



Environmental impacts of phosphoric acid production using di-hemihydrate process: a Belgian case study



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ABSTRACT

This paper undertakes an environmental evaluation of phosphoric acid production, using industrial data from Prayon SA in Belgium. Phosphoric acid is produced using the wet di-hemihydrate process also called Central Prayon process. Both grades of phosphoric acid are evaluated: fertilizer and purified grades. Specificities of this plant are highlighted and improvements of the process in terms of energy and facilities integration through years are quantified as environmental benefits. The implementation on site of two sulphuric acid production facilities and their energetic integration allow a reduction of climate change impact of 80%. Results also show the importance of phosphogypsum valorisation which is sold for the main part in this case study. Concerning the purified grade, this specific process has been compared to the thermal process, using Best Available Techniques (BAT) values for the modelling. It shows a reduced environmental impact for the wet process in the majority of categories studies.

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1. Introduction

Phosphoric acid is, after sulphuric acid, the most important mineral acid produced in the world. It is mainly consumed during the manufacturing of phosphate fertilizers or for direct use as acid. The use as fertilizer, which represents 80% of the overall use, requires a lower grade of purity than the second use (European Commission and Joint Research Centre, 2007). Phosphorus, traditionally expressed as P_2O_5 in the fertilizer industry, is the second nutrient consumed in the world after nitrogen. Its consumption achieved 41.8 Mt (as P_2O_5) in 2013 and is expected to reach 45.9 Mt P_2O_5 in 2018 (Heffer and Prud'homme, 2014). Phosphate fertilizer is usually produced from phosphate rocks and/or commercial phosphoric acid (Kool et al., 2012). Worldwide phosphoric acid production capacity was 41.6 Mt P_2O_5 in 2004. In Europe, the production capacity of this acid is about 3.08 Mt P_2O_5 (European

Commission and Joint Research Centre, 2007). Two production processes are available: the wet and the thermal one.

The thermal process uses elemental phosphorus produced from phosphate rocks but has been abandoned in the majority of European countries due to the high energy requirement (European Fertilizer Manufacturers' Association, 2000). This process is still employed in countries as China or Kazakhstan. The quality of this acid is higher than the one required for fertilizer production as it allows the production of a defluorinated and purified phosphoric acid. Therefore, the most common process for commercial phosphoric acid production, for 95% of the total phosphoric acid in EU, is the wet one but its main flaw is the coproduction of phosphogypsum, considered as one of the main hazards of wet-production of phosphoric acid (European Fertilizer Manufacturers' Association, 2000). This commercial phosphoric acid can be upgraded to a purified grade after solvent extraction (European Commission and Joint Research Centre, 2007).

To our knowledge, few papers related to the environmental impacts of commercial phosphoric acid production have been published and none was found about the purified acid produced from the wet process. A paper of Kapustenko et al. (2009) focused on the energy improvement and optimisation of the phosphoric acid production but without showing associated environmental impacts. The Ecoinvent report explains how databases have been

List of abbreviations: BAT, Best Available Technique; CTU_h, Comparative Toxic Units for humans; DHH process, Di-hemihydrate process; EU, European Union; IEA, International Energy Agency; ILCD, International Life Cycle Data; ISO, International Standardization Organization; kt/a, kilotonnes per year; LCA, Life Cycle Assessment; Mt, Mega tonne; PM, Particulate matter; US, United States.

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modelled for both US and Morocco sites at the commercial grade (Primas and Capello, 2004). Bojarski et al. (2008) modelled the wet phosphoric acid production process, varying the destiny of phosphogypsum and using data from a real process plant located in Greece. Two other papers compared wet and thermal processes for phosphate fertilizer production. The first one is based on the single superphosphate production (Silva and Kulay, 2003) and the second one compared from an environmental point of view the fused magnesium phosphate and the triple superphosphate (Silva and Kulay, 2005). Both plants are situated in Brazil. All previous papers are focused on wet production using hemi or dihydrate processes. By-product phosphogypsum is then a waste which is usually stacked or dumped into the sea. For each tonne of phosphoric acid (P_2O_5) produced, about four to five tonnes of phosphogypsum are produced: mass ratio of phosphogypsum (PG) side product to phosphoric acid produced, $\zeta(PG/P_2O_5) = 4-5$. Impurities contained in phosphate rocks as e.g. cadmium (Cd), mercury (Hg), heavy metals, and some radioactive elements, are partly recovered from the phosphogypsum. Due to its volume and the type and level of impurities in the phosphogypsum, it constitutes an environmental challenge to handle (European Commission and Joint Research Centre, 2007). Furthermore, in Europe, disposal to the sea is forbidden and land disposal must be used. Some prevention measures can be conducted to avoid environmental pollution but another way of dealing with this problem is to improve the quality of phosphogypsum, allowing its use in construction, agriculture or industrial sectors. The valorisation of phosphogypsum is easier if its transportation cost is low.

A Belgian company, called Prayon SA, already valorises a high part of its phosphogypsum (85%), mainly in the plaster industry. It uses a wet process with di-hemihydrate recrystallization type (called DHH process or Central Prayon process) with double stage filtration (European Commission and Joint Research Centre, 2007) which allows a sufficient purity of the phosphogypsum for further valorisation. For fertilizer grade phosphoric acid, only the wet route is used and the Prayon processes are applied for more than 50% of the worldwide production. Concerning the purified phosphoric acid production, the Prayon process represents about 5% of the worldwide production, with a P_2O_5 capacity of 180 kt/a, but this production is equal to 85% of the European production.

This paper will conduct the environmental life cycle assessment of phosphoric acid production at both fertilizer and purified grades to get a more accurate view of environmental impacts of this production, using di-hemihydrate process which has not been modelled yet in literature. Results of environmental impacts relative to this di-hemihydrate process will be compared to the thermal production process, especially for the purified grade of phosphoric acid. This paper will also draw some clues of improvement to reduce environmental impacts of phosphoric acid production.

