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Can Your P2O5 Be Commercially Exploited?

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Company Profiles

Phosphate Consulting LLC is a consulting and engineering company specializing in the development of phosphate beneficiation projects. In association with our business partners, we also provide consulting and engineering services for projects encompassing the entire spectrum of phosphate development, including: mining, geology, phosphoric acid, sulfuric acid, and granular fertilizers.

WorleyParsons is a technology independent engineering and services company that provides pit-to-fertilizer-to-port engineering and project services, and also offers a wide range of consulting services. The WorleyParsons Phosphate Center of Excellence, located in Melbourne, is used to support our global offices to offer an unmatched blend of global quality and local knowledge.

Statement of the Problem

- World reserves of high-grade, high-quality phosphate rock are steadily decreasing. As a result, lower quality rock is being increasingly evaluated to determine its potential for commercial exploitation.
- Most early stage phosphate feasibility studies tend to focus on the P_2O_5 content and de-emphasize the other chemical constituents or impurities in the rock. It is the remainder of the chemical constituents that define the quality of the P_2O_5 concentrate and its potential for conversion to phosphate fertilizers.
- Once the chemical analyses of a representative phosphate rock product are known, it is often possible to predict the suitability of the rock as feed for conventional wet process phosphoric acid production.
- Ultimately, phosphoric acid pilot plant testing is required.

This paper is presented to give a general understanding of the conventional wet acid process for conversion (acidulation) of phosphate rock as it relates to the presence and concentration of the major chemical constituents usually associated with phosphate rocks. Five case studies are presented.

