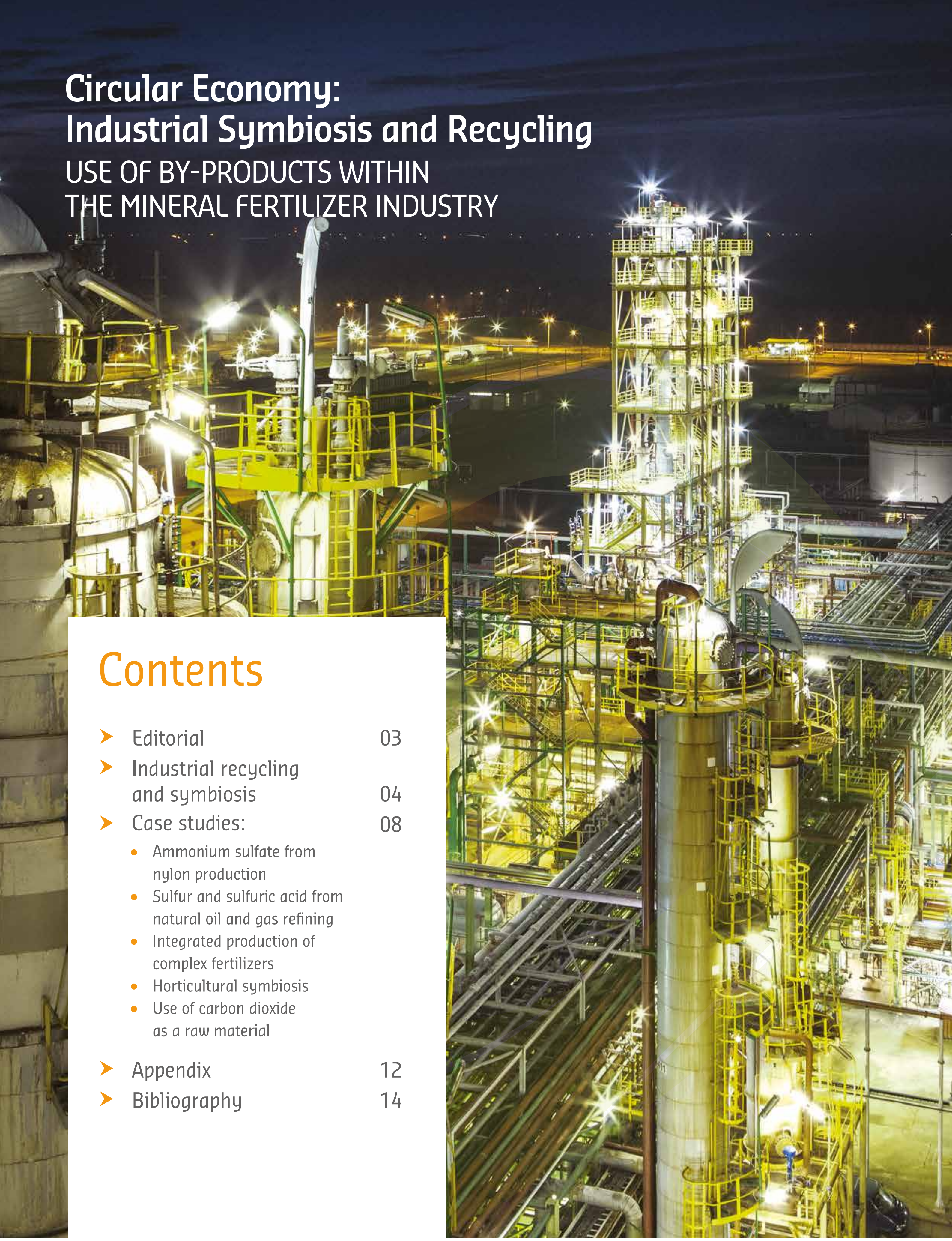
Infinite product stewardship

fertilizers europe

Circular Economy
& the European fertilizer sector



Circular Economy: Industrial Symbiosis and Recycling

USE OF BY-PRODUCTS WITHIN THE MINERAL FERTILIZER INDUSTRY

Contents

- Editorial 03
- Industrial recycling and symbiosis 04
- Case studies: 08
  - Ammonium sulfate from nylon production
  - Sulfur and sulfuric acid from natural oil and gas refining
  - Integrated production of complex fertilizers
  - Horticultural symbiosis
  - Use of carbon dioxide as a raw material
- Appendix 12
- Bibliography 14

Circular Economy is already here!

> *The fertilizer industry has always been circular.*
>
> ***Jacob Hansen,*** *Fertilizers Europe*

From the very beginning, the mineral fertilizer industry was a circular economy. In a typical fertilizer plant, by-products from one process are used as raw material for other processes and vice versa.

This brochure presents five case studies which illustrate how our industry utilizes the concept of circular economy. The case studies show how the fertilizer industry grew from foundations based on circular thinking, and today, it involves the recycling of millions of tons of material.

Already a leader in circular economy, the fertilizer industry understands that even more can be achieved to further strengthen our role within it. The goal of industrial symbiosis and recycling is to improve the industrial system by optimizing resource use, closing material loops, and minimizing emissions.

