

Simultaneous mineralization of CO₂ and recovery of soluble potassium using earth-abundant potassium feldspar

XIE HePing^{1,2*}, WANG YuFei^{1,2}, JU Yang³, LIANG Bin^{1,4}, ZHU JiaHua^{1,4}, ZHANG Ru¹, XIE LingZhi¹, LIU Tao^{1,2}, ZHOU XiangGe⁵, ZENG HongMei⁵, LI Chun⁴ & LU HouFang⁴

¹ Center of CCUS and CO₂ Mineralization and Utilization, Sichuan University, Chengdu 610065, China;

² Key Laboratory of Energy Engineering Safety and Mechanics on Disasters, The Ministry of Education, Sichuan University, Chengdu 610065, China;

³ State Key Laboratory of Coal Resources and Safe Mining, China University of Mining Technology, Beijing 100083, China;

⁴ School of Chemical Engineering, Sichuan University, Chengdu 610065, China;

⁵ School of Chemistry, Sichuan University, Chengdu 610065, China

Received July 30, 2012; accepted August 21, 2012; published online September 5, 2012

CO₂ capture and storage (CCS) is an important strategy in combatting anthropogenic climate change. However, commercial application of the CCS technique is currently hampered by its high energy expenditure and costs. To overcome this issue, CO₂ capture and utilization (CCU) is a promising CO₂ disposal method. We, for the first time, developed a promising method to mineralize CO₂ using earth-abundant potassium feldspar in order to effectively reduce CO₂ emissions. Our experiments demonstrate that, after adding calcium chloride hexahydrate as an additive, the K-feldspar can be transformed to Ca-silicates at 800°C, which can easily mineralize CO₂ to form stable calcium carbonate and recover soluble potassium. The conversion of this process reached 84.7%. With further study, the pretreatment temperature can be reduced to 250°C using hydrothermal method by adding the solution of triethanolamine (TEA). The highest conversion can be reached 40.1%. The process of simultaneous mineralization of CO₂ and recovery of soluble potassium can be easily implemented in practice and may provide an economically feasible way to tackle global anthropogenic climate change.

CCU, mineralization, potassium feldspar, potassium salts, CCS

Citation: Xie H P, Wang Y F, Ju Y, et al. Simultaneous mineralization of CO₂ and recovery of soluble potassium using earth-abundant potassium feldspar. *Chin Sci Bull*, 2013, 58: 128–132, doi: 10.1007/s11434-012-5466-7

Carbon dioxide (CO₂), produced from the combustion of fossil minerals, is considered to be one of the main factors responsible for global climate change. CO₂ emission reduction has become a significant issue of common concern worldwide. CO₂ capture and storage (CCS) is currently considered one of the most effective techniques for reducing emissions, maintaining the current atmospheric CO₂ concentration, and alleviating greenhouse gas effects [1,2]. While a number of countries or regions have carried out field demonstration projects related to CO₂ geological storage to test CCS, wide application of the CCS is mainly hampered by its high costs. To alleviate the associated costs, appropriate strategy should be focused on carbon capture

and utilization (CCU) [3–6]. By CCU, we mean CO₂ being captured and used as raw material to produce high-value products (or related by-products) thereby reducing CO₂ emissions. In industry, one of method of utilization of CO₂ is transforming CO₂ into organic chemicals or polymers. Another method was regenerate methanol and hydrocarbon from CO₂ and H₂O which can be used as fuel. These two methods confronted the problem of high material cost, high energy consuming and short lifetime of product. Therefore, many people considered that the CCU method can only transforming small amount of CO₂, which has little effect on reducing the emission of CO₂, and the CCU cannot be regarded as the main CO₂ disposal method.

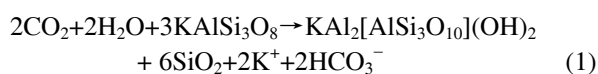
CO₂ mineralization is a relatively new technology in the field of CO₂ geological sequestration [7]. Compared with