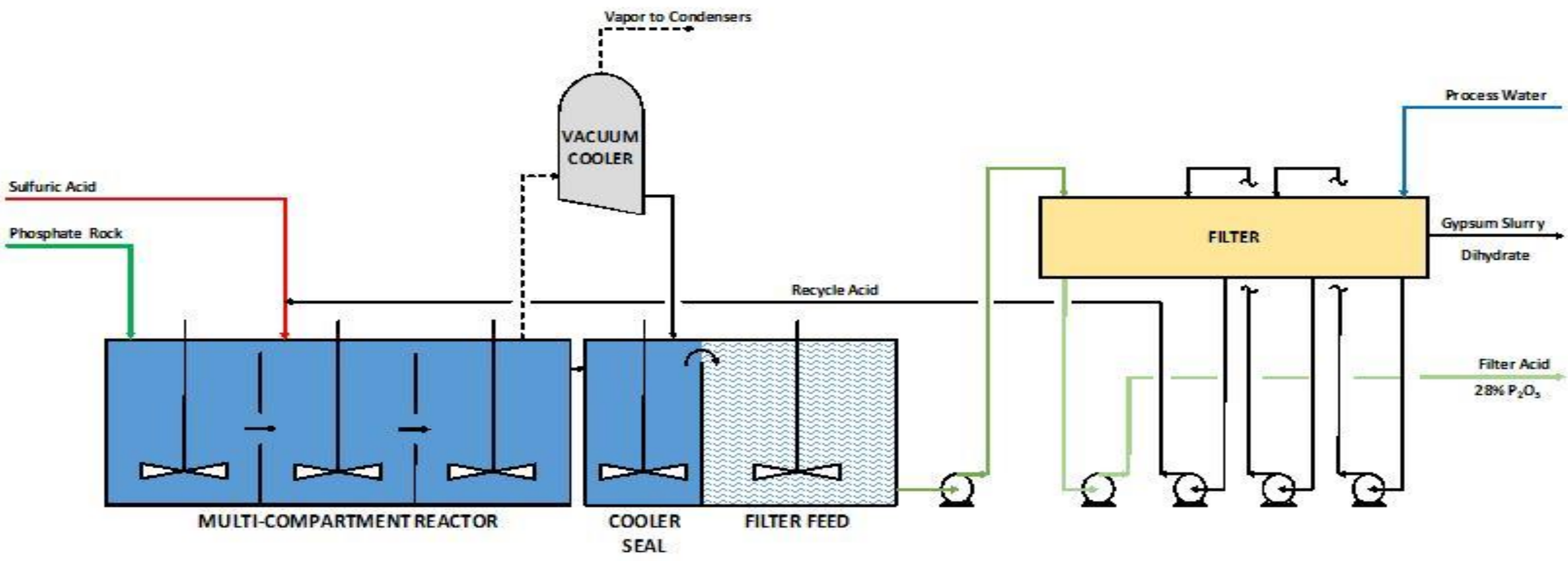
Background

- There is no substitute for phosphorus in agriculture. It is essential for plant nutrition and plays a critical role in photosynthesis and plant growth.
- Phosphate rock, when used in a natural or untreated form, is not very soluble and provides little available phosphorus to plants.
- Treating phosphate rock with sulfuric acid produces phosphoric acid, the water-soluble material from which most phosphate fertilizers are derived. Calcium sulfate (gypsum), the main byproduct of this reaction, can exist in three different forms.

Dihydrate:	$CaSO_4 \cdot 2H_2O$
Hemihydrate:	$CaSO_4 \cdot ½H_2O$
Anhydrate:	$CaSO_4 \cdot H_2O$

- Commercially, phosphoric acid is produced using several wet processing routes, each characterized by the form of gypsum produced. The processing routes most commonly offered today are the dihydrate (DH) and the hemihydrate (HH) methods. Approximately 80% of wet acid processing plants utilize the DH process and is described following.

The Dihydrate Process



Phosphate rock concentrate (fluorapatite, represented as $Ca_{10}(PO_4)_6F_2$) is reacted with sulfuric acid at a temperature and phosphoric acid concentration such that calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), or gypsum, is precipitated.

$$Ca_5(PO_4)_3F + 5\ H_2SO_4 + 10\ H_2O \rightarrow 5\ (CaSO_4 \cdot 2H_2O) + 3\ H_3PO_4 + HF$$

Phosphate Rock Impurities

- Phosphate rock is a complex raw material that affects plant operation in numerous ways.
- Considering the production of phosphoric acid, all phosphate rock elements that are not PO_4^{3-} or Ca^{2+} are considered to be impurities.
- If these impurities are not soluble, they typically have a limited impact on the wet phosphoric acid process.
- However, once the ions are in solution in the acid, problems can occur such as:
  - corrosion
  - poor filtration
  - scaling
  - poor fertilizer quality
  - production of sludge
  - increased acid viscosity
  - process instability

Typical Chemical Constituents of Phosphate Rock

Calcium (%CaO)
Magnesium (%MgO)
Iron (%Fe_2O_3)
Aluminum (%Al_2O_3)
Silica (%SiO_2)
Chlorine (%Cl)
Fluorine (%F)
Carbon Dioxide (CO_2) and Organics
Sulfides
Sodium (Na_2O) and Potassium (K_2O)
Heavy metals, rare earths, and other elements.

Traditional Concentrate Quality Guidelines for DH Phosphoric Acid Production and 18-46-0 DAP Manufacture

		Acceptable Range
Phosphate	% P_2O_5	28 to 36%
Calcium	weight ratio CaO/P_2O_5	1.3 to 1.6
Magnesium	%MgO	<0.6%
Iron+Aluminum	$\%Fe_2O_3+Al_2O_3$	<3.0%
Aluminium	% Al_2O_3	0.5 to 1.5%
MER	see next slide	0.03 to 0.1 ratio
Silica – insoluble	% SiO_2	>6%
Silica – soluble	% SiO_2	<0.8%
Chlorine	low/med/high	300/500/1000 ppm
Carbon Dioxide	CO_2+Organics	<4.5%
Fluorine	%F	3 to 4%
Sodium	% Na_2O	<0.8%
Potassium	% K_2O	<0.8%
Heavy Metals		

