




DECARBONISING

DIAMMONIUM

PHOSPHATE



Stephen B. Harrison, sbh4 Consulting, Germany, outlines methods that can be used to capture the carbon emissions generated during diammonium phosphate production.

Diammonium phosphate (DAP) is the most common phosphate fertilizer. High volume commodity crops such as wheat, maize, and rice all benefit from DAP. It is popular because it is safe to handle, can be applied conveniently as granules, and introduces both nitrogen and phosphorus to the soil.

OCP is the world's largest producer of phosphate fertilizers with 31% global market share. Jorf Lasfar is the world's largest phosphate processing plant and the largest fertilizer complex in the world, from which OCP exports phosphate fertilizers worldwide.

Florida, US, is also a major producer of phosphate fertilizers, exploiting locally mined fluorapatite ore. The Mosaic Company and Nutrien both operate fertilizer production plants there. Despite this local production, the US is the largest importer of DAP worldwide.

Geogenic CO₂ from DAP production

DAP is produced in locations where phosphate rock is mined. This ore is rich in a phosphorus-bearing mineral, fluorapatite. The ore is beneficiated to remove sand, clay, and as much calcite as possible.

In addition to CO₂ emissions from the heat and energy requirements of DAP production, geogenic CO₂ is produced during DAP production because the fluorapatite mineral is contaminated with calcite (calcium carbonate, or limestone).

The beneficiated fluorapatite ore is mixed with sulfuric acid, to yield phosphogypsum as a solid waste material and phosphoric acid. The phosphoric acid is reacted with ammonia, then granulated and sieved to produce DAP.

In addition to ore beneficiation, phosphoric acid production and DAP granulation, the end-to-end process generally involves on-site production of sulfuric acid from sulfur. Ammonia, another key input to the process, can be made on-site, but is generally purchased from off-site sources.

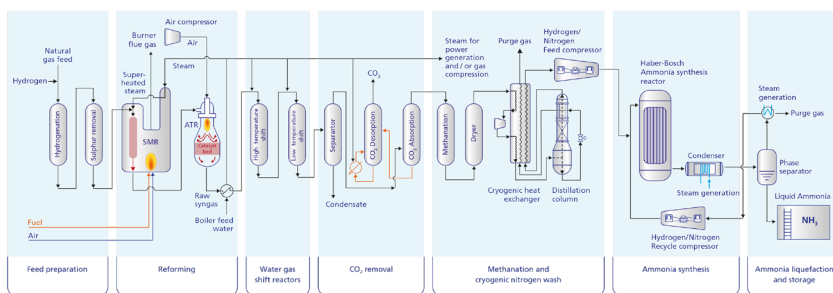
High quality ores, such those found in Morocco, and Jordan contain between 10 and 15% calcite. In other main phosphate rock mining locations such as Florida and Saudi Arabia, the calcite content can be up to 20%.

During phosphate rock beneficiation, clay and silica are easily removed. However, only about half of the calcite is separated from the fluorapatite and the calcite is mixed with the sulfuric acid, along with the fluorapatite. During the reaction between calcite and sulfuric acid, CO₂ is released.

The flue gas from the sulfuric acid mixing chamber is hot, moist, and contains hydrogen fluoride (HF), which is released from the fluorapatite ore. It is scrubbed with water to remove the HF. The resultant gas mixture is hot, moist CO₂ which is generally vented to atmosphere.

If the calcite content of the beneficiated ore is reduced to 6%, as would be the case in Morocco, approximately 0.05 t of geogenic CO₂ per tonne of DAP produced. For Saudi Arabian DAP production, the geogenic CO₂ emissions liberated during the production of phosphoric acid are close to 0.1 t of CO₂ per tonne of DAP.

To partially decarbonise DAP production, recovery and separation of the geogenic CO₂ from moist flue gas can easily be achieved using cooling and condensation. The resultant dry, pure CO₂ can then be liquefied for rail or sea shipment, or compressed for pipeline transmission at low marginal cost.