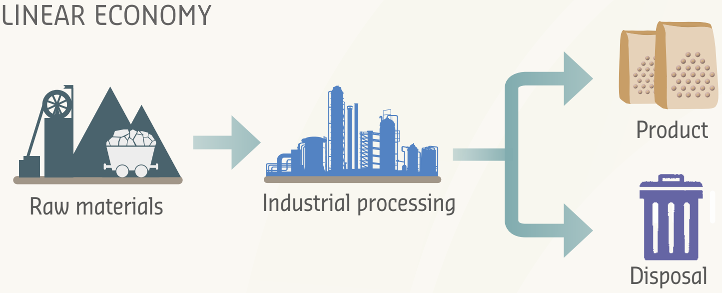
At the end of the brochure, you will find an appendix listing the most common materials which link to the circular nature of fertilizer production.

Jacob Hansen, Director General

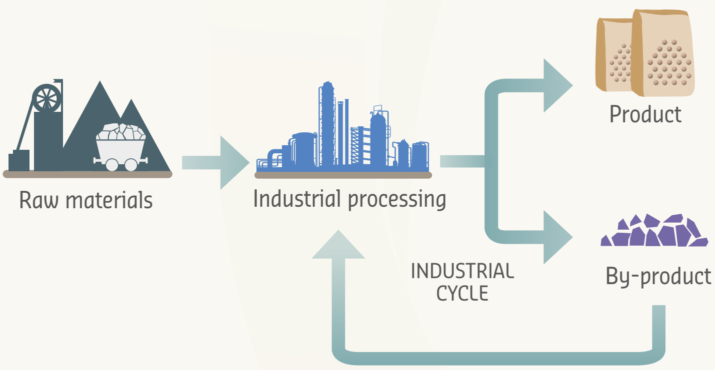
Industrial Recycling and Symbiosis

In simple words, industrial recycling consists of reintegrating parts of by-products or waste generated in the production process. Industrial symbiosis refers to the mutually beneficial exchange of materials and energy between separate industrial production processes. This concept is a strong characteristic in the mineral fertilizer industry.

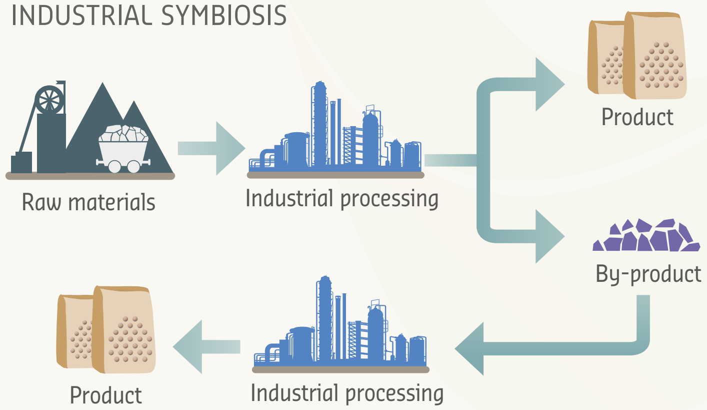
LINEAR ECONOMY



INDUSTRIAL RECYCLING



INDUSTRIAL SYMBIOSIS



Recycling and symbiosis in industry close the loop in material and energy flows during manufacturing. The concept of industrial symbiosis is intended to avoid waste by recycling products and using them as input for other production processes.

The principal objective in both instances is to optimize resource use, close material loops, and minimize emissions, thus reducing and possibly even eliminating the dependence on non-renewable energy resources. This is achievable by focusing on industrial networks on local, regional and European levels.

The European Union has recognized the potential contribution of industrial recycling and symbiosis towards sustainable production and competitiveness of the European industry. “The Roadmap to a Resource Efficient Europe” published by European Commission, indicates that better reuse of raw material could save 1.4 billion euros and generate 1.6 billion euros in additional sales annually.

Industrial symbiosis intends to avoid creating waste and move towards integrated systems in which every product has its use and value:

- keep resources in use for as long as possible
- minimize residual waste
- extract the maximum value from products
- recover and regenerate products and materials at the end of service life

