Chemical Engineering Journal 292 (2016) 255–263

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

An efficient milling-assisted technology for K-feldspar processing, industrial waste treatment and CO_2 mineralization

Wenjie Shangguan [a], Jimin Song [a], Hairong Yue [a,*], Siyang Tang [a], Changjun Liu [a], Chun Li [a], Bin Liang [a,b], Heping Xie [b]

[a] *Multi-phases Mass Transfer and Reaction Engineering Laboratory, College of Chemical Engineering, Sichuan University, Chengdu 610065, China*
[b] *Center of CCUS and CO_2 Mineralization and Utilization, Sichuan University, Chengdu 610065, China*

HIGHLIGHTS

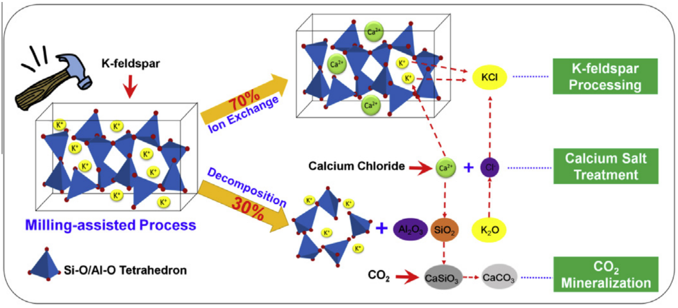
- An efficient milling-assisted technology to use K-feldspar and mineralize CO_2.
- Facilitation the potassium extraction under mild conditions (e.g. 30–40 °C).
- A maximum potassium extraction ratio of ~80% and CO_2 mineralization ratio of ~5%.
- Fragmentation, amorphization and lattice distortion enhance reaction activities.

ARTICLE INFO

Article history:
Received 12 December 2015
Received in revised form 8 February 2016
Accepted 9 February 2016
Available online 13 February 2016

Keywords:
Milling-assisted
Industrial waste treatment
Environmental chemical
CO_2 mineralization
K-feldspar
Mineral processing

GRAPHICAL ABSTRACT



ABSTRACT

This paper describes an environmentally friendly and efficient milling-assisted technology to produce soluble potassium from natural K-feldspar with the additive of calcium salts, and capture CO_2 via mineralization. The milling-assisted process could facilitate the extraction of potassium from K-feldspar under mild conditions (e.g. 30–40 °C), and mineralize CO_2 with reacted calcic slag. The milling-assisted and mineralization conditions (e.g. milling time and material ratio) were systematically investigated, reaching a maximum potassium extraction ratio of ~80% and a CO_2 mineralization ratio of ~5%. Characterizations indicated that the fragmentation, amorphization, and lattice distortion of the mineral particles during milling-assisted process are responsible for the enhanced K-feldspar decomposition reactions and ion-exchange reaction with calcium salt. Reaction principles of K-extraction and CO_2 mineralization are discussed, and a possible mechanism of milling-assisted process was proposed.

1. Introduction

The issues of sustainably utilizing natural mineral resources, dealing with industrial waste with low energy consumption and waste emissions offer challenging opportunities for sustainable development in energy and the environment. Soluble potassium resource reserves contain less than 1% of the global potassium, and are scarce in many parts of the world. Natural K-feldspar ($KAlSi_3O_8$) is an abundant and insoluble potash ore, with reserve in the range of billions of tons. However, utilization of potassium from K-feldspar is difficult because of its stable tetrahedron structure. Many methods have been developed to improve extraction of potassium from K-feldspar, such as hydrofluoric acid digestion, ion exchange, and high-temperature thermal activation (e.g. >1500 °C) [1–3], which are not economically practicable and environmentally friendly.

---

* Corresponding author.
E-mail address: hryue@scu.edu.cn (H. Yue).

http://dx.doi.org/10.1016/j.cej.2016.02.031

In addition, technologies of CO_2 capture and storage (CCS) have been intensively investigated for reduction the industrial CO_2 emissions in the past couple of decades [4–6]. While plenty of research has focused on CO_2 storage and its conversion to fuels and chemicals, mineralization is a promising alternative as it is thermodynamically favorable [7,8]. CO_2 mineralization via reaction with alkaline earth oxides form industrial slag to form carbonates is an effective method to permanently dispose a large amount of CO_2 [9,10].

Our previous work described a coupling method that could simultaneously process industrial waste (e.g. $CaSO_4$ from wet-process phosphoric acid process or $CaCl_2$ from the Solvay process), extract soluble potassium from natural K-feldspar and mineralize CO_2 [1,11,12]. Wang et al. reported [11] the use of natural K-feldspar and $CaSO_4$ to produce soluble potassium and mineralize CO_2. K-feldspar is reacted with $CaSO_4$ through an ion exchange process at 1200 °C. The highest K-extraction and CO_2 mineralization ratios reached ~87% and ~7.7%, respectively. Ye et al. [12] used $CaCl_2$ to reduce the activation temperature to 908.3 °C and increase the potassium extraction and CO_2 mineralization ratios to ~90% and ~12%, respectively. These results indicate a promising path to dispose atmospheric CO_2 and extract soluble potassium. However, the high-temperature activation in the solid–solid reaction produces HCl or SO_2 (from the decomposition of $CaCl_2$ and $CaSO_4$) in the exhaust gas, which hinders its industrial application.

