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Phosphate Beneficiation with Novel Collectors for Direct and Reverse Flotation: Beyond Low Cost Fatty Acids

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Phosphate Beneficiation with Novel Collectors for Direct and Reverse Flotation

BEYOND LOW COST FATTY ACIDS

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what is precious to you?

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Historical Review and Future Trends

- Direct flotation of phosphate with fatty acids has been practiced in Florida since the 1920s.
- In 1942, Arthur Crago patented a double float process using a “negative-ion agent” for a rougher float followed by a “positive-ion agent” to remove silica.
- Direct flotation alone or in a double float process is still the prevalent method for flotation of phosphates in the United States, Brazil, Russia, Vietnam, South Africa and many other parts of the world.
- Direction flotation collectors are mostly low cost fatty acids derived from either tall oil or vegetable sources
- Alternative uses for low cost fatty acids are emerging:
  - UPM Biofuels started production of tall oil-based biodiesel in Lappeeranta in January 2015. Capacity is 100,000 tonnes/yr.
  - SunPine started producing crude tall diesel from tall oil in Pitea, Sweden in 2010. Now producing 100,000 tons/yr.

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Historical Review and Future Trends

– The highest feed grades that are suitable to float with low cost fatty acids are being exhausted:
  - The southern part of the Florida bone valley is rich in dolomite
  - New deposits in South America and Africa contain significant amounts of carbonates
– Reverse flotation with amines and specialized anionic collectors is necessary in some regions of the world, particularly where carbonates are a significant portion of the gangue.
– Phosphate mine operators are beginning to value increased recovery of mined material, and the corresponding extension of mine life.
– Clariant is developing specialized anionic and cationic collectors to deliver increased recovery and grade using a global network of mining laboratories.

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Clariant's Global Mining Footprint

Clariant Mining Laboratories

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Reverse Flotation in Central Africa

– Cominco Hinda Project:

- Francolite ore with 19% P_2O_5, 3.5% MgO and 24.8% silica in flotation feed
- Flotation targets: 32% P_2O_5 and <0.80% MgO
- Targets achieved with reverse flotation in one rougher and one cleaner step

Figure 1. P_2O_5 Recovery versus P_2O_5 Grade for Central Africa flotation

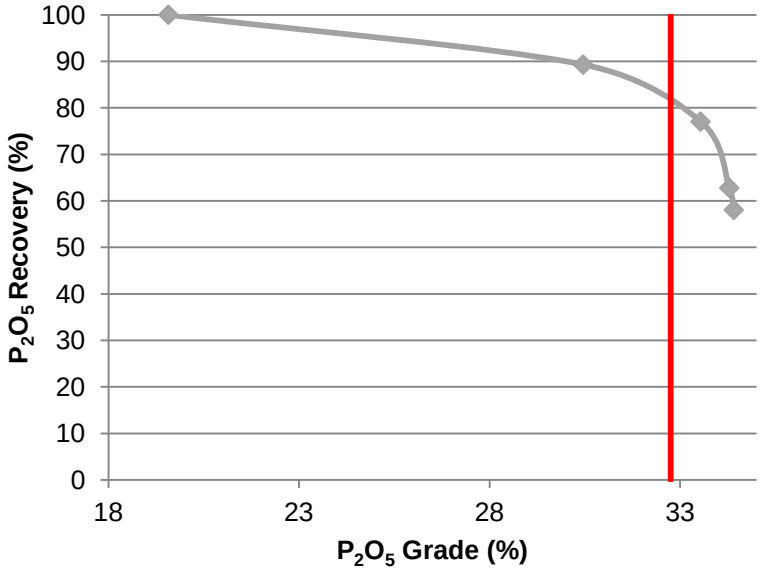
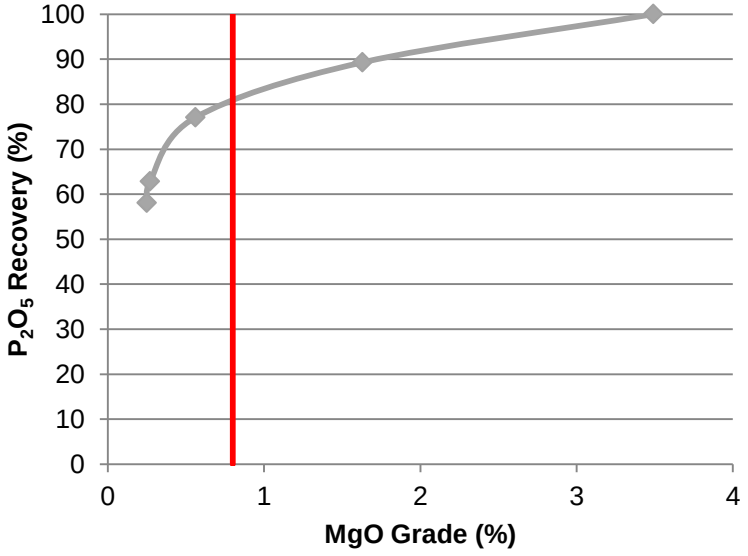