2. Materials and methods

2.1. Goal definition

Environmental impacts of phosphoric acid production at both fertilizer and purified grades, produced in Belgian industrial plant of Prayon SA, are assessed using attributional LCA methodology classified as Situation C from the ILCD handbook (European Commission – Joint Research Centre – Institute for Environment and Sustainability, 2010). They are calculated using both ILCD 2011 midpoint (European Commission – Joint Research Centre – Institute for Environment and Sustainability, 2011) and ReCiPe 2008 (Goedkoop et al., 2009) methods. The first one is recommended by the ILCD handbook and regroups the most relevant methods to assess the environmental impact in each studied

impact category. The last one regroups both midpoint and endpoint approaches and is relevant to evaluate separately the environmental impact of mineral and fossil fuel depletion which cannot be performed using the first method.

This study is made in accordance with the ISO standards 14040 (International Organization for Standardization (ISO), 2006a) and 14044 (International Organization for Standardization (ISO), 2006b) and tends to answer these questions: “Does purified grade phosphoric acid from wet process achieve better environmental results than the one produced with thermal process?”, “What are the environmental hotspots of commercial phosphoric acid production?” and “What are the clues of improvement to reduce environmental impacts of phosphoric acid (H_3PO_4) and therefore environmental impacts of P_2O_5 fertilizers?”.

2.2. Scope definition

The functional unit of P_2O_5 (1 t) means that specific (divided by mass) quantities are used for both fertilizer and purified phosphoric acid grades. Boundaries of the wet production process, presented in Fig. 1, include eight main stages: (1) production of so-called weak phosphoric acid, (2) concentration and production of fertilizer grade phosphoric acid, (3) production of special grade intended for purification and internally called D01, (4) effluents from those three first steps, (5) oxidation of previous acid, (6) extraction per solvent, (7) defluorination step and (8) effluents due to steps (5)–(7). Production of fertilizer grade acid includes steps (1), (2) and a fraction of (4) while production of purified acid goes from step (1) to step (8).

All information relative to allocation factors, data quality and source or exclusion criteria are explained in the paragraph 2.3.

2.3. Life cycle inventory analysis

Inventory concerning wet process is based on specific data for Belgium collected in the Prayon industrial plant located in Engis during the year 2012 (Prayon SA, 2012b). The nature and the quantity of each consumption and emission are specific to the plant and relative to primary data. To model these consumptions, commercial Ecoinvent databases v2.2 (Swiss Centre for Life Cycle Inventories, 2010), were used as the goal of the paper was not to model in details each chemical production. Inventory relative to thermal process is based on the Best Available Techniques (European Commission and Joint Research Centre, 2007) as no industrial data were directly available.

2.3.1. Phosphoric acid production

2.3.1.1. Phosphoric acid production in Prayon Engis. In Engis, the wet process and more specifically the di-hemihydrate recrystallization process (called DHH process or Central Prayon process) with double stage filtration (European Commission and Joint Research Centre, 2007) is used to produce phosphoric acid following both next steps. First, the tri-calcium phosphate present in the phosphate rock is attacked by sulphuric acid to produce phosphoric acid and an insoluble salt as co-product. Then, the co-product is filtered from the phosphoric acid H_3PO_4 . The previous reaction is limited by an insoluble layer of $CaSO_4$ but can be minimised by recirculation of phosphoric acid which allows the solubilisation as mono calcium phosphate which becomes calcium sulphate after precipitation with sulphuric acid. Equations (1)–(3) present simplified chemical reactions between rocks and sulphuric acid (European Commission and Joint Research Centre, 2007; European Fertilizer Manufacturers' Association, 2000).

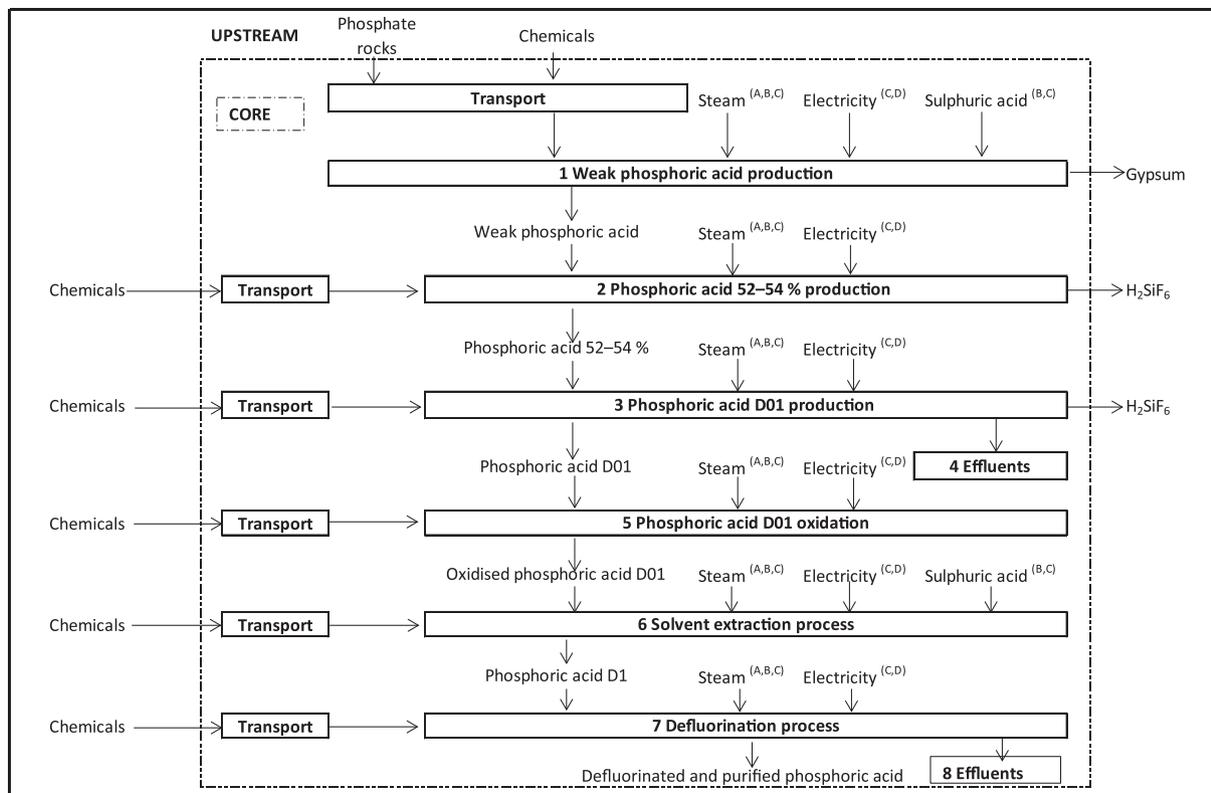
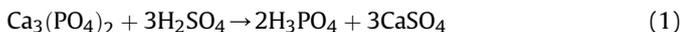


