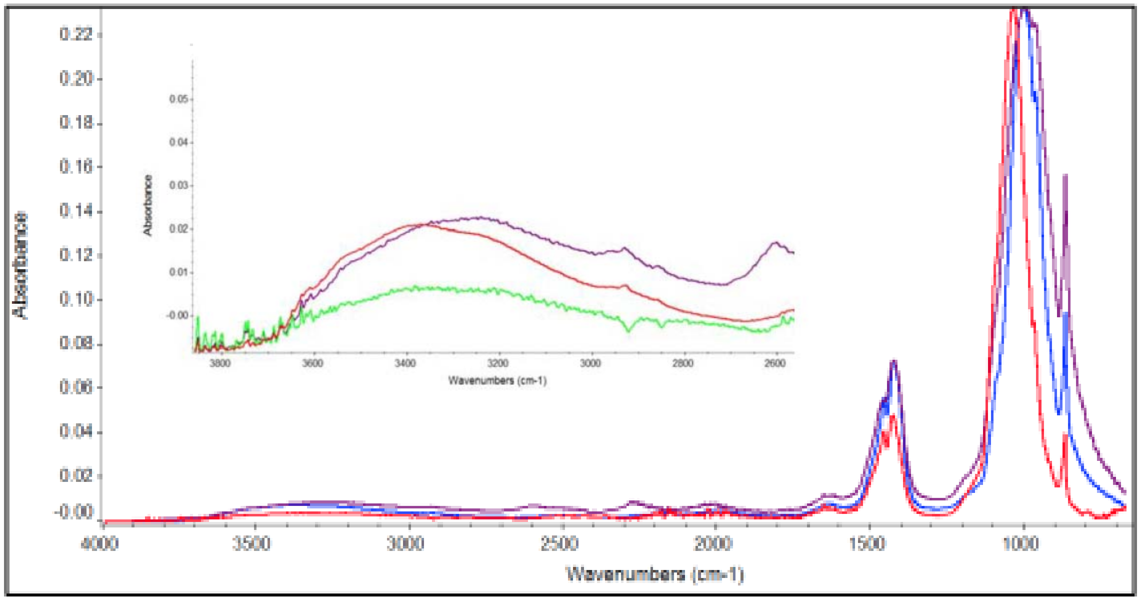


Figure 26. ATR Spectra of Three Coarse Black Particles Picked from the Concentrate of CF East Sample. Insert shows enlarged region due to stretching vibrations of the OH groups.

Absorption bands at ~2900-3000 cm^{-1} due to νCH vibrations of adsorbed oleate

- **Present in all concentrate phosphate particles but not on tailing particles**
- **What suppress oleate adsorption on tailings phosphate particles**
  - **acidic surface Al–OH–Al and SiOH groups and alumosilicate inclusions**

No noticeable difference in amount of dolomite and gypsum in tailings of bad or good samples

Somasundaran et. al., Similarities and dissimilarities in Florida phosphate ore types, IMPC, 2010
Effect of Particle Characteristics on Fatty Acid Flotation of Florida Phosphate Rock, Florida Institute of Phosphate Research, 2010

Conclusions

Isomorphically substituted carbonate groups typical of francolite

Descriptor of flotation performance

- **Carbonate substitution is not reason for poor flotation performance**
- **Dolomite or gypsum are not the culprits**
- **Fine phosphate tailing particles have surface silanols (from silica impurities)**
- **Coarse phosphate tailing particles have silicates**
- **Absorption bands at ~2900-3000 cm^{-1} due to vCH vibrations of adsorbed oleate**
  - **Present in all concentrate phosphate particles but not on tailing particles**

Oleate adsorption suppressed on tailings phosphate particles

- **acidic surface Al–OH–Al and SiOH groups and alumosilicate inclusions**

Key factors for poor flotation performance - slimes formation on surface and silicate inclusions in bulk

Tackling slimes formation – polymer flocculation of slime before flotation

A molecular dynamics study of the interaction of oleate and dodecylammonium chloride surfactants with complex aluminosilicate minerals

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Lithium minerals

Batteries - 39%; ceramics & glass - 30%; lubricating greases - 8%; & other uses - 22%

Chile & Argentina – major producer of lithium – from brine lakes

Lithium carbonate and chloride from brine lakes and salt pans

From complex silicate mineral

- **Spodumene [$LiAl(SiO_3)_2$]**
- **lepidolite, [$K_2Li_4Al_2F_4Si_8O_{22}$]**

https://minerals.usgs.gov/minerals/pubs/commodity/lithium/mcs-2017-lithi.pdf
https://minerals.usgs.gov/minerals/pubs/commodity/lithium/myb1-2014-lithi.pdf

