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Use of HTGR process heat for nitrogen fertilizers and chemical products

Authors : Mrs. Raimondas PABARCIUS (LEI)

Gemini Plus - Contract Number: 755478
Gemini Plus Dr. Panagiotis MANOLATOS

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Summary

In the frame of the Gemini Plus project, the Working Package 3 (?WP3 - Innovation and long-term perspective?) focus on innovation options which are of benefit for the demonstration of safety and performance, and which enhance the competitiveness and market potential of a nuclear cogeneration plant. The present report is one of the first WP3 deliverables presenting possible cogeneration HTR in fertilizers industry. This document contains an overview of EU chemical industry focusing on nitrogen fertilizers sector; main chemical plants and its production capacities are presented; manufacturing process of the main components for nitrogen fertilizers fabrication is analyzed pointing out the energy efficiency and required process parameters; as well as the main sitting requirements for nuclear cogeneration are discussed and possible coupling schemes with industrial site are referred. Resulting from information collected, operating window of the HTR technology employment in nitrogen fertilizers industry sector is viable, HTR can provide process steam of required parameters, and it can be coupled with industrial end user via steam based heat transport configuration scheme in the short-term horizon.

Approval

Date	By
2018-05-25 10:43:33	Dr. Michael FÜTTERER (EC-JRC)
2018-06-13 20:55:21	Pr. Grzegorz WROCHNA (NCBJ)

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Abbreviations

BDBA	Beyond Design Basis Accident
CHP	Combined heat and power (plant)
CRP	Coordinated Research Project
EIA	Environmental Impact Assessment
EU	European Union
JAERI	Japan Atomic Energy Research Institute
HT(G)R	High Temperature (Gas-cooled) Reactor
HRS	Heat Recovery System
ICCA	International Council of Chemical Association
IFA	International Fertilizers Association
IHX	Intermediate heat exchanger
LNG	Liquefied natural gas
LWR	Light Water Reactor
NPP	Nuclear Power Plant
PET	Polyethylene terephthalate
SPZ	Sanitary Protection Zone
UAE	United Arab Emirates
UK	United Kingdom
US	United States (of America)

Summary

In the frame of the Gemini Plus project, the Work Package 3 (“WP3 - Innovation and long-term perspective”) focuses on innovation options which are of benefit for the demonstration of safety and performance, and which enhance the competitiveness and market potential of a nuclear cogeneration plant. The present report is one of the first WP3 deliverables presenting the possible use of cogeneration HTR in the fertilizer industry.

This document contains an overview of the EU chemical industry focusing on the nitrogen fertilizer sector; main chemical plants and its production capacities are presented; manufacturing process of the main components for nitrogen fertilizers fabrication is analysed pointing out the energy efficiency and required process parameters; as well as the main siting requirements for nuclear cogeneration are discussed and possible coupling schemes with industrial site are referred. Resulting from information collected, operating window of the HTR technology employment in nitrogen fertilizers industry sector is viable, HTR can provide process steam of required parameters, and it can be coupled with industrial end user via steam based heat transport configuration scheme in the short-term horizon.

1 Introduction

In Europe HTR is not focusing on electricity production but also on heat production and is then a good candidate for coupling with process plant for cogeneration indeed massive reducing of CO₂ emissions and reduced dependence on fossil fuel. HTR deployment in nuclear cogeneration is specified in two timeframes. In the short-term horizon (5 – 10 ys), HTR can be coupled with industrial facility via schemes which are based of mature technology. Short-term horizon includes deployment of HTR for combined heat (at moderate temperatures up to 750°C) and power production for industrial sector. Medium and long term horizon (10–15 ys) is the time needed for additional technology development for tighter coupling schemes, additional applications or higher temperature proof materials (over 900°C) [1]. The concept of coupling nuclear unit with industrial site need to ensure very high reliability on availability, stable steam parameters, high level usage of existing infrastructure on industrial site as well as competitive economic factors. Today HTR, and more precisely modular HTR, is considered as an energy alternative for cogeneration and coupling with the conventional process heat market.

Many industrial sectors consume steam as process heat, ingredient of chemical reaction or working fluid for electricity production. Different processes and purposes require specific values of the steam parameters like temperature, pressure, mass flow and availability. About 99% of the users in the world industrial heat market require 1 to 300 MWth, and this range accounts for about 80% of the total energy consumed (at 150 - 600°C) [29]. The largest thermal capacity in EU is utilized in oil refineries, chemical industry, iron, steel and cement production. Plug-in market, covering all combined heat and power plants supplying one or more industrial facilities, is very attractive, because the existing cogeneration plant could be replaced by a HTR simply by switching the pipes. Nevertheless plug-in option is limited to existing cogeneration facilities, all producing steam under 550°C, where majority of application are chemical industry. Such application is interesting and for district heating as well.

The European chemical industry is a European manufacturing success story. A wealth generating sector of the economy, it is a valuable part of Europe's economic infrastructure. Having ridden out the recession, the European chemical industry is continuing its recovery. It aims to provide solutions for the achievement of a competitive, low carbon and circular economy in Europe and beyond [2]. At the EU level, the chemical industry (excluding pharmaceuticals) is the fifth largest industry, contributing to about 7% of total EU manufacturing added value. The top five leading sectors are machinery and equipment, motor vehicles, food products, fabricated metal products, and chemicals [3].

From the technological point of view the fertilizers production sector can be supplied by employing nuclear units to coupled production of process heat and electricity as well. Ammonia is mostly/mainly used in the production of nitrogen fertilisers. In fact, ammonia production needs massive volumes of hydrogen, but hydrogen produced from natural gas will be more and more expensive in the coming years (increasing of natural gas price). Therefore, HTR could replace natural gas for hydrogen production and steam for ammonia production, taking into account more stable predictable HTR fuel costs than fossil fuels, as well as the energy security benefits.

ICCA had quantified the greenhouse gas emissions reduction enabled by the chemical sector worldwide [4]. This study compared the greenhouse gas emissions of a chemical product in a specific application (for 102 individual chemical product applications in the year 2005 and 2030) over its lifetime with the next best non-chemical alternative. The study identifies a number of applications as the most important contributors of avoided emissions, including building insulation, fertilizers, lighting, packaging, and marine antifouling. The ICCA study reports net avoided emissions of 3.6 to 5.2 Gt CO₂ equivalents at global level for 2005.

The IAEA CRP project "Uranium – Thorium fueled HTGR applications for energy neutral sustainable comprehensive extraction and mineral product development" within the framework of the IAEA is ongoing, which aims to elaborate on the applicability and potential of using HTRs to provide process heat and/or electricity to power energy intensive mineral development processes [43]. Inter alia, the phosphate ore processing with uranium recovery using HTR is going to study,



thus HTR coupling with phosphate fertilizer plant will be analyzed and techno-economic feasibility studies will be performed. Preliminary estimates made regarding the mass- and energy balance using exemplary phosphate fertilizer plants and exemplary HTR, suggest that “energy neutral” phosphate fertilizer production may be possible [44]. An overview of the current progress of this IAEA multinational research project is presented in [45]. The Project is expected to end at April of 2019.

So taking these facts into account the fertilizers industry will represent an interesting potential of HTR deployment in the coming decades. This report presents information on topic focusing on nitrogen fertilizer sector.

2 Chemical industry

2.1 EU chemical sector

With 15.1%, the EU chemical industry ranks second, along with the US (14.2%), in total sales. When including both the EU and non-EU countries in Europe, total sales reached €597 billion in 2016, or 17.8% of world chemical sales. Worldwide competition has ratcheted up in the last ten years, however, as China holds the top ranking in sales – a position once firmly held by Europe [2].

The EU chemical industry is structured in five main sectors, i.e. petrochemicals, polymers, basic inorganics, specialties and consumer chemicals (Fig.1), broken down into 16 subsectors (Fig. 2).

The petrochemicals subsector covers manufacturing of chemicals using basic processes, such as thermal cracking and distillation. All processes are capital and energy intensive.

The basic inorganic chemicals subsector includes production of chemical elements, inorganic acids, bases, alkalis, and other inorganic compounds including fertilizers/nitrogen. All processes are capital and energy intensive.

Plastics in primary forms embraces the manufacture of resins, plastic materials and elastomers. Manufacture of polymers in primary forms is in most cases integrated into petrochemicals sites.

The specialty chemicals group is by far the most heterogeneous group with regard to products, applications, production processes, business structure. Specialty chemicals covers areas, such as paints and inks, crop protection, dyes and pigments.

Consumer chemicals are represented as soaps, detergents, perfumes and cosmetics.