Figure 2. P_2O_5 Recovery versus MgO Grade for Central Africa flotation



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Reverse Flotation in Central Africa

– Experimental Details:

- Feed ground to 80% passing 190 microns.
- Reverse flotation with sodium tripolyphosphate as a phosphate depressant and sequential treatment with an anionic collector (Flotinor 7463) and two cationic collectors (Flotigam 7457 and Flotigam 7510).
- Flotation at pH 5.5, controlled with sulphuric acid.
- Additional reagents dosed for each of three reverse cleaner stages
- Conditioning times for each reagent and each step optimized based on multiple experiments.
- Target results obtained with just rougher and the first cleaner stage.

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Reverse Flotation in Central Africa

Table 1. Detailed Analysis of Rougher + 3 Cleaner Stages in Reverse Flotation

Product streams	Mass (g)	Mass (%)	Grade						Recovery					
			P_2O_5 %	MgO %	Al_2O_3 %	SiO_2 %	CaO %	Fe_2O_3 %	P_2O_5 %	MgO %	Al_2O_3 %	SiO_2 %	CaO %	Fe_2O_3 %
Reverse Rougher Conc. 1 (RRC 1)	175.6	42.6	4.92	6.00	2.20	51.90	16.00	0.05	10.70	73.22	78.69	89.05	19.60	79.29
Reverse Rougher Conc. 2 (RRC 2)	51.3	12.4	19.30	5.50	1.40	16.80	37.20		12.26	19.61	14.63	8.42	13.31	0.00
Reverse Rougher Conc. 3 (RRC 3)	37.6	9.1	30.60	1.70	0.50	4.40	49.00		14.25	4.44	3.83	1.62	12.85	
Reverse Rougher Conc. 4 (RRC 4)	11.7	2.8	32.90	0.40	0.40	3.30	50.40		4.77	0.33	0.95	0.38	4.11	
Product +150um	50.8	12.3	35.10	0.01	0.10	0.40	53.30		22.08	0.04	1.03	0.20	18.89	0.00
Product -150um	85.4	20.7	34.00	0.40	0.05	0.40	52.40		35.95	2.37	0.87	0.33	31.22	
Calculated Feed	412.4	100.0	19.58	3.49	1.19	24.82	34.75	0.03	100.00	100.00	100.00	100.00	100.00	100.00

Cumulative products	Mass (g)	Mass (%)	Grade						Recovery					
			P_2O_5 %	MgO %	Al_2O_3 %	SiO_2 %	CaO %	Fe_2O_3 %	P_2O_5 %	MgO %	Al_2O_3 %	SiO_2 %	CaO %	Fe_2O_3 %
Product	136.2	33.0	34.41	0.25	0.07	0.40	52.74	0.00	58.03	2.41	1.90	0.53	50.11	0.00
Product +RRC4	147.9	35.9	34.29	0.27	0.09	0.63	52.55	0.00	62.80	2.73	2.86	0.91	54.23	0.00
Product +RRC4+RRC3	**185.5**	**45.0**	**33.54**	**0.56**	**0.18**	**1.39**	**51.83**	**0.00**	**77.04**	**7.18**	**6.69**	**2.53**	**67.08**	**0.00**
Product +RRC4+RRC3+RRC2	236.8	57.4	30.46	1.63	0.44	4.73	48.66	0.00	89.30	26.78	21.31	10.95	80.40	0.00
Product +RCC4+RRC3+RRC2+RRC1	412.4	100.0	19.58	3.49	1.19	24.82	34.75	0.02	100.00	100.00	100.00	100.00	100.00	79.29