Spodumene minerology

Spodumene ore occurs along with other silicate gangues and quartz

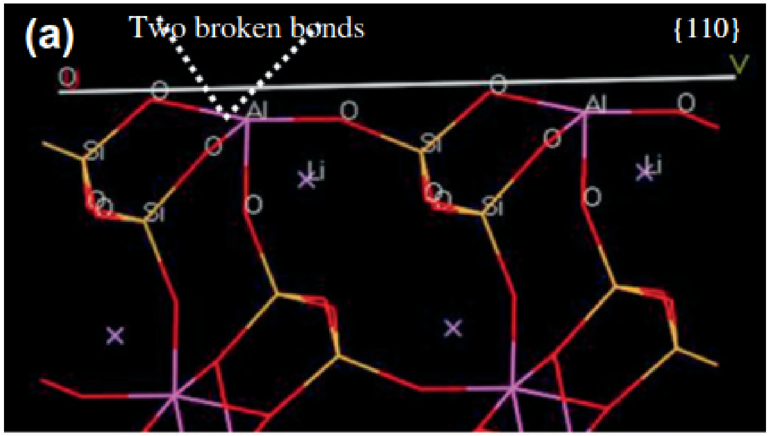
- For example, ore deposits from Kings Mountain, North Carolina contain by wt.
  - Spodumene [$LiAl(SiO_3)_2$] -20%,
  - Muscovite [$K_2Al_4(Al_2Si_6O_{20})(OH)_4$] -7%,
  - Feldspar [$KAlSi_3O_8$] – 43%
  - Quartz [SiO_2]– 30%

Spodumene is separated from other silicates using fatty acids (sodium oleate)

Prior literature

Moon and Fuerstenau (Int. J. Miner. Process. 72 (2003) 11)

1. Chemisorption of oleate on aluminum sites of the spodumene (1 1 0) plane as opposed to feldspar and muscovite
2. Oleate preferentially adsorbs on spodumene’s cleavage plane (1 1 0), as opposed to the nominal (0 0 1) plane Contact angle on (1 1 0) > (0 0 1)
   - two unsatisfied co-ordinations at Al sites on the (1 1 0) plane – ideal for oleate chemisorption.
   - Only one broken bond at Al sites on the (0 0 1) surface



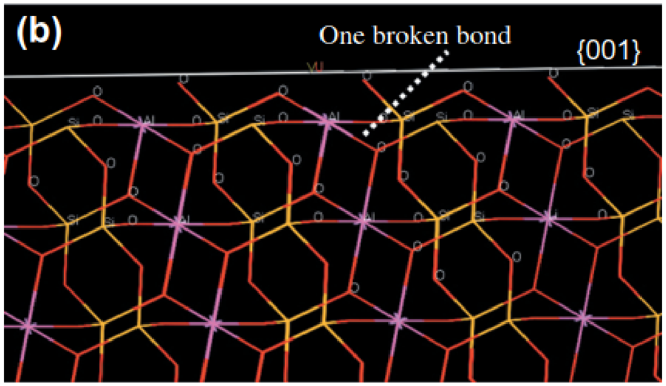


Fig. 2. Optimized model of spodumene (a) {1 1 0} and (b) {0 0 1} surfaces (color codes: Red – O, Yellow – Si, Pink – Al, and Violet – Li). (For interpretation of the