Fig. 1. Scheme of defluorinated and purified phosphoric acid production: consumptions and important steps.



A scheme of di-hemihydrate process is presented in Fig. 2. The main advantages of this process are that the yield is high and reaches an efficiency of 98% in P₂O₅ as well as it allows the valorisation of the phosphogypsum (European Commission and Joint Research Centre, 2007).

In order to produce phosphoric acid, suitable phosphate rocks can be found all over the world with a composition varying with

their geological origin. The supply of phosphate rock in Europe is provided mainly by Morocco and Russia. The majority of ores for Prayon study case comes from Russia and contain about 39% of P₂O₅ as mass fraction (European Commission and Joint Research Centre, 2007; Prayon SA, 2012b). The mining of rock requires an energy comprised between 0.5 GJ/t and 2.8 GJ/t of rock (Kool et al., 2012). In our study, as specific databases are not available for Russian rocks, we use Ecoinvent databases where the required energy is 1.15 GJ/t of Moroccan rock and 1.29 GJ/t of American rock, which is in the range published.

Inventory relative to the production of 1 t P₂O₅ in both fertilizer and purified grades phosphoric acid are presented in Table 1 (Prayon SA, 2012b). This table presents the total of specific energy required by the plant for the production of the functional unit as

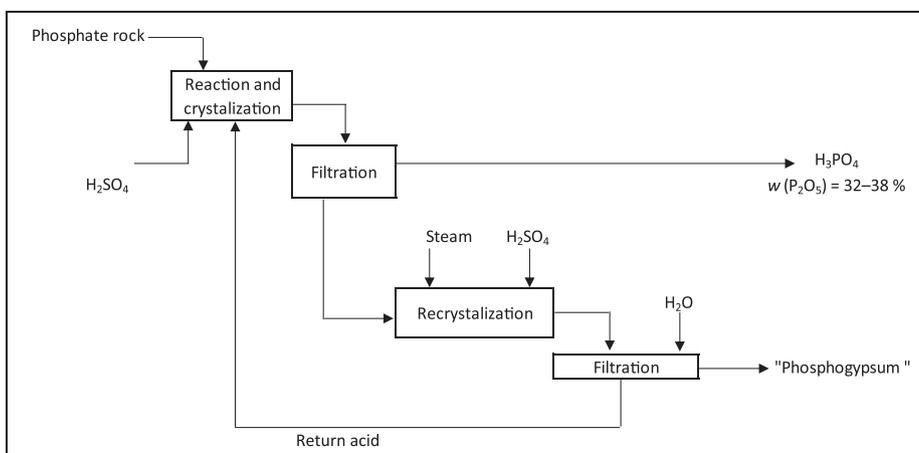


Fig. 2. Overview of the Di-Hemihydrate (DHH) recrystallization process with double-stage filtration based on European Commission and Joint Research Centre (2006).

well as main consumptions; specific inventory relative to each step cannot be published due to confidential aspects. The numbers between brackets represent the energy produced on site using natural gas boilers or electricity from the grid; they complete the supply of sulphuric acid facilities, as described below. For both phosphoric acid grades, electricity supply by the plant itself is equal to 50%. Concerning steam, both sulphuric facilities achieve at least 90% of the entire demand of the production process.

Sulphuric acid is produced on site with two different facilities both converting elemental sulphur recovered in the petroleum industry into sulphuric acid. 31% on the overall sulphuric acid is produced by the first facility which produces sulphur dioxide and also, as a co-product, steam which is used directly on site. Sulphur dioxide is then first converted into sulphur trioxide. This component is absorbed in water and transformed into sulphuric acid. The second unit which produces 69% of the total mass of sulphuric acid, in service for 5 years, uses the same principle but includes a cogeneration allowing the joint production of steam and electricity. This production of electricity allows the supply of around 50% of the needed electricity of the industrial plant. As both units produce several co-products, an allocation between all these co-products has been applied to divide the environmental impact of sulphur burning. This allocation is based on a physical relation between all products which is the thermodynamic relation between sulphur and the heat released during the combustion. For the cogeneration plant, electricity is produced from steam and then, a quantity of steam at 50 bar (gauge pressure) needed for this production can be calculated. This amount of steam is calculated using a turbine yield of 80% which was calculated after thermodynamic modelling. The energy included in steam at 6 bar (gauge pressure) is based on the total enthalpy of steam from which the enthalpy of water at 25 °C is subtracted. To be able to compare steam used for electricity or in the plant, the reference is the steam at 50 bar (gauge pressure). Then, the quantity of steam from step one at 6 bar (gauge pressure) is converted in a quantity of steam at 50 bar (gauge pressure), using the energy relation. Table 2 presents the calculated values for allocation for each facility. Another possibility is to assume that this surplus energy (as steam or electricity) is free and the entire burden of elemental sulphur combustion is given to sulphuric acid production. This possibility has been assessed in a sensitivity analysis in paragraph 3.1.2.