*Corresponding author (email: xiehp@scu.edu.cn)

other CCS technologies, it has the advantage of safely storing CO₂ for a very long, if not infinite, time, by converting CO₂ into a solid phase. Through a reaction between rich calcium and magnesium ions in natural alkaline ores [8–18] and alkaline wastes [19–23], CO₂ could be converted into stable solid carbonates, such as magnesium carbonate and calcium carbonate. Forsterite, with a high CO₂ conversion rate, is the main mineralization material. Current research shows that when reacting with CO₂ within a solution of NaCl and NaHCO₃, at a temperature of 185°C and pressure of 15 MPa, forsterite with a particle size of 37 μm can reach a conversion rate of 81% [1,18]. Unfortunately, forsterite (a magnesium silicate) tends to distribute along either present or ancient continental boundaries [1], and thus are not available in all countries with significant CO₂ emissions, such as China. Thus, it is difficult to obtain low-cost forsterite in many countries or regions important for reducing global CO₂ emission. Neither on-site nor off-site mineralization of CO₂ based on forsterite has been implemented. Seeking rich, low-cost alternative raw materials for CO₂ mineralization, and the means to fulfill high reaction efficiency, low reaction requirements, and easy industrialization, will likely be the future direction of CO₂ mineralization.

Feldspar is one of the most stable and abundant minerals in the earth, accounting for about 60% of the total mass of the earth's crust. Taking the average content of potassium within feldspar of 4% into account, within the scope of human use (about 5 km underground), the reserves of K-feldspar (KAlSi₃O₈) is about 95.6 trillion tons. If the K-feldspar were used for mineralization of CO₂ with a conversion rate of 50%, it could theoretically sequester more than 3.82 trillion tons of CO₂. According to a report by the International Energy Agency [24], global carbon dioxide emission in 2010 was expected to reach 30.06 billion tons. Potentially, in theory the earth's natural potassium feldspar can mineralize as much as 127 years of global CO₂ emissions.

Unfortunately, because of the structural stability of potassium feldspar, the feldspar does not easily react with weakly acidic CO₂—the reaction progress is given in eq. (1) [1].



Under natural conditions, the reaction between CO₂ and potassium feldspar usually takes hundreds to thousands of years [1,25]. Even after increasing the reaction temperature and the partial pressure of CO₂, it is still difficult to significantly increase the reaction rate of potassium feldspar with CO₂ [26]. Therefore, meaningful CO₂ mineralization, during the time period of interest for CCS, can barely be achieved by this chemical reaction. So far, there has been neither research nor industrial application of K-feldspar with respect to effective mineralization of CO₂.

Using earth's natural potassium feldspar to mineralize CO₂ with high efficiency and low cost faces at least two challenges: (1) how to destabilize the stable crystal structure

of potassium feldspar to make it react efficiently with CO₂; and (2) how to generate a stable mineralization product in nature, since the soluble carbonate generated through the reaction of natural potassium feldspar and CO₂ is easily decomposed. In this study, we use calcium chloride, a common by-product in alkali industry, which currently has limited practical use, to partially deal with these challenges. Resulting from the interaction between calcium and aluminosilicates, calcium chloride may help undermine the structure of potassium feldspar to form relatively active calcium aluminosilicates that react easily with CO₂ to produce stable solid calcium carbonate.

1 Experiments

1.1 Materials

Feldspar (reddish in color, from Shandong Province, China) was used as a raw material. By crushing and ball-milling the feldspar samples, the feldspar particle sizes reduced to 45 μm. X-ray diffraction (XRD) results indicate that the main mineral composition of feldspar includes microcline (KAlSi₃O₈) and Albite (NaAlSi₃O₈). Energy dispersive X-ray fluorescence (XRF) analysis shows that the silicon content in the ore is 32.7%, the aluminum content 9.3%, potassium content 8.5%, sodium content 2.5%, calcium content 0.17%, and copper content 0.15%. There are also trace amounts of zinc, iron, phosphorus, and chromium. A. R. grade calcium chloride hexahydrate (CaCl₂·6H₂O) and anhydrous calcium chloride (CaCl₂) was used without further purification. The CO₂ was purchased from Dong Feng (China) with the purity of 99.99%.

1.2 CO₂ mineralization procedures

In order to destabilize the structural of K-feldspar, two different pretreatment has been taken to transform K-feldspar to Ca-silicates. In high temperature pretreatment, 2.5 g K-feldspar and 2.5 g calcium chloride hexahydrate were mixed together and heated to 800°C in furnace. After activating 1h at 800°C, the reaction was stopped. The product was putted out and cooled to room temperature, then washed by distilled hot water (80°C) and filtered. The filtrate was diluted to 1 L. The solid was oven-dried at 110°C.

