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Research Article

Effect of phosphogypsum use as a waste recycling on GHG emissions by mineral carbonisation method

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ABSTRACT

The release of greenhouse gas emissions into the atmosphere as a result of anthropogenic sources and industrial applications has triggered the increase in global temperatures called global warming and related climate change. Phosphogypsum (PG) is a by-product of the wet process phosphoric acid (H_3PO_4) production process, which chemically consists of calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$) with some impurities. Annual PG accumulation has reached 300 Mtons and a strategy is needed to ensure efficient, continuous and bulk consumption. Due to the high amount of calcium it contains, PG is a material suitable for use in CO_2 capture and storage processes to form stable solid carbonate compounds. This process, called mineral carbonisation of PG, contributes to sustainable development goals by providing the multiple benefits of both the utilisation of an industrial by-product and the realisation of CO_2 capture and storage technology.

Keywords: Phosphogypsum, carbon capture, accumulation, waste management.

Mineral karbonizasyon yöntemiyle atık geri dönüşümü olarak fosfojips kullanımının sera salımları üzerindeki etkisi

ÖZ

Antropojenik kaynaklar ve endüstriyel uygulamalar sonucu atmosfere sera gazı emisyonlarının salınması, küresel ısınma olarak adlandırılan küresel sıcaklıklardaki artışı ve buna bağlı olarak iklim değişikliğini tetiklemiştir. Fosfojips (PG), kimyasal olarak bazı safsızlıklar içeren kalsiyum sülfat dihidrattan ($CaSO_4.2H_2O$) oluşan, ıslak proses fosforik asit (H_3PO_4) üretim prosesinin bir yan ürünüdür. Yıllık PG birikimi 300 Mton'a ulaşmış olup verimli, sürekli ve toplu tüketimi sağlamak amacıyla bir stratejiye ihtiyaç vardır. PG, içerdiği yüksek kalsiyum miktarı nedeniyle kararlı katı karbonat bileşikleri oluşturmak için CO_2 tutma ve depolama işlemlerinde kullanıma uygun bir malzemedir. PG'nin mineral karbonizasyonu olarak adlandırılan bu süreç, hem endüstriyel bir yan ürünün kullanımının hem de CO_2 yakalama ve depolama teknolojisinin gerçekleştirilmesinin birçok faydasını sağlayarak sürdürülebilir kalkınma hedeflerine katkıda bulunur.

Anahtar Kelimeler: Fosfojips, karbon yakalama, biriktirme, atık yönetimi.

1. INTRODUCTION

1.1. Greenhouse gas emissions and their effects on climate change

Global warming is caused by carbon dioxide emissions released as a result of industrial processes. Along with the carbon dioxide emission resulting from industrial processes, the increase in temperatures in sea water and other living spaces with the effect of sunlight draws attention. This temperature increase has negative consequences such as inefficiency for agricultural work, especially in agricultural areas.[1,2]

Carbon dioxide emissions generally occur from thermal power plants, industrial plants that apply the heating process, and processes that produce petrochemicals. Compared to other greenhouse gases, it is accepted that the main component of increasing greenhouse gas emissions is carbon dioxide (CO_2), which has a share of

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approximately 64%.[3] If current activities that cause CO_2 emissions continue, stabilisation of greenhouse gas concentrations will not be possible. Fossil fuels are the dominant form in meeting the energy needs on a global scale, and fossil fuel consumption accounts for approximately 75% of anthropogenic CO_2 emissions. It was stated that the annual average increase in CO_2 emissions between 1970 and 2000 had a share of 1.72%, and this rate increased to 2.75% between 2010 and 2014. CO_2 emissions from the energy sector are around 30 billion tons per year and are expected to nearly double by 2050.[4,5] For this reason, stabilizing the CO_2 concentration in the atmosphere is important and it is estimated that CO_2 levels can be reduced by about 85% in the next century, with a decrease of approximately 20 billion tons of CO_2 formation per year.[6,7] This approach requires the adoption of a common goal of controlling global warming by reducing global CO_2 emissions.[8,9] In this context, research on greenhouse gas and carbon neutrality has become widespread and important at the global level. There have been several initiatives in recent history to reduce carbon dioxide emissions. With these initiatives, efforts are made to prevent the worldwide temperature increase caused by carbon dioxide gas.[10,11]