Minor Element Ratio

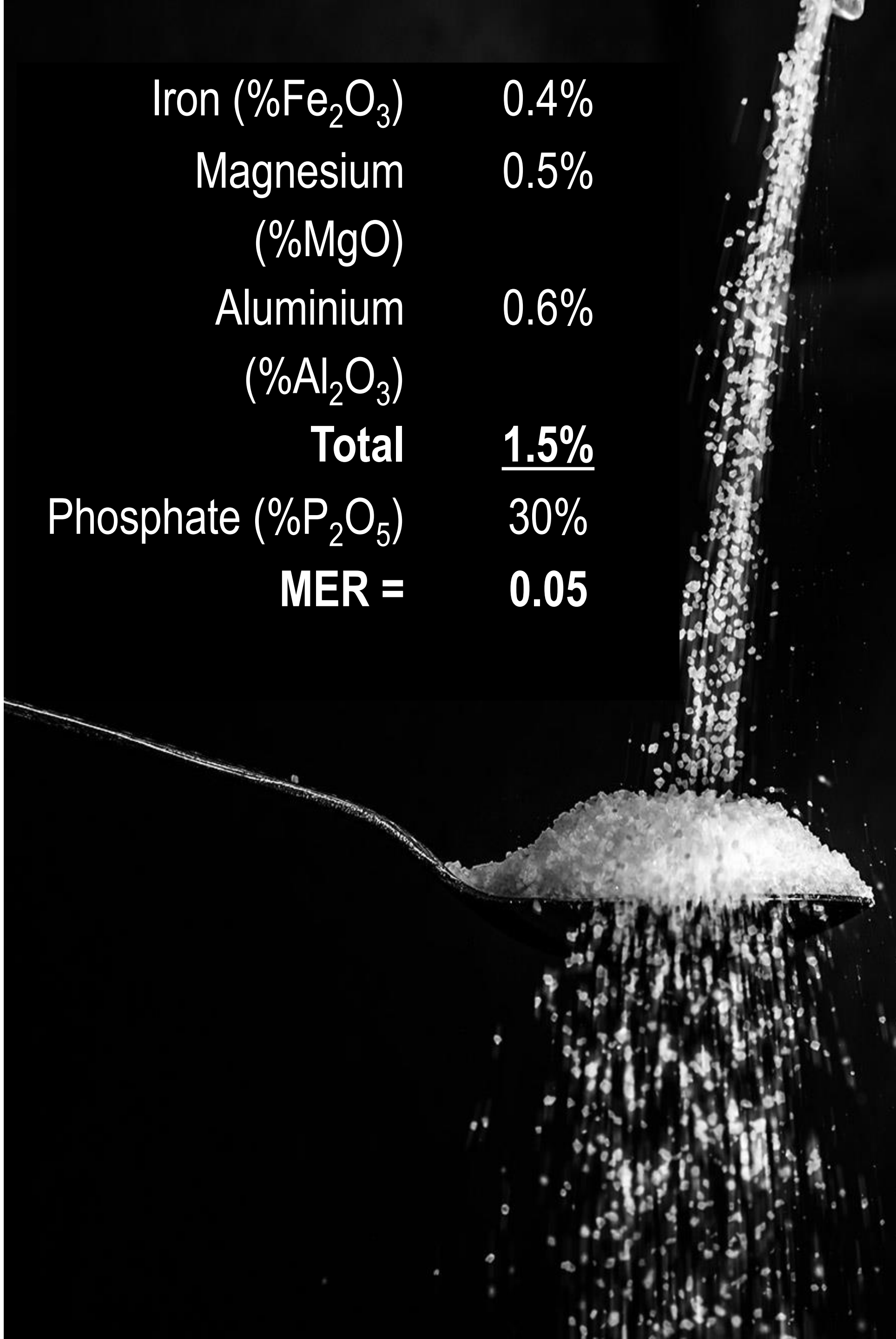
A little please but not too much!

- Minor Element Ratio (MER) =

$$\frac{\%Fe_2O_3 + \%MgO + \%Al_2O_3}{\%P_2O_5}$$

- MER specification 0.03 to 0.1
- MER < 0.01 gypsum crystal formation is difficult
- > 3% (Fe + Al) increases acid viscosity, impacts gypsum crystal growth and creates insoluble components

Iron ($\%Fe_2O_3$)	0.4%
Magnesium ($\%MgO$)	0.5%
Aluminium ($\%Al_2O_3$)	0.6%
Total	**1.5%**
Phosphate ($\%P_2O_5$)	30%
MER =	**0.05**



Case Studies

Five case studies are discussed. In all case studies, the phosphate rock concentrate was evaluated based on chemical analyses alone. The rock was subsequently acidulated in the continuous pilot plant using the dihydrate mode of operation and the phosphoric acid was evaluated to determine if commercial grade DAP with an N-P-K grade of 18-46-0 could be produced. The predicted test results were then compared to the actual test results.

