

The Role of the Merseburg Process in Industrial Decarbonisation and Waste Evaluation

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Abstract

Due to greenhouse gas emissions in industrial production, global warming and the resulting climate change pose significant threats to a liveable world. The emission of carbon dioxide, which is released as a result of industrial activities, is the most important component that triggers the global warming process. The use of waste material, which is the result of industrial activity, as raw material within the framework of circular economy is of vital importance in terms of the use of sustainable resources.

The problem of phosphogypsum, which is released during the production of phosphoric acid, can be eliminated by the Merseburg process. With such waste minimisation, the destruction caused by emission gases such as carbon dioxide in the atmosphere will also be prevented. In this evaluation study, the use of carbon dioxide gas as a raw material is discussed, while reducing the emission values of industries such as cement and thermal power plants that cause large amounts of carbon dioxide emissions from phosphogypsum waste. Although an ammonium sulphate production is foreseen with the evaluation of carbon dioxide and phosphogypsum waste with the Merseburg process, the effect of the impurity content of the waste material used on the recommended ammonium sulphate concentration will be an important research topic.

Various protocols are being worked on worldwide in order to minimise the emissions on international scale. The use of the Merseburg process for this and similar processes will provide significant advantages to the manufacturer in reaching the targeted emission amount.

Keywords

Phosphogypsum, Merseburg, global warming, climate change, waste minimisation

1 Introduction

1.1 Global warming, climate change, and CO₂ emissions

Greenhouse gas emissions originate from a variety of sectors such as energy systems, industry, buildings, transport, agriculture, forestry, and other land uses. Accumulation of greenhouse gases in the atmosphere enables the absorption of sunlight, resulting in an increase in surface and ocean temperatures. Global warming causes significant changes in the climate by irregular droughts, heat waves, together with flooding and freezing stress conditions on a local basis.^{1,2}

Global warming and related climate change differ from any other environmental problem since their effects are long lasting. In order to mitigate the environmental effects of greenhouse gases and adapt to climate change, transition to clean technologies play an important role. Control of environmental pollution and mitigating its negative effects have been a significant issue for countries, and protocols and agreements have been signed on the development of clean technologies.³ Research on greenhouse gases and carbon neutrality has spread globally. More than 100 national governments signed the Kyoto Protocol in 1997 within the scope of the United Nations Framework Convention on Climate Change in order to set net zero emission targets, and then came together in Paris in 2015,

again within the scope of the United Nations Framework Convention on Climate Change, in order to re-regulate the current carbon gas emissions. They agreed to keep pre-industrial levels below 2 °C and above 1.5 °C by signing the Paris climate agreement.^{4,5}

Anthropogenic impact together with the industrial revolution have triggered a constant increase in production and accumulation of greenhouse gases over the past decades.⁶ Carbon dioxide is the main contributor to greenhouse gases, and industry plays a significant role in mitigating CO₂ emissions and the effects of global warming by shifting to clean technologies. Global CO₂ emissions are attributed to mainly electricity, transportation, heating, and industrial applications, and have been increasing continuously with a rate of 2.4 % per year. Industrial applications account for 12 % of global CO₂ emissions.⁷ In order to reach the 1.5 °C target of the Paris Agreement, global CO₂ emissions should be below 9 Gt year⁻¹ by 2060, and net zero CO₂ emissions by 2100. However, projections show that the total industry-based CO₂ emissions reduction with available mitigation options would reach as high as 10.1 Gt year⁻¹ by 2050. Thus, continuously increasing energy demand and meeting net zero emission aims might be possible by introducing sustainable and renewable energy technologies.^{8,9}

Within the concept of combating the negative effects of global warming and climate change, research is focusing on decarbonisation processes. Studies on energy efficiency improvement for CO₂ emission reduction, carbon capture