Rai et. al, Journal of Colloid and Interface Science 362 (2011) 510–516

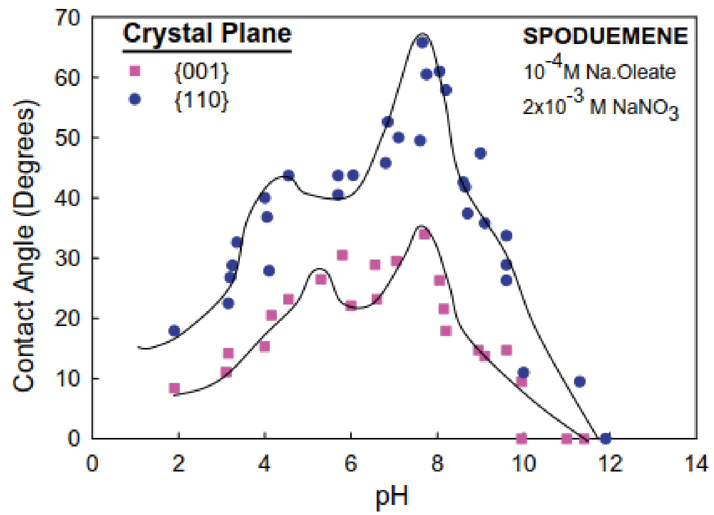
Prior literature

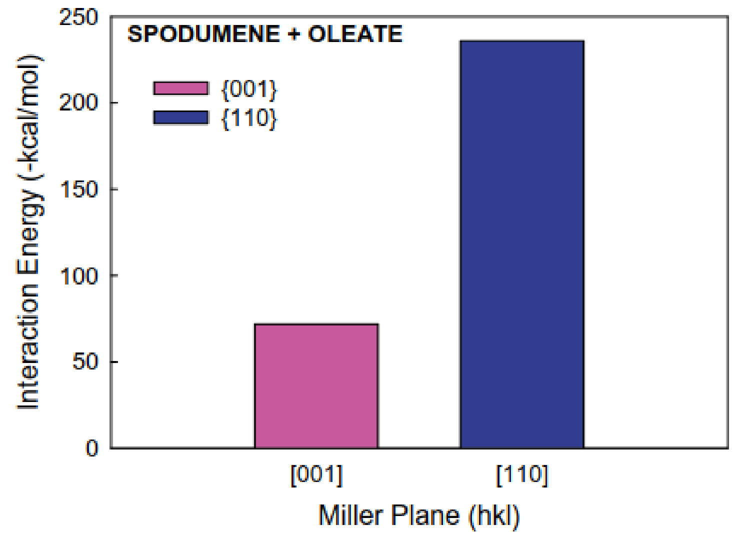
3. **Uniqueness of spodumene structure as opposed to muscovite and feldspar is confirmed with jadeite, $NaAl(SiO_3)_2$, which also chemisorbs oleate surfactant**

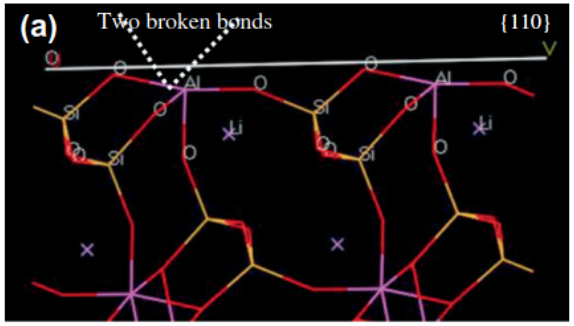
Goal

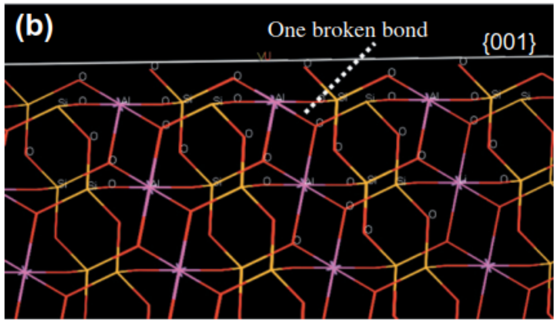
Can we theoretically capture these specific interactions using interaction energies evaluated through molecular dynamics simulations?

Oleate interaction with Spodumene (1 1 0) and (0 0 1)



