Sana Boulabiar and Matias Navarro, Veolia Water Technologies, USA, discuss how crystalline water-soluble fertilizers are the most efficient way for delivering the nutrients that boost the quantity and quality of crops the world desperately needs while protecting its soil and water resources.

The rising pressures from population growth, coupled with changes towards protein-rich diets driven by a more affluent class of global consumers, are testing the limits of the Earth's supply of land and water resources. These forces are not expected to diminish. The Food and Agriculture Organization (FAO) of the United Nations projects an approximate 50% increase in the demand for crops in 2050 from 2013 levels.

Over the course of recent history, no other modern agricultural practice has contributed more to solving the challenges of feeding more people than the application of mineral fertilizers. Fertilizers provide the three major essential nutrients: nitrogen (N), phosphorus (P) and potassium (K).

Nitrogen is the most important determinant of plants' growth, vigour, colour, and yield.

Phosphorus is essential to seed formation and photosynthesis, a vital process that converts sunlight to energy and is also critical to plant development and quality.

Potassium is a crucial 'building block' for plants, playing roles in water regulation, heat stress tolerance, and protein synthesis and enzyme activation.

These three vital macronutrients are essential but they are not the only ones required to sustain healthy and productive farms, as plants use 17 essential elements to thrive and survive. That is the reason for the growing fertilizer market of NPK formulations that add secondary nutrients with ideal ratios to each other.

An industry with burning environmental issues

Given the constraints imposed by limited resources, further boosting agricultural productivity is essential.

Converting more land to agriculture translates into negative impacts such as reduced biodiversity, deforestation, and increasing emissions, as has been seen in the recent fires that have ravaged what is left of the Amazon rainforest – some of which were intentionally started to further expand the agricultural frontier. Additionally, climate change worsens the situation with erosion and loss of topsoil.

Furthermore, water shortages are putting pressure on the sector and agriculture is a centrepiece at both ends: as a contributor and as a casualty of water scarcity problems. For instance, entire fields have traditionally been irrigated using water in high quantities at long intervals, whether by sprinklers or by flood irrigation, resulting in significant losses and high fluctuations in soil-moisture content which affect plant growth and crop yields.

The responsible answer to optimal plant nutrition

The need to minimise water usage and increase irrigation efficiency drove the shift to more modern irrigation methods such as drip irrigation (or micro-irrigation), which consists in delivering water directly into the root zone of plants. Drip irrigation systems are able to supply small amounts of water at high-frequency intervals and therefore maintain optimal moisture range in the soil. This promotes water savings, as well as enhancing growth and production.

Just as advanced irrigation saves water and improves yields, the application of fertilizers also results in higher returns and more intensive use of the land, helping to preserve forests and avoid new acreage being converted to cropland.

In short, to gain efficiencies in resource use and improve environmental performance, the global agricultural industry needs to do more with less, which means more sustainable solutions that boost productivity and fertilizers' efficiency with minimum water usage and more intense use of land. The market has adopted fertigation and foliar feeding techniques coupled with precision agriculture, a sensor-based technology assisted by drones and digital tools, to overcome these dual water and soil challenges.

Fertigation, a technique that distributes nutrients through irrigation systems, makes use of small and frequent applications of water and soluble fertilizers to enhance plant growth and increase yields. By feeding plants in exact amounts only when needed, fertigation increases the efficiency of nutrient uptake and minimises nutrient losses. In addition, selective wetting of the soil, as achieved by drip irrigation, allows for savings in both water and fertilizer.

Foliar feeding, another technique associated with higher yields and better crop quality, consists of spraying water-soluble fertilizers directly onto the plant leaves. It is a fast and effective solution when environmental conditions limit the uptake of nutrients by plants' roots. Such conditions may include high or low soil pH, temperature stress, too low or too high soil moisture, root disease, presence of pests that affect nutrient uptake, nutrient imbalances in soil, etc.

