There are many applications in the fertilizer market that involve evaporation and crystallisation techniques, either to make fertilizer products from a raw material feedstock or to recover valuable byproduct fertilizer from another process, or due to economic pressure, from waste streams.

Due to increasing water scarcity and the drive for more efficient fertilization practices, there has been a rise in demand for water-soluble fertilizer products. There are many examples of fertilizer production processes involving evaporation and crystallisation, including the following:

- Ammonium sulfate crystals can be made using pure ammonia and pure sulfuric acid, using reactive crystallisation, or produced by evaporative crystallisation of a dilute ammonium sulfate stream (i.e. using a byproduct from caprolactam production, coking, sulfuric acid gas scrubbing, nickel/cobalt production or recovery of waste nickel).
- MAP/DAP: crystalline mono-ammonium phosphate (MAP) and di-ammonium phosphate (DAP) can be made via reactive crystallisation using technical grade quality phosphoric acid and
Mono-potassium phosphate
Phosphoric acid: evaporation is used to concentrate phosphoric acid, H\(_2\)PO\(_4\).

Potash: cooling crystallisation is used extensively to make potassium nitrate, KNO\(_3\).

Nitrate-based fertilizers: evaporation is used to concentrate ammonium nitrate and to produce products such as calcium nitrate, Ca(NO\(_3\))\(_2\).

Potassium chloride (MOP), KCl

A forced circulation crystalliser is a mixed suspension, typically made using evaporation and crystallisation processes.

Potassium sulphate (SOP), K\(_2\)SO\(_4\)

Falling film evaporation is typically used to concentrate highly soluble salts, such as calcium chloride, to make high-concentration solutions.

Calcium nitrate, Ca(NO\(_3\))\(_2\)

Pre-concentrate a stream before a separate crystallisation process begins and can be used to concentrate highly soluble salts, such as calcium chloride, to make high-concentration solutions.

Table 1. Fertilizer products that are typically made using evaporation and crystallisation processes

<table>
<thead>
<tr>
<th>Product Type</th>
<th>Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium chloride, NH(_4)Cl</td>
<td>Phosphoric acid, H(_2)PO(_4)</td>
</tr>
<tr>
<td>Ammonium nitrate, NH(_4)NO(_3)</td>
<td>Potassium chloride (MOP), KCl</td>
</tr>
<tr>
<td>Ammonium sulfate, (NH(_4))(_2)SO(_4)</td>
<td>Potassium nitrate, KNO(_3)</td>
</tr>
<tr>
<td>Calcium nitrate, Ca(NO(_3))(_2)</td>
<td>Potassium sulphate (SOP), K(_2)SO(_4)</td>
</tr>
<tr>
<td>Calcium phosphate, Ca(_3)(PO(_4))(_2)</td>
<td>Mono-potassium phosphate (MOP), K(_2)HPO(_4)</td>
</tr>
<tr>
<td>Di-ammonium phosphate (DAP), (NH(_4))(_2)HPO(_4)</td>
<td>Di-potassium phosphate (DKP), K(_2)HPO(_4)</td>
</tr>
<tr>
<td>Mono-ammonium phosphate (MAP), NH(_4)H(_2)PO(_4)</td>
<td>Mono-ammonium diphosphate (MKDP), K(_2)(H(_2)PO(_4))(_2)</td>
</tr>
<tr>
<td>Magnesium sulfate heptahydrate (Epsom salt), MgSO(_4)(_7)H(_2)O</td>
<td>Urea, CO(NH(_2))(_2)</td>
</tr>
<tr>
<td>Magnesium sulfate monohydrate, MgSO(_4)H(_2)O</td>
<td>Urea phosphate, CO(NH(_2))(_2)H(_2)PO(_4)</td>
</tr>
</tbody>
</table>

Tables 1 and 2 list some of the products and byproducts of fertilizer production that are typically made using evaporation and crystallisation processes.

Table 2. Non-fertilizer byproducts that are typically made using evaporation and crystallisation processes

<table>
<thead>
<tr>
<th>Byproduct Type</th>
<th>Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium chloride, CaCl(_2)</td>
<td></td>
</tr>
<tr>
<td>Sodium chloride, NaCl</td>
<td></td>
</tr>
<tr>
<td>Magnesium chloride, MgCl(_2)</td>
<td></td>
</tr>
</tbody>
</table>

pure ammonia. Opportunities also exist to make these products using less expensive green phosphoric acid or raffinate.

Potash: cooling crystallisation is used extensively to produce potassium chloride (KCl or potash) from solution mining or it is used to make a higher grade KCl product from conventional mining.

SOP: potassium sulphate (SOP) demand is increasing due to its greater use (and higher selling price than KCl) as a fertilizer on high-value crops such as tobacco or nuts. This can be made via multiple approaches, often involving crystallisation steps.

Nitrate-based 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 sellable 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.