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Reverse Flotation in Central Africa

- Simplified Flow Sheet
  - only one cleaner float
  - testing the same amine in rougher and cleaner
- $Na_5P_3O_{10}$ used as a depressant at 780 g/ton

Table 2. Reagents and Dosages for Simplified Flowsheet

Test	Rougher Collectors	Dosage (g/ton)	Cleaner Collectors	Dosage (g/ton)
Test 1	Flotinor 7463	436	Flotinor 7463	97
	Flotigam 7457	436	Flotigam 7510	97
Test 2	Flotinor 7463	450	Flotinor 7463	100
	Flotigam 7457	450	Flotigam 7510	100
Test 3	Flotinor 7463	450	Flotinor 7463	100
	Flotigam 7457	450	Flotigam 7457	100

Table 3. Metallurgical Results of Testing Simplified Flowsheet

Test	P_2O_5 Recovery (%)	P_2O_5 Grade (%)	MgO Grade (%)
Test 1	77.04	33.54	0.56
Test 2	74.65	33.70	0.50
Test 3	73.64	33.90	0.60

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Reverse Flotation in Central Africa

– Further increase in P_2O_5 recovery by scavenging the combined froth of the rougher and cleaner reverse floats:

  - The cleaner underflow is the primary product stream
  - The scavenger underflow can be added back to the rougher feed to increase the feed grade and increase the overall recovery.

Table 4. Scavenger circuit metallurgical results

Stream	Mass (g)	Mass (%)	Grade (%)			Recovery (%)		
			P_2O_5	MgO	SiO_2	P_2O_5	MgO	SiO_2
Scavenger Froth	416.7	52.7	8.1	6.1	44.7	21.2	86.6	94.7
Scavenger Underflow	39.0	4.9	30.4	2.3	3.7	7.5	3.1	0.7
Cleaner Underflow	335.8	42.4	33.7	0.9	2.7	71.3	10.3	4.6
Feed	791.5	100.0	20.0	3.7	24.9	100.0	100.0	100.0

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Reverse Flotation in Central Africa

– Conclusions:

- Reverse flotation with anionic and cationic collectors and a phosphate depressant allows for recovery of 77% of the phosphate at a grade of 33.5% P_2O_5 and only 0.6% MgO.
- A scavenger circuit allows for recovery of additional phosphate quantities through scavenging of the rougher and cleaner froths from the primary circuit.
  - The scavenger underflow froth can be added to rougher feed to recover additional quantities of phosphate and improve overall feed grade.

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Reverse Flotation in North Africa

- Ore with 22.3% P_2O_5, 6.4% MgO and 6.9% silica in flotation feed.
- Ground to P100 150 microns.
- Target of <0.65% MgO achieved with reverse flotation in one rougher followed by four cleaner flotation stages.
- Sodium tripolyphosphate, Anionic collector Flotinor 7466 and cationic collector Flotigam 7470 added in each of the five flotation stages.

Table 5. Reagents and overall dosages for North African Phosphate

Reagent	Function	Total Dosage (g/ton)
$Na_5P_3O_{10}$	Depressant	1050
Flotinor 7466	Anionic Collector	600
Flotigam 7470	Cationic Collector	420