Compression duty for 1,000 tonne per day ammonia plant

Hydrogen/Nitrogen feed compression	11 MW
Air compressor (Air Separation Unit)	7 MW
Ammonia gas recycle	4 MW
Boiler water feed & cooling water pumps	1 MW

1. The SMR and the ammonia synthesis loop both generate steam, and the majority of the HP steam is from the SMR
2. Much of the compression energy is recovered from HP/NIP steam expansion turbines which may either generate power and / or drive compressors on the same shaft
3. Heat energy (MP steam) for the CO₂ capture is recovered from within the process
4. The overall process, including the SMR, can export a small amount (circa 2 MW) of MP steam

Figure 1. Air fed ammonia production process.

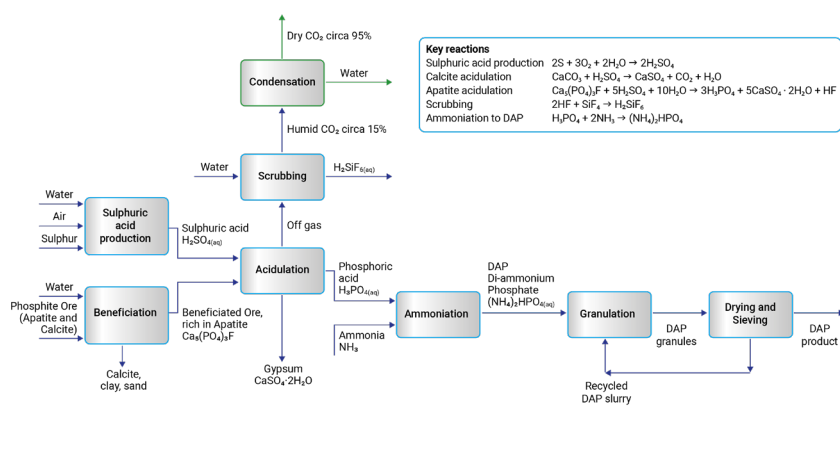


Figure 2. Geogenic CO₂ capture from phosphoric acid and DAP.

From theory to practice

The idea to capture CO₂ from phosphate fertilizer production will be implemented from 2027 by OCP Nutricrops in partnership with OCP Green Water and INNOVX at OCP's Jorf Lasfar industrial platform in Morocco.

The initiative is part of OCP Group's decarbonisation roadmap, which aims to achieve carbon neutrality across Scope 1, 2, and 3 emissions by 2040. It also addresses international competitiveness by reducing the CO₂ intensity of DAP which is important when exporting to the EU where the Carbon Border Adjustment Mechanism (CBAM) will impose tariffs on carbon-intensive imports starting in 2026.

The captured CO₂ will be used by OCP Green Water for pH adjustment and re-mineralisation of drinking water in support of a local reverse osmosis desalination plant. This will support Morocco's goal to meet 100% of the nation's water needs through unconventional resources by 2027.

INNOVX will develop a plant to use captured CO₂ and waste phosphogypsum to produce ammonium sulfate fertilizer. The Merseberg Process is one of the pathways to achieve this. It reacts aqueous ammonia with CO₂ to produce ammonium carbonate.

Phosphogypsum is reacted with ammonium carbonate to yield calcium carbonate and the target product ammonium sulfate. Calcium carbonate is a recognised permanent sink for CO₂, so this pathway sequesters CO₂ gas emissions from the DAP process and enables integrated production of ammonium sulfate.

Ammonium sulfate was the first commercially available nitrogen fertilizer.

However, it was displaced in many markets by ammonia and urea due to their higher nitrogen content. But, it is still used extensively in Brazil, which imports about 4 million tpy, mostly from China.

Ammonium sulfate is suitable for the Brazilian soils which contains very low sulfur levels. Sulfur is essential to grow high protein crops such as soya beans, which are exported to the US and used locally for beef cattle farming.

Ammonium sulfate also has a lower ammonia volatilisation rate than urea. This is an important factor in the warm Brazilian climate and leads to its use on South East Asia for growing wheat and rice.