Basically the output from the EU chemical industry covers three broad product areas: base chemicals, specialty chemicals and consumer chemicals. Base chemicals in 2016 represented 59.2% of total EU chemical sales. Specialty chemicals are produced in small volumes but they nevertheless made up 27.2% of total EU chemical sales in 2016. Consumer chemicals represented 13.6% of total EU chemical sales in 2016. Petrochemicals and specialty chemicals accounted for the majority – 53.1% – of EU chemical sales [2].

Petrochemicals and basic inorganic chemicals companies operating in the EU are mostly large multinational groups operating multiple production sites and trading chemicals in a global market.

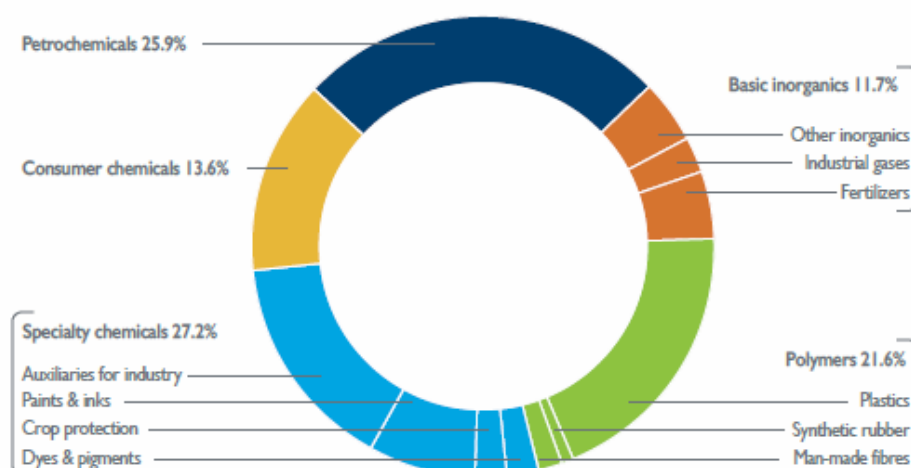


Figure 1: Sectoral breakdown of EU chemical industry [2]

C20.11: Industrial gases
C20.12: Dyes and pigments
C20.13: Other inorganics basic chemicals
C20.14: Other organics basic chemicals
C20.15: Fertilisers and nitrogen compounds
C20.16: Plastics in primary forms
C20.17: Rubber in primary forms
C20.20: Pesticides and other agrochemical products
C20.30: Paints, varnishes and similar coatings, printing ink and mastic
C20.41: Soap and detergents, cleaning and polishing preparations
C20.42: Perfumes and toilet preparations
C20.51: Explosives
C20.52: Glues
C20.53: Essential oils
C20.59: Other chemical products not elsewhere classified
C20.60: Man-made fibres

Figure 2: Subsectors of the EU chemical industry [5]

On the sectoral side, the chemical industry subsectors with the highest capital spending values (gross investments in tangible goods) are petrochemicals, inorganic basic chemicals, plastics in primary forms, fertilisers and nitrogen compounds [6]. The chemical companies that produce the fertilizers and other agrochemical products share 4.6% of whole EU chemical industry, but production of fertilizers is increasing [2].

Germany and France are the two largest chemicals producers in Europe, followed by Italy and the Netherlands. In Germany, the chemical and pharmaceutical industry is the third largest industry. These four countries together accounted for 61.7% of EU chemical sales in 2016, valued at €312.8 billion. The share rises to 82.6%, when including Spain, the United Kingdom and Belgium. The remaining EU Member States accounted for 17.4% of EU chemical sales in 2016. Poland and Austria are the two largest contributors to that Member State market [7].

Therefore, the EU chemical sector is characterised by geographical concentration, as about 70% of chemical companies are located in only seven EU countries (France, Germany, Italy, Spain, Poland and UK).

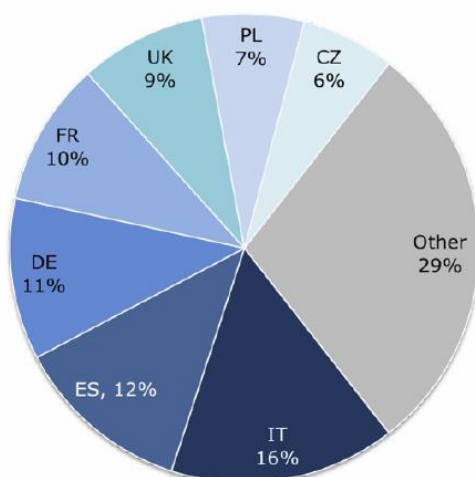


Figure 3: Share of EU chemical companies by country [6]

Europe has over 300 chemical production sites, the majority of which are located in clusters, in a triangle formed by the countries: Germany, Belgium and the Netherlands.

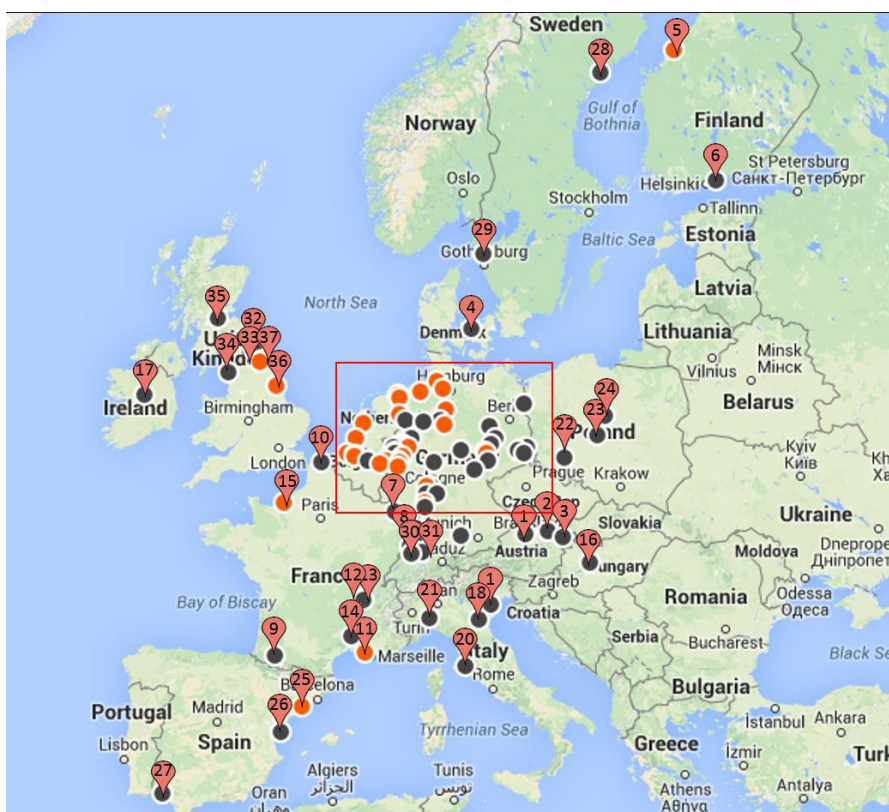


Figure 4: Chemical parks in Europe [8]

Installations EU chemical industry has a lifetime of 30-40 years and after this time is replaced with new system. For chemical clusters as other branches of industry price and availability of energy is fundamental aspect for profitability of the investment. Nuclear CHP unit could replace conventional CHP unit usually located at the cluster, or in its direct vicinity. But at the moment the biggest competitors for nuclear cogeneration is gas cogeneration.

The European heat demand has never been quantified for the chemical industry. However, the final energy use (not only for heat purpose) in the European chemical industry was estimated at around 3,000PJ in 2010. The particularity of the chemical industry is that energy such as oil and

natural gas are used to provide energy but are also used as feedstock. The main energy vectors used today in the chemical industry are natural gas and oil.

During execution of NC2I-R project more than 130 chemical sites in Central Europe were analysed to identify the energy needs for process heat and electricity. In chemical industry the steam is not only used as an energy carrier but also as medium required for processes, sometimes a direct ingredient of the chemical reaction.

It was determined that the thermal capacity of the majority of the chemical site is between 100 MWth and 200 MWth. The thermal consumption of several small parks was below 100 MWth and a minority of important parks has a thermal power higher than 500 MWth (for instance, in Poland). The electrical capacity was distributed in more uniform manner. Majority of chemical sites use less than 100 MWe but several sites (Romania, Ukraine) have an electrical power usage in 200-400 MWe [1]. For instance, the total heat demand of 13 largest chemical plants in Poland is 6500 MW (400-550°C) and the thermal consumption of single plant could be covered by 165 MWth HTG reactor [30].

