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Phosphates market report
Evaporation & crystallisation technology
Applying evaporators & crystallisers to fertilizer production

Véronique Bourgier, PhD, Karen Schooley and Rob Lawson, of Veolia Water Technologies HPD® Evaporation and Crystallization, explain the main applications of evaporators and crystallisers in the fertilizer industry – particularly in potash production. These include manufacturing fertilizers from raw materials, and the recovery of fertilizers as valuable by-products from waste streams or other processes.

Evaporation and crystallisation techniques have many applications in the fertiliser industry. Valuably, they allow fertilizers to be produced from primary raw materials or from the secondary by-products of another process, or, due to economic pressures, from waste streams.

The numerous applications of evaporation and crystallisation in the synthesis of N, P and K fertilizer products are shown in Figure 1. Demand for water-soluble fertilizer products is on the rise, driven by water scarcity and the adoption of more efficient fertilization practices. The diverse range of fertilizers produced using evaporation and crystallisation technologies include:

- **Ammonium sulphate**: Crystals can be made from pure ammonia and pure sulphuric acid by reactive crystallisation, or produced by evaporative crystallisation of a dilute ammonium sulphate stream (i.e. using a by-product from caprolactam production, coking, sulphuric acid gas scrubbing, nickel/cobalt production or recovery of waste nickel).

- **MAP/DAP**: Monoammonium phosphate (MAP) and diammonium phosphate (DAP) can be made via reactive crystallisation using technical-grade phosphoric acid and pure ammonia. Opportunities also exist to make these products using less expensive green phosphoric acid or raffinate.

- **Potash**: Cooling crystallisation is used extensively in solution mining to produce potassium chloride (KCl or potash), and in conventional mining to make higher grade KCl products. Many

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**Fig 1: Fertilizer production processes that involve evaporation or crystallisation**

Source: Veolia HPD
Potash deposits contain sylvinite (a double salt of NaCl and KCl). Sodium chloride removal via crystallisation can make up a major portion of the processing plants used to recover valuable potash.

- **SOP**: Potassium sulphate (SOP) can be made via multiple approaches, often involving crystallisation steps. SOP demand is increasing due to its greater use on high-value crops such as tobacco or nuts (and its higher selling price relative to potassium chloride).
- **Nitrate fertilizers**: Evaporation is used to concentrate ammonium nitrate and to produce products such as potassium nitrate and calcium nitrate.
- **Phosphoric acid**: Evaporation is used to concentrate dilute phosphoric acid into a marketable product, or as raw material for phosphate fertilizer production.
- **Calcium chloride**: Calcium chloride waste streams generated from the phosphoric acid process can be concentrated using evaporation technology to generate a saleable product.

Fertilizers manufactured using evaporation and crystallisation processes and the main by-products obtained are listed in Table 1 and Table 2, respectively.

### Process options

Evaporation and crystallisation encompasses a range of different process options. These include standard evaporation, evaporative crystallisation, cooling crystallisation and reactive crystallisation. Process selection is influenced by the types of raw materials, the desired quality of the end-product, the physical behaviour of materials and project-specific criteria.

**Evaporation and evaporative crystallisation**: This involves the removal of solvent, typically water vapour, to concentrate the solute – which is usually the desired product. The objective is to increase the concentration of dissolved salts as water is evaporated. Examples of the use of evaporation in the fertilizer industry include phosphoric acid and calcium chloride concentration, and the pre-concentration of dilute streams prior to crystallisation.

**Cooling crystallisation**: Certain compounds – those with relatively steep normal temperature-dependent solubility – are easily crystallised in cooling crystallisers. Crystallisation is initiated by cooling a hot solution to a temperature below the saturation point of the desired crystalline phase.
saturated solution until supersaturation is reached. The cooling is most often achieved by flashing the water vapour under vacuum. The main driving force for crystallisation is the cooling of the solute, but some concentration also occurs due to the removal of water vapour. This type of crystallisation is prevalent in potash production.