Focus on the fertilizer industry

INDUSTRIAL SYMBIOSIS & RECYCLING

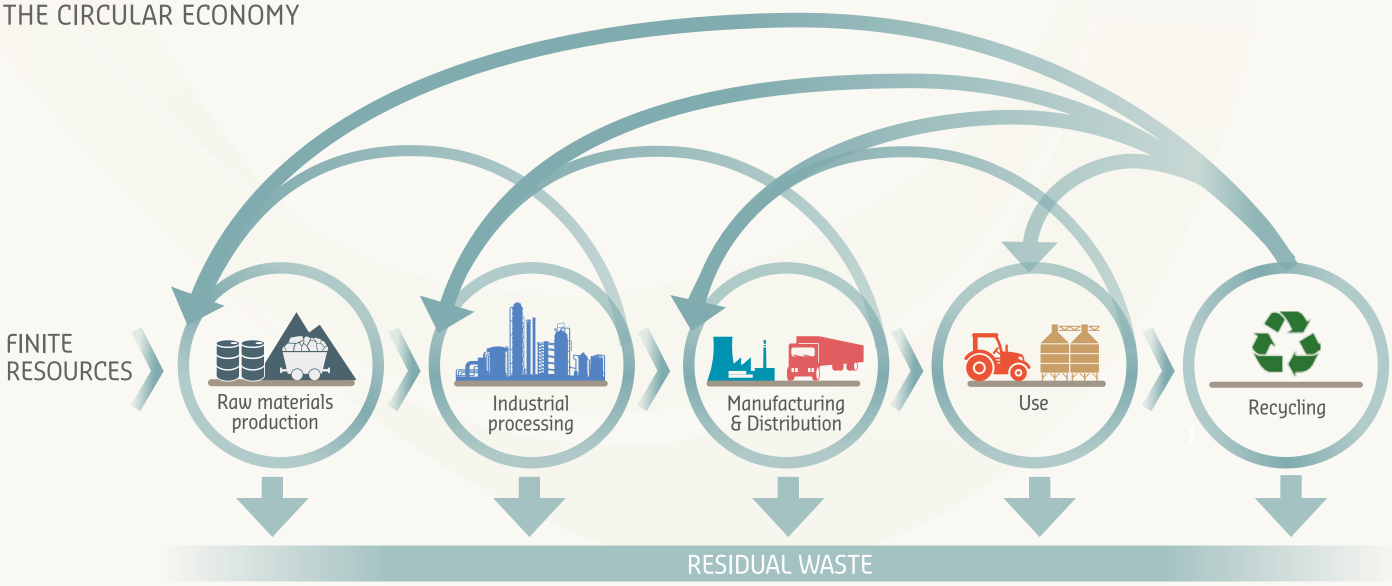
The fertilizer industry has had particularly optimized production systems for over one hundred years. It had always made use of spent raw material that derived from related production processes, today known as by-products.

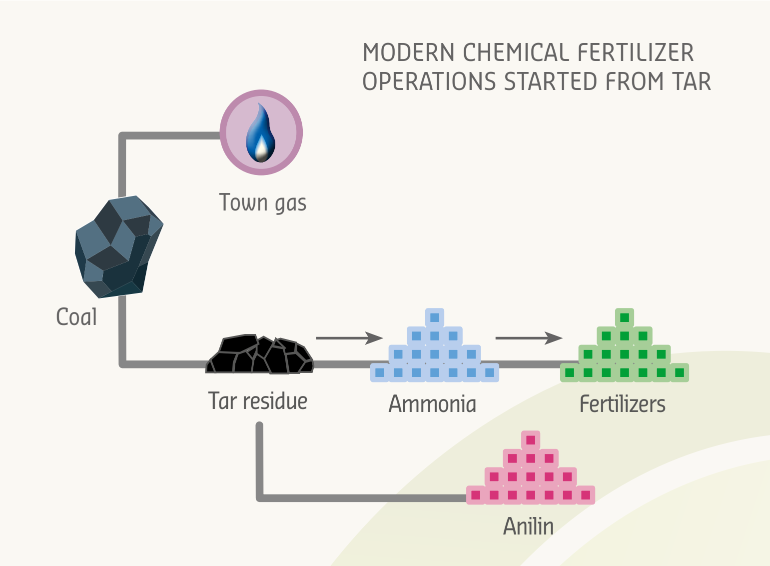
Modern chemical operations, as we know them today, began in the second half of the 19th century and were mainly fueled by coal. During that time, coal was also used to produce town gas for street lighting purposes. The tar residue, or by-product, of this process was found to contain a range of chemicals that could be extracted to provide aniline, the basis for artificial dyes, and ammonia, which is the basic raw material for modern fertilizers.

Throughout those times, the industry evolved greatly and the demand for ammonia to be used as a component in fertilizers substantially exceeded its availability, and thus the search began for an industrial route for ammonia production. This ultimately led to the Haber-Bosch process, which is still the most energy efficient production process in use today.

Nevertheless, the principles of recycling have always remained in the very DNA of our industry, which over the past 100 years, has continued to integrate a vast range of by-products from other industries.

THE CIRCULAR ECONOMY





Typical examples are:

- use of ammonium sulfate from nylon synthesis for making sulfate-containing mineral fertilizers.
- use of sulfur from oil and gas refining operations for making sulfuric acid
- application of used acids in dissolving insoluble rock phosphates for making water-soluble and therefore plant available phosphate fertilizers