The pretreatment test using low temperature was undertaken in 250 mL autoclave, 2.5 g K-feldspar was added with 75 mL solution, which contain 1.85 mol/L CaCl₂ and 0–1.5 mol/L triethanolamine (TEA). The pretreatment was kept 2 h at 250°C. When the autoclave cooled to room temperature, it was opened, and the suspension was filtered. The filtrate was diluted to 250 mL. The solid was oven-dried at 110°C. As a comparison, another test was done using NaOH instead of TEA. The pH of the solution used in this latter test was about 10.05 and the same as that obtained by adding 1.5 mol/L TEA.

The reaction of mineralization of CO₂ was undertaken in a 250 mL autoclave. After adding the solid from pretreatment and 75 mL distilled water, the autoclave was sealed and heated to the reaction temperature (150°C for high temperature pretreatment and 200°C for low temperature pretreatment). CO₂ was directly added into the solution by gas booster, until the partial pressure of CO₂ goes to 4 MPa. The reaction was going at a specific stirring rate (350 r/min). When the reaction time was elapsed (1 h), the autoclave was cooled to 70°C and depressurized, and opened. The suspension was filtered, and the solid was dried at 110°C.

1.3 Analysis of solid phases

The mineralogical composition was determined by X-ray diffraction (XRD). The amount of sequestered CO₂ in product was analyzed by thermal gravimetric analysis system (TG). Samples (10–20 mg) were heated in aluminum oxide ceramic cups under an oxygen atmosphere at 20°C/min. The amount of CO₂ sequestered as calcium carbonate was defined on the basis of its dry weight ($m_{105^\circ\text{C}}$) and the weight loss between 105 and 1000°C ($\Delta m_{105-1000^\circ\text{C}}$):

$$\text{CO}_2 [\text{wt}\%] = (\Delta m_{105-1000^\circ\text{C}} / m_{105^\circ\text{C}}) \times 100. \quad (2)$$

1.4 Conversion of K-feldspar

The concentration of K⁺ and Al³⁺ in solution was tested by ICP (Inductive Coupled Plasma Emission Spectrometer). The conversion rate of K-feldspar ζ was defined by comprising the total mass of K in solution m_{K^+} with that in the material M_{K} , which can be calculated by

$$\zeta = m_{\text{K}^+} / M_{\text{K}}. \quad (3)$$

2 Results and discussion

2.1 CO₂ mineralization with high temperature pretreatment

Figure 1 shows the XRD result of mineralogical composition of solids after high temperature pretreatment and mineralization of CO₂. The experimental results indicate that calcium chloride hexahydrate was decomposed at a high temperature into anhydrous calcium chloride and calcium oxide. Anhydrous calcium chloride and calcium oxide react with potassium feldspar at high temperatures and generate three different calcium silicate salts—pseudo-wollastonite (Ca₃Si₃O₉), anorthite (CaAl₂Si₂O₈) and mayenite (Ca₁₂Al₁₄O₃₃)—that mineralize CO₂ in the form of stable, solid calcium carbonate. These reactions are

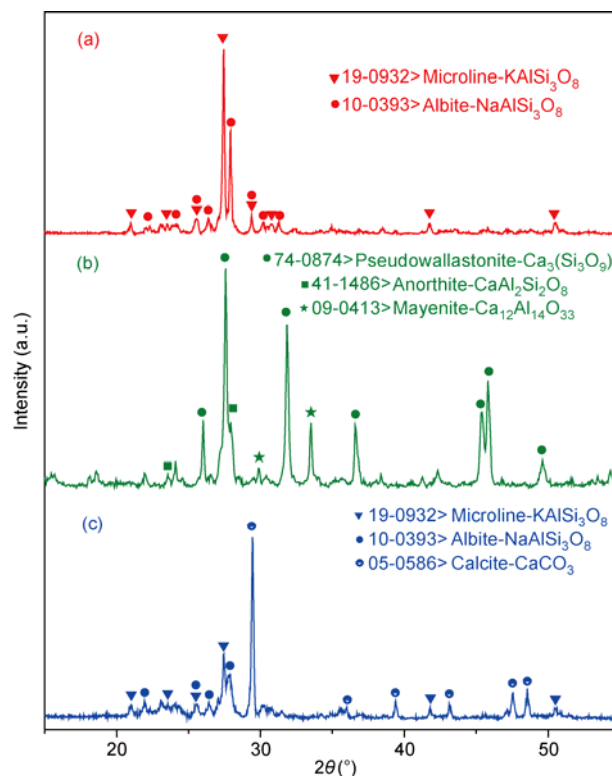
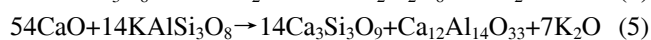