**Reactive crystallisation:** In this process, a crystalline product is formed by a chemical reaction when two species are mixed together. This type of crystallisation is used to make ammonium sulphate from ammonia (either gaseous or liquid) and sulphuric acid, or MAP/DAP by reacting ammonia with phosphoric acid. These types of crystallisers generally require relatively pure reactants, although there is increasing interest in using less pure, less costly compounds or waste streams in these applications.

**Equipment types**

The most common types of equipment adopted by the fertilizer industry (Figure 2) are as follows:

- A **falling film evaporator** is typically used to concentrate a solution in non-scaling applications. It is often used to pre-concentrate a stream prior to a separate crystallisation process, and can turn highly soluble salts such as calcium chloride into high concentration solutions.

- A **forced circulation crystalliser** is used for applications where it is easy to grow large crystals or where the particle size distribution of the product is not critical. Forced circulation crystallisers are often used for sodium chloride crystallisation in potash recovery from sylvinite deposits. This type of equipment is also known as a ‘mixed suspension, mixed product removal’ (MSMPR) crystalliser because the slurry is well-mixed and uniform throughout the system.

- The use of draft tube baffle (DTB) or HPD partitioned internal circulation (PIC™) crystallisers is widespread in the fertilizer industry. This type of crystalliser is used in applications that require a

**CASE STUDY 1**

**Potash from solution mining**

This case study is for a greenfield project in Saskatchewan, Canada. This will use solution mining to produce two million t/a of potash (KCl). The ore is mainly sylvinite (NaCl and KCl) but contains small amounts of carnallite (KCl.MgCl₂.6H₂O) and other minor impurities (CaCl₂, CaSO₄, NaBr, etc.).

**Process description with water and energy optimisation**

A block diagram of the solution mining process is shown in Figure 4. The ore is dissolved by injecting hot water underground. The brine solution produced is treated to recover pure, economically-valuable potassium chloride. Evaporation is used as an initial treatment step to remove sodium chloride. The use of an integrated thermo-compressor in the multiple effect evaporation system improves energy efficiency. NaCl removal takes place in a forced circulation crystalliser with an elutriation leg. The brine from the solution mine is saturated in calcium sulphate. This needs to be managed throughout the evaporator system to prevent scaling in the evaporator heaters.

The mother liquor obtained from the NaCl evaporator system is a hot solution nearly saturated in potassium chloride. KCl is crystallised from this pregnant liquor in a multiple-stage, adiabatic cooled crystalliser system comprised of DTB crystallisers. Each stage operates at a progressively lower pressure/temperature and KCl precipitates as the liquor cools. Product purity and crystal size is controlled by adding water and adjusting process flows.

Solution mining initially requires large volumes of water to dissolve the ore and additional water is also required throughout the evaporation and crystallisation process. However, evaporated water is recovered and reused to minimise the amount of make-up water consumed during the solution mining process.

**Complex supply logistics**

Due to the size of the project, it was necessary to source equipment from multiple locations. Some vessels were pre-fabricated in China and shipped to Houston then trucked to Saskatchewan (Figure 5). The vessels transported were over 12 metres high, in excess of 50 metres long and weighed about 330 tonnes. It was desirable to minimise the amount of site construction work and do as much of the vessel fabrication in shops as possible. Equipment supply logistics were therefore complex and required careful coordination.

![Fig 5: Veolia’s KCI crystalliser being transported to the project site.](source: Veolia HPD)
Evaporation and crystallisation plays a key role in emerging technologies. Narrower crystal size distribution and a larger crystal size. Common applications include potash, ammonium sulphate and MAP/DAP fertilizer production, among others.

The HPD Growth™ crystalliser is an Oslo type or ‘classified suspension, classified product removal’ (CSCPR) crystalliser. It typically involves the circulation of a crystal slurry and the classification of crystals according to size using a fluidised bed. The classification advantages of an HPD Growth™ unit have been demonstrated in many applications. These applications include from high-purity to fertiliser-grade potassium chloride production and from by-product to high purity ammonium sulphate production.