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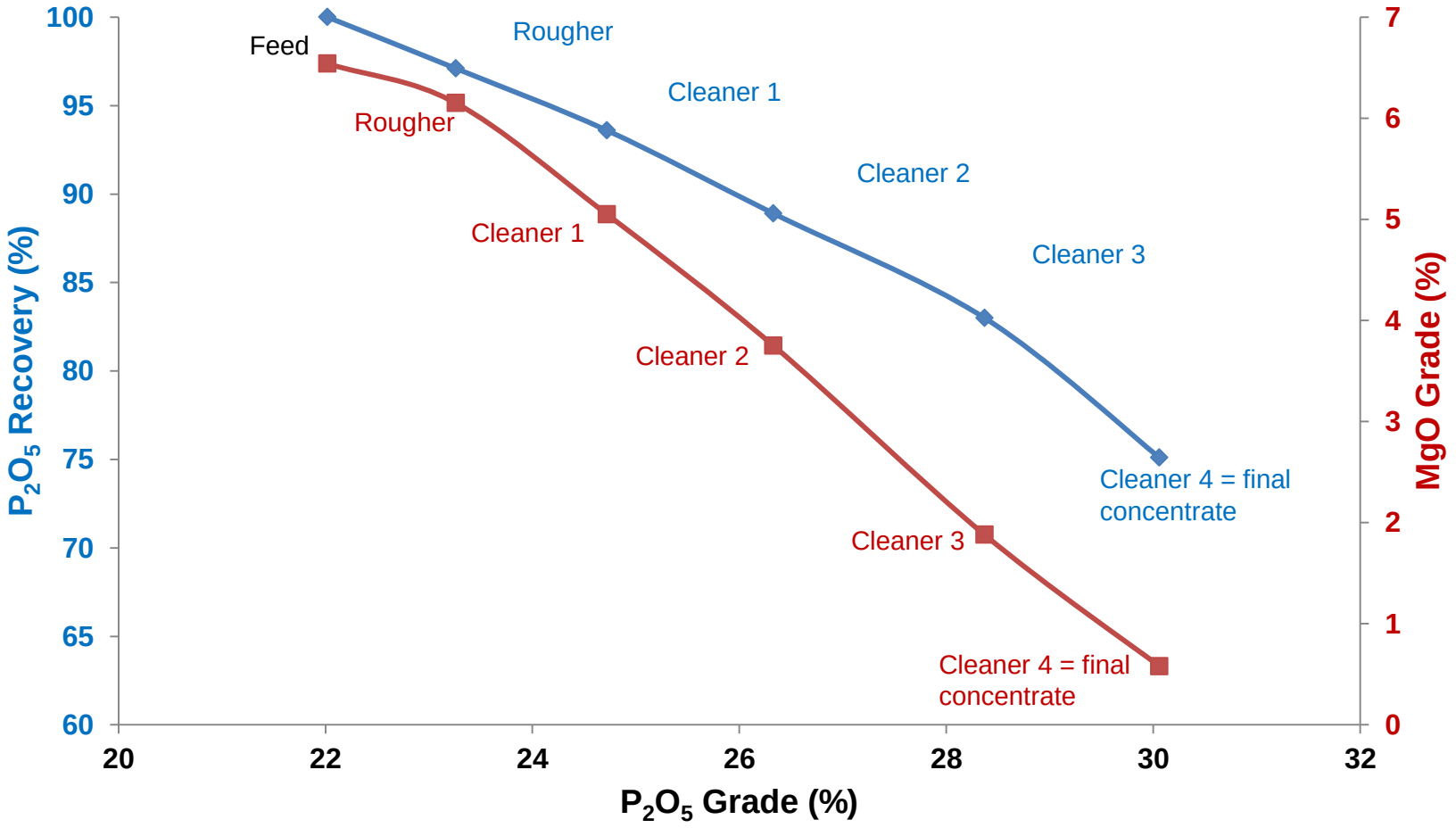
Reverse Flotation in North Africa

Figure 3. P_2O_5 Recovery and MgO Grade versus P_2O_5 Grade for North Africa Phosphate



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Reverse Flotation in North Africa

Table 6. Metallurgical Results of Flotation Experiments with North African Phosphate

Fraction	Recovery (%)		
	P_2O_5	MgO	SiO_2
Feed	100.0	100.0	100.0
Feed-T1	97.1	86.5	71.7
Feed-T1-T2	93.6	64.4	57.1
Feed-T1-T2-T3	88.9	42.7	46.9
Feed-T1-T2-T3-T4	83.0	18.6	39.6
Feed-T1-T2-T3-T4-T5	75.1	4.9	34.6

Fraction	Grade (%)		
	P_2O_5	MgO	SiO_2
Feed	22.02	6.54	6.92
Feed-T1	23.26	6.15	5.40
Feed-T1-T2	24.72	5.05	4.73
Feed-T1-T2-T3	26.33	3.75	4.37
Feed-T1-T2-T3-T4	28.37	1.88	4.25
Feed-T1-T2-T3-T4-T5	30.06	0.58	4.35

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Reverse Flotation in North Africa

- Target of <0.65% MgO achieved at 75.1% recovery of P_2O_5 and 4.4% SiO_2.
- The number of cleaner cycles required is ore dependent and generally increases as the dolomite content in the feed increases.
- Reagent dosages of anionic and cationic collectors are tuned to the specific requirements of each mine.

