Carbon Capture and Utilization via Mineral Carbonation of Alkaline Wastes without CO2 Purification and Pressurization

	ほう　しんろん
氏　　　　　　名	何　星融
授　与　学　位	博士（環境科学）
学　位　記　番　号	環博第152号
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指　導　教　員	東北大学教授　柴田　悦郎
論　文　審　査　委　員	主査　東北大学准教授　飯塚　淳　東北大学教授　柴田　悦郎 東北大学教授　井上　千弘　東北大学教授　松八重　一代

論 文 内 容 要 旨

Climate change is one of the most pressing issues currently facing society. There is therefore an urgent need to develop suitable and sustainable techniques that mitigate the impacts of climate change. The emission of greenhouse gases (GHG) is a significant contributor to climate change, specifically global warming. CO_2 emissions account for approximately three-quarters of GHG emissions; therefore, achieving a reduction in CO_2 emissions is an important part of minimizing the extent of global warming. Industries of particular concern for their environmental and climate impact are those that produce alkaline wastes. These include the cement and concrete industry, iron and steel manufacturing industry, and coal-fired power generation.

Carbon capture and utilization (CCU) is a promising process for reducing CO_2 emissions. The mineral carbonation of alkaline materials is of particular interest for CCU, as well as for addressing the environmental impacts of alkaline waste production. Most CCU methods require additional CO_2 purification and pressurization processes, which are costly, require high-energy input, as well as additional land use, decreasing their feasibility as an environmental strategy. Mineral carbonation of alkaline materials is possibly promising solution for developing without CO_2 purification and pressurization because the reaction is spontaneous. Additionally, the carbonated products are stable, with potential for use in further applications. Alkaline waste is regarded as a more suitable input material compared with alkaline rocks because alkaline wastes are generally

cheaper, more active, and do not require the exploitation of natural resources.

The primary objective of this research was to develop a promising CCU method using mineral carbonation of alkaline wastes, without the need for CO_2 purification and pressurization. Specifically, this study focused on the following processes:

(1) Development of direct aqueous carbonation of alkaline wastes.

(2) Development of circular indirect carbonation of alkaline wastes without chemicals consumption.

First, we investigated the direct aqueous carbonation of concrete fines under low-energy input. Concrete fines are a by-product of aggregate recycling from waste concrete, produced when the hydrated cement fraction, which decreases the quality of the recycled aggregate, is removed. Concrete fines need to be appropriately treated to improve the feasibility of aggregate recycling. In this study, we evaluated synthetic concrete fines and two types of concrete fines generated from the aggregate recycling processes from demolished concrete and solidified, returned fresh concrete. By varying the reaction parameters, we achieved a CO_2 uptake efficiency of 0.19 g-CO_2/g-synthetic concrete fines, and 0.13 g-CO_2/g-concrete fines, under low-energy input (14% CO_2, atmospheric pressure). The effects of solidification and particle collision were determined by carbonated product characterization. Compared with previous studies using high pressures and pure CO_2, this work achieved higher CO_2 uptake efficiency according to the high contents of active chemical forms of calcium such as $Ca(OH)_2$. Concrete fines are therefore a promising input for low-energy carbonation without the need for CO_2 purification and pressurization. Additionally, the carbonated products have the potential for use in diverse applications.

Second, we investigated the direct aqueous carbonation of coal fly ash under low-energy input. Mineral carbonation of coal fly ash under high-energy input has been investigated extensively; however, to our knowledge, there are limited studies investigating the process under low-energy input. We investigated mineral carbonation under low-energy input by using coal fly ash, which usually has a low Ca content, without CO_2 purification and pressurization. The carbonation reaction and reaction mechanisms, such as $CaCO_3$ redissolution, were monitored and the potential for CO_2

sequestration and utilization was evaluated. The carbonated product showed minimal risk of leaching and could therefore be considered for use in further applications. Our results demonstrated that coal fly ash was an appropriate input in direct aqueous carbonation under low-energy input. The maximum CO_2 uptake efficiency was 0.016 g-CO_2/g-coal fly ash. This is lower compared with the literature values for other materials; however, the high availability of low-Ca-content fly ash means that its total CO_2 reduction potential remains competitive.

