Evgeny Fedoseev and James Samuelson, Novaphos Inc., USA, outline a new economic and sustainable approach to effectively deliver high quality phosphate for the fertilizer market.

Phosphorous, and thus phosphate, is crucial to all living organisms, and the use of phosphate fertilizer has been instrumental in bringing food security to the world. However, the current technology used to make almost all phosphate fertilizers, the wet-acid process or WAP, is decades old and burdened with significant problems; it requires large deposits of high quality phosphate rock, which is increasingly scarce, and creates large volumes of noxious waste. As the world's population continues to grow and the amount of arable land declines, sustainable phosphate production will remain essential to maintain food supplies. The industry does not have the luxury to wait to change how essential phosphate products are made; our future depends on a better phosphate industry.

Novaphos has developed a technology that aims to change the future of phosphate production. The process is based upon carbo-thermal reduction of phosphate rock ore, concentrate and even mine tailings, integrated with oxidation, and followed by scrubbing in water to produce a phosphoric acid that can be used to make any number of phosphate products, including liquid and water-soluble fertilizers, animal feed ingredients, and even purified phosphoric acid (PPA).

This process produces a useful co-product, J-Rox®, instead of phosphogypsum waste. J-Rox is a calcium silicate compound that can be used in concrete as a replacement for cement or as a light-weight aggregate. The radon gas emanation from J-Rox is about 50 times lower than most phosphogypsum and very close to, if not less than, background levels. This is accomplished by the

PHOSPHATE TECHNOLOGY

FOR A NEW ERA

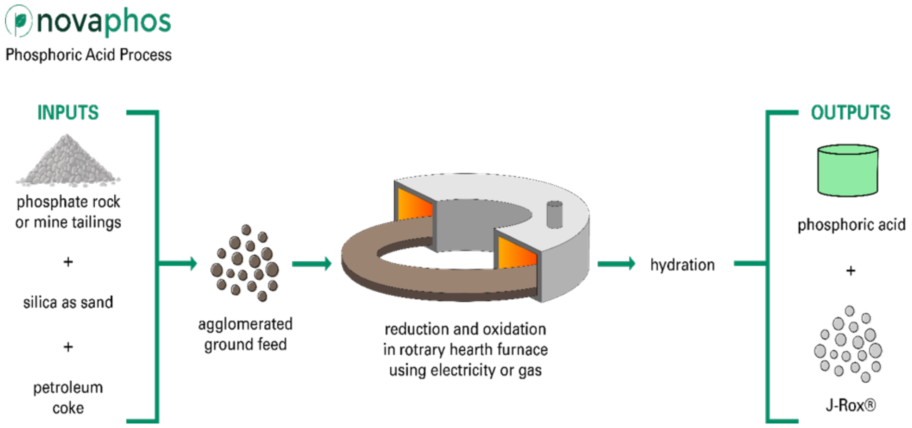

Figure 1. A newly developed phosphoric acid process.

crystaline structures formed under the high temperatures required to facilitate the process reactions. J-Rox also contains a significant amount of plant available silicon and is suitable as a soil amendment for crops requiring silicon. The process is illustrated in Figure 1.

The current standard for phosphate production is the wet-acid process (WAP), where sulfuric acid is reacted with phosphate rock to produce phosphoric acid and phosphogypsum waste. Economy-of-scale considerations have driven these plants to production rates of over 500 000 tpy of P_2O_5, with each plant requiring up to 2 million tpy of high quality phosphate rock concentrate. In order to support a 30-year useful life, a new WAP plant could require a quality phosphate rock reserve of 100 million t or more depending on ore characteristics and beneficiation requirements. The number of such phosphate deposits are in rapid decline and are simply non-existent in most of the world. High impurity levels that result from near complete dissolution of the phosphate rock are also a problem for WAP phosphate producers.

The Novaphos process can be commercialised at production levels from 20 000 tpy of P_2O_5, allowing for the utilisation of much smaller phosphate deposits which are numerous throughout the world. In addition, the process does not require high quality ore, and in many cases the run of mine ore at a lower cut-off value is quite suitable. Many phosphate mine tailings can also be used, especially if they are high in silica, as sand is also a reactant in this process.

The wet-acid process also requires sulfuric acid, which is produced by burning sulfur, most of which is recovered from hydrocarbons. As humanity strives to become carbon free, the world's recovered sulfur supply will decline, requiring the mining of natural sulfur at a much higher cost. Even more unfortunate, all the sulfur purchased and consumed in a WAP phosphoric acid plant is used and then discarded in the waste phosphogypsum. The production of sulfuric acid adds significantly to the capital cost of a WAP facility and brings safety and environmental risks, as well as the logistics of handling sulfur.

The Novaphos process does not require sulfur, however, it does need a small amount of carbon in the form of pet coke or coal. The process requires the input of energy to initiate the reaction, and the source is quite flexible – this can be natural gas, electricity, or green energy sources. The process can also be configured to capture any carbon emissions as industrial grade CO_2, bringing it very close to the 'zero-waste' ideal.