•Case Study 1: Sedimentary rock from North Africa. Crushing, grinding, desliming, and two stages of reverse flotation were utilized to lower the concentration of carbonates and iron minerals.

•Case Study 2: Sedimentary rock from West Central Africa. Crushing, closed-circuit screening/grinding, desliming, and two stages of reverse flotation, were utilized to increase the P_2O_5 concentration and to lower the concentration of silica and carbonates.

•Case Study 3: Sedimentary rock from Central Asia. Simple beneficiation, consisting of crushing and selective screening, was utilized to increase the P_2O_5 concentration.

•Case Study 4: Igneous rock from Southeast Africa. Crushing, closed-circuit grinding, desliming, wet magnetic separation, and multiple stages of reverse flotation, were utilized to increase the P_2O_5 concentration and to lower the concentration of iron and carbonates.

•Case Study 5: Sedimentary rock from Central Australia. Crushing, drum scrubbing, grinding, desliming, and multiple stages of cationic flotation, were utilized to increase the P_2O_5 concentration and to lower the concentration of iron, aluminum and silica based minerals.

Case Study 1 (Sedimentary Rock, North Africa)

Chemical Constituent		Chemical Analyses		Comments[1], [2]
		Ore	Product	
P_2O_5	%	27.1	31.8	Typical
CaO	%	42.5	47.4	See CaO/P_2O_5 ratio
MgO	%	1.3	0.6	Typical
Fe_2O_3	%	3.7	2.7	See $Fe_2O_3 + Al_2O_3$
Al_2O_3	%	0.9	0.4	**Slightly Low**
SiO_2 (sol.)	%		0.1	**Very Low**
SiO_2 (insol.)	%		3.9	Typical
Cl	ppm		180	Typical
F	%		3.2	Typical
CO_2 & Organics	%		4.0	Typical
Na_2O	%		1.0	**Slighty High**
K_2O	%		0.3	Typical
CaO/P_2O_5		1.57	1.49	**Slightly Low**
$Fe_2O_3 + Al_2O_3$			3.10	**High**
MER		0.22	0.12	**High**

[1] Comments based on chemical analyses of the product.

[2] Color coding: **red** denotes possible adverse impact on acidulation and/or fertilizer production; **green** denotes the opposite impact.

Based on the beneficiated rock chemical analyses, in particular the high Fe_2O_3 content (2.7%) and high MER (0.12), it was predicted that effective manufacture phosphoric acid would be difficult, gypsum filtration rates would be marginal, and since the concentrate was low (deficient) in soluble silica (0.1%), the addition of soluble silica was expected to be required during acidulation. Production of DAP from the acid generated from this rock sample was predicted to be extremely difficult, if not impossible.

Case Study 1 (Results)

Test Results

- Defoamer was needed to reduce foaming and diatomaceous earth (DE) was added to the rock feed to control corrosion.
- Although the concentrate was slightly high in sodium, excessive scaling was not apparent during acidulation. However, sodium fluoride compounds were a major component of the sludge that precipitated during filter acid clarification.
- P_2O_5 recoveries across the reactor and gypsum filter were excellent, at 97%, but filtration rates were low, at nominally 4 tonnes P_2O_5 per m^2 per day.
- Filter acid strength was about 27% P_2O_5. Filter acid Fe_2O_3 was 2.2% and the MER was 0.12.
- Kaolin was added to the rock feed to compensate for the slight deficiency in aluminum.

Conclusions

Bench-scale batch DAP tests conducted on the unclarified MGA concentrated from the pilot plant filter acid demonstrated that 18-46-0 DAP could not be made, likely because the high concentration of iron resulted in the formation of citrate insoluble iron-phosphate salts.

In conclusion, the predicted results, based solely on the concentrate chemical analyses, were quite accurate. The issues concerning low filtration rate, and kaolin addition were anticipated and realized. Scaling during acidulation was expected, but did not materialize until clarification of the filter acid.