Usually more than one type of steam is used onsite. Most of the investigated chemical sites occupied with CHP produce fresh steam (max 3.5 MPa) which is then converted into medium or low pressure required for particular technology processes. Usually fresh steam is converted into 3-4 types of steam using infrastructure available onsite. In most of the chemical sites, several steam networks are available at different pressures: a low pressure (a few bars), an intermediate pressure (between 10 and 20 bars) and a high pressure (over 30 bars). The process steam temperature of the steam networks varies but is not higher than 600°C, and is usually between 200 and 500oC [1].

There are some examples on the technical feasibility studies performed for nuclear cogeneration for chemical plants. Attempt to site a reactor in a major city was made in 1967, when BASF planned to build a PWR on its ground at Ludwigshafen (Germany), to supply process steam to the large integrated chemical complex. The project was withdrawn by BASF as being too close to a large centre of population and also as being both a risk to the chemical plant and at risk from the chemical plant [46].

Fictive realistic process heat application was assessed under ARCHER project, using the reference HTR system coupled to a typical European process heat application (provided by Prochem, Poland). This application represents a large chemical complex, i.e. an oil and refinery complex.

Under high-temperature engineering test reactor demonstration program in Japan a high temperature gas-cooled reactor (HTTR, 30MWt) was developed, designed, constructed, and is operated by JAERI. It is expected to be the first-of-its-kind nuclear reactor to be connected to hydrogen production processes. The process to be tested first is the steam reforming of natural gas. Currently valuable data to support commercialization of HTTR is being accumulated through safety and performance, operations and maintenance.

2.2 EU fertilizers production

Fertilizer production is an energy-intensive industry. It has been estimated that fertilizer production accounts for approximately 1.2% of the world's energy, of which about 93% is consumed by nitrogen-based fertilizers [10]. Nitrogen fertilizers represent a major industry worldwide accounting for more than 100 million tons of various products per year. The world nitrogen fertilizer demand increased by years. It is expected to be around 119.4 million tons in 2018 at the annual growth of 1.4 % [31].

Yara International ASA is a Norwegian chemical company. Its largest business area is the production of nitrogen fertilizer, however it also encompasses the production of nitrates, ammonia (the largest trader of ammonia in the world), urea and other nitrogen-based chemicals. The company has around 16,000 employees, production sites on six continents, operations in more than 60 countries and sales to about 160 countries. Most of *Yara's* production sites are in Europe.

In 2016, Yara's total energy consumption in production was 273 million GJ. About 90% of the energy is consumed in ammonia production [11].

Due to the historical structure of mainly nationally owned fertilizer industries, nitrogen fertilizers are still manufactured in relatively small plants. With the exception of Norwegian-based *Yara International*, nitrogen fertilizer manufacturers operate mainly within the EU, the production and sales of the different types of fertilizers appears concentrated in a few EU countries. Germany, France, Poland, the United Kingdom, and The Netherlands are the countries with the largest values of fertilizer sold, accounting for more than 50% of the total fertilizer turnover realized in the EU-28 [12].

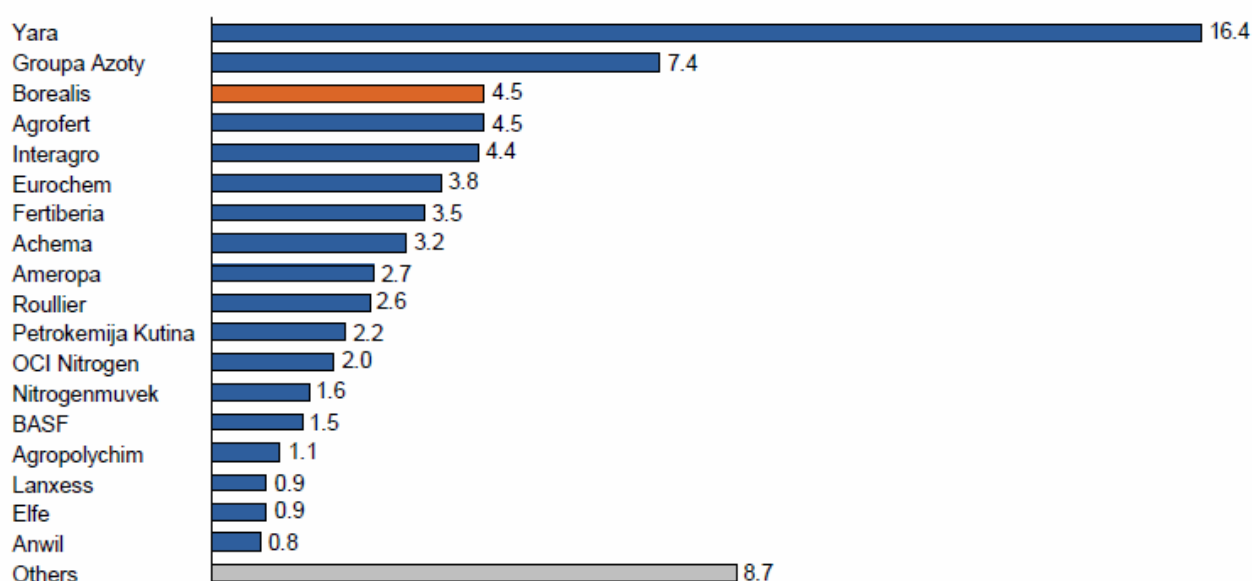


Figure 5: The biggest players in European Fertilizers market incl. non-EU Balkans and Norway (in Mt) [13]

The **Grupa Azoty Group** (Poland) is one of the leading players on the European fertilizer and chemical markets. The Agro Fertilizers segment manufactures nitrogen and compound fertilizers, as well as ammonia and other nitrogen-based intermediate products. The segment's manufacturing activities are conducted by the companies in Tarnów (the parent), Puławy, Kędzierzyn, Police, Gdańsk, and Chorzów. The Group is Poland's largest and EU second largest manufacturer of mineral fertilizers [14].

The main plants of the *Grupa Azoty Group* have their own power and heat generating units, their own power media and energy distribution network. For instance, the total consumption of energy inside the *Grupa Azoty Puławy Company* (the main fertilizers producer, 850 MW) is $\sim 2 \cdot 10^7$ GJ. Until 2020, the existing coal-powered co-generation facilities will continue as the main source of heat and electricity for the production plants in Tarnów and Police. The existing CHP units will be gradually modernised, with the scope of upgrades adapted to the changing legal requirements, particularly the environmental regulations [15].

At *Grupa Azoty Kędzierzyn Company* (474 MW), there is a plan to restore the plant's electricity and heat generation capacity, to increase its output to satisfy demand for electricity and heat, and to implement solutions that would ensure compliance with the increasingly stringent environmental requirements. March 23rd 2017 saw the completion of the first stage of construction of a new CHP plant at *Grupa Azoty Kędzierzyn site* [16].

At *Grupa Azoty Puławy*, the project to construct a 400 MWe Combined Cycle Gas Turbine unit (high-efficiency cogeneration of heat to be used for technological/heating purposes and electricity) was abandoned, and a decision was made not to select any bid and to close the tender procedure.

It was also announced that the project will be discontinued. On March 31st 2017, the Company's Supervisory Board authorized the Management Board to commence work on the preparation of an investment project to construct a hard coal-fired generating unit, including in particular conceptual and analytical work. Such unit, tailored to the Company's needs, would secure electricity and heat supplies to *Grupa Azoty Pulawy*. The Group's ability to secure long-term access to heat and electricity will mainly depend on changes in the regulatory regime and market conditions [16].

Borealis Company (Austria, UAE) is a leading provider in the fields of polyolefins and base chemicals. The company has around 6,600 employees, production sites on 5 continents, operations in more than 120 countries. *Borealis* takes Top 3 position in Fertilizer in Europe. *Borealis* produces and then distributes and supplies around five million tonnes of fertilizers and technical nitrogen products each year: nitrogen-based straight fertilizers; complex fertilizers – a combination of nitrogen, phosphate and potassium as well as speciality fertilizers; and a range of technical nitrogen products, from ammonia and ammonium nitrates to nitric acid and urea solutions. Main sources of energy are electricity, heat (primarily from steam), natural gas and fuel gas. For reasons of commercial confidentiality, *Borealis* does not disclose specific data on energy consumption, broken down into the different sources. Relative energy efficiency, converted into primary energy, is as follows:

- Fuels (including natural gas): 100% conversion to energy,
- Steam: 90% boiler efficiency,
- Electricity: 40% efficiency,

Meanwhile in 2017, *Borealis'* total primary energy consumption in whole production including fertilizers was 22,400 GWh [17].

