Surface Properties of Cement Kiln Dust with Water Treatment for Selective Extraction of Calcium and Potassium

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ABSTRACT: Water and hydrochloric acid were employed as solvents to extract K and Ca from K- and Ca-rich cement kiln dust (CKD). It has been shown that hydrochloric acid effectively extracts Ca and K from CKD with efficiencies of more than 85 and 99%, respectively. On the other hand, water, as a solvent, selectively extracts K and Cl with an efficiency of 99%. The selectivity of Ca extracted using hydrochloric acid from treated CKD increased from 37 to 87%. Scanning electron microscopy and energy-dispersive X-ray spectroscopy revealed that K and Cl were dominant on the surface of fresh CKD. After extraction with water, the portion of Ca increased more than twice, and Ca species became dominant. Thus, extraction of CKD with water is capable of selectively removing KCl, leaving Ca on the surface; hence, treated Ca-rich CKD can serve as a suitable raw material for mineral carbonation.

1. INTRODUCTION

Cement is a key material for the construction industry, with the annual production of cement in 2016 estimated to be at 4174 million tons.1 The corrosive and harmful cement kiln dust (CKD) generated as the major byproduct (15−20% of the cement amount) of cement production is generally buried or stockpiled, which causes environmental problems.2,3 Hence, CKD management and reduction technologies are highly sought after because cement production is expected to steadily increase.4

The cement industry is a leading CO₂ emission source, accounting for 8% of anthropogenic emissions.5,6 Since CO₂ is a major greenhouse gas contributing to abnormal weather and global warming, much effort has been globally directed at the development of CO₂ reduction technologies, such as mineral carbonation. This technology relies on the reaction of CO₂ with alkaline materials to generate thermodynamically stable carbonates.7−9 In addition, industrial byproducts that contain alkaline material such as CKD can be used as raw materials and find applications in the cement industry.10,11

Mineral carbonation can be divided into direct and indirect carbonation. The former technique involves a single-step carbonation process in which a solid-state alkaline earth metal compound reacts with CO₂ in a gaseous or aqeous phase, which has the advantages of simplicity and low consumption of chemicals. However, this method is more appropriate for CO₂ storage since the final product has a low purity and slow reaction rate and is formed at high temperatures and pressures.12,13 Conversely, indirect carbonation is a two-step process with the stages of alkaline material extraction and CO₂ injection-induced carbonation. The use of solvents and additives as well as relatively large sites results in high carbonation efficiency and the production of highly pure precipitated calcium carbonate (PCC), thus allowing for CO₂ storage and use.13 However, to increase the economic feasibility of indirect carbonation and promote its commercialization, one should increase the value of the corresponding products (e.g., PCC).

Table 1 summarizes the compositions of industrial byproducts used in recent studies on mineral carbonation technologies, revealing that these byproducts contain cations (Al, Si, Fe, K, etc.) as well as alkaline earth metals, such as Ca and Mg. Ca was more than 20% of the contained byproducts for mineral carbonation. Most of the above constituents originate from raw materials but can also be affected by the choice of fuel, e.g., the use of alternative fuels in a cement kiln can provide byproducts rich in KCl.15 The presence of elements other than Ca or Mg may reduce PCC purity and make CKD unsuitable for use as a raw material for cement production. Therefore, in order for industrial byproducts to be used as resources, a technique for the selective extraction of alkaline earth metals from these byproducts has to be developed.