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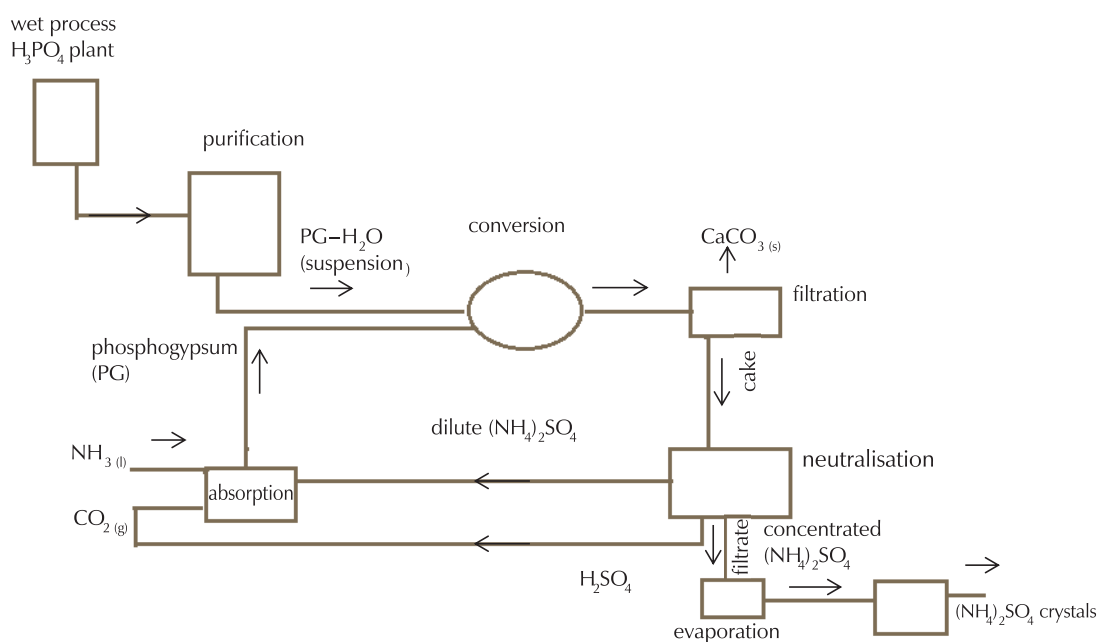


Fig. 1 – Schematic illustration of industrial-scale Merseburg Process³⁷

and storage technology, substitution of low-carbon raw material sources such as biomass have been assessed to mitigate CO₂ emissions.^{10,11}

1.2 Value of phosphogypsum as raw material

The use of by-products during industrial production as raw materials in an industrial process is an important part of the circular economy process. Similarly, phosphogypsum is released as a by-product in the production of phosphoric acid. The production of ammonium sulphate from the phosphogypsum by-product is a good example of circular economy. However, although the production of ammonium sulphate from phosphogypsum is called the Merseburg process, the produced ammonium sulphate is among the most needed nitrogen fertilisers.

PG is chemically in the form of calcium sulphate dihydrate, also containing impurities such as residual acids, fluorides, rare earth elements, heavy metals, and radionuclides, and therefore is not as pure as natural gypsum.^{12–15} Resulting PG is, in slurry form, filtered and sent to the storage area. During long storage periods, slurry loses its water content and sedimentation occurs.

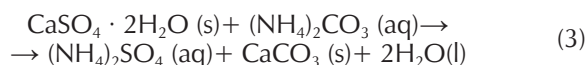
There are many studies on the use of PG in the extraction of rare earth elements, as soil improver in agricultural applications or re-used as a secondary raw material in the production of sodium/ammonium sulphate.^{16–19} Cement industry utilises PG as a setting retarder or as a mineralising agent in clinker production process.^{20–22} PG is also used as a filler in the construction material industry, in plasterboards, brick manufacturing or roadbed construction.^{23,24} Although there are more examples of the utilisation of PG in agricultural applications, manufacturing of building materials and roadbed material in the literature, these studies

are still being developed, and do not ensure regular consumption in large quantities.²⁵

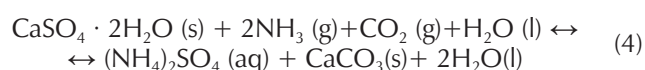
The production rate of PG, which is produced as a by-product in the production of phosphoric acid, increases in parallel with the production rate of phosphoric acid.^{26,27} Due to water-soluble phosphates, heavy metals and radionuclides in the PG structure, its re-use area is limited, and only 15 % of the PG formed per year is being re-used, while the remaining 85 % is stored as piles where they are sent after process.^{28–31} The amount of PG used for recycling is at a very low level when compared to the amount of PG that is formed annually, so studies on researching bulk consumption of PG are of importance.³²