Despite their many advantages, fertigation and foliar feeding cannot fully deliver these benefits through the use of conventional fertilizers. In other words, advanced farming techniques need advanced fertilizer products such as fully-soluble, crystalline products which have proven superiority over traditional crop nutrition. Other forms of granulated or powder-like grades are not as effective as crystalline water-soluble fertilizers. And when it comes to large-scale field operations, crystalline water-soluble fertilizers are even less expensive than commonly used liquid fertilizers.

Figure 1. Mono-ammonium phosphate (MAP) crystals under the microscope.

Table 1. Most common crystalline water-soluble fertilizers

Fertilizer	NPK			Form	Approximate pH (5% wt solution)
	N %wt	P_2O_5 %wt	K_2O %wt		
AMS – $(NH_4)_2SO_4$	21	0	0	Crystals	5.5
MAP – $NH_4H_2PO_4$	12	61	0	Crystals	4.2
DAP – $(NH_4)_2HPO_4$	21	53	0	Crystals	7.5 – 8
MKP – KH_2PO_4	0	52	34	Crystals	4.4
DKP – K_2HPO_4	0	40	54	Crystals	9
MKDP – $KH_5(PO_4)_2$	0	60	20	Crystals	2.2
NOP – KNO_3	13	0	46	Crystals	7 – 10
MOP – KCl	0	0	60	Crystals	7
SOP – K_2SO_4	0	0	53	Crystals	7

Feeding plants with crystals

The attributes of high-quality fertilizers for fertigation and foliar feeding applications are centred on high solubility and low impurities at acceptable pH levels that fit within the farm management programme. Crystalline water-soluble fertilizers achieve the highest performance in the global fertilizer market as they are fully water-soluble, highly pure with almost none of the water-insoluble impurities (usually less than 0.1% wt) that cause clogging of spray systems and dosing devices as well as having very low (or no) sodium, chlorine, or heavy metals.

The production of crystalline water-soluble fertilizers takes place in a crystallisation plant, usually composed of a crystalliser vessel followed by solid/liquid separation and drying/cooling. The key to crystalline fertilizers reaching maximum solubility and high purity relies on crystallisation technologies. Contrary to other production processes such as granulation, blending or atomisation, the crystallisation unit operation performs two key roles:

- Crystallisation, which achieves consistent levels of production at a specific size and shape.
- Purification, to reach very high purity (usually higher 99 wt%) and remove water-insoluble impurities.

Only through crystallisation can purification be achieved. By extracting a purge stream from the crystalliser, impurities are diluted which prevent their co-precipitation with the desired fertilizer crystals. Other techniques available through the crystallisation process contribute to further upgrades and purifies the product, achieving the differentiating attributes the market looks for: full solubility and minimum impurities. One of them is the use of a second crystallisation stage that allows for minimising the waste purge and achieving higher production yields. It also allows the possibility to use lower grade raw materials and still produce higher value fertilizer product.

One of the greatest advantages of fertilizer production through crystallisation is its ability to adapt the process to different feedstock grades or sources such as waste streams. This is most evident in the production of mono-ammonium phosphate (MAP), one of the most popular water-soluble phosphorus fertilizers. MAP is produced by adding ammonia to phosphoric acid. Crystallisation technologies enable the production of high-value MAP even from low-grade phosphoric acid, which is typically a waste compound with little to no value unless it is subject to costly purification steps.

Picking a crystal

A diverse range of crystalline water-soluble fertilizers available in the market are produced through the crystallisation process. The most commonly used 'straight' water-soluble fertilizers are shown in Table 1. Many NPK blends also exist and must be combined properly to ensure fertilizer compatibility and prevent any unwanted precipitation.

Ammonium sulfate (AMS) combines N and sulfur (S) required to meet essential nutritional needs. It provides an excellent source of S, which supports or drives numerous vital plant functions, including protein synthesis. AMS crystals can be made from pure ammonia and pure sulfuric acid by reactive crystallisation or produced by evaporative crystallisation of a dilute AMS stream (i.e. using a byproduct from caprolactam production, coking, sulfuric acid gas scrubbing, nickel/cobalt production or recovery of nickel production waste).