Equipment configurations

There are many different ways to configure evaporation and crystallisation equipment (Figure 3) to ensure that project economics and process efficiency are both maximised. Among the design factors that must be considered are:

- Utility (steam, power and cooling water) availability and costs
- Capital equipment size and metallurgy
- Installation costs
- Process requirements
- Environmental constraints

In a steam driven system, steam is introduced into a heater to transfer the heat from the steam to a solution being concentrated in heater tubes. The vapour generated as a consequence of evaporation must be condensed in a water- or air-cooled condenser. The multiple effect process improves the energy efficiency by using the vapour that is generated as the heat source to evaporate additional water. This occurs at progressively lower pressure in each additional effect. This configuration greatly increases the steam economy, namely the amount of water evaporated per the amount of steam used. If high pressure steam is available, it is possible to reduce the steam consumption by using a thermo-compressor.

Mechanical vapour recompression (MVR) uses electrical energy to drive the evaporation in lieu of steam. The water evaporated is compressed using a mechanical vapour compressor. The resulting high-pressure vapour is then used in the heater to drive the evaporation. This results

CASE STUDY 2

Potash from brine

A new crystallisation production system was required as part of a brownfield expansion of a Dead Sea brine plant in Israel. This was designed to increase potash capacity by 30%. The new system needed to be integrated into the existing plant and replace an older production line. The site also produces bromine and magnesium chloride from highly-concentrated brine feed.

Process description

The customer’s original expansion plan was based on a four-stage train. However, after discussion, this was changed to a five-stage train using PIC™ (draft tube baffle), HPD® crystalliser technology (Figure 6). This design improved heat recovery and the additional cost was more than justified by the sizable savings in energy consumption. The bypass capabilities added to the system by the modified design would also help keep plant capacity at a stable rate.

Challenges and solutions

Veolia designed and built the system on a turnkey basis using HPD crystallisation technology. The design goal for a minimum nameplate capacity of 153 t/hr (1.3 million t/a) for potassium chloride crystal production was met with high system availability. To reach this goal, the production process needed to generate crystals of consistent size at high purity (> 98% KCl).

The location of the new crystalliser train was another project challenge. Field erection of large vessels was necessary due to clearance issues in accessing the proposed expansion area. Other difficulties were the limited communication windows, the regional climate and the extremely tight battery limits.
in much higher energy efficiency than a steam-driven system and is beneficial and practical option where steam or cooling sources are limited.

A multiple stage vacuum flash configuration is often used for products that have an inverse solubility. These types of crystallisers use adiabatic cooling, i.e. the evaporation caused by the vacuum in the crystalliser cools the liquor and the product precipitates as a result of this cooling. This is a typical configuration used in KCl production.

**Process challenges**

To develop or validate design parameters, performing bench or pilot-scale tests is generally an imperative (Figures 7, 8). These should ideally be performed with the actual feed solution to be used in the full-scale commercial plant, or by using a synthetic substitute where this not available. The main process challenges in designing a commercial plant are:

**Production of high quality product salts:** Fertilizer products often need to meet specific crystal habit, size or purity requirements.

**Heat integration and water balance optimisation:** Some production processes, such as potash from solution mining, have large recycle flows and place very high energy demands on the system. It is vital for such systems to have a highly-integrated heat balance.

**Choice of construction materials:** Because the feed or mother liquor is often at high temperature and contains high concentrations of corrosive compounds, a balance needs to be struck between the need for corrosion resistance and ensuring that the design remains cost-competitive.

**Conclusions**

Evaporation and crystallisation processes are prevalent in many commercial fertilizer production plants. New fertilizer production technologies continue to be developed in response to rising fertilizer demand and the decreasing availability of low-cost raw materials. Evaporation and crystallisation plays a key role in these emerging technologies. Research, bench-scale and pilot-scale testing and process development will also remain vital in bringing new applications to market.

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**PK**

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