The fertilizer industry is the largest single sectoral consumer of natural gas in the EU's manufacturing sector (~13 billion cubic metres per year). The EU is amongst the world's most carbon efficient in this field. Carbon emissions in ammonia production is ~2t CO₂ per t NH₃ (2011 data). An average, one-third of emissions from natural gas-based ammonia production are associated with the burning of fuel and two-thirds with the use of fossil fuel feedstock to obtain the hydrogen needed to synthesize ammonia [49]. Nitrogen fertilizer is extremely fossil fuel-intensive, requiring 1.5 tons of oil equivalents to make 1 ton of fertilizer.

2.3 LT fertilizers industry

Chemical sector is the third-biggest industry in Lithuania after oil refining and food production. Total sales in 2016 were €1.6 billion. The production of main chemicals, fertilizers and primary forms of plastics accounts for over 80 % of the country's chemical industry turnover. More than 80 % of production is exported to more than 120 countries around the world [20].

Key manufacturers within the chemical sector are Lithuanian companies *Achema* (a leading manufacturer of nitrogen fertilizers and chemical products in the Baltic States) and *Lifosa* (a producer of nitrogen-phosphorus fertilizer), and foreign-capital companies *Neo Group* and *Orion Global Pet* (makers of PET raisin, based in the seaport city Klaipėda). Lithuania covers a 1.7 % share of the global fertilizers exports in the world.

The stock company **Achema** is a leading manufacturer of nitrogen fertilizers (2.5 million tons per year) and chemical products in Lithuania and the Baltics. Out 25 % of products are marketed in Lithuania; the remaining part is exported to France, Germany, Benelux countries, United Kingdom, Scandinavia, USA, Estonia, Latvia and other destinations. The company has around 1300 employees [21].



Figure 6: Achema site [21]

Capacity of production: ammonia (the most important raw-material for the production of fertilizers) – 1117 thousand tons per year; Nitric acid - 1410; Urea - 785; Ammonium nitrate – 561; Urea ammonium nitrate solution – 1336; Calcium ammonium nitrate – 450; “AdBlue” (a liquid additive used to reduce NO_x in diesel exhaust gas) – 64; Formalin – 66.5; Urea formaldehyde resins and urea melamine formaldehyde resins – 82.5. Gas accounts for 70% Achema’s raw materials. Achema consumed about 70 % of all natural gas consumed in Lithuania [21]. Lithuania imports LNG from Norway under a supply deal with Statoil. The terminal is located in LNG floating storage and regasification unit terminal in the port of Klaipeda.

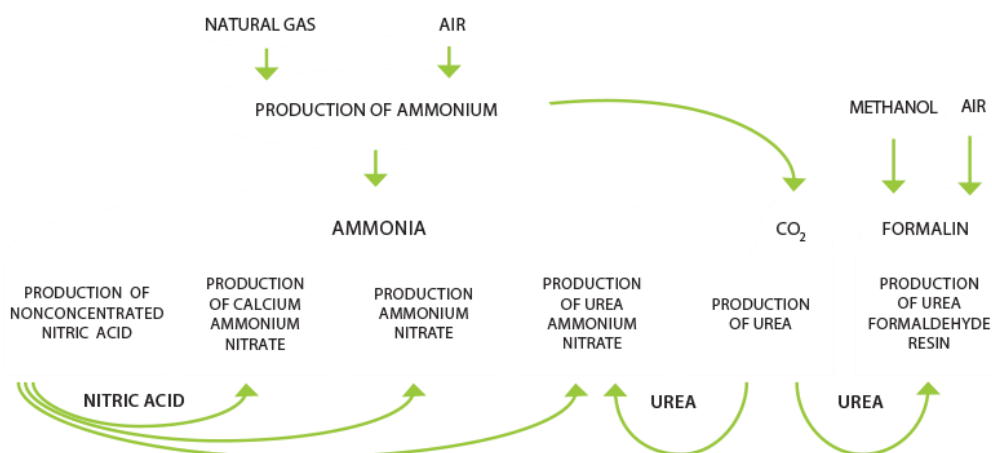


Figure 7: Production flowchart in Achema Company [21]

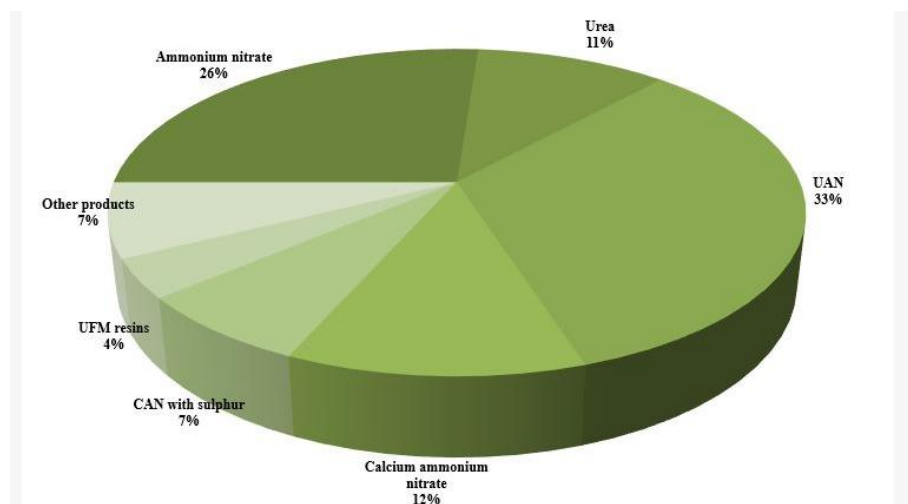


Figure 8: Achema Company sales [21]

Achema has two gas-fired cogeneration plants No.1 (21 MWe, 38 MWth) and No. 2 (47 MWe, 70 MWth). The last one is the only plant of such capacity in Lithuania, that fully complies with the EU CHP (cogeneration) Directive. Power efficiency of this plant is very high - over 90 %. Used German Siemens turbine SGT-800 is considered the most effective among the world's industrial turbines. It can supply steam 70 t/h and needed electricity for the production of products. Both gas-fired cogeneration plants can entirely supply the company with power and steam [21].

The basic product manufactured at Joint-stock company *Lifosa* is the nitrogen-phosphorus fertilizer Diammonium Phosphate, the process of which requires phosphoric acid and sulphuric acid, which are also produced at the Company. Lifosa produce heat and electricity on-site (37 MW). Most of the energy produced is consumed in the company's needs. In 2007 *Lifosa* completed the installation of the HRS. This system enables to produce more heat and electricity by more efficiently utilizing the sulphuric acid process heat. The installed capacity of steam boilers is 44 MWth, but it is used not all the time. The excess heat of technological process is used for district heating [22].

3 Production of nitrogen fertilizers

3.1 Manufacturing process

Fertilisers are additives that provide nutrients essential to the plants, and they can be broken in two groups: primary and secondary nutrients. There are three main primary nutrients: nitrogen, phosphorus and potassium. Nitrogen-based fertilizers account for the majority of fertilizer use (67% of total consumption in Europe) [32].

Nitrogen fertilizers come in many different forms containing high levels of nitrogen, they include many types of liquid and solid products, among which the most common ones are ammonia, ammonium nitrate, and urea. Ammonia is produced by reacting nitrogen from the air with hydrogen from natural gas at high pressure and temperature. Anhydrous ammonia is stored as a liquid under pressure or refrigerated. For ease of handling, it is often converted to other types of fertilizers (Fig. 9). As a first step, nitric acid is produced by mixing ammonia and air in a tank followed by the absorption of the nitric oxide gas in water. Concentrated nitric acid and ammonia gas are then mixed together producing ammonium nitrate. The urea is produced by a reaction of ammonia with carbon dioxide at high pressure. Both ammonium nitrate and urea can be further concentrated and converted into a solid form. Another process step can combine urea with ammonium nitrate solution to make liquid urea ammonium nitrate [9].