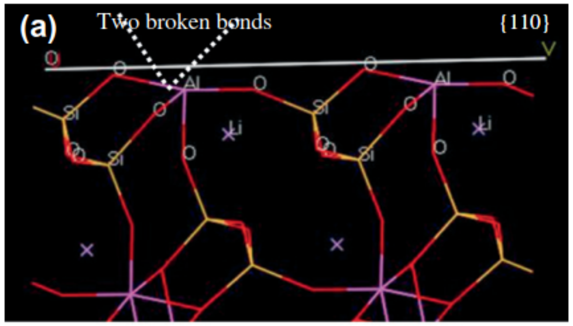




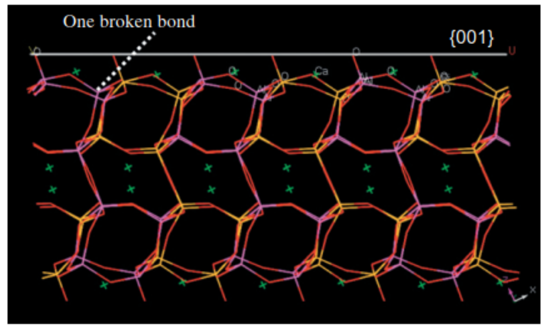


Rai et. al, Journal of Colloid and Interface Science 362 (2011) 510–516

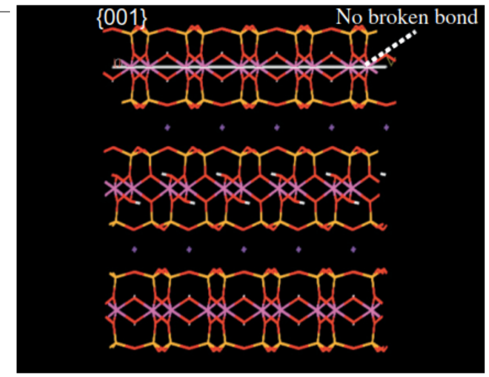
Spodumene vs. muscovite vs. feldspar



Spodumene (1 1 0)



Feldspar (1 1 0)



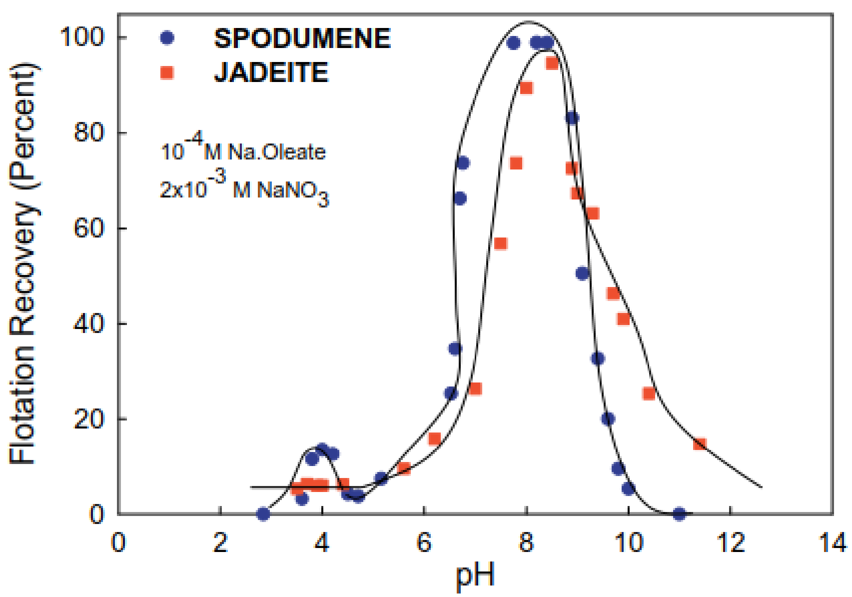
Muscovite (1 1 0)

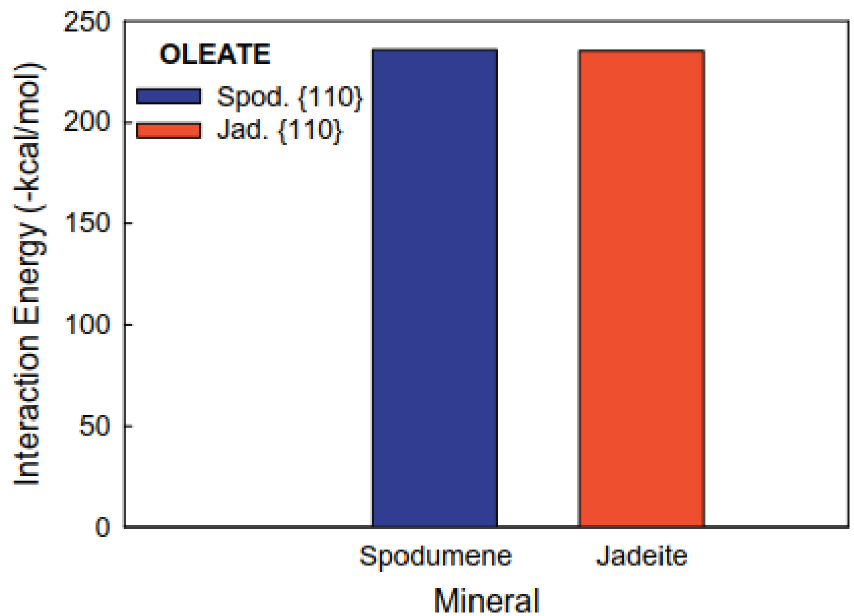
A comparison of computed interaction energies (kcal/mol) of oleate and water molecules on different aluminosilicate mineral surfaces [24,25,53,54].