Reducing industrial carbon dioxide emissions, which cause worldwide temperature rise, has been the main goal. Therefore, various processes such as carbon capture and capture come to the fore as an industrial carbon removal method. However, the use of raw materials with low carbon content is also considered as another method to reduce carbon gas emissions. [12,13] The carbon capture and storage method is a critical method accepted by the authorities within the scope of global greenhouse gas emission reduction studies and included in the scenarios.[14] The basic steps of carbon capture and storage methods consist of post-combustion and pre-combustion CO_2 capture, separation from other gases, transport and isolating CO_2 from the atmosphere by storage.[15-17]

1.2. Mineral carbonisation method

Mineral carbonisation is expressed as a decarbonisation process for industrial plants that emit carbon dioxide, using the carbon gas release to create raw materials using the mineralisation method.[18,19] However, there are also challenges such as slowing the kinetics of mineral-fluid reactions and accelerating the carbonation process throughout the process.[20,21]

Alkaline earth metals such as Ca and Mg are the most suitable metals for the mineral carbonisation method. However, due to their highly reactive nature, these metals are rare and generally found in silicate forms.[22] The most common natural silicate minerals are olivine (Mg_2SiO_4), wollastonite ($CaSiO_3$) and serpentine ($Mg_3Si_2O_5(OH)_4$). In addition to natural minerals, industrial solid wastes such as waste ash, waste cement, steel production slag and mine waste are also potential materials that can be used as raw materials in the carbonisation process.[23-25]

1.3. Phosphogypsum as an industrial waste and its recycling mechanism

Phosphogypsum (PG) is a by-product of the "wet process" based on the production of phosphoric acid (H_3PO_4) by the decomposition of natural phosphate rock in sulfuric acid (H_2SO_4) at 70-80 °C. Phosphogypsum is formulated as calcium sulfate containing two moles of water and must be cleaned of toxic elements before it can be used as raw material.[26-30] The PG formed as a result of the process is in the form of sludge in the first stage and is sent to the storage area after the filtering stage. During the long storage period, the sludge loses its water content and sediment formation is observed over time.

Various research studies have been reported in the literature regarding the use of phosphogypsum in agricultural areas.[31-34] PG is used as a setting retarding additive or mineralizing agent in the clinker production process in the cement industry.[35-37] Although there are applications in the building material sector for its use as a filler in gypsum boards, brick manufacturing or road construction, these studies are still under development and cannot yet provide regular and bulk consumption of PG.[38]

Phosphogypsum is formed during the production of phosphoric acid and its amount may increase depending on the production capacity of phosphoric acid.[39,40] Due to the internal contamination of phosphogypsum, its use as a raw material is not common and requires pretreatment for cleaning before use.[41-45]

Since the use of phosphogypsum, which is produced as a waste in phosphoric acid processes, as a raw material is very limited, it is necessary to work on various methods to improve the raw material properties.[46,47] In recent studies carried out within the scope of reuse studies of PG, it has been stated that natural ores or industrial wastes show good efficiency in the production of sulfate compounds, and there are various studies for the conversion of gypsum to alkaline sulfates such as $(NH_4)_2SO_4$, K_2SO_4, Na_2SO_4. Studying the mineral carbonation process by reacting phosphogypsum with magnesium, calcium and silicon salts can be considered as important steps towards carbon dioxide removal. It has been stated that the use of PG or FGD is more advantageous than other industrial wastes.