Case Study 2 (Sedimentary Rock, West Central Africa)

Chemical Constituent		Chemical Analyses		Comments[1], [2]
		Ore	Product	
P_2O_5	%	10.6	30.4	Typical
CaO	%	26.9	45.0	See CaO/P_2O_5 ratio
MgO	%	6.4	1.2	Very High
Fe_2O_3	%	0.9	0.6	See $Fe_2O_3 + Al_2O_3$
Al_2O_3	%	2.3	0.4	Slightly Low
SiO_2 (sol.)	%		0.7	Slightly Low
SiO_2 (insol.)	%	38.0	5.7	Typical
Cl	ppm		130	Typical
F	%		3.5	Typical
CO_2 & Organics	%		5.7	High
Na_2O	%		0.9	Slightly High
K_2O	%		0.3	Typical
CaO/P_2O_5		2.54	1.48	Slightly Low
$Fe_2O_3 + Al_2O_3$			1.00	Low
MER		0.91	0.07	Typical

[1] Comments based on chemical analyses of the product.

[2] Color coding: **red** denotes possible adverse impact on acidulation and/or fertilizer production; **green** denotes the opposite impact.

Based solely on the beneficiated rock chemical analyses, it was predicted that effective manufacture of phosphoric acid would be difficult, primarily due to the high MgO content (1.2%). MgO, in excess of 0.6%, can form precipitates with fluorine in the reactor which, in turn, may inhibit (blind) the gypsum filter cloth, thus adversely affecting the filtration rates. High MgO in the filter acid can cause higher P_2O_5 losses via post precipitation (sludge). Since the concentrate was low (deficient) in soluble silica (0.7%), the addition of soluble silica was expected to be required during acidulation. Based on the expected high MgO in the filter acid, production of DAP from the acid generated from this rock sample was also predicted to be difficult.

Case Study 2 (Results)

Test Results

- Although the MgO level was high, the viscosity of the weak and concentrated acid was manageable.
- The low level of soluble SiO_2 required the use of an additive (kaolin) to reduce corrosion by free fluorine.
- P_2O_5 recoveries across the reactor and gypsum filter were excellent, at 97%, however filtration rates were low, at nominally 4 tonnes P_2O_5 per m^2 per day. Kaolin addition increased the filtration rate to approximately 4.5 tonnes P_2O_5 per m^2 per day.
- Foam generation was not an issue and no defoamer was utilized.
- The 28% P_2O_5 product acid was good quality (the MER was 0.05) with few solids. The level of fluorine and sodium in the solids indicated the formation of sodium fluorosilicate induced by the high level of sodium in the rock.
- Weak and strong acid clarification steps were easy and the viscosity was acceptable.

Conclusions

Commercial quality DAP was successfully produced from the unclarified MGA concentrated from the pilot plant filter acid. The water and citrate solubility's of these products were good and, except for some foam formation, ammoniation was not difficult and demonstrated that commercial grade, 18-46-0, DAP could be made.

In conclusion, the predicted results, based solely on the concentrate chemical analyses, were partially accurate. Issues concerning the high MgO rock were not realized during the pilot plant run. The issues concerning low filtration rate and kaolin addition were anticipated and realized. Overall, this rock acidulated better than anticipated.

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Case Study 3 (Sedimentary Rock, Central Asia)

Chemical Constituent		Chemical Analyses		Comments[(1), (2)]
		Ore	Product	
P_2O_5	%	11.1	18.2	Very Low
CaO	%		29.3	See CaO/P_2O_5 ratio
MgO	%		0.3	Low
Fe_2O_3	%		1.5	See $Fe_2O_3 + Al_2O_3$
Al_2O_3	%		1.1	Typical
SiO_2 (sol.)	%			
SiO_2 (insol.)	%		35.2	Very High
Cl	ppm		41	Very Low
F	%		2.2	Low
CO_2 & Organics	%		3.9	Typical
Na_2O	%		0.7	Typical
K_2O	%		0.4	Typical
CaO/P_2O_5		0.00	1.61	Slightly High
$Fe_2O_3 + Al_2O_3$			2.60	Slightly High
MER		0.00	0.16	Very High

(1) Comments based on chemical analyses of the product.

(2) Color coding: **red** denotes possible adverse impact on acidulation and/or fertilizer production; **green** denotes the opposite impact.

