Giedrius Rutkauskas, Arionex Wasseraufbereitung Gmbh, Switzerland, outlines why the fertilizer industry should take the opportunity to mitigate pollution created from water demineralisation.

GRASPING A UNIQUE OPPORTUNITY

Water plays a crucial role in the fertilizer industry, primarily in steam generation, cooling cycles, and, more recently, hydrogen production. Two main technologies are relied upon for water demineralisation: ion exchange and reverse osmosis. Ion exchange technology generates 5 – 10% wastewater as a byproduct, contaminated with regenerants like NaOH, H_2SO_4, or HCl. In contrast, reverse osmosis technology produces a discharge stream of 20 – 30% from the input water, with salts concentrated four to five times higher than raw water. Both technologies create pollution that is environmentally undesirable for disposal.

However, the fertilizer industry has a unique opportunity to mitigate this environmental pollution using a combined ion exchange-membrane technology.

This approach employs HNO_3 and NH_3 solutions for regenerations. The regeneration process of ion exchange resins results in effluents enriched with salts removed during demineralisation, producing both demineralised water and concentrated effluents (15 – 18%). These effluents contain approximately 50% of Ca, Mg, K, Na, SO_4, Cl, and Si salts and 50% of NH_4NO_3. Rich in minerals extracted from water and ammonium nitrate, the effluent serves as raw material for the production of liquid or solid NPK fertilizers. In this way, minerals originally present in the water return to the soil and plants, completing a sustainable cycle.

History

Half a century ago, a specialised ion-exchange treatment and recovery process known as Fertarex was invented. This process aimed to address issues related to condensate contaminated with ammonium nitrate. Utilising specific cation and anion ion-exchange resins, regenerated with 50 – 60% nitric acid (HNO_3) and 15 – 20% ammonia (NH_3), the Fertarex process is now used in many nitrogen fertilizer complexes. Its purpose is to produce demineralised water and recover the discharged nitrogen products as an 18 – 20% NH_4NO_3 solution, obtained from the regeneration of cation and anion resins. This recovered solution is either recycled directly into the ammonium nitrate production plant or concentrated to 75 – 80% NH_4NO_3 through a supplementary vacuum evaporation plant. Due to the production of demineralised water and the recovery of all discharged nitrogen products as ammonium nitrate fertilizer, no contaminated nitrogen (N) wastewater is discharged into the environment, resulting in significant cost savings. A medium-sized ammonium nitrate production plant can save up to US$1 – 1.5 million per year, making it possible to recoup the initial investment in less than five years.

Figure 1. Fertarmix plant.

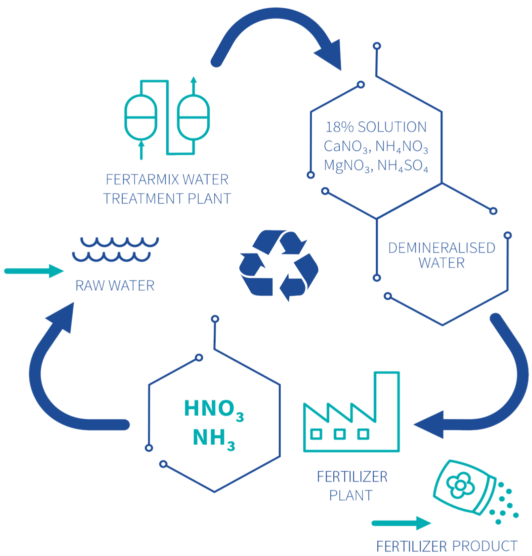

Figure 2. Recycling scheme.

Existing water demineralisation technologies

Demineralised water is a critical product, especially for the chemical industry and as boiler feed water for power stations. For over a century, demineralised water has been primarily produced using ion-exchange techniques. This approach employs cation resins (R-H) to remove calcium (Ca), magnesium (Mg), sodium (Na), and anion resins (R-OH) to remove sulfate (SO_4), chloride (Cl), nitrate (NO_3), bicarbonate (HCO_3), silica (SiO_2), and more. Mixed bed ion-exchange polishing yields high quality demineralised water with conductivity values below 0.1 μS/cm. When the ion-exchange resins become exhausted, they are regenerated using acids such as hydrochloric acid (HCl) or sulfuric acid (H_2SO_4) for cation resins, and caustic soda (NaOH) for anion resins. Typically, the waste effluents from resin regeneration contain high levels of salts and excess acids or caustic, leading to significant environmental pollution.

A more advanced technology is reverse osmosis membrane technology, which separates water into two streams: demineralised and concentrated flow (with low and high salt concentrations, respectively). Pressure is applied to the membrane to achieve this separation. While membrane technology does not employ regenerants, its recovery rate varies between 70 – 80%, resulting in a concentration factor four to five times higher than the inlet water. This technology generates less polluted wastewater than ion exchange but in significantly larger quantities.

Both processes produce wastewater, which, under certain environmental conditions, cannot be discharged into natural water sources such as rivers and lakes.