1.3 Merseburg process and the value of phosphogypsum

The Merseburg process (Fig. 1) is defined as the reaction of gypsum (or anhydrite) with ammonium carbonate ((NH₄)₂CO₃) to yield ammonium sulphate ((NH₄)₂SO₄) and calcium carbonate (CaCO₃).^{33,34} The use of the Merseburg process has been restricted due to the development of more economical and alternative processes for the production of ammonium sulphate. Therefore, various modification studies have been carried out in the reaction kinetics to increase the economic feasibility of the reaction.³⁵ The reaction sequence is given by Eqs. (1)–(3).³⁶



The overall reaction (combination of Eqs. (1)–(3)) can be shown by Eq. (4).



The cost of the operation is closely related to the reactor system and NH_3 prices. Phosphogypsum and CO_2 prices can be associated with various industrial applications, mostly by-products of the phosphoric acid production process and the cement industry.³⁷

Ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$), as the main product of the Merseburg process, is the first produced nitrogen fertiliser containing both nitrogen (N) and sulphur (S) in the form of ammonium (27.27 % by weight) and sulphate (72.72 % by weight), respectively.^{38–40} During production, an intense greenhouse gas production takes place in terms of carbon emissions.^{41,42} In this respect, the realisation of the decarbonisation process in the process will ensure that the carbon emission problem is significantly minimised.⁴³

2 Historical development of the Merseburg process and its environmental benefits

The Merseburg process is also known as the ammonia-carbonation reaction, and was first developed in Germany between 1913 and 1918. In 1923, production started in the United Kingdom and Korea. The first plant to use PG in the Merseburg process in 1942 was in Selzeate, France. In the 1950s and 1960s, plants in Germany, India, Pakistan, Austria, and Japan were using PG as a source of gypsum in the ammonia-carbonation reaction (Table 1).^{33,34}

Table 1 – Historical development of the Merseburg process

Year	Development
1913	Merseburg process was developed in Germany
1923	Merseburg processes were built in England and France
1942	Phosphogypsum was used for the first time in France in the Merseburg process
1950	Natural gypsum was used in the Merseburg process in India, Pakistan, Austria, Italy, and Turkey
1960	Phosphogypsum was used in Merseburg porcelain in India, Japan

The use of the Merseburg process has been restricted due to the development of more economical and alternative processes for the production of ammonium sulphate. Therefore, various modification studies have been carried out in the reaction kinetics to increase the economic feasibility of the reaction.

Continuous increments in the global CO_2 emissions have led to a steady increase in the global temperature, being

one of the most important precursors of global warming and climate change phenomena. Carbon capture and storage technologies developed for the mitigation of CO_2 emissions are also widely studied, and various studies have been conducted for efficient application.

Phosphogypsum comprises a wide range of impurities including heavy metals, radionuclides and REEs. Disposal and landfill of PG poses significant environmental problems in the long term, since its recycling is limited due to its chemical structure, which hinders its efficient use in construction and other industrial applications. Although there have been many studies conducted in PG recycling, there are still some challenges to overcome for its effective re-use. Besides, re-use rate is very low when compared to the accumulation rate, and long-term storage might pose some environmental risks.

The Merseburg process is based on the ammonia-carbonation reaction of gypsum. However, due to the nature of the raw material, alternative processes are being studied to prevent carbon dioxide emissions due to ammonia production. Any type of gypsum (dihydrate, hemihydrate or anhydrous) can be used in the Merseburg process. In the case of using PG, satisfactory conversion efficiencies can be obtained. In the case of PG utilisation, satisfactory conversion yields can be achieved. Gypsum can be carbonated by either ammonium carbonate or using NH_3 solution together with gaseous CO_2 mixture. The latter approach offers an environmental approach for both CO_2 capture and PG recycling.^{44,45}

Merseburg process allows the consumption of PG as a gypsum source and capture of CO_2 as solid CaCO_3 . Also known as the mineral CO_2 sequestration method, it is possible to achieve a permanent CO_2 capture and manufacture environmentally friendly and stable solid carbonates, suitable for valorisation in various kinds of industries.⁴⁶ Phosphogypsum, being an industrial by-product of wet process H_3PO_4 production method, rich in calcium content, is a promising candidate for the carbonation process. The use of PG waste and carbon dioxide gas during the Merseburg process is an important industrial gain in terms of minimising greenhouse gas emissions.³⁸ In this framework, Merseburg process offers a simple and efficient route for the mineral sequestration of CO_2 , utilising PG as a calcium source.⁴⁷ Consuming an industrial by-product and performing CO_2 capture technology are both contributing sustainable development goals.