Figure 1 (Color online) XRD results of the reaction (conversion and mineralization) of CO₂ using K-feldspar and calcium chloride hexahydrate at high temperature. (a) Result from natural K-feldspar; (b) result from reaction of K-feldspar and calcium chloride hexahydrate at 800°C; (c) result from the reaction of the conversion production at 800°C and CO₂.

The result of XRD proved the possibility of simultaneous mineralization of CO₂ and recovery of soluble potassium. The conversion of K-feldspar reached 84.7% after reaction. Figure 2 illustrates the thermogravimetric results of the mineralization production. The content of CO₂ reached 13.15% in product.

Although CO₂ mineralization with high temperature pretreatment showed a good results in activating K-feldspar and mineralizing CO₂, the pretreatment temperature of 800°C is not desirable, because it corresponds to high energy consumption and therefore high CO₂ emissions. Obviously, converting natural K-feldspar with a higher conversion

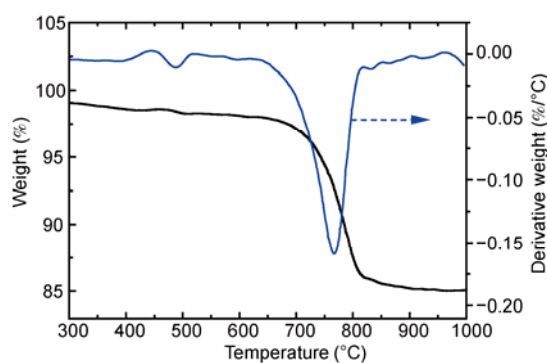


Figure 2 (Color online) Thermogravimetric test results of the conversion product.

rate and lower energy consumption (corresponding to a low required temperature) is the key to developing practically feasible approaches for CO₂ mineralization and cogeneration of soluble potassium salt, using the Earth's natural potassium feldspar.

2.2 CO₂ mineralization with low temperature

Thermodynamic calculations show that, at 400 K (122.85°C), the ΔG , the Gibbs free energy, of reaction (3) is -41.3 kJ/mol [27]. This means that K-feldspar could theoretically convert into anorthite through a reaction with calcium chloride at low temperatures. Previous studies have shown that K-feldspar could react with low-concentrated calcium chloride under hydrothermal conditions with a temperature of 250°C, though with a conversion rate of only 2.1%, this conversion rate is too low for practical applications.

K-feldspar can be dissolved in alkali solution. Casey et al.'s results [29] indicate that the mechanism for alkali-dissolving K-feldspar is as follows: the K-feldspar reacts with OH⁻ and generates Al(OH)₄⁻ in the solution, and then a poor aluminum-rich-silicon precursor polymer (SiO₂ · *n*H₂O) is formed on the surface of the K-feldspar to undermine K-feldspar's stable crystal structure, which finally leads to the dissolution of potassium feldspar. A number of experimental results [30–32] have indicated that Al³⁺ in the solution controls the dissolution rate of K-feldspar.

Therefore, a compound that could chelate the Al³⁺ ion might enhance the conversion of K-feldspar. And this compound should be also stable in relative high temperatures, weakly alkaline, and easy to get. To this end, triethanolamine (TEA) was chosen as a catalyst and calcium chloride as an additive, to convert potassium feldspar and mineralize CO₂ at a relatively low temperature—thereby finding a way to achieve efficient conversion of potassium feldspar to effectively mineralize CO₂ and produce valuable, soluble potassium salt.