Mineral	Molecule	
	Oleate	Water
Spodumene (1 1 0)	−235.8	−19.7
Anorthite (0 0 1)	−141.9	−3.7
Muscovite (0 0 1)	127.0	−3.4

Rai et. al, Journal of Colloid and Interface Science 362 (2011) 510–516

Similar recoveries of spodumene and jadeite





Rai et. al, Journal of Colloid and Interface Science 362 (2011) 510–516

Conclusions

1. **Oleate selectivity to spodumene is theoretical captured (matching the experimental observations)**
2. **A predictive methodology developed using**
   - **Combination of interaction energies from molecular dynamics simulations and an analysis of surface geometric features and surfactant packing**

Acknowledgements

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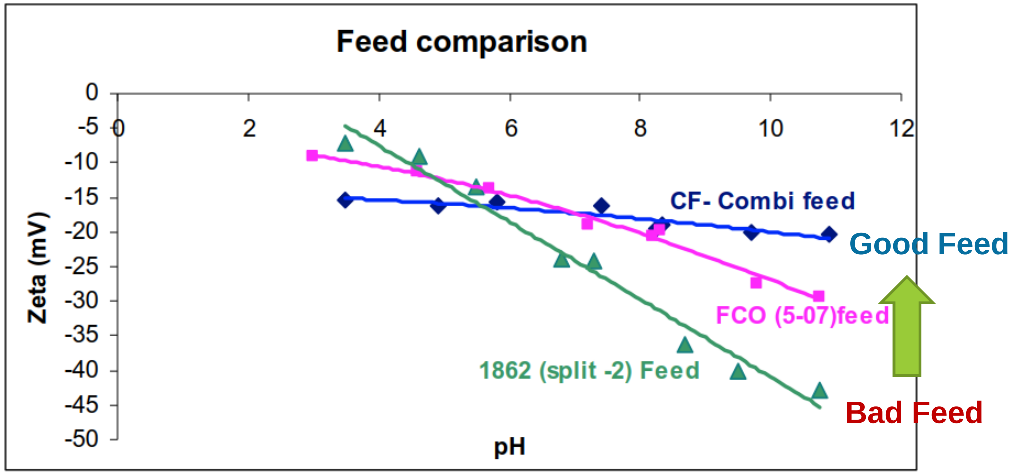
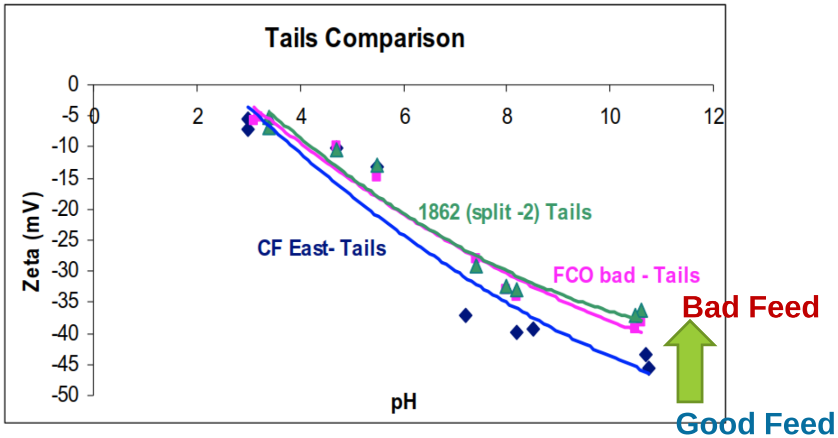
Thank you!

Electrokinetics: Zeta potentials



Zeta Potential of Phosphate Samples (FCO 5-07, 1862-S2 and CF Combined Feed).



Zeta Potential of Phosphate Samples (FCO Bad, 1862-S2, and CF Combined Tails).

Bad-feed: surface presence of quartz or siliceous minerals (either as inclusions or as slimes)

Tails of Bad-feed: less siliceous (because of reporting of phosphate minerals)

Concentrates: both good and bad feeds similar or inconclusive

Somasundaran et. al., Similarities and dissimilarities in Florida phosphate ore types, IMPC, 2010