3 Conclusion

The amount of CO_2 being released from industrial applications has reached about 30 Gt year⁻¹; such large and continuous release of CO_2 causes some climatic consequences, primarily global warming and climate change issues. Carbon capture and storage technologies have been developed to combat global warming, aiming to reduce CO_2 emissions. Mineral carbonation processes offer the capture of CO_2 as stable solid carbonates, disabling further CO_2 releases.

Phosphogypsum, a by-product of the phosphoric acid wet production process, is widely used in road construction, used as an alternative to gypsum in cement production, agricultural applications, and building materials production. However, the recycle rate of PG is much lower than the accumulation rate, and annual PG accumulation has reached up to 300 Mt. Storage of such huge amounts of PG poses some risks, such as release to ground water or radionuclide exposure, and is of significant environmental concern. Research for the re-use of PG on an industrial scale has been gaining importance in recent years. Although PG is valorised in various industrial applications, it still lacks a promising solution that would provide efficient, continuous, and bulk consumption.

Merseburg process is basically defined as the ammonio-carbonation reaction of gypsum. Phosphogypsum can also be utilised in the reaction as pure gypsum, and both have satisfactory conversion efficiencies. Ammonium carbonate is the other reactant in the reaction. However, gypsum, ammonium hydroxide and CO₂ can also undergo the reaction. In both cases, CO₂ consumption is provided. Merseburg process allows the consumption of two environmentally risky outputs, PG and CO₂. On the other hand, the products are ammonium sulphate and CaCO₃, which have an economic value and their own share in global markets. Ammonium sulphate is a type of nitrogenous fertiliser, the use of which has become widespread, and the demand for ammonium sulphate is expected to increase in the next 10-year projection. CaCO₃ is a functional material for various industries.

Circular economy studies aiming at the reduction of carbon emissions on an industrial scale (industrial decarbonisation) are of great importance to achieve the net zero carbon emission target. In terms of enabling regular consumption of PG, serving the increase in ammonium sulphate demand in the upcoming years, and reducing CO₂ emissions, the Merseburg process is a promising approach for consumption of an industrial by-product and minimisation of CO₂ emissions.

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SAŽETAK

Uloga Merseburg procesa u industrijskoj dekarbonizaciji i evaluaciji otpada

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Globalno zatopljenje i klimatske promjene, kao rezultat emisija stakleničkih plinova u industriji, predstavljaju veliku prijetnju živom svijetu. Ugljikov dioksid, koji se oslobađa kao rezultat industrijskih aktivnosti, najvažnija je komponenta u procesu globalnog zagrijavanja. Otpadni materijal, kao još jedan produkt industrijske aktivnosti, može se u okviru kružnog gospodarstva upotrebljavati kao sirovina.

Problem fosfogipsa, koji se oslobađa tijekom proizvodnje fosforne kiseline, može se otkloniti Merseburg procesom. Takvim smanjenjem otpada smanjit će se i destrukcija uzrokovana emisijom plinova, poput ugljikova dioksida, u atmosferu. U ovoj studiji komentirana je uporaba plinovitog ugljikova dioksida kao sirovine, uz smanjenje njegovih emisija u cementarama i termoelektrana, gdje se emitiraju velike količine ugljikova dioksida iz fosfogipsnog otpada.

U svijetu se radi na različitim protokolima da bi se smanjile emisije na međunarodnoj razini. Primjena Merseburg procesa za taj i slične procese pružit će značajnu prednost proizvođačima u postizanju ciljanih količina emisija.

Ključne riječi

Fosfogips, Merseburg, globalno zagrijavanje, klimatske promjene, smanjenje otpada

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