Chemical Engineering Journal 352 (2018) 151–162

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Integrated absorption–mineralisation for energy-efficient CO_2 sequestration: Reaction mechanism and feasibility of using fly ash as a feedstock

Long Ji[a,b,c], Hai Yu[b,*], Bing Yu[b], Kaiqi Jiang[b], Mihaela Grigore[d], Xiaolong Wang[e], Shuaifei Zhao[a], Kangkang Li[b,*]

[a] Department of Environmental Sciences, Macquarie University, Sydney, NSW 2109, Australia
[b] CSIRO Energy, Newcastle, NSW 2304, Australia
[c] School of Chemical & Environmental Engineering, China University of Mining & Technology (Beijing), Beijing 100083, China
[d] CSIRO Energy, North Ryde, NSW 2113, Australia
[e] Huaneng Clean Energy Research Institute, Beijing 102209, China

HIGHLIGHTS

- The application of fly ash in integrated CO_2 absorption and mineralisation for energy efficient CO_2 sequestration.
- Low energy penalty and cost.
- Detailed investigation of amine regeneration by mineralisation.

ARTICLE INFO

Keywords:
CO_2 capture
Chemical regeneration
MEA
Multicycle
Fly ash

ABSTRACT

The most critical challenge for the large-scale implementation of amine-based carbon dioxide (CO_2) capture is the high energy consumption of absorbent thermal regeneration. To reduce the energy requirement, absorbent thermal regeneration can be replaced by a chemical method that integrates amine scrubbing, chemical regeneration and CO_2 mineralisation in one process. However, the mechanisms of the process and the application of industrial waste as feedstocks have not been fully investigated. In the present work, we studied the integrated CO_2 absorption–mineralisation process using the benchmark solvent monoethanolamine (MEA) as an amine absorbent and fly ash as a chemical regeneration agent. We investigated the mechanism involved in the mineralisation in detail and studied the performance of MEA in regeneration by mineralisation of calcium oxide (CaO) at various CO_2-loadings. The performance stability of MEA was verified in multicycle CO_2 absorption–-mineralisation experiments. We also investigated the technical feasibility of using fly ash as a feedstock for absorbent regeneration. Our results show that MEA can be regenerated after a carbonation reaction with both calcium oxide and fly ash at 40 °C, and that the CO_2 absorbed by MEA is precipitated as calcium carbonate. Compared with traditional thermal regeneration-based CO_2 capture, the integrated CO_2 absorption–mineralisation process displays a similar cyclic CO_2-loading (0.21 mol/mol) but has great advantages in energy reduction and capital cost savings due to the smaller energy requirement of amine regeneration and the limitation of CO_2 compression and pipeline transport. This technology has great potential for industrial application, particularly with CaO-containing wastes such as fly ash and carbide slag.

1. Introduction

Carbon dioxide (CO_2) emissions resulting from human activity are widely accepted as the major greenhouse gas contributing to global warming [1]. Despite fossil-fuelled power plants being the greatest contributor (~37%) of global CO_2 emissions, the use of fossil fuels will continue to power the world's economic growth in the foreseeable future [2]. Post-combustion CO_2 capture (PCC) technology is a promising strategy to directly reduce CO_2 emissions from coal and gas-fired power plants and mitigate global climate change in the short to intermediate term [1]. A variety of PCC technologies have been developed, including amine scrubbing [3], membrane separation [4–8], solid adsorption [9] and mineralisation [10–13]. Of these, amine scrubbing, used for decades in the gas processing industry to absorb CO_2, is the

---

* Corresponding authors.
E-mail addresses: hai.yu@csiro.au (H. Yu), kangkang.li@csiro.au (K. Li).

https://doi.org/10.1016/j.cej.2018.07.014
Received 21 March 2018; Received in revised form 22 June 2018; Accepted 1 July 2018
Available online 02 July 2018
1385-8947/

most mature technology available for large-scale CO_2 capture. Monoethanolamine (MEA) is commonly considered as a benchmark amine absorbent for CO_2 capture, due to its commercial availability, relatively low cost, fast absorption rate and extensive experience in industrial applications [14,15]. However, its large energy penalty and high capital cost make it economically unviable. For instance, integrating the state-of-the-art MEA capture process into a coal-fired power plant would reduce power generation efficiency by 25–40% and raise the cost of electricity by 70–100% [16].