We next investigated indirect carbonation with chemicals regeneration via electrodialysis, using coal fly ash. Indirect carbonation requiring the continuous addition of chemicals results in the formation of waste by-products. Therefore, a circular indirect carbonation method, which incorporates an electrochemical process for chemicals regeneration, has been proposed as a more sustainable approach to indirect carbonation. However, the concept has only so-far been discussed in the context of using waste concrete in the cement and concrete industry. There is a need to explore the applicability of this method in more industries. This is the first study to investigate the indirect carbonation method using coal fly ash and electrodialysis. The process is composed of four main steps: leaching, CO_2 capture, $CaCO_3$ precipitation and solution regeneration by bipolar membrane electrodialysis (BPED). The effects of the HNO_3 concentration, L/S ratio and N/C ratio (molar ratio of nitric acid to calcium in fly ash) on fly ash leaching were investigated and the N/C ratio was determined to be the key factor influencing the leaching efficiency of the Ca and impurities. By varying the N/C ratio through adjusting the HNO_3 concentration and the L/S ratio, the mass fraction of Ca in solution changed because of the changing concentration of dissolved impurities such as Si and Al. The leaching behavior of impurities was mainly related with the colloidal precipitation reaction. After the leaching step, 97.3% of the Ca in solution had successfully reacted with the Na_2CO_3 solution (produced through reaction of NaOH solution with absorbed CO_2) to form precipitated $CaCO_3$. The remaining salt solution was then treated by BPED. The effects of the electric potential and current density on the BPED regeneration process of the acid (HNO_3) and alkaline (NaOH) solutions, was investigated. The overall power consumption was used to evaluate the method's performance in terms of the cost and total CO_2 balance. Because this is a preliminary study, further research is needed to improve the process through additional optimization of the experimental parameters discussed. With that said, indirect carbonation of coal fly ash with BPED shows potential as a promising CCU method with considering various scenarios of using different energy supplies including renewable energy.

In conclusion, this study investigated methods of CCU via mineral carbonation of alkaline wastes, without the need for CO_2 purification and pressurization. Our results show that direct aqueous carbonation under low-energy input using alkali-activated wastes such as concrete fines, is a potentially promising method. Concrete fines generated from aggregate recycling proved to be a suitable material for developing CCU techniques without CO_2 purification and pressurization. Indirect carbonation of relatively inert alkaline wastes, i.e., coal fly ash, with electrodialysis chemicals regeneration, was also investigated as a potential CCU technique with discussing several parameters and various scenarios which proves the potential of CO_2 reductions is great. Overall, our study adds to the evidence that mineral carbonation is a promising CCU method.

（別紙）

論文審査結果の要旨及びその担当者

論文提出者氏名	何 星融（Hsing-Jung HO）
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論文審査担当者	主査　准教授　飯塚 淳 教 授　柴田 悦郎　　教 授　井上 千弘 教 授　松八重 一代

論文審査結果の要旨

本論文は、二酸化炭素の高純度化及び圧縮を必要とせずに、塩基性廃棄物の炭酸塩鉱物化によって二酸化炭素の有効利用を行う技術の開発に関するものである。

第一章では、地球温暖化対策技術及び廃棄物処理の問題に関する研究の背景を示すとともに、炭酸塩鉱物化技術に関する概説を行い、本研究の目的を述べている。

第二章では、各種排ガス中の二酸化炭素の濃度と圧力についてまとめるとともに、各種の二酸化炭素の有効利用技術が要求する二酸化炭素の純度や圧力とのギャップについて言及している。また、炭酸塩鉱物化技術は排ガス中の二酸化炭素を直接利用可能な技術であることを述べ、本研究の必要性と目的を更に明確化している。

第三章では、コンクリート廃棄物を対象とした直接炭酸化技術について、固液比と二酸化炭素の濃度が二酸化炭素の固定速度に及ぼす影響について検討するとともに、炭酸化反応生成物の粒度分布変化や溶出性について確認を行っている。また、二酸化炭素の固定効率はその他の廃棄物を対象とした既存の報告よりも大きく、コンクリート廃棄物が有望な対象であることを示している。

第四章では、コンクリート廃棄物よりもカルシウム含有率が低く、反応性の小さな石炭飛灰を対象とした直接炭酸化技術に関して各種条件下での検討を行っている。検討されたカルシウム含有率の低い石炭飛灰の場合には、直接炭酸化による二酸化炭素固定効率は抑制的であることが示されている。

第五章では、バイポーラ膜電気透析法による酸と塩基の再生を利用した石炭飛灰の間接炭酸塩化技術に関する検討についてまとめられている。強酸を用いた石炭飛灰からのカルシウムの抽出、抽出液と炭酸塩溶液との混合による炭酸カルシウムの析出、電気透析による塩溶液の再生に関する実験的検討の結果が示されている。石炭飛灰を利用して二酸化炭素を炭酸カルシウムへ化学的に転換することが可能であること、発電コストと二酸化炭素排出原単位の低い再生可能エネルギーを利用することで二酸化炭素の有効利用を効率的に行える可能性があることが示されている。

第六章では、本研究結果の総括と今後検討されるべき課題を示している。

以上のように本論文は、今後、更に重要となる二酸化炭素の有効利用技術の開発に関して基礎的な検討を詳細に行なっており、価値は十分に高いと評価できる。

よって、本論文は博士（環境科学）の学位論文として合格と認める。