Figure 3 illustrates that within the solution with the additive calcium chloride, triethanolamine has a significant promotion effect on the conversion process of potassium feldspar. Without adding TEA, the conversion rate of K-

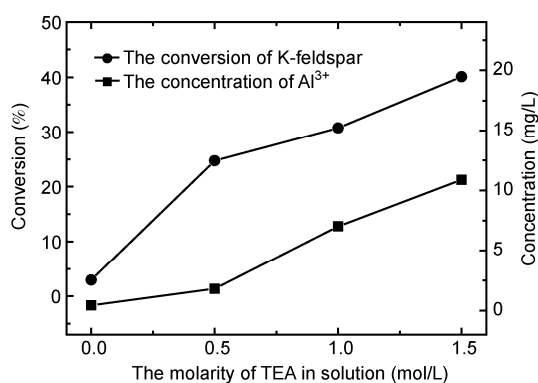


Figure 3 Effect of triethanolamine TEA concentration on potassium feldspar conversion.

feldspar was only 3%. For a triethanolamine concentration of 1.5 mol/L, the potassium-feldspar conversion rate increased to 40.1%, much higher than that in the comparison test (about 5.1%). The XRD test results have shown (Figure 4) that Si-Al-calcium salt, generated by potassium feldspar under hydrothermal conditions at 250°C, more easily reacts with CO₂ to mineralize CO₂ into stable, solid calcium carbonate.

The conversion rate of K-feldspar increases significantly with increasing concentration of aluminum ions in the solution (Figure 3). This is because in an alkaline solution, Al ions on the surface of the potassium feldspar react with OH⁻ to form Al(OH)₄⁻ in the solution. Then, Al(OH)₄⁻ and TEA together result in chelation that enhances the solubility of Al³⁺ within the solution. As a result, more Al ions enter the solution and undermine the stable structure of the potassium feldspar crystals. The additive calcium chloride prompts potassium feldspar's conversion into Si-Al-calcium salt, which more actively reacts with CO₂ and increases the rate of CO₂ mineralization.

3 Conclusions

CO₂ capture and utilization (CCU) based on CO₂ mineralization was a new and promising CO₂ sequestration method. Because of the great reserve of natural K-feldspar in earth, it

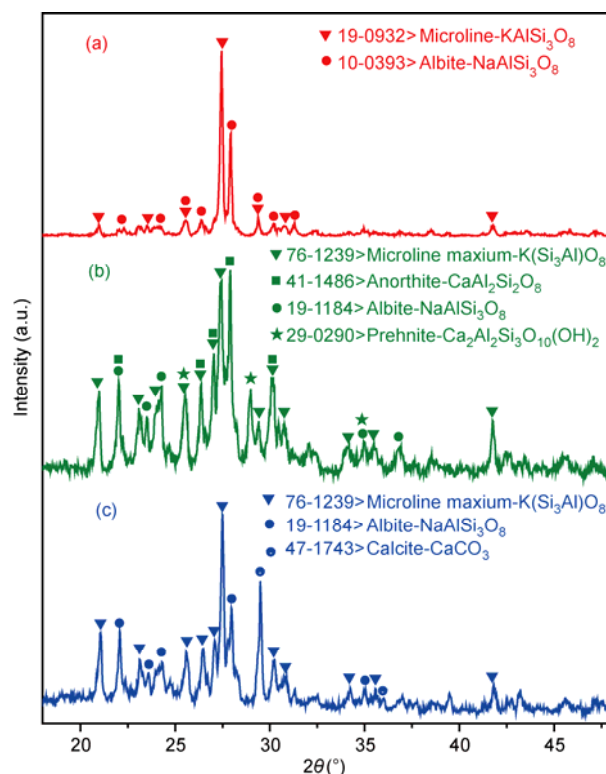


Figure 4 (Color online) XRD results of the mineralization of CO₂ by potassium feldspar at low temperature conversion. (a) Results from natural K-feldspar; (b) result from reaction of K-feldspar and calcium chloride at triethanolamine solution with hydrothermal condition of 250°C; (c) result from reaction of the K-feldspar conversion production and CO₂.

is potential to mineralize plenty of CO₂ and supply valuable soluble potassium salt.

The stable K-feldspar can be activated at 800°C using calcium chloride hexahydrate as additive. After activation, the reactive Ca-silicates were formed and soluble potassium was recovered. The conversion of K-feldspar can be reached 84.7%. CO₂ can be easily reacted with reactive Ca-silicates and sequestered as stable calcium carbonate. The temperature of pretreatment can be reduced to 250°C by adding solution of triethanolamine. At low temperature pretreatment, the highest conversion of K-feldspar can be reached 40.1% using hydrothermal method, which makes it possible to mineralize CO₂ effectively, either *in situ* or based on engineered processes, using the Earth's natural K-feldspar stone. It is also important to emphasize that this technique generates soluble potassium chloride as a value-added product that can be used in the production of potash.