Evaporator and crystalliser processes

There are multiple processes available to achieve evaporation and crystallisation. These processes include evaporation, evaporative crystallisation, cooling crystallisation and reactive crystallisation. The process that is implemented depends on the raw materials, desired end-product quality, physical properties of the materials and any specific project criteria.

Evaporative crystallisation

Evaporation is the removal of solvent, i.e. water vapour, resulting in the concentration of the solute, which is usually the desired product. As water is evaporated, the concentration of dissolved salts increases. Examples using evaporation in the fertilizer industry include concentrating phosphoric acid or calcium chloride, or pre-concentrating dilute streams before crystallisation.

Cooling crystallisation

Compounds with a relatively steep normal temperature dependent solubility are easily crystallised in cooling crystallisers. A hot saturated solution is cooled, creating supersaturation, which results in crystallisation. The cooling is most often achieved by flashing the water vapour under vacuum. The main driving force for the crystallisation is the cooling of the solute, but some concentration also occurs as water vapour is removed. This type of crystallisation is prevalent in KCl production.

Reactive crystallisation

This is a process where two species are mixed together resulting in a chemical reaction to form a crystalline product. This type of crystallisation is used to make ammonium sulphate from ammonia (either gaseous or liquid) and sulfuric acid, or MAP/DAP by reacting ammonia with phosphoric acid. Typically, relatively pure reactants are used in these types of crystallisers. However, there is increasing interest in using less pure (and less costly) compounds or waste streams for these applications.

Types of equipment

The most common types of equipment used for the fertilizer industry are as follows:

- Falling film evaporation is typically used to concentrate a solution in non-scaling applications. It is often used to pre-concentrate a stream before a separate crystallisation process begins and can be used to concentrate highly soluble salts, such as calcium chloride, to make high-concentration solutions.

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

- The draft tube baffle (DTB) crystalliser or HPD® partitioned internal circulation (PIC™) crystalliser is commonly used in the fertilizer industry. This type of
crystalliser is used in applications that require narrower crystal size distribution and larger crystal size. These crystallisers are common for KCl, ammonium sulfate, MAP/DAP production, among others. The crystalliser consists of an internal draft tube with an agitator and a baffled section that overflows to an external recirculation loop for heating and/or fines destruction. The agitator, a vertically mounted axial flow impeller, provides the high recirculation flow through the draft tube.

- The Oslo type or HPD growth crystalliser design is a classified suspension classified product removal (CSCPR) crystalliser with well-developed bed fluidisation and circulation of a magma or crystal slurry. The fluidised bed provides classification of the crystalliser inventory by crystal size. The classification advantages of an HPD growth unit have been demonstrated in applications from high-purity to fertilizer grade KCl and from byproduct to high-purity ammonium sulfate.

**Equipment configurations**

There are multiple ways to configure equipment for evaporation and crystallisation in order to maximise project economics and process efficiency. Factors that must be considered in the design are:

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

In a steam driven system, steam is introduced into the heater in order to transfer the heat from the steam to the solution that is being concentrated in the heater tubes. The vapour that is generated as a result 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 at a progressively lower pressure in each additional effect. This greatly increases the steam economy, which is 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 in lieu of steam to drive the evaporation. The water that is evaporated is compressed using a mechanical vapour compressor. The resulting higher pressure vapour is used in the heater to drive the evaporation. This results in much higher energy efficiency than a steam driven system and is beneficial where steam or cooling sources are limited.

The multiple stage vacuum flash configuration is often used for products that have an inverse solubility. The crystallisers use adiabatic cooling whereby the evaporation caused by the vacuum in the crystalliser cools the liquor. The product precipitates as a result of the cooling. This is a typical configuration used for KCl production.

**Process challenges**

Often it is imperative to perform bench or pilot scale tests to develop or confirm the design parameters, using ideally the actual feed solution expected for the commercial plant or, if not available, a synthetic solution.

The process challenges to design a commercial plant are:

- Production of high-quality product salts: fertilizer products may have specific crystal habit, size or purity requirements.
- Adaptation to environmental constraints, which may include a limitation upon waste liquid or other discharged material into the environment, a limited energy supply or a restricted cooling media supply.
- Valuable product recovery from waste streams or byproducts.
- Heat integration and water balance optimisation.
- Choice of materials of construction: balance between resistance to the corrosive environment (feed or mother liquor is often at high temperature and contains high
concentrations of corrosive compounds), and cost competitive solution.

**Case study 1: potash from solution mining**
A recently commissioned greenfield project in Saskatchewan, Canada, will use solution mining to produce 2 million tpy of potash (or KCl). The ore is mainly sylvite (NaCl and KCl) and contains small amounts of carnallite (KCl·MgCl₂·6H₂O) and other minor impurities (CaCl₂, CaSO₄, NaBr, etc.).