The remaining part of electricity needed by the industrial plant is produced using the Belgian energy mix of fuels. The model has been performed using the IEA statistics (International Energy Agency, 2015) and is presented in Table 3.

As mentioned previously, a co-product is obtained at the first stage of weak acid production. 85% of this phosphogypsum is sold and the remaining part is stacked. Even if there is a physical relation, based on stoichiometry, between weak phosphoric acid and phosphogypsum, the total impact has been associated to phosphoric acid H_3PO_4 as it reflects the market reality. Furthermore, this choice allows the comparison of the environmental impact of DHH process with the other ones. Sensitivity analysis using other

Table 2

Used allocations between co-products of sulphuric acid production facilities, data are given in %.

Unit	SO ₂	Steam	H ₂ SO ₄	Electricity
First facility	37	63	/	/
Second facility – first step	45	45	/	10
Second facility – second step	/	29	71	/
Second facility – global		32	58	10

Table 3

Energy mix for electricity in Belgium in 2012 from International Energy Agency (2015) China and Kazakhstan in 2011 from International Energy Agency (2012). Data are given in %.

Fuel	Belgium	China	Kazakhstan
Coal	6.0	79	81.1
Natural gas	28.2	1.8	9.2
Hydroelectricity	1.6	14.8	9.1
Nuclear energy	53.5	1.8	0.0
Wind	2.6	1.5	0.0
Waste	2.2	0.2	0.0
Biomass	4.3	0.7	0.0
Solar PV	1.3	0.0	0.0
Oil	0.3	0.2	0.6

allocation factors for phosphogypsum has been performed and results are presented in paragraph 3.1.3.

Another co-product, called fluosilicic acid, is also recovered during the production of fertilizer grade phosphoric acid. It is produced during the attack, by the sulphuric acid, of the rock which contains between 2% and 4% of fluoride (European Commission and Joint Research Centre, 2007; European Fertilizer Manufacturers' Association, 2000). This acid is sold and then a part of the environmental impact due to the concentration stage must be allocated to this co-product. An allocation based on stoichiometry relation has been used and fluosilicic acid is responsible of around 2% of these impacts. This allocation factor is in accordance with the Ecoinvent report specific to phosphoric acid production (Primas and Capello, 2004). Furthermore, due to the small quantity of H_2SiF_6 produced, these mass factors also reflect the economy factors and then no sensitivity analysis is required between both allocation factors. Considering H_2SiF_6 as a waste will not change anything in the overall results for the same reasons as explained just before.

Effluents of the first three steps are mainly emitted in water and comprise phosphorus and fluorine. Some metals as Cr, Cd or Pb are also emitted. The values taken into account are based on environmental reports published by Prayon SA for 2012 (Prayon SA, 2012a).

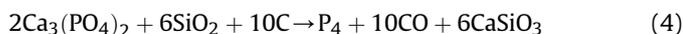
To obtain a purified and defluorinated phosphoric acid, three further steps are needed. The first one consists to oxidise the previous acid using steam and electricity. The next step is the extraction per solvent, using NaOH and sulphuric acid, and also using energy, too. The last step is dedicated to the acid defluorination using also energy.

Table 1

Main specific consumptions for fertilizer and purified phosphoric acid production – per tonne of P_2O_5 .

Consumption	Quantity per tonne of P_2O_5		Unit
	Fertilizer grade (1.92 t H_3PO_4 71.7%)	Purified grade (1.85 t H_3PO_4 72.5%)	
Phosphate rock	2.6	3	t
H_2SO_4	2.5	3	t
Electricity	142 (72)	263 (133)	kW h
Steam	2.1 (0.13)	3.9 (0.38)	t
NaOH	/	55.5	kg

2.3.1.2. Phosphoric acid production using thermal process. Production of purified and defluorinated phosphoric acid can also be achieved using the thermal process. This process consists in producing elemental phosphorus from phosphate rock and then oxidising it into P_2O_5 , which is hydrated to obtain phosphoric acid. The reaction due to the passage of grinded phosphate rock, mixed with a slurry consisting of water, clay, carbon and various waste streams containing phosphorus through a furnace can be summarised by Equation (4). This reaction produces elemental phosphorus, carbon monoxide and a liquid slag (European Commission and Joint Research Centre, 2007; European Fertilizer Manufacturers' Association, 2000).



The efficiency of phosphorus recovery is equal to 94%. The next step of phosphoric acid production is the oxidation of elemental phosphorus with the air to P_2O_5 . This reaction is exothermic and the heat release is used for high temperature steam generation. The P_2O_5 produced by oxidation is contacted with diluted phosphoric acid and reacts with the water content to produce phosphoric acid. Reactions are described by equations (5) and (6).



Thermal process for phosphoric acid production in European countries is now only performed in Czech Republic and Poland (European Commission and Joint Research Centre, 2007). Currently, this process is widely used in China and Kazakhstan, which are the main producers of thermal process phosphoric acid.

As no specific values are available for the modelling of the thermal process, average values from the Best Available Techniques (BAT) for the manufacture of large volume Inorganic Chemicals – Ammonia, fertilizers and acids, concerning consumptions are used and shown in Table 4 (European Commission and Joint Research Centre, 2007). Due to this non-specificity of data, uncertainties relative to inventory can appear but the results of environmental impacts obtained will be treated as a range of accessible values for thermal process and not as absolute values. Mass of needed phosphate rocks is given by the stoichiometry of the process so a weak uncertainty is then associated to this value. Information relative to emissions and energy consumptions should be considered as an accessible range of values.