Sonication-assisted, temperature-swing, and pH-swing extraction techniques were reported for the (selective) removal of impurities from industrial byproducts. Said et al.19 used...
sonication to remove Si, forming a porous layer on the surface of steel slag, and achieved an extraction efficiency exceeding that realized using a mechanical mixer. De Crom et al. precipitated Si by lowering the temperature of the leachate extracted from slag and removed Mg and Al by adjusting pH to 8.4. Hu et al. precipitated 99% of Al after cation extraction from blast-furnace slag by controlling pH at 5.5 by injecting NH₃, and Azdarpour et al. precipitated and separated impurities in the extract by using NH₄OH to adjust pH. Among the impurity-separation methods, those involving sonication and cooling require additional equipment. On the other hand, the pH-swing technique employs chemicals for pH adjustment and has drawn much attention because the resulting high pH aids CO₂ absorption and carbonate production in the carbonation stage. However, since this method exploits the differences in ion solubilities, its adequacy for impurity removal should be reviewed based on the composition of industrial byproducts.

In this study, we suggest a sequence for selective extraction of Ca and K from KCl-rich CKD using hydrochloric acid and water as extraction solvents and NaOH as a pH control agent. Extract compositions are characterized by inductively coupled plasma (ICP) analysis to probe the suitability of the pH-swing method, and the effects of extraction with water on CKD surface properties are investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analyses to reveal that this extraction results in changes in the dominant species. In addition, the effect of solvent concentration was determined for high extraction efficiency and selectivity of Ca. Finally, we conclude that the extracted Ca from treated CKD can be used as a raw material for mineral carbonation.

2. RESULTS AND DISCUSSION

Given the results of previous studies on Ca extraction from industrial byproducts, we selected hydrochloric acid as an extraction solvent because it has been widely used for extracting Ca and Mg, and the obtained extract was pH adjusted with NaOH to separate Ca from impurities (including those containing K). Whereas Ca, K, Si, and Mg were extracted in step 1, Si and Mg were mostly removed in step 2. Moreover, Ca and K were partially removed in the latter step because of their solubility decrease with increasing pH. In step 3, most of the Ca was removed, but K was still present in the solution because KCl is more soluble than CaO(Figure 1). However, some K precipitated as soon as Ca was removed. Ca precipitation selectivity was found to be 85.7% based on the concentrations of Ca and K in the filtrate of step 3. Thus, extraction with hydrochloric acid followed by pH adjustment with NaOH was inadequate for the separation of Ca from K.

In view of the exceedingly high solubility of K, as concluded from the above results, we used water as an extraction solvent. ICP analysis of the corresponding extract (Figure 2) revealed the presence of K (26,237.5 mg/L) and Ca (1271.5 mg/L) as well as that of Mg (0.1896 mg/L) and Si (0.2884 mg/L), which are found in most industrial byproducts. The levels of Al and Fe were below the detection limits and could not be measured. Compared to the HCl extract, the water extract contained 92% less Ca and 5.5% less K. Thus, K could be selectively extracted with water, and the corresponding extraction selectivity was calculated as 95.4%.

An aliquot of the water extract was evaporated to dryness, and we subjected the resulting solid to XRD analysis (Figure 3). The major peak of the acquired pattern matched that of KCl, but no CaO peak was observed, which confirmed the high selectivity of K extraction with water. The conditions of water extraction and the recovery of KCl could be further optimized, which, however,
is beyond the scope of this paper. Notably, extraction with water does not require the use of additional reagents (e.g., NaOH) and facilitates the use of KCl and extracted CKD as raw materials.

Subsequently, we attempted to extract Ca from water-extracted CKD by a 10 min treatment with hydrochloric acid (1.2−2.0 M) (Figure 4). Compared to the case when 2 M hydrochloric acid was used in step 1, the amount of extracted K was reduced by 94%, and Ca extraction selectivity increased from 37 to 87%. Thus, the two-step water-hydrochloric acid extraction was shown to selectively separate K from Ca.

Figure 5 shows the results of SEM analysis conducted to identify changes in CKD surface characteristics after extraction with water. Pristine CKD contained almost spherical particles with sizes of 100−700 nm, whereas water-treated CKD featured pores on its surface and in the bulk, which we assumed were formed via the dissolution of KCl. This finding confirmed that KCl was evenly distributed throughout CKD, not present only on the surface or within the bulk.