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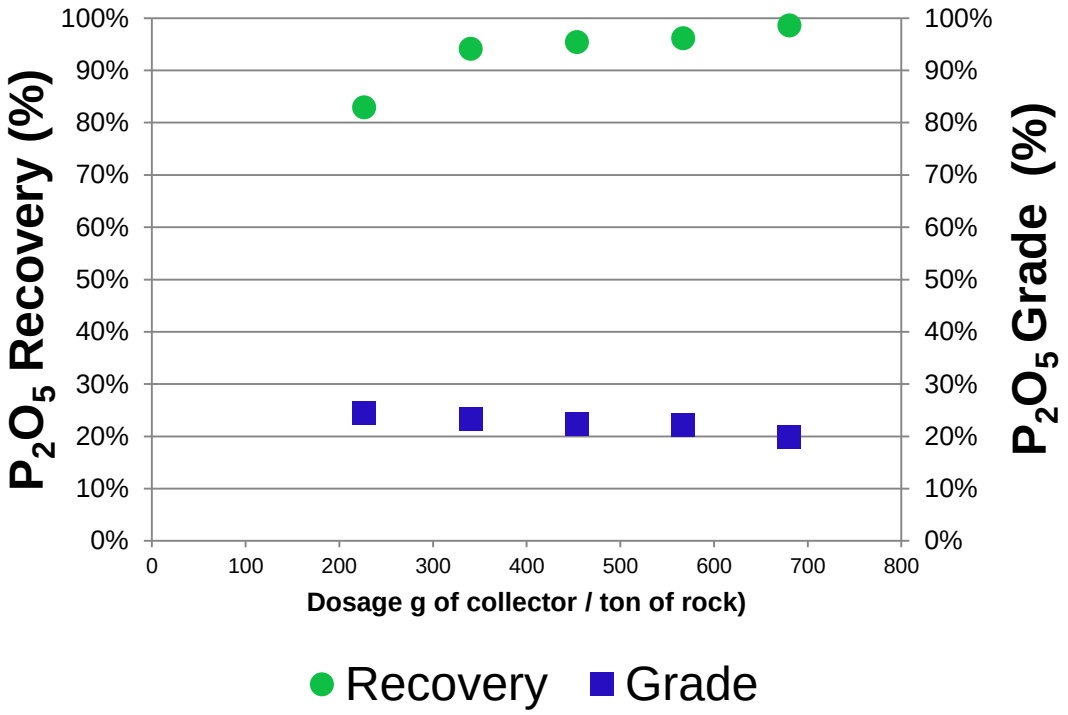
Direct Flotation in North America

- Sedimentary Francolite Phosphate ore, 5.3% P_2O_5
- First step of Crago process using published laboratory procedure*
- 72% solids conditioning with unsaponified collector and fuel oil at pH 9.3, 50 seconds
- 20% solids in flotation
- Adjusted water (50 ppm Ca)
- Collector Flotinor 7474

Figure 4. Flotation results for a North American sedimentary ore



*Glen Oswald, Glenn Gruber, Charles Guan, ***How to Conduct a "Standard" Florida Phosphate Lab Flotation Test***, Beneficiation of Phosphates, SME, 2010, pp. 337-344

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Direct Flotation in North America

– Acid Insolubles in feed 82.7%

Figure 5. Acid Insolubles versus collector dosage for a North American sedimentary ore