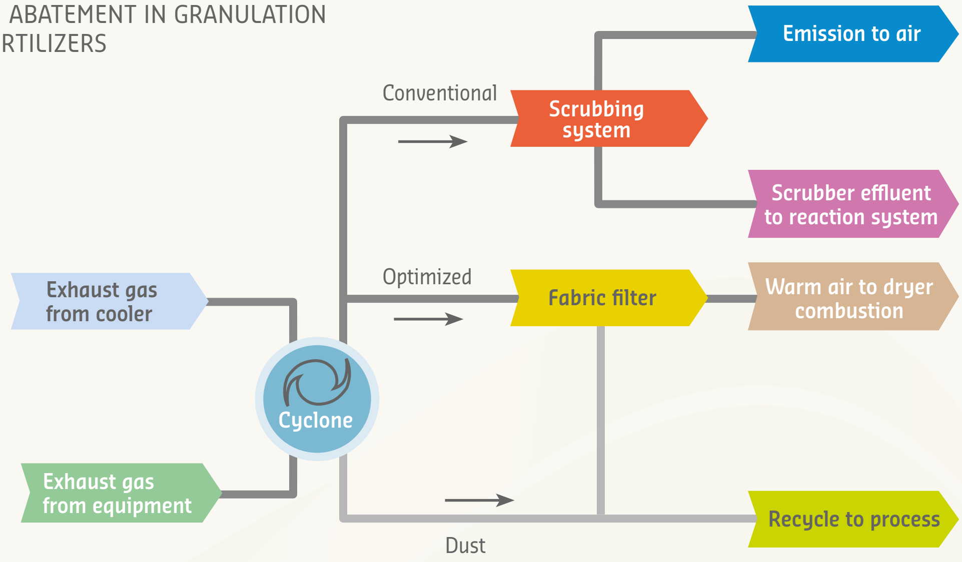
More details on the above as well as other case studies are presented in later chapters of this brochure. Furthermore, a non-exhaustive list of recycled by-products is given in the appendix.

ENERGY USE OPTIMIZATION

Waste heat from one process is used as heat input in another process.

Recycling in the fertilizer industry is not limited to only chemical products. The production of fertilizers requires significant amounts of energy (such as in the case of ammonia production) and also produces large amounts of energy and heat (such as in the case of nitric acid production). All processes can be optimized for best energetic performance, as both energy and heat are required in all industrial production systems.

RECYCLING OF EFFLUENT STREAMS FROM ABATEMENT IN GRANULATION OF FERTILIZERS



INTERNAL RECYCLING

Fertilizer manufacturing processes have abatement systems installed in order to minimize emissions into air and water. For example, in the granulation of calcium ammonium nitrate (CAN) or multi-nutrient NPK fertilizers, dust particles generated from the production process are recovered through methods such as cyclones, fabric filters and scrubbing systems.

The image above describes a system related to the abatement in granulation of fertilizers where the dry recycling material and the liquid solutions are reused within the same installation. This minimizes emissions and makes full use of the original raw material. Besides recycling within one production plant, a process of recycling products between different fertilizer plants is also often incorporated.

The reference document "Best Available Techniques for the manufacture of Large Volume Inorganic Chemicals - Ammonia, acids and Fertilizers" (LVIC-AAF), published by the European Commission, shows a number of examples of emission abatement, recycling and reuse of by-products, as well as recovery of heat.

Case studies

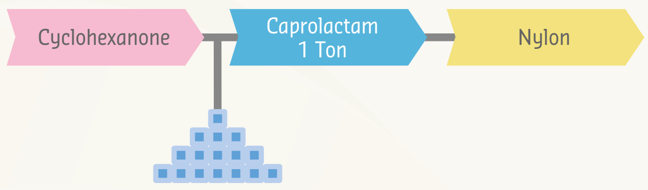
1 Ammonium sulfate from nylon production

Nylon 6 is a synthetic polymer. It is manufactured through polymerization of caprolactam. Caprolactam itself is made from cyclohexane or cyclohexanone in a process that cogenerates ammonium sulfate (see image below). 2,0 to 2,2 tons of ammonium sulfate are produced per ton of caprolactam.

Globally, the production of caprolactam amounts to 4,5 million tons per year, which are linked to generating approximately 10 million tons of ammonium sulfate.

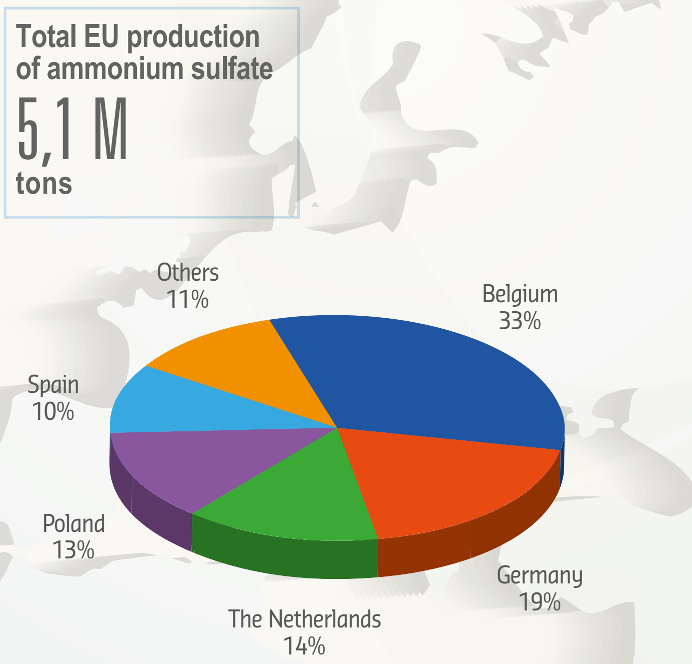
In Europe, the annual production of the by-product ammonium sulfate amounts to about 5,1 million tons generated through the manufacturing process of caprolactam out of 7,5 million tons of ammonium sulfate produced in total.