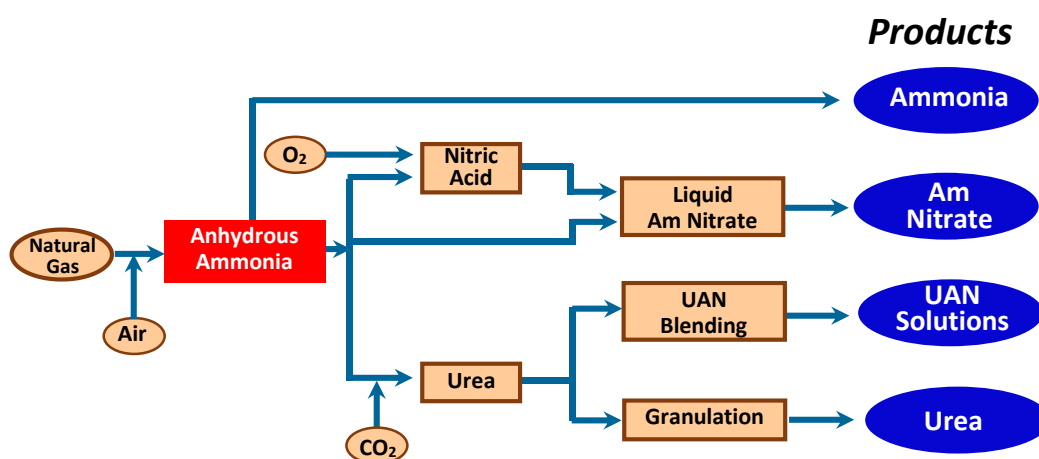


Figure 9: Production flowchart of nitrogen fertilizers [9]

3.2 Heat demand and process parameters

Nitrogen is one of the most widely distributed elements in nature, since it's the most abundant gas in the atmosphere. Atmospheric nitrogen (N_2) is relatively inert, thus it does not easily react with other chemicals to form new compounds. Among various types of fertilizers, nitrogenous fertilizers require maximum energy for a preparation of raw materials, especially for nitrogen fixation process. More than 90% of total energy used in fertilizers industry is for the production of ammonia [19].

3.2.1 Ammonia [23]

Ammonia is produced by the reaction of hydrogen and nitrogen in the so-called Haber-Bosch process. There are two main hydrogen production processes used:

- *Steam/air reforming.* Feedstocks to this process include natural gas or other light carbon fuels such as natural gas liquids, liquefied petroleum gas, and naphtha.
- *Partial oxidation.* Feedstocks to this process include heavy feedstocks such heavy oils and coal.

The key difference between conventional steam reforming (Fig. 10) and partial oxidation production route is in the way synthesis gas is produced. Synthesis gas is primarily composed of H_2 and CO that is produced by the steam reforming or partial oxidation of hydrocarbons. The other parts of ammonia production process, from shift conversion to ammonia synthesis, are identical for both production routes, except for the liquid nitrogen wash in partial oxidation [24]. Natural gas is the preferred feedstock for ammonia production, as it has the highest hydrogen to carbon ratio, leading to reduced energy consumption and lower CO_2 emissions. Ammonia produced during Haber-Bosch process is used as feedstock for all other nitrogen fertilizers.

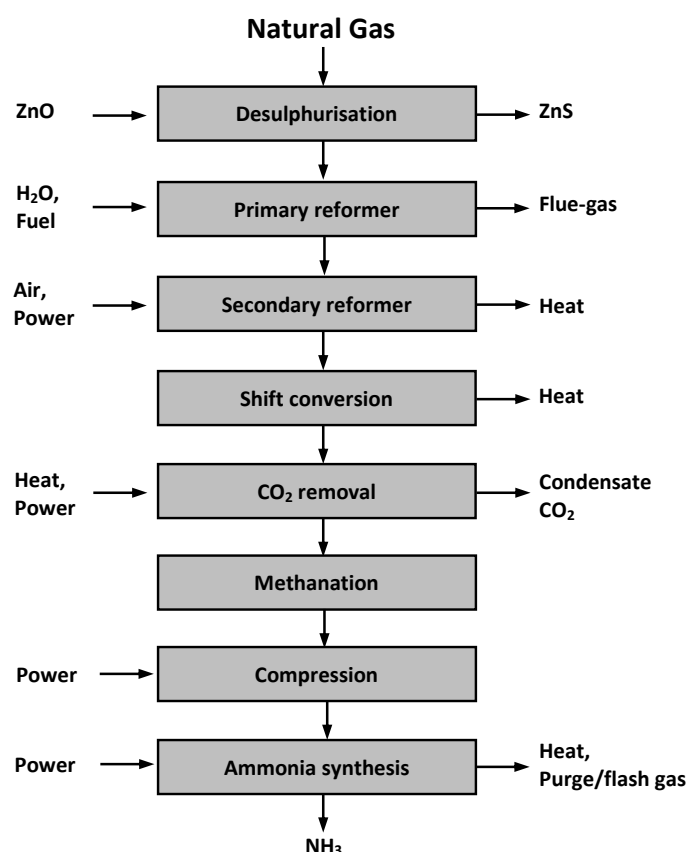
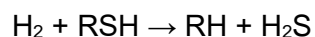


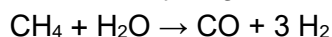
Figure 10: Block diagram of the steam/air reforming process [23]

Thus hydrogen needed for production of ammonia is mainly produced by steam reforming of hydrocarbons, with natural gas (methane) being the most common feedstock. In order to produce synthesis gas (N_2 , H_2), which also contains CO , CO_2 and H_2O , the feedstock of natural gas is reformed with steam in a heated primary reformer and subsequently with air in a secondary reformer. After removal of H_2O , CO and CO_2 from the synthesis gas is compressed and synthesis of ammonia takes place on an iron catalyst. Anhydrous ammonia then is stored as a liquid under pressure or refrigerated. It is often converted to other types of fertilizers in purpose to ease of handling and safety.

Because sulphur poisons the catalyst used in subsequent steps, the first step in the process of ammonia production is a removal of sulphur compounds from the natural gas feedstock. The removal of sulphur compounds requires catalytic hydrogenation to convert sulphur poisons to gaseous hydrogen sulphide, which is later adsorbed and removed from feedstock:



To achieve catalytic hydrogenation the feed gas is preheated up to 350-400 °C. The hydrogen used for the hydrogenation reaction is usually taken from the ammonia synthesis section of the plant. Desulphurised natural gas is then heated up to 400-600 °C and led into the primary reformer. In the reformer the natural gas and steam mixture is led over a tube filled with nickel catalyst. The applied steam to carbon molar ratio is typically around 3. At high temperatures (up to 1200 °C) and pressures (up to 40 bars) in the presence of a metal-based catalyst (nickel), steam reacts with methane to yield carbon oxides and hydrogen:

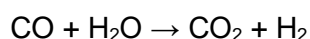


The hydrocarbon conversion rate in the primary reformer is about 60% in a conventional plant. High temperatures are required by the catalyst since this is an endothermic reaction, thus the heat must be supplied to the process for the reaction to proceed. The reformer is heated externally, that is to say the necessary heat for reaction is supplied as indirect heat by firing the burners.



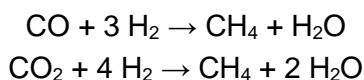
The preheated air is mixed with gas mixture, which leaves the primary reformer, and passed over a nickel catalyst in the secondary reformer. The process air is compressed and heated in the primary reformer convection section to around 550 °C. The heat required for the steam and methane reaction to proceed in this reformer is supplied as direct heat by combustion of the gas mixture with air. The introduction of air in the secondary reformer provides the nitrogen required for ammonia synthesis in the exit gases.

The exit gases mixture from the secondary reformer contains carbon monoxides, which can be used to recover additional hydrogen through the water-gas shift reaction. Higher carbon monoxide conversion thermodynamically is favoured at lower temperatures. Thus the exit gas mixture is cooled in the waste heat boiler to 330-380 °C. The excess heat from shift reformer is used to produce high pressure steam (30-100 bars). In the shift reformer carbon monoxides is converted to carbon dioxide and hydrogen:

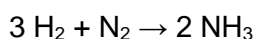


After these reactions a mixture of N₂, H₂, CO₂ and some inert gases is formed (syngas). The CO₂ has to be removed before the ammonia synthesis step to prevent poisoning of the catalyst. Thus CO₂ from syngas is removed with chemical absorbants. The removed CO₂ can be later used in the urea synthesis.

The final part of the gas purification is the methanation step. Small amounts of CO and CO₂ is left in the syngas even after CO₂ removal. The methanation step takes place in the methanator, and the reactions involved are the reverse of the reforming catalyst:



The equilibrium condition for methanation reaction is the temperature range from 280 °C to 400 °C. By using the right methane air mixture at the input, after all these steps a syngas of about 75% H₂ and 25% N₂ is left. The ammonia synthesis takes place in the ammonia synthesis converter:



High temperatures from a kinetic point of view and low pressures from a practical point of view are favourable for the final ammonia synthesis reaction. The reaction temperature and pressure is therefore a typical compromise, namely 350-500°C and 100-250 bars. Iron oxide is used as a catalyst for the reaction. The final result is a 20-30% ammonia yield. This is separated out of the mixture by condensation. The unreacted gases are recycled, and eventually a high conversion is achieved.

The ammonia production processes depend highly on plentiful supplies of energy. During the 2008 IFA benchmarking survey, which included participation by 93 plants located in 33 countries and representing approximately one quarter (40 million tonnes) of total world ammonia production, was determined that the average net energy efficiency was 36.6 GJ/t NH₃ (ranging from 27.0 to 58.2 GJ/t NH₃). The top quartile performed in the range of 28 to 33 GJ/t NH₃. These figures are comparable to theoretical design efficiencies and are near the optimum efficiency level, for a new plant, of approximately 28-29 GJ/t [18].