EDX mapping showed that in the case of pristine CKD, Ca was mostly found in large particles, whereas K was distributed more evenly, i.e., was dominant on the CKD surface (Figure 6). However, after extraction with water, the content of K decreased from 13.52 to 2.08 wt %, and that of Ca increased from 11.84 to 26.27% (Table 2).

3. CONCLUSIONS
In this study, K and Ca were selectively extracted from CKD, and changes of surface properties were characterized. It was found that the pH swing is not suitable for efficient separation of Ca and K from CKD extract. Water was employed to separate K because of high solubility of K in an aqueous environment. When water was used as a solvent, K was selectively extracted with an efficiency of 99% and a selectivity of 95%. Ca could be selectively extracted from the treated CKD with a selectivity of 87% using hydrochloric acid.
Aqueous extraction of K generated pores on the surface of CKD. This was created by the removal of 84% of the KCl salt, while the Ca content increased to 26.27% simultaneously, i.e., Ca became the dominant element. It is believed that the separation method showed in this study was well suited for the K-rich CKD. In addition, the further optimization of Ca/K separation and KCl recovery processes will be able to provide more environmental friendly and cost-effective pathway for conversion of CKD into more resources otherwise waste material.

4. EXPERIMENTAL SECTION

4.1. Physicochemical Properties of CKD. The ionic composition of CKD was probed by X-ray fluorescence (XRF; ZSX Primus, Rigaku) and ICP (Waters 600E/431/125, Waters) analyses, and phase composition was probed by X-ray diffraction (XRD; X’Pert PRO MRD, PANalytical) analysis in the 2θ range of 20−80° at a scan rate of 6°/min. In addition to the components listed in Table 3, XRF confirms various cations such as K, Ca, Si, Fe, and Al from untreated CKD. The ions with relatively high proportion (approximately over 1 wt %) are summarized in Table 3. ICP analysis (Table 4) identified the key components of CKD as K, Ca, Mg, Al, Fe, and Si, and XRD analysis (Figure 7) identified the major phases as KCl and CaO. Surface changes induced by pretreatment with H₂O were probed by SEM/EDX mapping (S-4800, Hitachi). The corresponding sample was prepared by mixing CKD (10 g) and water (100 mL) for 10 min, filtering, and 24 h oven drying of the residue at 105 °C.

4.2. Cation Extraction and Impurity Separation. Selective extraction of Ca from CKD was carried out as follows. CKD (10 g) and hydrochloric acid (2 M, 100 mL) were placed in a 250 mL Erlenmeyer flask and mixed at room temperature for 10 min using a magnetic stirrer to extract Ca (step 1). Afterward, pH was adjusted to 9.5−9.6 with saturated NaOH solution to precipitate impurities, which are the minerals except Ca (step 2). The solution with precipitants was filtered through a GF/C filter (CAT no. 1822-047, Whatman), leaving high-Ca content solution. Sequentially, the pH of filtrated Ca solution was raised to ≥13 (Step 3) to precipitate Ca. The filtrated impurities obtained from NaOH treatment and Ca extracted by pH swing were characterized by ICP. Additionally, water treatment was carried out for CKD prior to hydrochloric acid treatment (step...
1) in order to remove K to enhance the Ca selectivity. Extraction efficiency and selectivity can be calculated as the follows:

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\text{extraction efficiency (\%)} = \frac{C_{\text{ion}} \times V}{m_{\text{kiln dust}} \times X_{\text{ion-kiln dust}}} \times 100
\]

\[
\text{selectivity (\%)} = \frac{C_{\text{ion}}}{C_{\text{total ion}}} \times 100
\]

Where \(X_{\text{ion-kiln dust}}\) is ion mass fraction in the kiln dust, and \(C_{\text{ion}}\) is the concentration of ion obtained by the ICP analysis (g/L) in the filtrated solution after the extraction; \(m_{\text{kiln dust}}\) is kiln dust mass, and \(V\) is volume of the solvent.

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