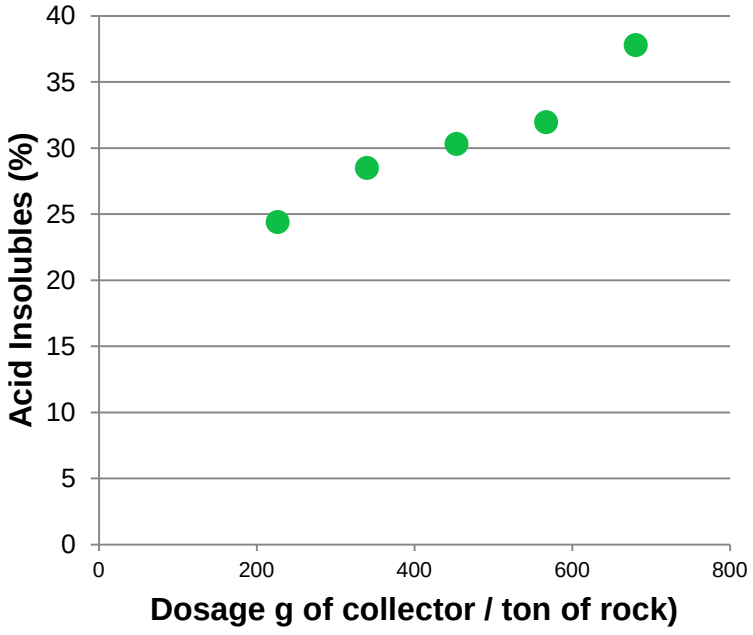
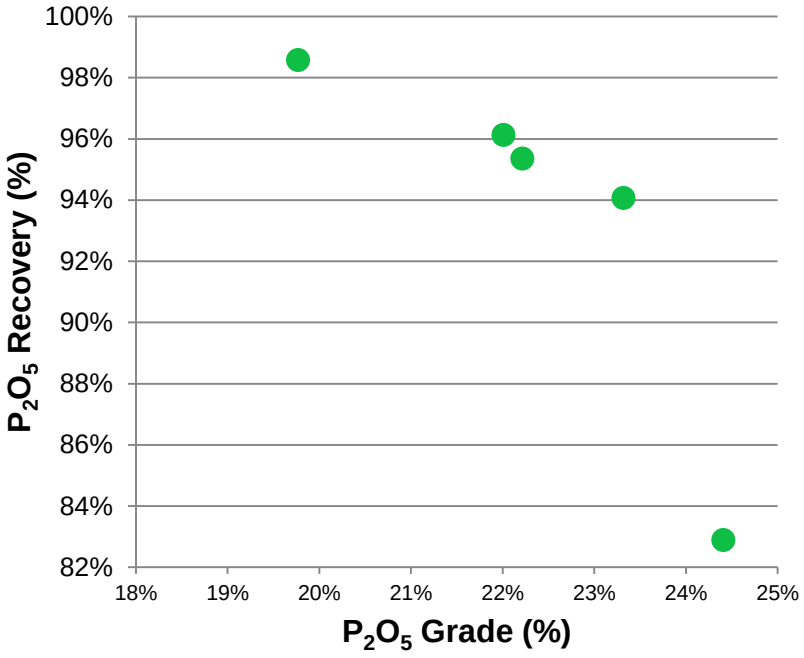


Figure 6. Recovery versus grade for a North American sedimentary ore



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Direct Flotation in Africa

- Weathered stockpile of Igneous Phosphate ore (pyroxenite)
- Low feed grade (<6.5% P_2O_5)
- High solids conditioning:
  - with alkylbenzene sulphonic acid depressant (300 g/ton, 3 min),
  - followed by saponified collector, 3 min
- 20% solids flotation with Rougher (2 min) + Cleaner (45 s) + Recleaner (45 s) flotation scheme

Table 7. Flotation results for an African igneous phosphate ore

Collector	Dosage (g/ton)	Concentrate Grade (% P_2O_5)	P_2O_5 Recovery (%)
Local fatty acid	300	26.20	82.02
Flotinor 7496	300	28.20	84.74
Flotinor 7496	200	28.20	82.48

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Direct Flotation in South America

- Igneous Phosphate ore
- 35% P_2O_5 required
- Starch depressant (500 g/ton)
- 200 g/ton collector
- Rougher (3 min) + Cleaner (2 min) flotation scheme
- P80 = 248 microns