For electricity generation, energy mixes relative to China and Kazakhstan have been modelled using the IEA values presented in Table 3 (International Energy Agency, 2012). Energy mix has been modelled with 50% for each electricity type considering a production in both countries.

3. Results and discussion

3.1. Results

Fig. 3 presents a breakdown of the results for ILCD 2011 environmental impact categories of our study. It presents the importance of specific consumption or emission for the product at fertilizer grade using wet process in Prayon SA. The overall process has been divided between 8 contributions: “phosphate” which refers to phosphate rock mining, “ H_2SO_4 ” which is relative to sulphuric acid production on site, “emissions in the air” specific to the plant, “emissions in water” due to process effluents, “steam” which is produced on site using sulphuric acid facilities or natural gas boilers, “electricity” produced on site or supplied by the grid, “chemicals” which refer to all chemicals consumptions of the

Table 4
Specific consumptions for P_2O_5 equivalent production using thermal process.

Consumption	Average quantity per tonne of P_2O_5	Unit
Phosphate rock	3.2	t
Clay	0.25	
Coke	0.55	
Process water	40	m^3
Cooling water	120	
Electricity	5850	kW h

process and finally “transport” which is relative to the phosphate rock and chemicals transportation. Fig. 4 compares both production processes for purified phosphoric acid, using Prayon specific data and BAT based thermal process data. Results relative to mineral and fossil fuel depletion categories modelled with ReCiPe 2008 method are added in both figures. Categories of ILCD 2011 method do not express directly the impact of fossil fuel consumption, which is an important factor for interpretation especially with energetic processes. Absolute values of impacts for each category are presented in Table 5 and are commented in further paragraphs.

Concerning fertilizer grade acid, the contribution of phosphate consumption including mining and beneficiation for fertilizer grade production achieves between 4% of the total impact for (h) acidification category and 65% for (o) mineral, fossil and renewable resources depletion. In the majority of categories, it reaches around 30% of the total impact. Transportation of phosphate and chemicals impact is not negligible and achieves more than 10% except in (e) particulate matter formation, (h) acidification and (o) mineral, fossil and renewable energy depletion. Sulphuric acid and steam reach together 76% of the (e) particulate matter formation impact and 86% for the (h) acidification impact. Emissions in water, composed of mainly phosphate obtain 82% of the total impact of (j) freshwater eutrophication.

Production of wet process purified phosphoric acid leads to specific environmental impacts around 1.5 times higher than the fertilizer grade for the 1 t of P_2O_5 contained in the final product. Production of fertilizer grade acid achieves, depending on impact category, 54–73% of the total impact of purified acid. Previous information concerning the importance of preliminary steps for fertilizer grade is still available for purified grade.

Production of purified thermal process phosphoric acid, assumed to be produced both in China and Kazakhstan, gives environmental impacts at least 7 times higher for (a) climate change and (q) fossil fuel consumption, and 6 times higher for (e) particulate matter formation than the wet process, as shown in Fig. 4. Wet process leads to higher emissions in (j) freshwater eutrophication category compared to thermal process. Electricity production and consumption included in the thermal process induce 90% of the total impact in all categories.

3.1.1. Benefits of the second facility of sulphuric acid production

In 2009, production of sulphuric acid was performed using exclusively the first production facility. The first facility was not able to supply the overall consumption of sulphuric acid and then the remaining part was bought on the market. Supply of electricity was obtained using exclusively the grid and the required steam using natural gas boilers. Environmental impacts of this situation have been assessed and compared with the current situation. Without the second facility, results show an increase of 10% for (j) freshwater eutrophication impact but around 80% for (a) climate change category. The implementation of a second facility allowing co-generation and then energy integration allows a non-negligible reduction in terms of environmental impacts in all impact categories.