MAP is an excellent source of P and N, and has a pH that is moderately acidic, which makes it a highly desirable fertilizer in neutral and high-pH soils. High-quality MAP can be made via reactive crystallisation using technical-grade phosphoric acid and pure ammonia followed by solid-liquid separation and drying. Another alternative to produce MAP is from merchant grade phosphoric acid which further reduces production costs because it does not require the installation of an acid purification plant. MAP producers rely on crystallisation experts, such as Veolia, to provide the know-how to selectively crystallise high-quality water-soluble MAP despite the impurities coming with the feed acid. Test works are very often essential in tailoring the best process solution to the feed quality and required crystal purity.

Di-ammonium phosphate (DAP) is another source of N and P. DAP is the most widely used phosphate fertilizer among growers today. It is an excellent fit for low pH or alkaline soil. Crystalline DAP is suitable for use in fertigation and foliar feeding as water-insoluble particles can reach less than 0.1% wt when dissolved in a 10% solution at ambient temperature. DAP crystals are produced by reactive crystallisation from ammonia and purified phosphoric acid or, alternatively, from ammonia and MAP solution or crystals.

Mono potassium phosphate (MKP) is a preferred source of P and K when nitrogen fertilization should be limited. MKP is a highly soluble crystalline fertilizer with moderate pH. It can be produced by reactive crystallisation starting from potassium hydroxide (KOH) and purified phosphoric acid followed by solid/liquid separation and drying. Another cost-effective alternative is to produce MKP from lower grade phosphoric acid. As a result of the crystallisation process that plays a purification role, impurities coming from KOH and phosphoric acid can be removed and fully water-soluble MKP can be produced.

Di-potassium phosphate (DKP) is a specialty fertilizer combining P and K. DKP is unique due to its very high pH, which makes it suitable for enhancing plant nutrition in acidic soils. DKP is a highly soluble and pure crystalline fertilizer produced from KOH and phosphoric acid.

Mono potassium di-phosphate (MKDP) is another specialty fertilizer product combining P and K. Because of its very low pH, it increases phosphorus and micronutrient uptake and it also has an anti-clogging action to the fertigation equipment. MKDP can be produced in crystal form from KOH and phosphoric acid. Crystalline MKDP has exceptional purity and solubility. Because of its low pH, it is compatible with calcium and magnesium fertilizers.

Muriate of potash (MOP), also known as potassium chloride or KCl, is an excellent plant fertilizer when soils cannot supply the amount of K required by crops. High-grade potassium chloride crystals can be produced from different feedstocks such as sylvanite brine (NaCl.KCl) from solution mining or conventional mining or carnallite brine $KCl.MgCl_2.6H_2O$ from the sea. The feed can also be a waste stream from an industrial salt production facility. In all these cases, the crystallisation process allows the selective production of high purity water-soluble KCl crystals with very low sodium content.

Potassium sulfate (SOP) is a source of K when crops are sensitive to the addition of chlorides. It is also an excellent source of sulfur which is required for protein synthesis and enzyme function. While the traditional and most common SOP production method is through the old and energy-intensive Mannheim process reaction of KCl and sulfuric acid, there are other more efficient production routes of high-grade SOP crystals using crystallisation technologies. One of these options is to produce SOP crystals from natural brines, including polyhalite brine ($K_2SO_4.2CaSO_4.MgSO_4.2H_2O$), schoenite brine ($MgSO_4.K_2SO_4.6H_2O$) or even kainite brine ($KCl.MgSO_4.3H_2O$). The source of these feedstocks can be solar evaporated lake or solution mining. Another option is to produce SOP from waste streams of pulp and paper mills. In this process, glaserite (SOP and sodium sulfate double salt) is first recovered from the black liquor ash treatment system and then converted to high-quality SOP crystals for fertilizer use. In both options, the crystallisation process is key to controlling the purity and the size of the final SOP crystals.