Milling-assisted technology via applying mechanical forces to solid reactants is known to increase the rates and lower the temperature in many reactions [13,14]. Milling has been reported to significantly increase the chemical reactivity of solid–solid minerals via fragmentation of particles and change of crystal structures (amorphism and lattice distortion) [15]. Li et al. have found that increasing the lattice strain in the *c* axis direction of the ilmenite crystal contributes substantially more to ilmenite leaching than increasing the lattice strain in the *a* and *b* directions [16]. Mechanical treatments considerably affect the physicochemical properties of solid minerals, such as microstructure and dissolution rate [17]. In mineral processing and material synthesis, mechanical force has caused structural changes that could strengthen the reactivity [18,19]. These physicochemical changes induced by milling-assisted process in the structure may be favorable to the potassium extraction and CO_2 mineralization reactions.

Motivated by this idea, milling-assisted technology was introduced to intensify the solid–solid reaction of natural K-feldspar with calcium salts ($CaCl_2$, $CaSO_4$, or CaO) for production of soluble potassium and mineralization of CO_2. The reaction conditions of milling-assisted process, extraction, and mineralization were systematically investigated to obtain optimized operating parameters. Raw mineral and products after milling were systematically characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and particle size analysis to explore the role of milling assistant on the reactions. The mechanism of reaction intensification was proposed on the base of the experimental results.

2. Materials and methods

2.1. Materials

The K-feldspar ore used in the experiments was mined in Baoxin, China. The ore was crushed and milled to a particle size of 200–300 μm. The composition of raw K-feldspar ore was measured with Energy Dispersive Spectroscopy (EDS, Oxford IE 250) with the result listed in Table 1. Chemicals used in the experiments were analytical reagents and listed in Table S1 in the Support Information.

Table 1
Elemental composition of the K-feldspar ore.

Element (as oxide)	K_2O	Al_2O_3	SiO_2	CaO	Na_2O	Fe_2O_3
Mass percentage (%)	12.9	15.94	66.88	0.95	0.08	2.56

2.2. Methods

2.2.1. Milling-assisted and mineralization procedures

K-extraction ratio and CO_2 mineralization ratio were used to evaluate the extent of K-extraction and mineralization reactions. Milling time, additive agents ($CaCl_2$, $CaSO_4$, or CaO), mass ratio of mill balls to K-feldspar, and the mass ratio of K-feldspar ore to additive were taken into account to describe K-extraction process. The experimental conditions of mineralization reaction were at 150 °C and 4 MPa CO_2 pressure for 1 h.

The prepared K-feldspar ore powder and calcium salt were mixed proportionally (K-feldspar/$CaCl_2$ weight ratio from 0.5 to 16) and mechanically activated using a planetary ball mill (QM-QX2, Nanjing University Instrument Plant, China) with four symmetrical pots of 500 mL. The rotation speed of the pot is twice that of the disk. Approximately 10 g raw ore powder and one of the calcium salts were added to the pots and mixed with 100 mL deionized water and Φ5 grinding balls (steel or zirconia). The planetary ball mill was operated at 580 rpm for 2–20 h with an operation temperature of 30–40 °C. After milling, the solid–liquid mixture was filtrated, and the filtrate was collected to obtain K-rich solution while the filtration cake (i.e. millied slag) was dried and used to mineralize CO_2.

The CO_2 mineralization described here is a three-phase reaction. About 3 g of the dried milled slag and 60 mL deionized water were added to a 250 mL cylindrical titanium vessel placed in an autoclave for ease of product collection. The mineralization reaction was tested at 150 °C (an optimal temperature chosen in our precious work) [11]. CO_2 was introduced into the autoclave until the pressure reached 4 MPa. The magnetic stirrer was turned on and adjusted to a rate of 300 rpm for 1 h. The slurry after mineralization was quickly cooled to room temperature and filtered to obtain the mineralization slag.

2.2.2. Analysis the K-content of the ore

Accurate K-content of the ore was measured by chemical analysis, after first digesting the raw ore in a mixture of acids to completely extract K^+. About 0.2 g of ore sample was soaked in 10 mL of hydrofluoric acid (40 wt.%), 1 mL of sulfuric acid (50 wt.%), and 5 mL of nitric acid (50 wt.%) in a platinum crucible. The suspension was kept boiling till no more white smoke emerged from the crucible. Then slag in the crucible was dissolved in 2 mL nitric acid and 10 mL distilled water (refer to ICS 73.080). Then the K-content was measured by potassium tetraphenylborate precipitation. This analysis method (ISO 5317:1983 and ISO 5318:1983) is quite accurate, with an uncertainty of 0.12% within 10% and an uncertainty of 0.30% in the 10–20% range. The K-content in the ore (in terms of K_2O%) is linearly related to the mass of precipitation

$$K_2O\%(\eta) = \frac{M_1}{M_0} \times 0.1314 \times 100\%$$

where M_1 represents the mass of potassium tetraphenylborate precipitation and M_0 the mass of K-feldspar ore.