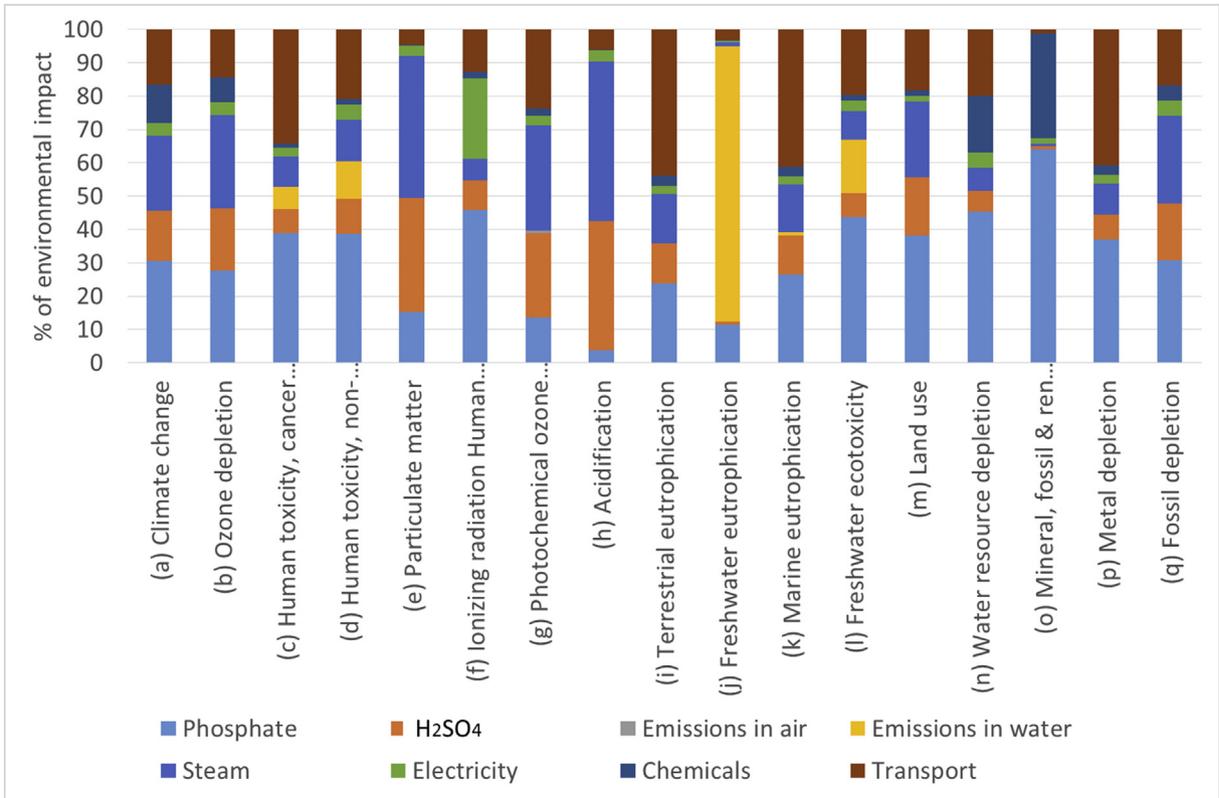


Fig. 3. Characterization results of environmental impacts for fertilizer grade phosphoric acid: importance of flows.

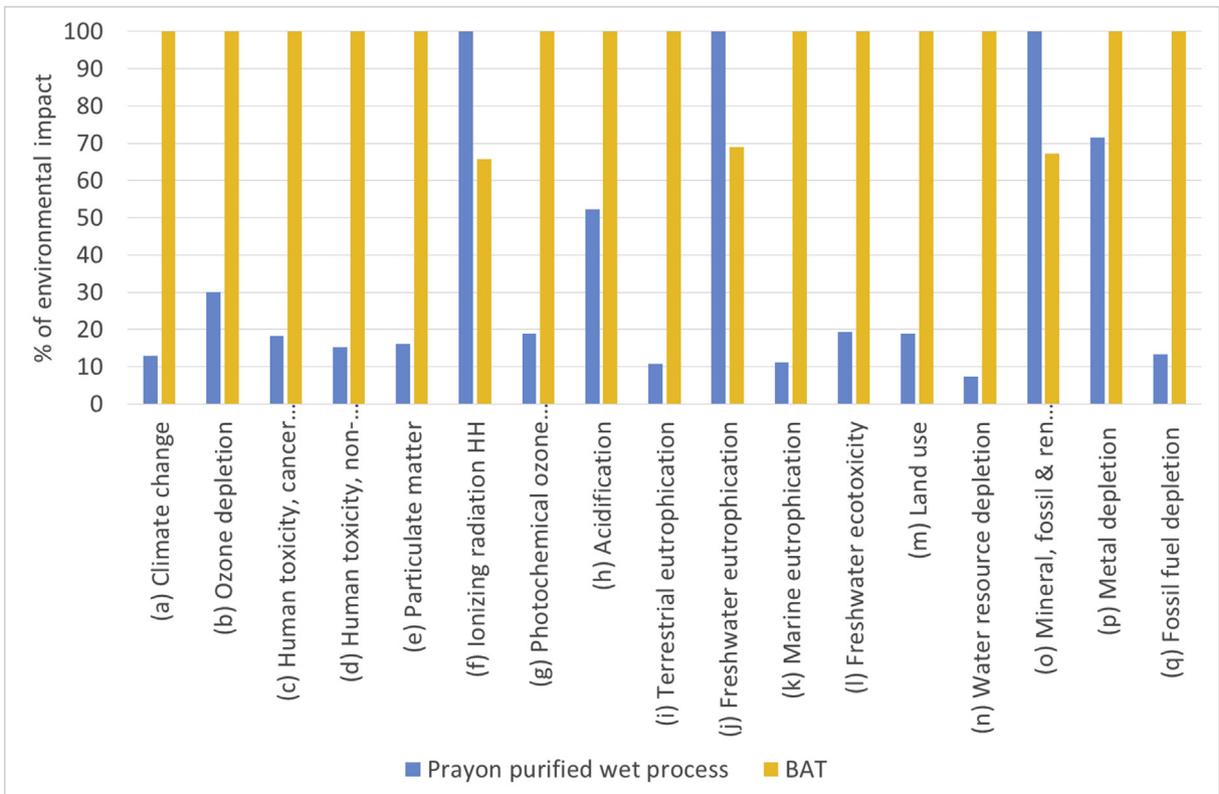


Fig. 4. Comparison between wet and thermal processes for purified acid production: characterization stage of environmental impacts.

Table 5
Specific environmental values for P₂O₅ using wet (fertilizer and purified grades) and thermal processes.

Category	Quantity and symbol	Unit	Usual unit	Fertilizer grade (1 t P ₂ O ₅)	Purified grade (1 t P ₂ O ₅)	
					Wet	Thermal BAT
Climate change	Mass of CO ₂ equivalent, m_{eq} (CO ₂)	kg	kg _{eq} CO ₂	626	950	7365
Human toxicity	Comparative Toxic Units for humans	CTUh	CTUh	1.07 10 ⁻⁴	2 10 ⁻⁴	1.27 10 ⁻³
Particulate matter formation	Mass of particulates 2.5 equivalent, m_{eq} (PM _{2.5})	kg	kg _{eq} PM 2.5	1.78	2.63	16.2
Acidification	Equivalent acidification amount, n_{eq} (H ⁺)	mol	mol _{eq} H ⁺	28.7	43.4	83
Freshwater eutrophication	Mass of phosphorus equivalent, m_{eq} (P)	kg	kg _{eq} P	1.1	1.5	1.04
Land use	Mass of carbon deficit, m_{eq} (C)	kg	kg C deficit	1394	1927	10 197
Fossil depletion	Mass of oil equivalent, m_{eq} (oil)	kg	kg _{eq} oil	187	293	2193

3.1.2. Sensitivity analysis – allocation for sulphuric acid production

In this study, an allocation has been used between sulphuric acid or sulphur dioxide, steam and electricity. This analysis is based on a physical relation given by thermodynamic values. Another possibility is to allocate the overall impact to sulphuric acid, based on the fact that it is the wanted product. Electricity and steam jointly produced are assumed to be free of burdens and then used in all facilities without any environmental impact. Fig. 5 presents variation of results for the main case and the sensitivity analysis.