PRODUCTION OF NYLON

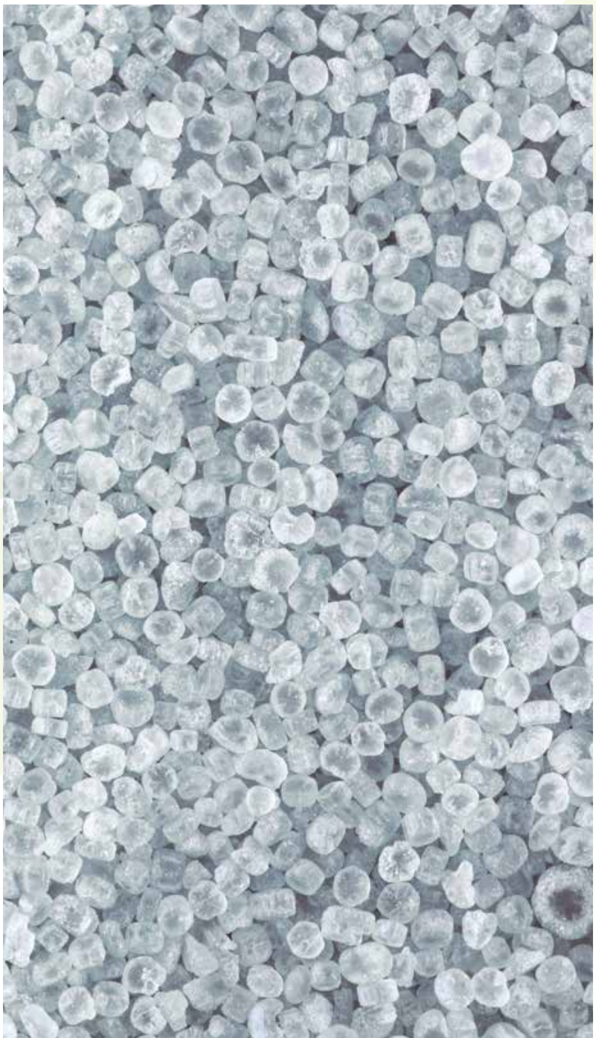


These white crystals are used for direct fertilization (particularly on crops that prefer nitrate-free forms of nitrogen), multi-nutrient fertilizers such as NPK, or single-nutrient formulations. Ammonium sulfate is a water-soluble component of fertilizers, and in that way, supplies needed sulfur to soil.

AMMONIUM SULFATE PROVENANCES IN EUROPE



Source: IFA 2015



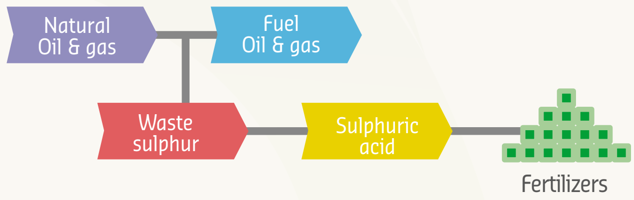
2 Sulfur and sulfuric acid from natural oil and gas refining

Natural oil and gas contain significant amounts of sulfur. If this sulfur is not removed, it is transformed during the combustion process into sulfur oxides which contribute to the formation of acid rain. Refining crude oil into final products requires desulfurization of the oil.

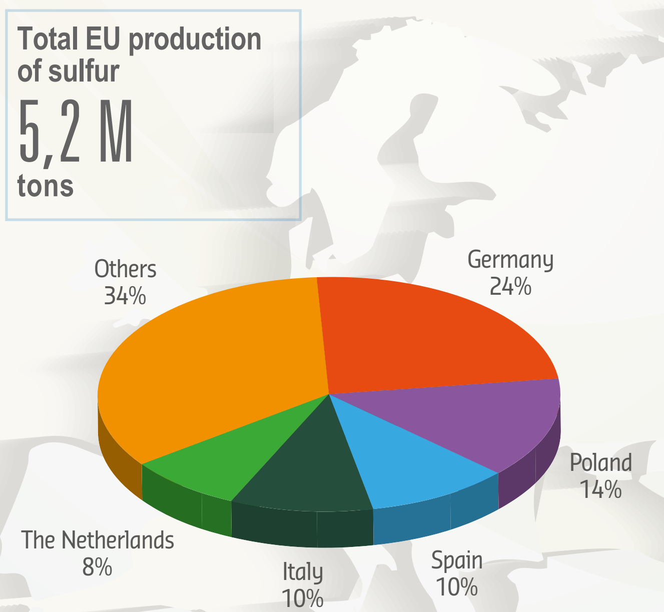
Specifications for fuel have become increasingly stringent with respect to the sulfur content. Likewise, many petrochemical products are produced to be nearly sulfur-free. Removal of sulfur from oil is consequently one of the central conversion requirements in most refineries.

Sulfur, as a by-product from refineries is converted into sulfuric acid that is used for the production of phosphoric acid. Phosphoric acid is an important preliminary material for production of granulated phosphate containing fertilizers.