This process uses similar chemistry to the classic thermal process to produce elemental phosphorus, but it is simpler and lower in cost, due to a simplified raw material preparation process, flexibility in energy sources, energy integration and a continuous operation. The process occurs in the solid phase because it does not require melting of the feed; this allows for a continuous process utilising a single piece of equipment, the rotary hearth furnace, to accomplish direct reduction followed by oxidation. The rotary hearth furnace is being used successfully in a number of industries and is considered reliable and robust. The process has a low carbon footprint and little environmental risk.

This process directly produces a phosphoric acid with very low impurities, enabling the production of high quality phosphate products including water soluble phosphates and superphosphoric acid (SPA) for use in liquid fertilizers. The production of animal feed ingredients and purified phosphoric acid can be accomplished with minor downstream processing steps. The basic phosphoric acid derived from the wet process typically has ten times more impurities than the Novaphos acid; as such, it can be very hard, if not impossible to make high-value phosphates economically. These WAP operations struggle sometimes to make the expected grade of basic granular di-ammonium phosphate (DAP) or even mono-ammonium phosphate (MAP).

The difficulty of purifying WAP phosphoric acid has created a bias in the phosphate industry towards solid products, like DAP and MAP, which tolerate higher levels of impurities. Unfortunately, solid fertilizers are fundamentally less suited to 'precision agriculture,' where farmers try to place nutrients close to plant roots at times when the plants require those nutrients (e.g. the 4 Rs: right source, right rate, right time, and right place). Liquid and high-solubility fertilizers help meet these sustainability goals, but adoption has been limited due to cost and availability. As much as 80% of the phosphate in solid fertilizer never makes it to the plant and negatively impacts storm water runoff from agricultural production.

Fundamental technical limitations in WAP production of phosphoric acid contribute to these limitations; phosphate rock typically contains a large amount and variety of impurities. The acidulation process causes most of these impurities to become dissolved in the resulting phosphoric acid, which also contains an excess of sulfate to ensure an adequate reaction of phosphate rock. In the wet acid dihydrate process, there might be impurity levels in the range of 6 – 9% (60 000 – 90 000 ppm) in the filter grade phosphoric acid, which is typically at only about 28% P_2O_5 concentration.

In contrast, technical grade phosphoric acid requires impurities in the range of 500 – 2000 ppm at about 56% – 61% P_2O_5 concentration. This represents a substantial reduction of impurities, and most purification of WAP phosphoric acid is accomplished with solvent-extraction technologies combined with pre-and post-processing steps to obtain the required specification. Producers have also sought to use membrane technologies with limited success. Regardless of the approach, purification processes can be inefficient, rejecting large amounts of phosphate along with impurities.

Purification technology inefficiencies combined with environmental regulations mean that these impurities must be absorbed in other products. Most purification reject streams contain meaningful amounts of phosphate, and the most logical destination for these reject streams is a phosphate fertilizer. The product that is most able to absorb these impurities while still making grade is granular MAP; however, phosphoric acid going into MAP can only absorb so much of these impurities before it becomes impossible to make commercial-quality MAP.

This balancing act between impurity removal and use in commercial products limits production of higher-value products like water-soluble products and even SPA, particularly where the underlying phosphate rock resource is high in impurities, like most sedimentary phosphate rock. This explains why a large number of phosphate producers are unable to make more – or indeed any – higher value phosphate products.

The Novaphos process sequesters a large proportion of the impurities from phosphate rock in the co-product J-Rox, where they are trapped in non-reactive chemical compounds and nano-scale microscopic crystal structures formed by calcium silicates. This means that a large proportion of the impurities never get into the phosphoric acid and therefore do not need to be removed in downstream purification. It also explains why the process can use low quality phosphate rock.

The quality of phosphoric acid means that a production facility can avoid production of solid fertilizers, thereby also avoiding ammonia purchases and storage, granulation operations, and solid storage and shipping. A plant could focus on producing only higher-value phosphoric acid products like SPA and technical grade PPA, even battery grade PPA for the production of lithium iron phosphate (LFP) cathode material utilised in the lithium-ion battery industry.

To summarise, the process can expand effective phosphate resources in multiple ways:

- Capturing P_2O_5 currently lost in mine tailings.
- Using low quality ore that is not currently mined.
- Enabling smaller deposits that are not currently economic.

Taken together, these benefits can make an enormous impact on the amount of phosphate rock that is available, particularly in regions without large, high quality deposits remaining to be exploited. The process provides higher quality phosphate fertilizer products that allows for better utilisation and more efficient use by the crop. It also produces a co-product that can be used in many construction applications. Finally, it does not generate any large-scale solid or liquid wastes.

Conclusion

Stepping back, we see a traditional phosphate industry that is limited by the kind of phosphate rock it can use and the kind of products it can make. It is also burdened with the need to purchase sulfur and dispose of that same sulfur in the form of phosphogypsum waste. These limitations are highly problematic in an industry on which the world depends for food security. It is time for a new approach that is more economic and sustainable. WF