In that case, a reduction in the total impact of the purified phosphoric acid is obtained for impact categories considered but value changes are comprised between 0.2% for (o) mineral, fossil and renewable energy depletion and 10.7% for (h) acidification with a majority of variations inferior to 5%. Using thermodynamic allocation is then relevant in our case, as all co-products are used for their energy content, relative to the thermodynamic values.

3.1.3. Sensitivity analysis – allocation for phosphogypsum

In this study, the unavoidable co-product, phosphogypsum, has been considered as a waste, assuming that the overall impact of the

Table 6

Allocation factors for weak phosphoric acid and phosphogypsum. Data are given in %.

Product	Waste	Stoichiometry	Price
Weak H ₃ PO ₄	100	49	95.3
Phosphogypsum	0	51	4.7

first step (weak phosphoric acid production) is only related to the main product. Another possibility is to divide this impact between phosphogypsum and phosphoric acid using different allocation factors which are presented in Table 6. Only the valorised part of phosphogypsum has been used in the calculation of these factors.

The physical relation, recommended by ISO standards leads to an environmental impact for weak phosphoric acid step divided by 2 which does not reflect the reality of the market. Concerning the economic allocation, the results obtained are quite the same as the ones used in the main text which confirms the robustness of this choice. A variation of around 5% for the weak phosphoric production step leads to a total variation lower than 5% for each impact

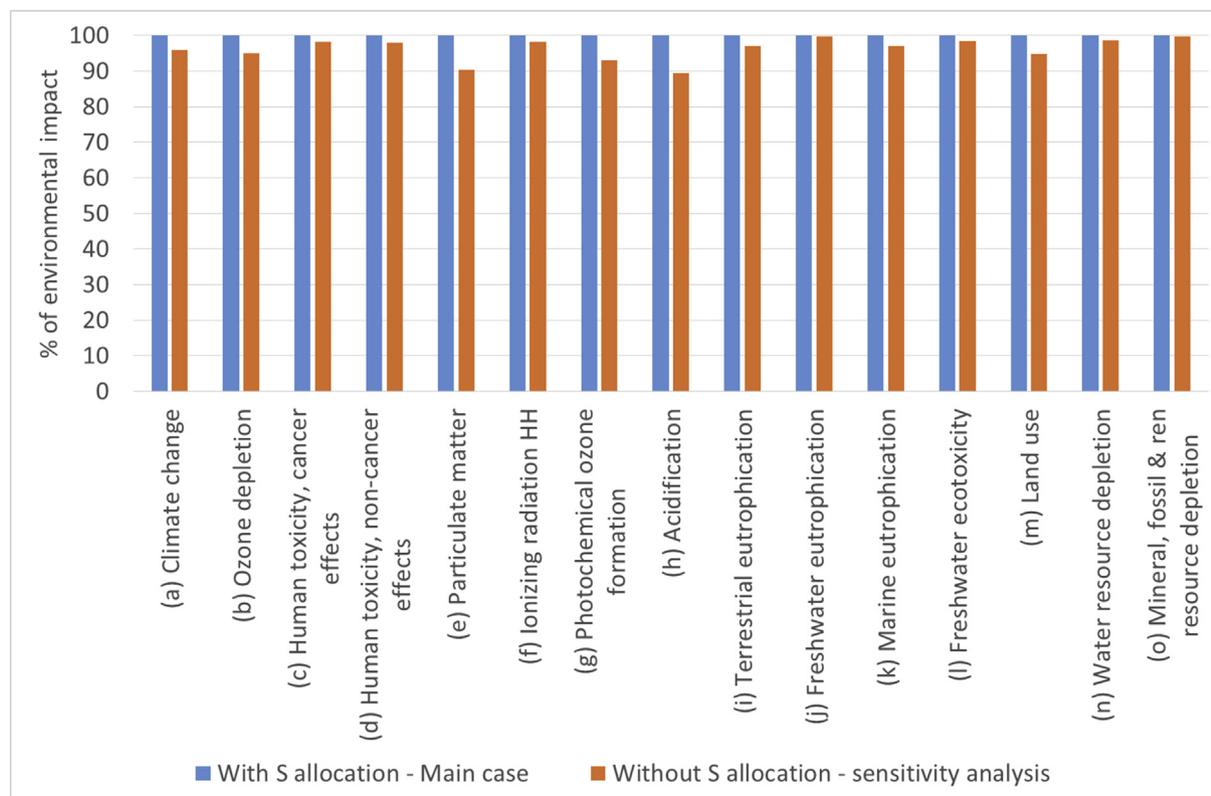


Fig. 5. Comparison between allocation on sulphur or not: characterization stage of environmental impacts.

category concerning purified phosphoric acid. If the physical allocation is used, the overall impact for each category is reduced by at least 10% for (j) eutrophication category and reaches more than 20% for (a) global warming, (b) ozone layer depletion and (q) fossil fuel depletion categories. Thus, practically, phosphogypsum was considered in this work as a waste, with no allocation at all, which is really the case for nearly all other phosphoric acid factories in the world.