Steam reforming ammonia plants have high-level surplus heat available for steam production in the reforming, shift conversion, and synthesis sections, and in the convection section of the primary reformer. Most of this waste heat is used for high pressure steam production for use in turbines for driving the main compressors and pumps and as process steam extracted from the turbine system. A modern steam reforming ammonia plant can be made energetically self-sufficient if necessary, but usually a small steam export and electricity import are preferred [23]. The steam supply for the turbines used for driving the synthesis gas compressor, the air compressors and the refrigeration compressors are about 3.9-6.3 GJ/t NH₃ [47] (higher values due to increased process air supply to the secondary reformer).



3.2.2 Urea [26]

Urea is the most common nitrogen fertilizer and is the largest end use of ammonia. Urea contains 46% nitrogen by weight. It contains higher nitrogen content than other nitrogen fertilizers. Therefore, it has the lowest transportation costs per unit of nitrogen nutrient. Urea is produced by a reaction of ammonia and carbon dioxide at elevated temperature and pressure. Urea production plants are almost always located adjacent to the site of ammonia production plants since large quantities of carbon dioxide are produced during the ammonia manufacturing process as a by-product from hydrocarbons. The production of urea consists of two main equilibrium reactions. The first is carbamate formation reaction, which is fast exothermic reaction of liquid ammonia with gaseous carbon dioxide at high temperature and pressure to form ammonium carbamate ($\text{H}_2\text{N}-\text{COONH}_4$). The second is urea conversion reaction, which is slow endothermic decomposition of ammonium carbamate into urea and water. Urea synthesis takes place at temperatures of around 190 °C and at pressures of about 140-175 bar.



According IFA [18] the energy intensity of a conventional urea total recycling plant is 3.7 GJ/t urea employing the best today practice and 3.2 GJ/t urea based on best available technology.

3.2.3 Ammonium nitrate [27]

Ammonium nitrate contains 34% nitrogen by weight. The production of ammonium nitrate entails the acid-base reaction of ammonia with nitric acid. As a first step, nitric acid is produced by mixing ammonia and air in a tank to form nitric monoxide (NO). NO is further oxidised to form nitrogen dioxide (NO_2), which finally is absorbed in water to produce HNO_3 . Ammonium nitrate is produced then concentrated nitric acid and ammonia gas are mixed together in a tank, in which a neutralization reaction occurs at 100-180 °C.

The net energy use in ammonium nitrate best practice plants is 0.5 GJ/t ammonium nitrate, while plants using best available technology have net zero energy use [18].

3.2.4 Urea ammonium nitrate [26]

Ammonium nitrate (AN) and urea are used as feedstocks in the production of urea-ammonium nitrate (UAN) liquid fertilizers. The combined solubility of ammonium nitrate and urea is much higher than that of either component alone. Thus it is possible to obtain a stable solution with a total nitrogen content (32%) approaching that of solid ammonium nitrate (33.5%). Continuous and batch type processes are used and in both processes concentrated urea and ammonium nitrate solutions are measured, mixed and then cooled. Steam and electricity consumption is about to 10-11kWh per tones (~0.04 GJ/t) but are a function of raw material type (solid or solution) and ambient temperature.

3.2.5 Nitric Acid [28]

Nitric acid is an intermediate product used in the manufacture of ammonium nitrate (AN), calcium nitrate (CN) and potassium nitrate that are used as straight fertilizers or mixed into compound fertilizers. The fertilizer industry uses the weak nitric acid production method/process with an acid concentration ~60%. In the weak nitric acid production process, three high-temperature catalytic reactions take place. Initially, ammonia is oxidized with air on a catalyst to produce nitric oxide. The heat produced during the exothermic reaction is recovered and used to produce steam and/or preheat the tail gas. The nitric oxide produced from the oxidation of ammonia is then oxidized as the mixture is cooled at the second stage. In the final step, nitrogen dioxide comes in contact counter currently with water in the absorption column to form HNO_3 and NO.

The total nitric acid production process is highly exothermic, generating more energy than consumed. The net energy use in best practice plants is -2.3 GJ/t nitric acid, while best available technology consumes -3.1 GJ/t nitric acid [18]. The waste heat boilers are usually used to generate superheated pressurized steam.

Hence in the fertilizer industry energy requirements are primarily associated with ammonia production, the average net energy efficiency is ~ 37 GJ/t NH_3 . The production of other types of fertilizers requires less energy, for instance, only 10% of energy used for ammonia is needed for urea production (~ 3.7 GJ per tonne of urea).

It can be noted, that the steam at various pressures and temperatures supporting chemical processes at fixed temperatures is used. The reaction temperature during fertilizers production does not overrun 600°C , the maximum process steam temperature is $\sim 550^\circ\text{C}$, and it is compatible with HTR. Various steam pressures are used during different processes, chemical plants generally have a network of pipelines exclusively for providing steam at low pressure, medium pressure, and high pressure. The maximum process pressure ~ 10 MPa.

4 Siting requirements for cogeneration

As was mentioned, for chemical plants (nitrogen fertilizers production plants) HTR is a good choice as potential heat source which could ensure very high reliability on availability of stable steam parameters which are required in technological process. In general, the location of nuclear facility close to the industry site is desired. However, the siting issue should be oriented to choose remote, but accessible, locations to mitigate any consequences of any accident.

In 2014 IAEA CRP project (I31026) was initiated to investigate and make proposals on modular HTGR safety design criteria. It is expected that these criteria would refer to LWR safety standards, and the deterministic and risk-informed safety design standards under development for existing and planned HTGRs worldwide that apply to the wide spectrum of design basis and beyond design basis events [33]. The Project is expected to end at December of 2018.

Some siting safety aspects must be taken into account during designing phase for coupling of nuclear site with industrial plant.

4.1 Exclusion / sanitary protective zone

Because of potential radiological impact on neighbouring populations in the event of a severe accident with a release of radioactivity, the nuclear site is usually located far from densely populated areas and near a large amount of cooling water. The exclusion area is a few kilometres around the nuclear plant, outside of which the cogeneration factory should be built. For existing industrial facilities, the co-location or proximate location of a nuclear plant may be further complicated by the likelihood of nearby population centres [34].

Regarding the potential impact of the reactor on the end users facility it should be noted that because of the passive safety characteristics of HTR's, low power density and consequential elimination of scenarios comparable to LWR core melting scenarios, the derived HTR exclusion zone is smaller than for other NPP types, allowing a closer distance to the end user facility or other public infrastructure (schools, stadium, etc.). Demonstrated by investigations on the size of the exclusion zone this area may be limited to the NPP/industrial site itself [35].

The HTR and the industrial end user facility shall not influence each other in particular in case of BDBA on the chemical site, such as explosions or release of corrosive materials. During assessment of the minimum distance between HTR and industrial site the hazards induced by the chemicals on the NPP (plume effects, explosion, fire, toxic and corrosive effects, etc.) shall be considered. The safety related risk by external hazards for the HTR shall be independent from the cogeneration components and the end user facility. Therefore, any external hazard for the reactor by the end user facility has to be evaluated in particular. For fertilizer (ammonia) plants the specific high risks are: fire and explosion hazards resulting from the leakage of flammable materials, and detonation pressure wave as the result of an inadvertent release of natural gas from the storage tank into the environment and its ignition, including potential domino effects [48].

In addition to the standard nuclear safety issues encountered at a nuclear site and the common safety hazards of the industrial site, there is also the potential interaction of the two. Any single failure of one system should not weaken the safety of the other. In particular, the defence in depth shall call for appropriate protective barriers against any radioactive transfer from the nuclear to the industrial site [36].

It is required to define a specific area, additional barrier, with special security treatment around facilities and plants, being sources of effect on life environment and health (referred to as the sanitary protection zone SPZ) the size of which ensures reducing of air pollution (chemical, biological, physical) up to the values established by the national sanitary-hygienic standards. Usually nuclear site protection zone area requirements fulfil the ones defined for industrial site. For example, the sanitary protection zone for Ignalina NPP site is 3 km [37] as for industrial plants depending on hazard classification can be up to 1,5 km (for *Achema* chemical plant the sanitary zone is 500 meters [38]). The SPZ size of the chemical site is determined taking into account the chemical, physical environmental pollution, smell or other pollution caused by the industrial site, the limit values of which are regulated by normative acts (concentrations, noise level, etc.). The pollution caused by industrial site outside the SPZ must not exceed the threshold values established in the legislation on the public and recreation environment. Normally, the normative SPZ size is specified in the legislation, taking into account the class of harmfulness of the industrial object. The size of the SPZ may be changed taking into account the results of the assessment of impact of the planned economic activity on public health and the results of EIA, assessing the potential risks of explosion, fire and other incidents.