1.4. Mineral carbonisation of phosphogypsum

Although the impurities it contains limit the usage area, there are also environmentally friendly applications for the recovery of PG. One of these approaches includes the use of PG as a calcium source in the CO_2 capture capture

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process to reduce greenhouse gas emissions.[48-50] Phosphogypsum contains a significant amount of calcium and does not require a different granulation process due to its low particle size, therefore, it does not cause any energy cost in terms of pre-treatment of phosphogypsum.[51-54]

The carbonisation process of PG can be done with various alkaline sources. In the mineral carbonisation of PG, PG acts as a carbon scavenger in the form of $Ca(OH)_2$ in the first stage. Sulphate is obtained by alkali dissolution using soda, and then mineral carbonate is formed by the instantaneous reaction with CO_2.[55] In another mineral carbonisation approach, ammonium hydroxide (NH_4OH) is used as an alkali source. In this case, in the first stage, ammonium carbonate ($(NH_4)_2CO_3$) is formed by the reaction of $(NH_4)OH$ with CO_2, in the next stage ammonium sulfate ($(NH_4)_2SO_4$) and limestone ($CaCO_3$) are formed by the reaction of $(NH_4)_2CO_3$ and PG.[56-58]

Carbonate and sulfate salts formed as a result of mineral carbonisation of PG are used as filling materials for various applications in the fertilizer and building materials industry. As a result of the mineral carbonisation process, both economically valuable products are obtained and large amounts of CO_2 are converted into stable solids in the form of carbonate in accordance with carbon emission control strategies. Mineral carbonisation can be carried out by processes such as membrane electrolysis or thermal degradation.[59]

2. RESULTS AND DISCUSSION

2.1. Environmental evaluation of mineral carbonisation of phosphogypsum

Phosphogypsum may contain various elemental contamination such as Fe and Al during storage due to process conditions and raw material properties. Environmental problems may occur in the long term due to the disposal and regular storage of PG, its limited recycling due to its chemical structure, and the limitation of its use in different industrial areas, especially its radionuclide content. While there are various studies on the use of phosphogypsum as a raw material, the use of phosphogypsum as a raw material in these processes is well below the production amount of phosphogypsum, and its use in the decarbonsation process by using it together with carbon dioxide will provide significant benefits to the greenhouse gas emission process.[60,61]

The high amounts of calcium and sulfur in phosphogypsum make it a valuable by-product. In this context, the methods to be developed for the evaluation of PG can be evaluated as a positive solution both in terms of using the stored material as raw material in the production of products with added value, and as an environmentally positive solution within the framework of waste minimisation.[62] Previous studies on environmental applications of PG indicate that PG is a suitable raw material as a mineral carbonisation process to reduce CO_2 emissions, especially within the framework of the CO_2 capture capture method.[63-65] Again, according to literature studies, 100-280 Mtons of PG can bind 26-72 Mtons of CO_2. In this context, approximately 1:5 mass ($PG:CO_2$) consumption can be achieved as a result of mineral carbonisation of PG.

3. CONCLUSIONS

The amount of CO_2 released into the atmosphere as a result of industrial applications has reached 30 Gtons per year. Such a large and continuous release of CO_2 causes some climatic consequences, especially global warming and climate change problems. Within the scope of combating global warming, which aims to reduce CO_2 emissions, carbon capture and storage technologies are at the forefront. Mineral carbonisation processes ensure that CO_2 is stored as stable solid carbonates, preventing further CO_2 release.

Phosphogypsum, which is released as a reaction product in the production of phosphoric acid, can be used as an industrial raw material in processes such as the ceramic industry. However, the amount of use in these processes is far below the production rate. Storage due to the toxic contamination it contains brings environmental risks. Therefore, the use of phosphogypsum as a raw material in larger scale industries is becoming important.

The increase in carbon dioxide emissions as a result of industrial processes causes an increase in temperature in the atmosphere and climate irregularities. Various decarbonsation methods are being studied to reduce carbon dioxide emissions. Mineral carbonsation is one of the important processes that stand out among these processes. Increasing the raw material properties with the phosphogypsum mineral carbonsation process will be a very important step in reducing industrial carbon emissions.

Conflict of interests

I declares that there is no a conflict of interest with any person, institute, company, etc.

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