Table 8. Flotation results for a South American igneous phosphate ore

Collector	Grade P_2O_5 (wt %)	Recovery P_2O_5 (wt %)
Local Fatty Acid	33.04	61.00
Flotinor 7493	28.66	96.05
Flotinor 7487	36.87	90.58
Flotinor 7498	36.48	91.24
Flotinor 7505	36.33	92.74

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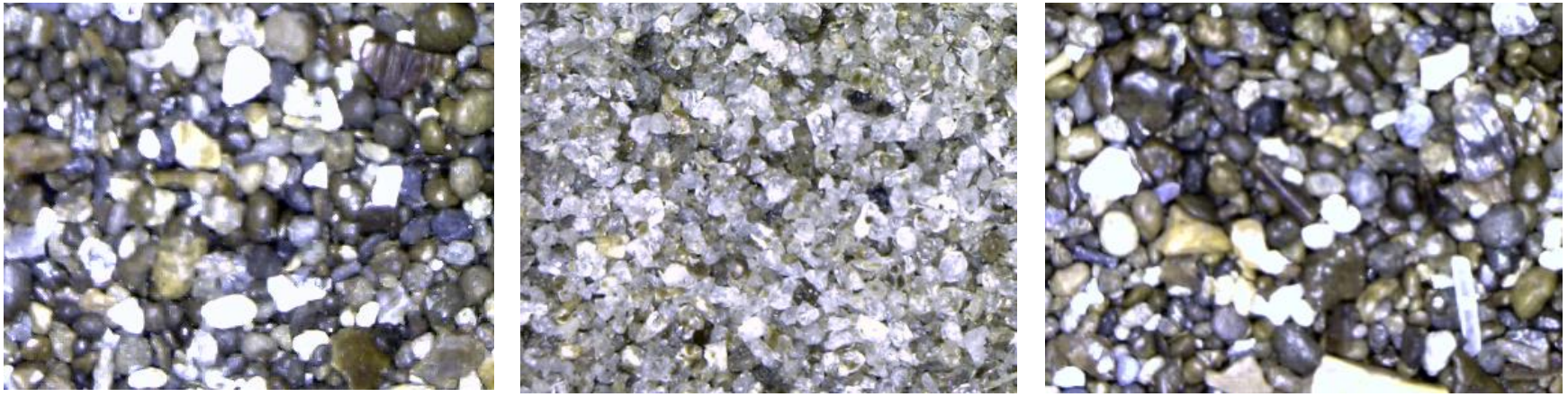
Reverse Flotation in North America

- Ore with 6.5% SiO_2 in flotation feed. The target is to achieve less than 3% SiO_2.
- Flotigam 7454 and Flotigam 7516 amine collectors evaluated in single reverse floats, and SiO_2 grade versus dosage curves were developed.
- 1.8% SiO_2 achieved at 98% P_2O_5 recovery with Flotigam 7516 with 180 g/ton.
- 2.5% SiO_2 achieved at 99% P_2O_5 recovery with Flotigam 7454 with 180 g/ton.

Feed | Tails | Concentrate



Representative images for Flotigam 7454 with 360 g/ton

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Reverse Flotation in North America

Figure 7. Phosphate recovery and acid insolubles versus collector dosage for Flotigam 7516