4.2 Heat transmission length

The supply of steam to an industrial process by a nuclear plant generally implies the need to have the nuclear facility in close proximity to the industrial process to reduce transmission line costs [34]. Distance between the industrial site and HTR unit should assure safe operation for both units and at the same time not cause extensive heat and/or pressure losses at long distances. It was pointed out [35] that a 2 km distance is sufficient to prevent hazards from industrial site to affect HTR. Whereas from technical and economical point of view it was determined that distance from HTR to utilizing location should not exceed 5 km [8]:

- a. If heat is transported in the form of hot water, the distance is not the main issue. Heat pipes can be designed to offer very low heat losses ($<0.02\%/km$) [34]. Safety considerations should prevail.
- b. If heat is transported in the form of steam (relevant for fertilizer production plants), transmission line costs rapidly increase with distance and steam pressure. The use of compressors in a steam system is generally not economical, so the transmission line length should be as short as possible (just beyond the exclusion zone boundary) [34].

4.3 Restricted flight zone

The restricted flight zone around units impacts the probability of design bases accident. Here the requirements for a nuclear unit also are stricter compared to the industrial site. For example, for Ignalina NPP the restricted flight zone -10 km, as for *Achema* chemical plant – 5 km [37].

4.4 Construction area

Area to potential HTR plant site is design dependent, but 40ha per unit should be considered as lower limit, to allow ease construction work [8].

5 Coupling schemes

Resulting from information collected above on different processes taking place in chemical industry, operating window of the HTR technology employment in this industry sector is viable.

In R&D project EUROPAIRS [39] the assessment studies for coupling HTR to conventional industrial processes were presented. The industrial heat end-users can be grouped into the classes (according to EUROPAIRS):

- steam class, where steam 150-600°C is used, both to the heat transport and heating processes (desalination, drying, paper industry, chemical industry incl. fertilizers, plastic, etc.);
- chemical class, where 600-900°C heat is mainly consumed as the driver of chemical reactions delivering required reaction enthalpy (plastic, hydrogen, coal liquefaction);
- mineral class, where heat above ~1000°C is used to melt solids or to drive reactions between solids (lime, cement, ore sintering, coke making, and metallurgy).

End-users in chemical industry refers mainly to the steam class, however some chemical plants require higher parameters for technological processes (oriented to the chemical class).

The temperature available for the chemical processes is limited mainly by the properties of candidate materials used for heat transfer (high temperature strength and corrosion resistance) for reasonable expected lifetime of the heat transport loop. Within the EUROPAIRS project, the following three power conversion system configurations have been considered:

- steam based heat transport loop with steam generator;
- gas based heat transport loop with gas-gas IHX;
- molten salt based heat transport loop with gas-molten salt IHX

With existing or near-term technology, HTR with the steam coupling loop can deliver process steam at temperatures up to 600°C, sufficient for most chemical products manufacturing. Steam is the most commonly heat utility used in chemical plants, as a heating fluid, feedstock, stripping agent in absorbers and adsorbers, and as utility to drive pumps, compressors, ejectors, etc. Chemical plants generally have a network of pipelines exclusively for providing steam at low pressure, medium pressure, and high pressure. The limitations related to employing the steam coupling loop in such case are related to the resistance to creep, fatigue and corrosion of the applicable high-temperature materials, and appear virtually the same as in conventional supercritical steam systems [40]. The near-term coupling scheme for nuclear cogeneration proposed in EUROPAIRS project is shown in Fig. 11.

IHX gas-gas heat transport loop may be sufficient for some chemical class end-users. However, this technology cannot be regarded as ready to use because at these temperatures there are still challenges concerning applicable materials, as well as further development of appropriate heat exchangers is also required. Molten salts IHX heat transport requires lower pressures, higher power densities and more efficient heat transfer. However, due to serious corrosion problems, high pressure drop and high risk of freezing, this configuration would require intensive R&D and probably cannot be considered even as a medium term option. [40]

Several configurations are possible to transfer heat from HTR as the heat source to the end-user process [39]. This transfer process can be directly coupled with the fluid of a secondary circuit, or indirectly by means of a tertiary circuit requiring additional heat transfer equipment. In parallel to the heat process supply, it is possible to add a turbine for electricity generation, either on the secondary or the tertiary circuit. Depending on the temperature required for the heat process, the turbine could be placed in a bottoming or a topping cycle configuration. Removal of part of the steam from the turbine allows the steam to be used in different ways, as process steam for industrial processes and for generation of electricity [39].

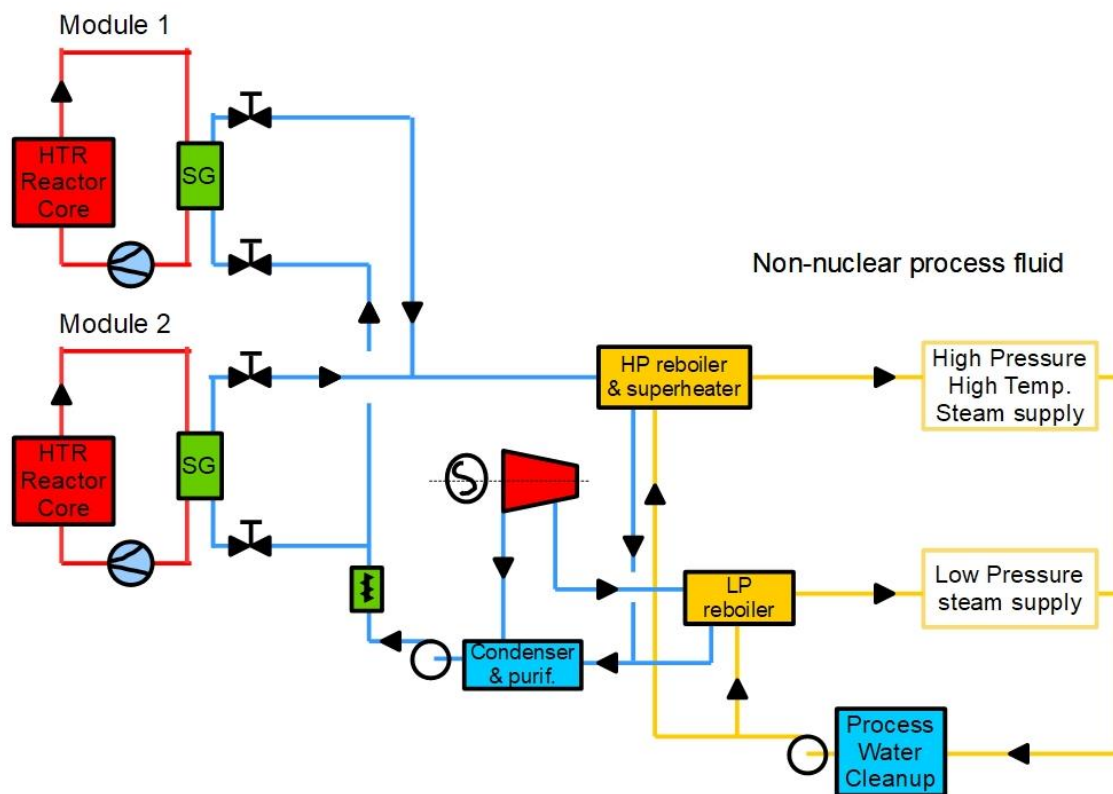


Figure 11: Steam based heat transport configuration [39]

The direct coupling between the secondary circuit and the industrial heat process seems to be very simple. However, it might not be acceptable from the point of view of tritium release and the contamination of industrial equipment. Although several technical measures enable to reduce radioactive contamination of this circuit below currently applicable effluent limits [50]. The usage of a turbine in heat transfer scheme with steam generator is advantageous, because it allows more flexibility in the operation of both, nuclear and industry, sites. Moreover, the tertiary circuit and a turbine reduce the amplitude of the transients generated by events on the heat process side [39].

Some chemical industry sectors (not fertilizers) require steam above 600°C, which is not compatible with HTR applications with standard steam based heat transport loop with steam generator. As it was mentioned above, a direct heating by means of gas-gas IHX is indeed possible as a medium-term option, but the near-term solution can utilize the proven and relatively inexpensive steam loop technology with one additional step in which the temperature is raised to the level required by the industry end-users. The simplest method is to use external heating (e.g. electric), but some authors consider employing a mechanical high temperature heat pump to achieve higher efficiency [41].