Compared to other wet production processes in the world, where the quality of phosphogypsum does not allow its use, the di-hemihydrate process avoids the stack of phosphogypsum or its disposal in the sea and then reduces the emissions in water due to leachates and also the land needed. This environmental improvement is very important, especially in countries where areas are limited due to high population density as it is the case in Belgium.

3.2. Discussion

Production of phosphoric acid using wet di-hemihydrate process has as main advantage the valorisation of a high share of the produced phosphogypsum. As mentioned in literature, it is generally well accepted that the destiny of phosphogypsum and its associated leachates are the main environmental hazards in phosphoric acid process and should be handled with care to avoid high eutrophication impact (Bojarski et al., 2008; Silva and Kulay, 2005). Even if the phosphogypsum is not as economically profitable as phosphoric acid, its valorisation avoids disposal costs.

Phosphate rock mining and use induce one third of the (a) climate change impact as well as in (q) fossil fuel and (p) mineral depletion categories. Its transportation from mines to the production plant is also an important factor. Silva and Kulay (2005) highlighted this factor in the case of H_3PO_4 produced in Brazil for global warming potential, ozone layer depletion, human toxicity and freshwater aquatic ecotoxicity categories. This is explained by the important distance between ore processing units and production sites with sometimes more than 700 km as it is the case in our study (Silva and Kulay, 2005). Concerning (j) freshwater eutrophication, emissions of phosphate are the main contributor of this category but in the Brazilian case (Silva and Kulay, 2003, 2005), they are due to phosphogypsum being disposed in open areas and leading to leachates compared to our study case where emissions only come from the production process.

Thanks to both sulphuric acid production facilities integrated on the site at Prayon, the part of fossil fuel used for energy generation as steam or electricity is reduced. Using an allocation factor for sulphuric acid facilities and their co-products is not significantly different from not using it; the results are similar from one case to the other which confirms the robustness of our choice. Furthermore, the implementation of the second sulphuric acid facility allows a reduction of grid electricity about 50%. The steam produced with natural gas boilers constitutes maximum 10% of the overall demand of the site. The total consumption of sulphuric acid is completely supplied by the plant which allows a high reduction of the environmental impacts of fertilizer and purified grades phosphoric acid. The production of sulphuric acid has been cited as a determinant factor for GHG emissions in the manufacture of phosphate fertilizer (Kongshaug, 1998; Wood and Cowie, 2004).

The comparison between purified wet and thermal phosphoric acids leads to the environmental benefit for the wet process. The electricity consumption (see Tables 1 and 4) of the thermal process reaches the highest part of the impact in all impact categories. The energy mix of electricity, mainly composed of coal in countries as China or Kazakhstan, is responsible of this important impact. The high energy consumption has been often evocated as the main reason to abandon this process in Europe followed by the handling

of slags and dust (European Commission and Joint Research Centre, 2007; European Fertilizer Manufacturers' Association, 2000).

This study case highlights the importance of phosphate rocks and their transportation from Russia to Belgium in the total impact. Producers of phosphoric acid have generally no influence on this impact, due to the geographical position of the rocks and economic reasons. Type of transportation, here mainly performed by boat, is also important. The lorry transport should be avoided as much as possible for environmental and economic purposes. Even if di-hemihydrate process for phosphoric acid production requires sophisticated materials of construction and also a close customer for phosphogypsum, this process avoids the disposal of phosphogypsum and its implementation in new plants could be driven by these cost benefits but also thanks to its flexibility to rock source (European Commission and Joint Research Centre, 2007). Furthermore, the sulphuric acid production on site, coupled with a cogeneration facility, has improved the process in a non-negligible way especially in (a) climate change category. Heat recovery and its transformation in facilities is a key point for acid phosphoric process improvement.

4. Conclusions

The life cycle assessment methodology, in accordance with the ISO standards, is applied to wet di-hemihydrate process also called Central Prayon process for fertilizer and purified grades phosphoric acid. The purified phosphoric acid is compared with thermal acid and results show a reduction in all impact categories when using wet process instead of thermal one, excepted for (i) eutrophication.

Using di-hemihydrate process for phosphoric acid production avoids the disposal of phosphogypsum and allows its use, in this case, in plaster industry. This permits a reduction of environmental impacts e.g. in (i) eutrophication due to the avoidance of leachates or sea disposal but also the reduction of the area of occupied land which is an important factor especially in countries where available space is limited.

Sulphuric acid production is, after the valorisation of phosphogypsum, the main parameter in the environmental impact of phosphoric acid production. The excess heat produced jointly with the sulphuric acid allows an energy recovery in terms of heat and electricity which reduces in a significant way the environmental impacts of phosphoric acid production. The implementation five years ago of a modern sulphuric acid production plant achieving a cogeneration process permits a reduction of 80% of (a) climate change impact. The energy integration coupled with the valorisation of co-products is then the best way to reduce environmental impacts of a high energy consuming chemical.

As the environmental impacts of fertilizer and purified grades of phosphoric acid for Belgium are now available, the next step of this study will be the evaluation of the environmental impacts of phosphate salts. This study will highlight the hotspots of this production and gives clues of improvement in an environmental point of view.

As the fertilizers are one of the main important factor in the agricultural sector, which is also related to numerous products of our daily life, it is important to get an accurate value of the environmental impacts of their production.

As wet process is used worldwide for the production of fertilizer grade phosphoric acid, and as Prayon processes represent around 50% of the production, this study can help in modelling other specific industrial plants. Then, only specific data concerning electricity mix, sulphuric acid production or specific regulations (e.g. the sea disposal of phosphogypsum is forbidden in Europe which is not the case in other continents) would be necessary to

model the fertilizer grade or purified phosphoric acid production in another location in the world.

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