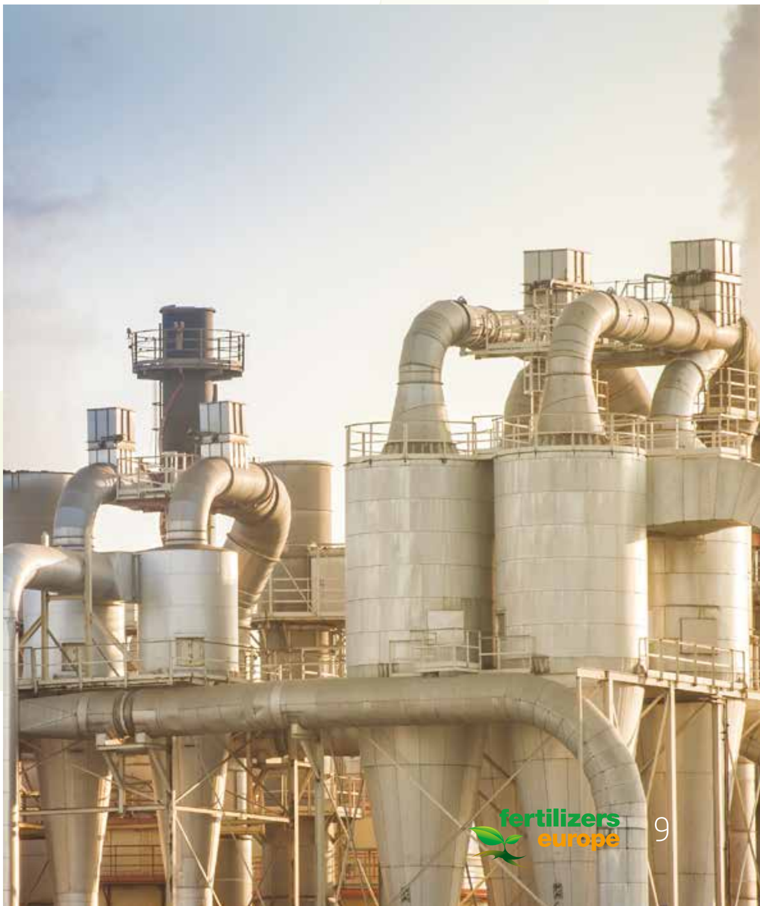
NATURAL OIL & GAS



SULFUR PRODUCTION IN EUROPE



Source: IFA 2013



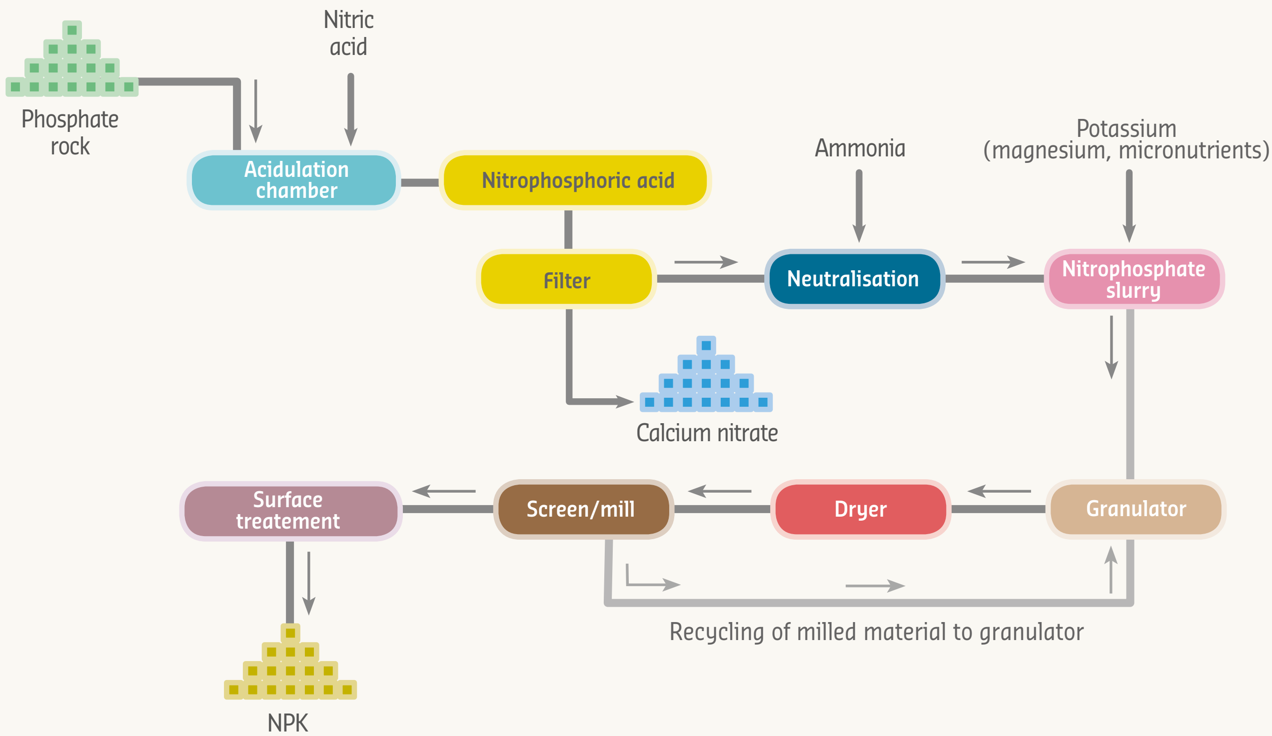
3 Integrated production of complex fertilizers