The paper [40] presents the results of the analysis done for various configurations of the steam transport loop coupled with high-temperature heat pump designed for chemical class applications. The analysed steam-based nuclear heat supply system generally follows the configuration proposed in EUROPAIRS project for the steam class coupling. The helium on HTR outlet has a temperature of 700°C and the steam leaves steam generator at 550°C and 10 MPa. The steam is transported over the long loop configured as a classical bottoming-cycle CHP, where the heat at ~530°C is directed through the heat exchanger towards the end-user installation, and the waste heat is used for power generation. The steam leaving the heat exchanger is expanded in a steam turbine providing mechanical work which can be used directly or converted into electrical energy, subsequently required to raise the output temperature. Increase of temperature could be done by electrical heating (Fig. 12) or by using the mechanical heat pump (Fig. 13). It was concluded that in

chemical class applications the only HTR heat supply system feasible in a near-term is a steam loop with electric heating, and total efficiency will be limited by efficiency of electricity production. Taking into account the qualified materials from the aerospace industry the configuration with high-temperature heat pump is feasible in the near-term.

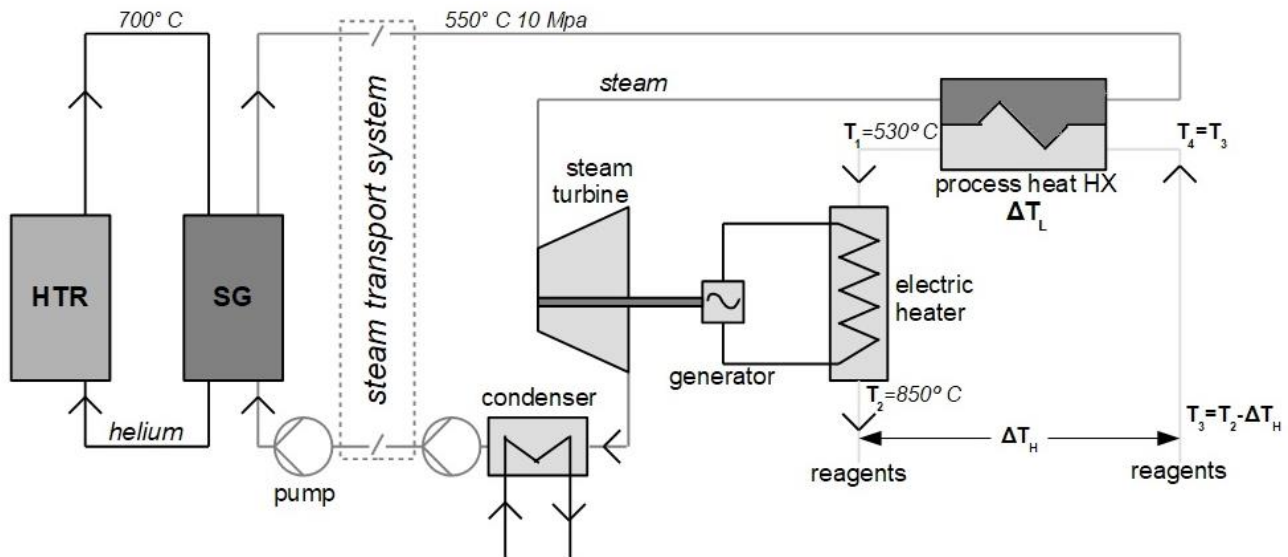


Figure 12: Configuration of the heat transport system with electrical heater [40]

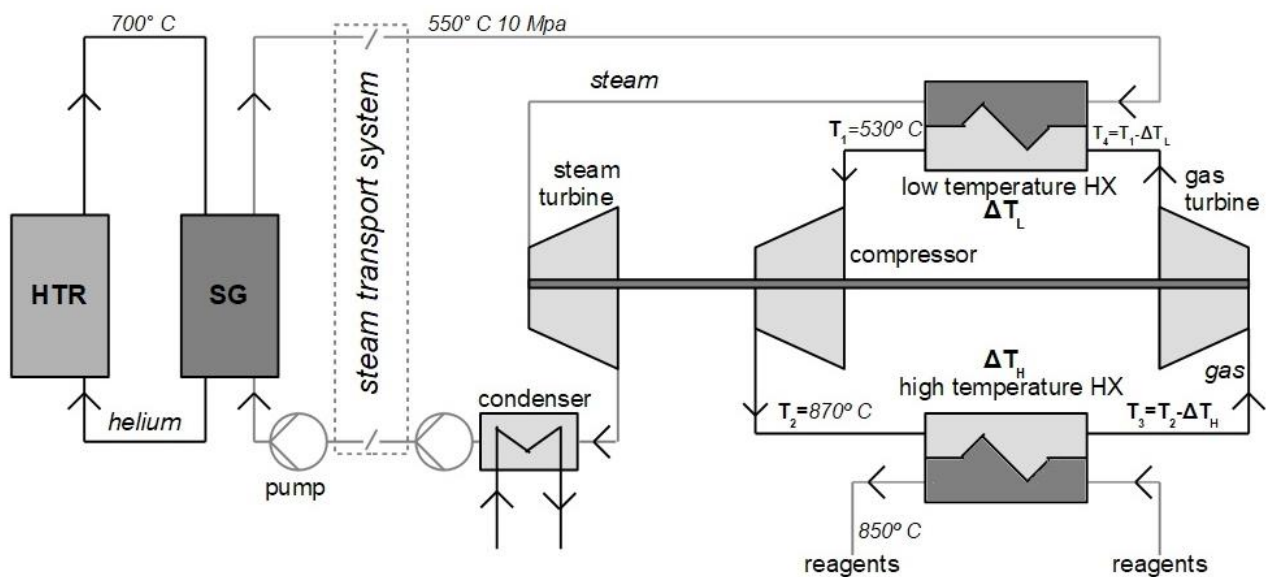


Figure 13: Configuration of the heat transport system with mechanical heat pump [40, modified]

It seems obvious that steam based heat transport configuration would be the most appropriate scheme for near future applications in chemical/fertilizers industry sector. Nonetheless, each chemical plant having its own specificities, a dedicated assessment is required for each site to ensure that HTR heat supply is meaningful.

6 Concluding remarks

Nuclear energy is an excellent source of process heat for various industrial applications including chemical industry and production of nitrogen fertilizers as well. The heat source required for the production of fertilizer production and usually provided by partial combustion of natural gas and by combustion of all purge gases can be replaced by the heat from nuclear energy. The gas-cooled reactors are a sustainable alternative in this case.

Heat carrier in chemical plants is often steam at a temperature of ~ 450 - 550°C. HTRs offer this temperature, they can deliver high-quality steam that can either be used directly for chemical processes or be expanded through a turbine to cogenerate electric power and supply process steam. In the short-term horizon, the HTR can be coupled with industrial end user via schemes, which are based on mature technology. The steam based heat transport configuration would be the most appropriate scheme for near future applications in chemical/fertilizers industry sector. Taking into account the limitations on conventional operation temperature of the heat exchangers as steam generators, HTR can provide outlet maximum steam temperature of 570°C and pressure of about 17 MPa. This range of parameters covers majority of applications for HTR in chemical/fertilizers sector [8]. The plug-in application will allow to replace the existing (gas) boiler with HTR, and to connect it to chemical plant without any need for adaptation of the steam distribution infrastructure. It would not be necessary to modify the chemical installation and facility as well. This approach can reduce the amount of required funding and simplify deployment of nuclear unit at the industrial site.

HTR can propose environmentally friendly and sustainable thermal process for fertilizers production. The production of fertilisers demands much energy and generates considerable greenhouse gas emissions. According IFA, the fertilisers manufacture accounts for approximately 1% of global greenhouse gas emissions. Major emissions associated with nitrogen-containing fertiliser production are carbon dioxide (CO₂) emitted when natural gas is combusted as part of ammonia synthesis, and nitrous oxide (N₂O) emitted during nitric acid production. Thus, application of non-carbon HTR cogeneration system is one of possible solutions to greenhouse gas emissions reduction.

Steam reforming of natural gas covering worldwide about half of the hydrogen demand, is one of the essential processes in the chemical/fertilizers industry. The coupling with nuclear as process heat source may save large amount of feedstock needed. For instance, up to 35% of the methane feedstock could be save in the petrochemical and refining industries [42].

Due to intrinsic safety features HTR passive heat removal system allows to limit core and fuel temperatures in order to prevent structural damage or radioactive release in case of accidents. Because of extremely low radiological consequences levels, the emergency planning zone may be limited to the footprint of the nuclear plant site. This is an important advantage of the HTR that allows it to be sited close to the end user.

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