Deep decarbonisation

For each tonne of DAP, 0.2 t of ammonia is required to react with the phosphoric acid. Grey ammonia production releases about 1.8 t of CO₂ per tonne of ammonia. Thus, 0.36 t of CO₂ is released from the ammonia required to produce 1 t of DAP.

Comparing the CO₂ emissions from ammonia production to the geogenic CO₂ emissions for the Moroccan and Saudi Arabian cases above, this is about 3.5 - 7 times more than the amount of CO₂ released from phosphoric acid production. To achieve deep decarbonisation of DAP production, capture of CO₂ from ammonia production is also essential.

When ammonia is made from steam methane reforming (SMR) of natural gas, CO₂ leaving the reformer in the syngas must be removed to enable the catalytic Haber-Bosch ammonia

synthesis reaction to take place. This is normally achieved using an amine solvent based CO₂ capture process.

The active ammonia catalyst is iron. All molecules containing oxygen, such as water, carbon monoxide or CO₂ must be removed from the syngas before it is fed to the ammonia synthesis loop. Otherwise, the catalyst is oxidised and becomes ineffective. Therefore, every natural gas-fed ammonia plant already has a CO₂ capture facility.

In some facilities, about 60% of the captured CO₂ is combined with ammonia to make urea. However, the residual 40% of the CO₂ from the SMR and ammonia plants that do not utilise captured CO₂ for urea production can sequester the captured CO₂ to reduce the CO₂ intensity of DAP and nitrogen fertilizer production with only a small incremental cost for CO₂ sequestration.

In China, coal-fed ammonia production is more common than the use of natural gas. Immediately after coal gasification the raw syngas is fed to a Rectisol unit where CO₂ and sulfurous gases are removed.

This captured CO₂ from ammonia synthesis coal gasifiers can also be sequestered at low-cost incremental since the capital and operating costs of the Rectisol plant are absorbed into the overall costs of ammonia production. To reduce the CO₂ intensity of coal to ammonia, the only incremental costs are CO₂ transmission and sequestration.

Process integration

OCP Group's third integrated fertilizer production plant, Jorf Fertilizers Company 3 (JFC 3), has been fully operational since 2017. JFC 3 has a capacity of 1 million tpy of granulated phosphate fertilizers.

JFC 3 includes a sulfuric acid line with a capacity of 1.4 million tpy, as well as a phosphoric acid line of 0.45 million tpy. The chemical reactions involved in the production of these acids are exothermic and the heat is used to generate steam for 62 MW of electricity generation on a thermal power plant. This process integration makes the JFC 3 unit autonomous in terms of energy consumption and reduces the requirement to burn fossil fuels for electricity generation.

Phosphogypsum recycling

Ma'aden Phosphate is collaborating with thyssenkrupp Uhde, with additional expertise from thyssenkrupp Polysius, to recycle phosphogypsum at Ras Al Khair.

Phosphogypsum is the solid waste material that is generated during phosphoric acid production. It is produced when sulfuric acid combines with the phosphate ore to produce phosphoric acid. Effectively, liquid sulfuric acid and solid phosphate rock is converted into liquid phosphoric acid and solid phosphogypsum.

Towering white phosphogypsum mountains are common close to phosphoric acid and phosphate fertilizer plants. Through calcination of phosphogypsum using high temperature heat, this waste can be converted to lime (CaO), sulfur dioxide (SO₂), oxygen, and water. The SO₂ gas can be converted to sulfuric acid to introduce circularity to the DAP production process.

The lime can be used for cement and steel production. Also it is used in the pulp and paper industry and for pH modification of soils. Alternatively, the lime can be used to mineralise CO₂ emissions from DAP production to produce calcite (CaCO₃). This mineral is insoluble and is recognised as a permanent CO₂ storage mechanism. **WF**



Figure 3. OCP Jorf Lasfar sulfur unloading.



Figure 4. Phosphogypsum in Heulva, Spain.