Complex mineral fertilizers can be produced via various processes and production routes. An important step in production is the conversion of insoluble phosphate contained in natural phosphate rock into plant available form. One of the possible processes to do so is via the nitrophosphate route, which includes the so-called Odda process. The advantage of the integrated Odda process is not only converting phosphate into plant-available forms, but also that the co-product calcium nitrate is used for the production of nitrate containing straight fertilizers.

In this integrated process, no solid waste is produced and, importantly, the by-product calcium carbonate (lime) can be obtained. This is the starting raw material for the synthesis of calcium ammonium nitrate, a highly efficient straight nitrogen fertilizers.

In the formation of lime, carbon dioxide from adjacent plants, such as an ethylene oxide, a waste incineration or an ammonia plant, is consumed. The process is exemplary of an integrated production, and closes material loops.

FLOW CHART FOR THE NITROPHOSPHATE PROCESS



4 Horticultural symbiosis

Greenhouse horticulture is the pillar of agricultural economy of the Netherlands. Dutch greenhouses are recognized worldwide for their innovation, resource-efficiency, and their ability to supply premium horticultural products all year round. Energy use, however, is a major challenge and accounts for some 30% of total operating costs.

Residual heat and carbon dioxide from ammonia operations from fertilizer manufacturing were once considered as waste. However, the use of available residual heat from neighboring industries is a promising option to reduce energy costs.

This type of industrial symbiosis can be realized using a pipeline network that supplies residual heat and carbon dioxide and by-products from an adjacent ammonia manufacturing plant to the neighboring greenhouses.

In the Netherlands, 60 kilotons (kT) of carbon dioxide are now used annually in horticulture through this process, whereas the use of the residual heat avoids the emission of another 135 kT of carbon dioxide annually.

Greenhouse in the Netherlands using CO_2 from a neighboring ammonia plant.

It is a successful example of industrial symbiosis on a large scale that implements benefits to the environment, horticulture, and the fertilizer industry in spite of significant challenges and costs.

5 Use of carbon dioxide as a raw material

In a usual fertilizer production process, an average of two tons of carbon dioxide is produced per one ton of ammonia. Part of that carbon dioxide is captured during the production process of ammonia and used for commercial markets. Some companies have been using this practice for over 30 years. Removing carbon dioxide is done before nitrogen and hydrogen react to ammonia. It is purified for use in a wide range of applications, including beverages such as sparkling water. Commercial carbon dioxide is transported under careful conditions and further used in the production of food, beverages, cleaning products, other chemicals, and fire extinguishers.

Sparkling water is made with CO_2 from ammonia production

Appendix

Materials commonly used in the production of fertilizers and their source process (non-exhaustive)

Material	Processes
Ammonium sulfate ($(NH_4)_2SO_4$)	Caprolactam
	Formic acid
	Gas scrubbing
	Titanium dioxide (TiO_2) pigment production
	Methyl methacrylate
	Acrylonitrile
	Steel
	Ammonia gas scrubbing in fertilizers production
Sulfur and derived products	Oil and gas industry, fuel oil methanation
Sulfuric acid (H_2SO_4)	Caprolactam
	Titanium dioxide (TiO_2)
	From by-product pyrite (copper/zinc mines)
Carbon dioxide (CO_2)	Ethylene oxide
	Ammonia - NH_3
Gypsum (calcium sulfate dihydrate)	Phosphoric acid production
	Hydrofluoric acid
Hexafluorosilicic acid (H_2SiF_6)	Phosphoric acid production
Nitric acid (HNO_3)	Nitrite production
Diluted nitric acid (diluted HNO_3)	Nitric acid operations
Ammonia (NH_3)	Melamine
	Caprolactam
	Urea
Ammonium nitrate (NH_4NO_3)	Melamine
	Scrubbing of hot combustion gases
	Scrubbing of fertilizer granulation off-gas
Ammonium nitrate (NH_4NO_3)	Manganese nitrate
	Acidic absorption of ammonia
Internal stabilizers, e.g. magnesium oxide (MgO), magnesium sulfate ($MgSO_4$), magnesium nitrate ($Mg(NO_3)_2$), aluminium sulfate ($Al_2(SO_4)_3$), iron sulfate ($Fe(SO_4)$)	Various operations (pigment production, e.g. titanium dioxide - TiO_2)
Calcium carbonate ($CaCO_3$, lime)	ODDA process
Calcium nitrate ($Ca(NO_3)_2$)	NP/NPK ODDA process
Diluted sulfuric acid (H_2SO_4)	Concentrated nitric acid production
Magnesium sulfate ($MgSO_4$)	Titanium dioxide (TiO_2) pigment production
Potash	Salt production
Natural gas	Fermentation processes
Iron sulfate ($FeSO_4$)	Titanium dioxide (TiO_2) pigment production