Extensive research has been conducted to reduce the energy consumption of solvent regeneration by improving solvent performance and implementing process improvements. For instance, amine regeneration duty consists of three components: the heat of CO_2 desorption, sensible heat and latent heat. The heat of CO_2 desorption can be reduced by using an advanced absorbent formulation [2,17]. A widely developed absorbent formula combines primary or secondary amines that have fast absorption rates with cyclic, tertiary or sterically hindered amines that have high CO_2 absorption capacity and low heat of CO_2 desorption [18,19]. Sensible heat and latent heat can be reduced by process improvements, such as absorber inter-cooling, rich-split and stripper inter-heating [16,20,21]. Process modifications can reduce the overall energy consumption of the MEA process by 8–20% compared to the conventional configuration [16]. Although the energy consumption of PCC has been largely reduced by advanced absorbent formulations and process configuration modifications, the energy consumption from thermal regeneration, which accounts for greater than 50% of total PCC energy consumption [16], is still too high for large-scale application. In addition, amine volatilisation and degradation are still environmental concerns, and equipment corrodes as a result of the high regeneration temperature. CO_2 transportation and subsequent geological storage also require further energy and capital costs. To deal with these problems, an alternative CO_2 capture technology is required to reduce the energy consumption of traditional thermal regeneration. CO_2 mineralisation is an attractive technology that provides leakage-free CO_2 sequestration and does not require post-storage monitoring [13]. The basic idea of CO_2 mineral carbonation is to mimic the process of natural rock weathering, where carbonic acid from the dissolution of CO_2 in rainwater is neutralised with alkaline metal minerals to form stable carbonate minerals [11]. The carbonation reactions can occur at moderate temperatures and release significant amounts of heat. Natural silicates (serpentine, olivine and wollastonite) can be used as feedstocks for CO_2 mineralisation, as can alkaline industrial wastes such as fly ash, carbide slag and steel slag [22–30]. These raw materials have low costs, high reactivity, and are readily available near CO_2 emission sources without further pre-treatment. However, CO_2 mineralisation is confronted by several challenges, the most critical being slow reaction kinetics.