Based solely on the chemical analyses and noting in particular the very high percentage of silica (35.2%) in the beneficiated rock, coupled with the very high MER, it was predicted that that effective manufacture of phosphoric acid would be difficult and gypsum filtration rates would be marginal, at best. Production of DAP from the acid generated from this rock sample was also predicted to be extremely difficult, if not impossible.

Case Study 3 (Results)

Test Results

- The filter acid analyzed 26% P_2O_5 with a P_2O_5 recovery of over 95%.
- Gypsum filterability was exceedingly low (varied from 2.1 to 3.4 tonnes P_2O_5 per m^2 per day)
- A significant amount of defoamer was required
- The gypsum cake was observed to have an organic layer that impeded the washes. A polymer was only partially successful in dispersing the organic layer and improving filterability.
- Corrosion testing indicated that the acid was not highly corrosive and that standard materials of construction could be used for handling the acid and slurry.
- The acid filter acid produced had an MER of nominally 0.16, which is typically much too high to produce 18-46-0 DAP. The MER of the acid did not change significantly as it was clarified and evaporated to 52% P_2O_5.

Conclusions

Bench-scale batch DAP tests conducted on the unclarified MGA concentrated from the pilot plant filter acid confirmed that it was not possible to produce commercial grade DAP due to the high concentrations of iron and aluminum impurities that likely formed phosphate salts that are citrate insoluble during the production of DAP. The test results confirmed that the N, P_2O_5, and water soluble P_2O_5 were not within specification.

In conclusion, the predicted results, based solely on the concentrate chemical analyses, were partially accurate. The acidulation and concentration steps went far better than expected considering the low P_2O_5 and high silica contents of the rock feed. The major issues during acidulation were foam generation (unexpected) and low filtration rates (predicted). As expected, the high acid MER was instrumental in preventing the production of commercial grade, 18-46-0, DAP.

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Case Study 4 (Igneous Rock, Southeast Africa)

Chemical Constituent		Chemical Analyses		Comments[1], [2]
		Ore	Product	
P_2O_5	%	7.5	32.3	**Typical**
CaO	%		46.7	See CaO/P_2O_5 ratio
MgO	%	3.9	1.0	**Very High**
Fe_2O_3	%	13.6	0.6	See $Fe_2O_3 + Al_2O_3$
Al_2O_3	%	1.9	0.2	**Very Low**
SiO_2 (sol.)	%			
SiO_2 (insol.)	%	5.1	6.0	Typical
Cl	ppm		1340	**Very High**
F	%		1.8	**Low**
CO_2 & Organics	%		5.9	**High**
Na_2O	%		0.2	**Low**
K_2O	%		0.1	**Low**
CaO/P_2O_5		0.00	1.45	Typical
$Fe_2O_3 + Al_2O_3$			0.80	**Low**
MER		2.59	0.06	Typical

[1] Comments based on chemical analyses of the product.

[2] Color coding: **red** denotes possible adverse impact on acidulation and/or fertilizer production; **green** denotes the opposite impact.

Based solely on the beneficiated rock chemical analyses, it was predicted that effective manufacture of phosphoric acid would be easy because of the high P_2O_5 content, low CaO/P_2O_5 ratio, and very low MER. However, the very high chlorine content (1340 ppm) was a potential corrosion concern and the high %MgO was predicted to be a potential concern for production of DAP.

Case Study 4 (Results)

Test Results

- The test run went very smoothly and the free sulfide level was easily controlled.
- Process performance was good with filtration rates ranging from 5 to over 6 tonnes P_2O_5 per m^2 per day. P_2O_5 recovery averaged 96% and sulfuric acid usage was in the expected ranges.
- The product acid had a low MER (at 0.08).
- The gypsum produced was in the form of needle crystals, typical of the dihydrate process.
- No defoamer was required
- The corrosion coupons used had surprisingly low corrosion rates although high corrosion activity was noted early in the run in the 316 SS filter feed pots. The material with the lowest corrosion rate was UR-52N. The REDOX potential (EMF) was not measured during the test.

Conclusions

Bench-scale batch DAP tests conducted on the unclarified MGA concentrated from the pilot plant filter acid demonstrated that the manufacture of international quality, 18-46-0, DAP was feasible.