Material	Processes
Iron sulfate ($FeSO_4$ x $7H_2O$)	Titanium dioxide (TiO_2) pigment production
Iron sulfate ($FeSO_4$ x H_2O)	Titanium dioxide (TiO_2) pigment production
Potassium sulfate (K_2SO_4)	Various industries
Ammonium thiosulfate	Gas treatment in energy industry
Ammonium carbonate ($(NH_4)_2CO_3$)	Production of baking agents (e.g. E 503), specific scrubbing
Nitrous oxide (laughing gas, N_2O)	Adipic acid
Carbon monoxide/hydrogen (CO/H_2) mixture	Acetylene off gas
Calcium ammonium nitrate (CAN)	Nitro-phosphate NPK production
Ammonium chloride (NH_4Cl)	Solvay process for the production of sodium carbonate
Potassium hydroxide (KOH)	Chlorine operations
H_2	Various industries (petrochemical/refineries)
Coating agents	Various industry by-products
Lignosulphonates	Wood-pulp production

Fertilizers Europe
Product Stewardship publications

Transport

- Guidance for UN Classification of Ammonium Nitrate Based Substances
- Transporting Ammonia by Rail
- Sea Transport of Ammonium Nitrate Based Fertilizers
- Transporting Nitric Acid in Tanks

Storage

- Safe and Secure Storage of Fertilizers on Farms
- Storage, Handling and Transportation of Solid Mineral Fertilizers
- Storage of Hot Ammonium Nitrate Solutions
- Inspection of Atmospheric Refrigerated Ammonia Storage Tanks
- Guidance for the Compatibility of Fertilizer Blending Materials
- Safe Handling and Utilization of Non-conforming Solid Fertilizers and Related Materials for Fertilizer Importers, Distributors and Merchants
- Short version of Guidance for Handling Non-conforming Ammonium Nitrate Based Fertilizers in the Distribution Chain
- Safe Handling and Use of Non-conforming Fertilizers and Related Materials for Producers
- Do's and Don'ts for Safe Storage of Fertilizers containing AN
- Stress Corrosion Cracking leaflet
- Guidance for Fighting Fires and/or Decomposition involving Solid Mineral Nitrogen-based Fertilizers

Production

- Inspection of and Leak Detection in Liquid Ammonia Pipelines
- Booklet nr. 1: Production of Ammonia
- Booklet nr. 2: Production of Nitric Acid
- Booklet nr. 3: Production of Sulphuric Acid
- Booklet nr. 4: Production of Phosphoric Acid
- Booklet nr. 5: Production of Urea and Urea-Ammonium Nitrate
- Booklet nr. 6: Production of Ammonium Nitrate and Calcium Ammonium Nitrate
- Booklet nr. 7: Production of NPK Compound Fertilizers by Nitrophosphate Route
- Booklet nr. 8: Production of NPK Compound Fertilizers by Mixed Acid Route

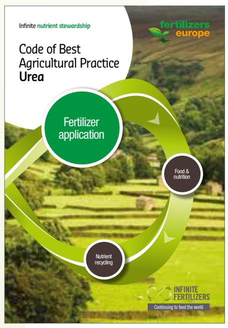
All Fertilizers Europe Product Stewardship publications are available at: www.fertilizerseurope.com

Bibliography

- EC, Roadmap to a Resource Efficient Europe, 2011.
- EC, A stronger European Industry for Growth and Economic Recovery, 2012.
- EC, Circular Economy Package, 2015.
- EC, Press release, 02.12.2015, "Closing the loop: Commission adopts ambitious new Circular Economy Package to boost competitiveness, create jobs and generate sustainable growth".
- EC, IPPC, LVIC-AAF, August 2007.

Available publications

Fertilizers Europe has developed a variety of publications, each corresponding to the product stewardship and nutrient stewardship side of Infinite Fertilizers. Should you be interested in obtaining any of these publications, please contact the secretariat of Fertilizers Europe.



INFINITE FERTILIZERS

Continuing to feed the world

Infinite fertilizers guides the European fertilizer industry's initiatives to ensure that Europe's farmers have access to a variety of safe, high quality, locally produced products, as well as information on their use, environmental impact and nutrient recycling opportunities.

fertilizers europe

This brochure is published under Fertilizers Europe's Infinite Fertilizers initiative to increase the efficient use of nutrients and reduce the carbon footprint of food production. Product Stewardship is defined as "management of the safety, health and environmental aspects of a product throughout its life cycle in an ethically responsible way". It is Responsible Care applied to products. Fertilizers Europe's application of Product Stewardship covers the total value chain as well as addresses additional issues such as Best Practice, which do not necessarily only deal with product characteristics. The scope of its Product Stewardship Program is limited to EU legislation and does not cover any specific national requirements.

www.productstewardship.eu

Fertilizers Europe asbl
Avenue E. Van Nieuwenhuyse 4/6
B-1160, Brussels, Belgium
Tel: +32 2 675 3550
Fax: +32 2 675 3961
technical@fertilizerseurope.com

www.fertilizerseurope.com

Fertilizers Europe

@FertilizersEuro