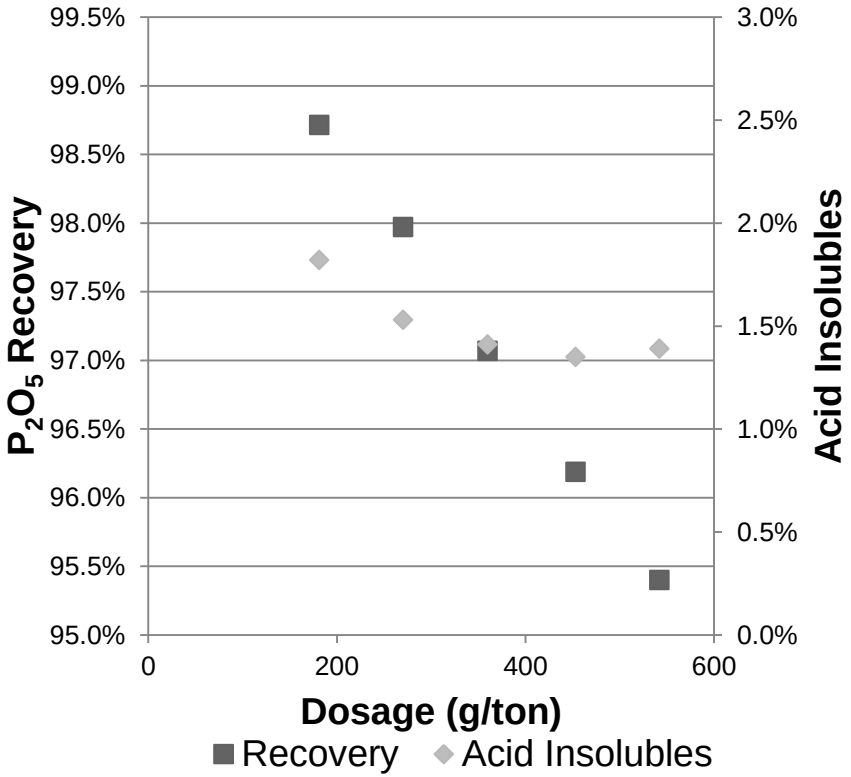
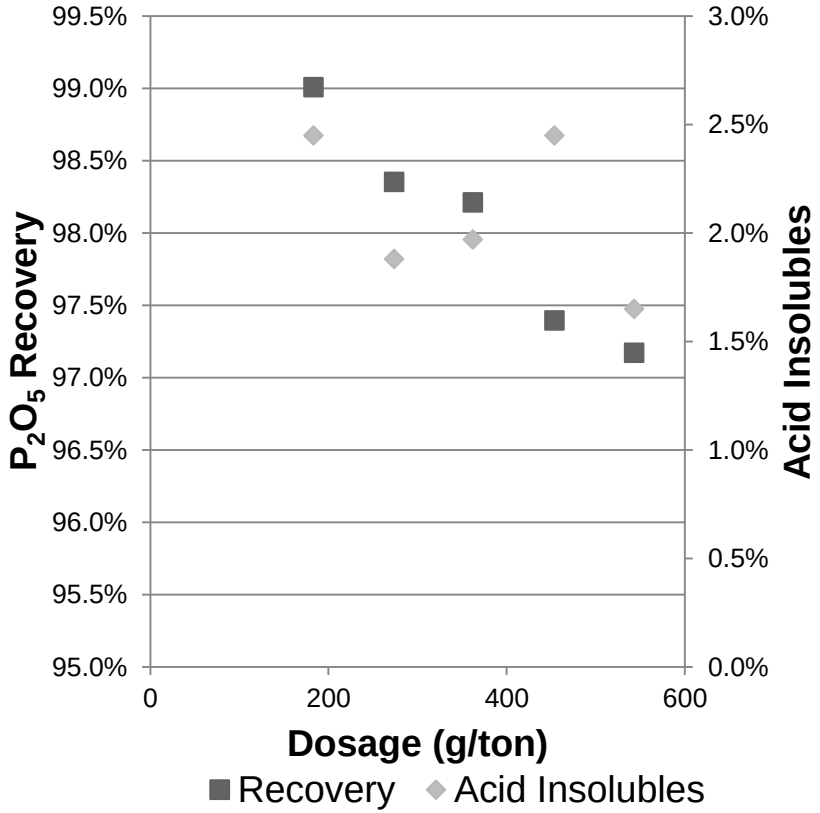


Figure 8. Phosphate recovery and acid insolubles versus collector dosage for Flotigam 7454



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Conclusions

- Difficult to float ores that cannot be beneficiated with low cost anionic collectors can be effectively beneficiated with new anionic and cationic collectors.
- Central Africa Phosphate ore can be beneficiated to less than 0.8% MgO with 78% recovery by reverse flotation and the use of scavenger circuits.
- North Africa Phosphate can be beneficiated to less than 0.65% MgO with 76% recovery by reverse flotation.
- Recoveries as high as 98% were obtained in North American francolite samples using the standard Florida flotation method as described in the literature.
- Recoveries of 99% achieved in reverse flotation to remove silica to less than 3%.
- Recoveries over 90% were obtained by direct flotation for a South American igneous ore where local low cost fatty acids could only deliver 61% P_2O_5 recovery in laboratory testing.

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