In conclusion, the predicted results, based solely on the concentrate chemical analyses, were fairly accurate. Issues concerning the high MgO rock were not realized during the pilot plant run, nor in the subsequent production of DAP. Potential concern of high rock CO_2 and organics also did not materialize. The high chlorine content of the rock (1340 ppm) was a concern, but far less than anticipated. The REDOX potential was not monitored during the pilot plant test run, so it was never determined if the REDOX potential was a factor for the apparent mitigation of chlorine induced corrosivity.

Overall, this rock acidulated very well with only minor issues.

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Case Study 5 (Sedimentary Rock, Central Australia)

Chemical Constituent		Chemical Analyses		Comments[(1), (2)]
		Ore	Product	
P_2O_5	%	18.1	32.6	Typical
CaO	%	24.3	44.4	See CaO/P_2O_5 ratio
MgO	%	0.7	0.2	Low
Fe_2O_3	%	4.4	1.2	See $Fe_2O_3 + Al_2O_3$
Al_2O_3	%	6.8	1.4	Slightly High
SiO_2 (sol.)	%		4.1	Slightly High
SiO_2 (insol.)	%	34.1	12.1	Slightly High
Cl	ppm		48	Very Low
F	%		3.5	Typical
CO_2 & Organics	%		2.2	Typical
Na_2O	%		0.2	Low
K_2O	%		0.3	Typical
CaO/P_2O_5		1.34	1.36	Low
$Fe_2O_3 + Al_2O_3$			2.60	Slightly High
MER		0.66	0.09	Typical

(1) Comments based on chemical analyses of the product.

(2) Color coding: **red** denotes possible adverse impact on acidulation and/or fertilizer production; **green** denotes the opposite impact.

Based solely on the chemical analyses and noting, in particular, the low % MgO, low CaO/P_2O_5 ratio, it was predicted that that effective manufacture of phosphoric acid would be straightforward with low consumption of sulfuric acid and typical gypsum filtration rates. Production of DAP from the acid generated from this rock sample was predicted to be a potential concern based on the slightly high MER.

Case Study 5 (Results)

Test Results

- The test run went very smoothly and the free sulfide level was easily controlled.
- The filter acid analyzed 26% P_2O_5 with a P_2O_5 recovery of over 98%.
- Sulfuric acid usage was low (at 2.5 tonnes 100% H_2SO_4 per tonne P_2O_5 feed). The filtration rate averaged 6 tonnes P_2O_5 per m^2 per day.
- There was no foam generated during acidulation.
- The rhombic shape and large size of the gypsum crystals made the dihydrate cake easy to wash.
- The filter acid had a low MER (at 0.063). The chemical constituent mass balance showed that 85% of the iron and only 30% of the aluminum solubilized into the filter acid.
- The filter acid was rapidly clarified (about 1 hour without flocculant and 2 to 3 minutes using flocculant).

Conclusions

Bench-scale batch DAP tests conducted on the unclarified MGA concentrated from the pilot plant filter acid demonstrated that the manufacture of international quality, 18-46-0, DAP was feasible. The water solubility of the DAP was acceptable and the citrate solubility was very high (at 99%).

In conclusion, the predicted results, based solely on the concentrate chemical analyses, were very accurate. The potential concern of the high MER on the ability to produce commercial quality DAP did not materialize because of the partial solubility of the iron and aluminum minerals.

Overall, this rock acidulated very well.

Closing Comments

- ✓ The case studies presented show that P_2O_5 alone is not an adequate indicator of the suitability of a rock as feed for conventional wet process phosphoric acid production. Other chemical constituents listed in this paper must also be evaluated.
- ✓ Chemical analyses can provide a reasonable indication of the suitability of a phosphate rock as feed for conventional wet process phosphoric acid production as well as an indication of the potential for conversion of the acid into phosphate fertilizers.
- ✓ Given the variety of form and content in which these chemical constituents can be present, acidulation pilot plant testing must be carried out during the latter feasibility study project phase in order to properly assess the quality of the phosphoric acid, the efficiency of the conversion process, the deportment of the chemical constituents into the acid and/or gypsum, and to determine the quality of the downstream fertilizer that can be produced
- ✓ Only pilot plant test results from well established, reputable laboratories with a proven "track record" should be used to design the commercial phosphoric acid plant.