**Process description with energy and water optimisation**
A block diagram of the solution mining process is shown in Figure 3. The ore is dissolved by injecting hot water underground resulting in a brine solution that must be treated to recover the KCl. The initial treatment step is to remove NaCl via evaporation. The NaCl evaporation system consists of multiple effect evaporation that integrates a thermo-compressor for improved energy efficiency. Each NaCl crystalliser effect is a forced circulation crystalliser with an elutriation leg for removal of the NaCl. The brine from the solution mine is saturated in calcium sulfate, so it is necessary to manage this throughout the evaporator system to prevent scaling in the evaporator heaters.

The hot pregnant mother liquor from the NaCl evaporator system is a nearly saturated KCl solution. The KCl is crystallised in a multiple stage, adiabatic cooled crystalliser system consisting of DTB crystallisers. Each stage operates at a progressively lower pressure/temperature and KCl precipitates as the mother liquor is cooled. Water is added and flows are adjusted to control product purity and crystal size.

Solution mining requires large volumes of water to dissolve the ore and additional water is used throughout the evaporation and crystallisation process. The water that is evaporated is recovered and reused in the solution mining process in order to minimise the amount of make-up water that is required.

**Complex equipment supply logistics**
Due to the size of the project, it was necessary to source equipment from multiple locations. Some of the vessels were pre-fabricated in China and were shipped to Houston then trucked to Saskatchewan. It was desirable to minimise the amount of site construction work and do as much of the vessel fabrication in off-site shops as possible. This resulted in some complex equipment supply logistics. The top of the equipment being transported was over 12 m off the ground, over 50 m long and weighed about 330 t.

**Case study 2: ammonium sulfate production**
A reactive ammonium sulfate crystallisation unit with a production capacity of 300 000 tpy was designed and installed, with operation commencing in 2014.

The plant process technology is a reactive HPD PIC draft-tube crystalliser (Figure 5) followed by solid-liquid separation, drying in a counter current rotary dryer/kinetic cooler, screening, product storage, packaging and auxiliary storage. Veolia provided the process design and supplied the equipment for the entire production facility. This includes raw material offloading and storage, the crystallisation plant for producing the high-quality ammonium sulfate crystals, including final product drying and solids handling.

**Process description and challenges**
The basic process block flow diagram is shown in Figure 6. Ammonium sulfate is produced in the crystalliser by reacting gaseous ammonia and sulfuric acid dissolved in the mother liquor. Various sources of these feed materials were considered in order to provide system flexibility and are allowed for in the design. The primary source of sulfuric acid is a byproduct from a urea production facility. An option exists to use waste ammonia produced in a nearby refinery. The reaction is highly exothermic. No external heat source is used. While this offers significant energy advantages,
it also presents a more challenging process control scheme to assure ease of operation and consistent product output.

Cooling water usage had to be minimised due to the high cost of water on site. Veolia used air-cooled condensers to condense vapours from the crystalliser providing significant cooling water savings.

The slurry from the crystalliser is dewatered using two pusher-type centrifuges. The centrifuge wet cake is discharged to a counter current rotary air dryer. The dried product is conveyed to a vibrating screen. The over- and under-sized product are sent to the dissolution tank via gravity for reprocessing while the granular and standard product are conveyed to storage. The final product is sold in bulk and in 25 kg bags.

**Performance**

The process needs to consistently produce very large crystals to achieve the highest product value. The development of large crystal size is a key design benefit of the HPD PIC crystalliser design. A performance test was then carried out successfully, achieving the results shown in Table 3.

**Case study 3: potassium sulfate from polyhalite ore**

The process involves several key unit operations to process conventionally extracted polyhalite ore (K₂CaMg(SO₄)₂·2H₂O) from the mine to produce more than 700 000 tpy of sulfate of potash (SOP, K₂SO₄) products.

Veolia was selected to refine, confirm and validate the process, using HPD evaporation and crystallisation technologies. Process validation was achieved through a series of bench and pilot-scale testing programmes performed in Veolia’s HPD research and development facility.

**Process testing description**

Figure 7 illustrates the leaching and crystallisation block diagram. The scope of the testing extended from the ore leaching to the SOP (K₂SO₄) crystallisation process, including crystallisation/redissolution of leonite (K₂Mg(SO₄)₂·4H₂O) and calcium sulfate removal.

**Results**

For this system, the challenge was to develop a cost-effective process to produce a premium potassium sulfate fertilizer. The series of tests proved to be a success as the produced SOP achieved the purity, crystal size and habit requirements for a fertilizer application. Based on the results, the testing provided the confidence that a commercial system would perform as designed and meet the product quality specifications.

**Conclusion**

Evaporation and crystallisation processes are currently prevalent in commercial fertilizer production facilities. As fertilizer demand continues to rise and there is decreased availability of low-cost raw materials, new fertilizer production technology is being developed. Evaporation and crystallisation also plays an important role in these emerging technologies. To develop these new applications it is often necessary to conduct development work, including research, bench scale and pilot scale testing and process development work.