Zero discharge water demineralisation processes

Considering the principles of the circular economy, the idea emerged to use historically-used technology for concentrating ammonium nitrate from condensate in a new water demineralisation process. This approach enables the recycling of salts extracted from water, as natural water from surface or ground sources inherently contains minerals that have dissolved into it. Water acts as a natural solvent, and minerals originate from the soil and rocks. Returning these minerals to the soil in small quantities creates a fully recyclable demineralisation process, as opposed to accumulating minerals in one place and causing pollution. Growing plants require not only nitrogen, phosphorus, and potassium for their growth, but also other elements like calcium, iron, manganese, magnesium, and sulfur.

In this way, minerals from water are incorporated into fertilizers as part of their composition, ultimately returning to the soil and plants where they originally came from. The Fertarmix ion-exchange water demineralisation process is primarily applicable in NPK complex fertilizer fabrication plants for producing demineralised water from pretreated surface water. Fertarmix is a modern ion-exchange demineralisation system that regenerates loaded cation and anion resins with nitric acid (HNO_3) and ammonia (NH_3).

Through selective fractioning of the regeneration effluents and neutralisation of excess NH_3 with HNO_3 to a pH value of 4.5, the process results in 12 – 16% TDS effluents, primarily containing NH_4NO_3 and small amounts of NO_3 and NH_4 salts. These effluents are then recycled back into NPK production plants.

Utilising on-site-produced HNO_3 and NH_3 regenerants, the process significantly reduces water demineralisation operation costs and eliminates the discharge of contaminated waste effluents into the environment, achieving a zero discharge system.

The process

To implement this process, the inlet water must undergo pretreatment using the same technologies as conventional water treatment plants. This involves removing suspended solids and reducing organic content, which can be accomplished using conventional clarifiers or ultrafiltration technology. The effluents from these processes can be easily converted into more or less dry cakes, suitable for disposal in landfills or use as inert material for various products. The pretreated water is then recycled back into the process. Subsequently, the water passes through cation and anion ion-exchange filters to remove Ca, Mg, K, Na on cation resins and SO_4, Cl, HCO_3, NO_3 on anion resins. After a filter cycle, the cation resin is regenerated with concentrated HNO_3, while the anion resin is regenerated with NH_3. The effluents from these regeneration processes are fractionated, with the most concentrated effluents collected separately as raw material for NPK production. Other regeneration waters are recycled within the process. The water emerging from the cation-anion filters undergoes further polishing using electrodeionisation (EDI) technology, which combines membrane and ion-exchange technologies. The resulting demineralised water, with a salt content of just 0.1 ppm, is suitable for various industrial processes. The EDI concentrate passes through an ion exchange filter to remove silica (Si). This filter is regenerated with KOH, and the effluents containing K and Si are mixed with the main process effluents, which are used to feed NPK production.

While this process description is general, the main mineral conversion technology can be combined with other technologies, such as nanofiltration, lime clarification, pellet softening, and reverse osmosis, depending on the quality of the inlet water. A thorough analysis of water quality is essential to determine the optimal combination of technologies, aiming for the best capital expenditure (CAPEX) and operational expenditure (OPEX).

Tests

In 2019, a pilot plant was built, and numerous tests were conducted using river water with ultrafiltration pretreatment. The tests were focused on process safety checks (when surface or ground water is treated) and process potential to achieve the highest possible effluent concentration. One of the test results is as follows:

- Cation-anion exchangers, each filled with 14 l resins.
- Inlet water TDS: 205 ppm.
- Flow rate: 250 l/h.
- Filter cycle: 3200 l.
- Effluents quantity: 20 l, representing 0.62% of the cycle.
- Effluents TDS: 177 000 ppm.
- Treated water quality at the end of the cycle: 10 – 12 microS/cm.

These tests demonstrated that the resins functioned reliably, high effluent concentration could be achieved, the process operated smoothly, and that there were no indications of cation resin degradation.

Experience

The most recent ammonium nitrate condensate treatment plants, utilising cation-anion technology with concentrated HNO_3 and NH_3 regenerants, were built in fertilizer plants – one in 2005 at Romania's Azomures S.A. Ameropa Holding, and another in 2010 at Turkey's Gemlik S.A. These plants have operated successfully for many years. Despite some resin producers not recommending the use of HNO_3 acid for cation regeneration due to its strong oxidising properties, practical experience has shown that a special configuration of resins and safety techniques for regeneration results in stable equipment operation without any incidents over extended periods.

Limitations

There are limitations to applying the aforementioned technology. In cases of high salinity (above 5000 ppm), it may not be economically efficient to treat water using this technology due to the high regenerant consumption and the generation of excessive effluents that cannot be utilised in existing NPK production. Additionally, the salt composition of the inlet water, especially the presence of heavy metals and high chloride (Cl) content, might be unacceptable for inclusion in NPK compositions. Each case for the combination of feed water composition and customer's production/products possibilities to use obtained salts as additives should be analysed or even tested. This consumes some time and effort.

Conclusions

The circular economy is an important approach to preserving the environment. Any technology that helps protect nature should be considered and evaluated alongside conventional technologies. In some instances, it becomes evident that environmentally friendly technologies can also be economically beneficial for industries. WF

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