Inspired by the fast CO_2 absorption of aqueous amines and low energy consumption of CO_2 mineralisation, one promising scenario makes use of the dual benefits of the two processes to achieve energy-efficient CO_2 sequestration. Fig. 1 shows the concept of the integrated CO_2 absorption–mineralisation (IAM) process. CO_2 is first captured by an amine absolvent in a CO_2 absorber, resulting in a CO_2-rich solution. The solution is then transferred to a carbonation reactor for amine regeneration and CO_2 sequestration by alkaline oxide or alkaline oxide-rich industrial wastes. The regenerated solvent is sent back to the top of the absorber for continuous CO_2 absorption. In this cyclic process, CO_2 is sequestrated in the form of calcium carbonate ($CaCO_3$), while the amine is chemically regenerated through pH swing, instead of the temperature swing used in the conventional amine scrubbing process. As a new developed process, the technical feasibility and the reaction mechanism of IAM should be investigated. The mechanism of CO_2 absorption by MEA solution was well studied and can be simply described by the reaction: $2MEA + H_2O + CO_2(aq) \leftrightarrow MEAH^+ + MEACOO^-$, while the thermal regeneration was the backward reaction. However, the mechanisms of MEA regeneration by mineralisation is unclear, which involves the reactions between CaO and the species of CO_2-loaded MEA solutions including MEAH+, $MEACOO^-$, $HCO_3{}^-$, and $CO_3{}^{2-}$. Arti et al. [31] investigated the technical feasibility of amine regeneration by introducing calcium chloride ($CaCl_2$) into CO_2-loaded amine solutions, including MEA, diethanolamine (DEA), N-methyldiethanolamine (MDEA) and 2-amino-2-methy-1-propanol (AMP). The results indicated that the absorbed CO_2 in amine solutions was converted to solid $CaCO_3$ without additional energy input, but the amine absorbents were not regenerated after carbonation reaction, which makes the process non-recyclable and chemical consuming. Also, the reaction pathways between $CaCl_2$ and CO_2-loaded amines were not investigated in their study. Kang et al. [32] improved the process by introducing calcium oxide (CaO) instead of $CaCl_2$ into CO_2-loaded AMP solutions, in which CO_2 was released from AMP solutions to form $CaCO_3$ precipitate and AMP was recovered in the carbonation reaction without thermal energy consumption. The reaction pathways in the carbonation of CaO and CO_2-loaded AMP solution were well investigated in their study, and the reaction mechanism was directly evidenced by Carbon-13 nuclear magnetic resonance (^{13}C NMR) results. However, as a sterically hindered amine, the species of CO_2-loaded AMP solution were very different from other primary and secondary amines, which were much more complex. Thus, the mechanisms involved in the IAM, especially the reaction pathways between CO_2–amine mixtures and CaO, were not fully understood. The key performance of the whole IAM process — including amine regeneration efficiency, CO_2 cyclic loading and performance stability using industrial waste — has not been reported. Furthermore, the technical and economic feasibility of the IAM process using industrial wastes as feedstocks has not yet been investigated.

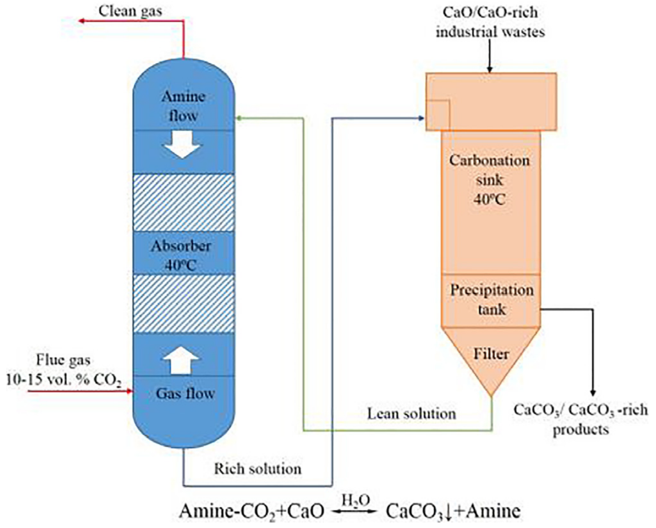

Fig. 1. Concept of the integrated CO_2 absorption–mineralisation process.

In the present study, the benchmark MEA absorbent was selected to investigate the technical performance and the reaction mechanisms of the IAM process. The CO_2 mineralisation feedstock material chosen were industrial wastes that contain alkaline oxide, such as fly ash, with the purpose of simultaneous disposal of CO_2 and wastes. Considering the highly heterogeneous nature and diverse components of the wastes, we first employed the reaction-active chemical CaO to gain insights into the carbonation mechanisms and fundamental reaction pathways. Since CaO provides two types of ions — calcium ions (Ca^{2+}) and hydroxide ions (OH^-) — into the MEA–CO_2–H_2O system, they have different action mechanisms in the reactions with the species in MEA solution. This makes it very difficult to monitor the behaviours of both ions at the same time. We also added sodium hydroxide (NaOH) and $CaCl_2$ separately into the CO_2-loaded MEA solution to clearly investigate the reaction mechanisms of Ca^{2+} and OH^- separately. The performance of MEA in the IAM process, including cyclic CO_2-loading and regeneration