Nitrate of potash (NOP), also known as potassium nitrate, is a source of K for chloride-sensitive crops. It is also an excellent source of N as nitrates requires no additional microbial action and soil transformation. Growers of high-value crops prefer to use a nitrate-based source of nutrition in an effort to boost yield and quality. KNO_3 is usually produced from the reaction between KCl and a nitrate source such as nitric acid, sodium nitrate or ammonium nitrate. The production of water-soluble KNO_3 crystals consists of reaction, concentration, crystallisation, solid/liquid separation, and drying processes.

Case studies

Ammonium sulfate

In the state of Sergipe in Brazil, Petrobras, a publicly-held energy and petrochemicals company, used the HPD® crystallisation technology to produce 875 tpd of fertilizer-grade AMS crystals, resulting from the reaction of waste ammonia and waste sulfuric acid from adjacent refinery and urea production plant. The plant, supplied by Veolia, consists of a HPD PIC™ draft-tube crystalliser, integrated with solid-liquid separation, drying, screening and packaging. The solution enabled Petrobras to

Figure 2. Installation of crystallisation technology to produce high-quality ammonium sulfate fertilizers.

Figure 3. Large-scale potassium chloride crystallisation system en-route to its final destination.

Figure 4. Process flowsheet under test to produce crystalline fertilizers of maximum purity and solubility.

generate additional revenues from waste streams by converting them into a high-quality ammonium sulfate fertilizer.

Ammonium phosphate

The Alkimia group, a Tunisian chemical holding company that specialises in the production of phosphate salts for industrial applications, will soon diversify its revenue streams by starting up the operations of a new 25 000 tpy MAP plant that will export higher-value fertilizer product from its facility in Gabes, Tunisia, to growth markets in the African agricultural sector. The solution proposed to Alkimia followed a series of laboratory tests conducted to simulate and develop the right process flowsheet. The fertilizer plant designed and delivered by Veolia integrates two crystallisation stages along with centrifugal separation, drying, cooling, and screening systems.

The plant uses low-grade phosphoric acid (merchant grade) and ammonia to produce fully water-soluble MAP crystals with high purity (i.e. 99% wt minimum) and very low water insolubles (i.e. below 0.2% wt).

Potassium chloride

K+S Group, a supplier of fertilizer products, built the Bethune potash mine, the largest solution mining site in North America, in order to produce more than 2 million t of potassium chloride (potash) in the Canadian province of Saskatchewan. With engineering and equipment supply under its scope, Veolia delivered HPD evaporation and crystallisation technology that recovered and crystallised potash from solution mining sylvanite brine while providing the lowest operating costs thanks to energy savings and water conservation. The potash is then refined into a high-quality end product.

Sulfate of potash

Compass Minerals, a North American fertilizer company, needed to expand production of potassium sulfate at its facility near Ogden, Utah, US. Veolia simulated and developed the process at its research facility near Chicago before validating the design. A HPD PIC draft tube baffle crystalliser was integrated into the existing plant, which enabled it convert schoenite feed brine into high purity potassium sulfate fertilizer product, known in the market as Protassium+®. In addition, due to the resultant more efficient recycling, Veolia's process solution enabled Compass Minerals to significantly reduce water consumption compared to the existing SOP plant.

The future of fertilizer production

Veolia and its HPD evaporation and crystallisation technologies support the global fertilizer industry in enhancing the value of its products and optimising their economics thanks to deep fertilizer crystallisation experience, know-how and state-of-the-art research and development capabilities.

To cope with population and resource pressures, the agricultural value chain has evolved and adopted modern practices. It is the responsibility of the fertilizer industry to make them more efficient by providing high purity fully-soluble crystalline products.

Although the future of fertilizers is crystal clear, the path to reach it is not. To be successful and develop the most economical solutions, crystallisation technology is the key to obtaining deep technical and process design expertise. **WF**