At present, the world's water-soluble potassium mineral resources are unevenly distributed—many countries lack such resources. Take China as an example: its water-soluble potassium salt reserves total 137057500 tons (KCl), only 1 percent of the world's reserves [23]. About half of consumption in China is from imports, leading to a high price for potassium chloride. Therefore, the co-production of soluble potassium salts can significantly compensate for the costs of CO₂ storage in China, and perhaps in other countries as well.

This work was supported by the International Cooperative Research Project of CO₂ Storage and Utilization in Saline Aquifer (2012DFA60760) from the Ministry of Science and Technology, and Basic Research for Chinese Energy Storage in Caverns Built in Highly Impure Rock Salt (51120145001) from the Natural Science Foundation of China, the National Natural Science Funds for Distinguished Young Scholars (51125017), the National Basic Research Projects of China (2011CB201201, 2010CB226804) from the Ministry of Science and Technology, and Key Research Program from the Ministry of Education of China. The authors are greatly grateful to Dr. Huihai Liu from LBNL USA and Dr. Derek Elsworth from Pennsylvania State University USA for their valuable discussions, review and comments.

- 1 Melt B, Davidson O, Connick H D, et al. Report on Carbon Dioxide Capture and Storage. Cambridge: Cambridge University Press, 2005
- 2 Haszedeine R S. Carbon capture and storage: How green can black be? Science, 2009, 325: 1647–1652
- 3 Xie H P. CO₂ storage and climate change (in Chinese). Sci Technol Rev, 2010, 28: 3
- 4 Xie H P. Developing low-carbon technology and promoting green economy (in Chinese). Energy China, 2010, 32: 5–10
- 5 Xie H P. Simultaneous recovery of national resources and mineralization of CO₂: A new CCU method (in Chinese). Technical Report, Energy and Mining Science, Chinese Academy of Engineering, 2012
- 6 Xie H P, Xie L Z, Wang Y F, et al. CCU: A more feasible and economic strategy than CCS for reducing CO₂ emissions (in Chinese). J Sichuan Univ: Eng Sci. 2012, 44: 1–5
- 7 Seifritz W. CO₂ disposal by means of silicates. Nature, 1990, 345: 486
- 8 Huijgen W J J, Witkamp G J, Comans R N J. Mechanisms of aqueous wollastonite carbonation as a possible CO₂ sequestration process. Chem Eng Sci, 2006, 61: 4242–4251
- 9 Koukouzas N, Gemeni V, Ziocok H J. Sequestration of CO₂ in magnesium silicates, in Western Macedonia, Greece. Int J Miner Process, 2009, 93: 179–186
- 10 Daval D, Martinez I, Corvisier J, et al. Carbonation of Ca-bearing silicates, the case of wollastonite: Experimental investigations and kinetic modeling. Chem Geol, 2009, 265: 63–78
- 11 Valer M M M, Fauth D J, Kuchta M E, et al. Activation of magnesium rich minerals as carbonation feedstock materials for CO₂ sequestration. Fuel Process Technol, 2005, 86: 1627–1645
- 12 Fagerlund J, Teir S, Nduagu E, et al. Carbonation of magnesium silicate mineral using a pressurized gas/solid process. Energy Proc, 2009, 1: 4907–4914
- 13 Kakizawa M, Yamasaki A, Yanagisawa Y. A new CO₂ disposal process via artificial weathering of calcium silicate accelerated by acetic acid. Energy, 2001, 26: 341–354
- 14 Munz A I, Kihle J, Brandvoll O, et al. A continuous process for manufacture of magnesite and silica from olivine, CO₂ and H₂. Energy Proc, 2009, 1: 4891–4898
- 15 Park A H A, Fan L S. CO₂ mineral sequestration: Physically activated dissolution of serpentine and pH swing process. Chem Eng Sci, 2004, 59: 5241–5247
- 16 Huijgen W J J, Comans R N J, Witkamp G J. Cost evaluation of CO₂ sequestration by aqueous mineral carbonation. Energ Convers Manage, 2007, 48: 1923–1935
- 17 Krevor S C, Lackner K S. Enhancing process kinetics for mineral carbon sequestration. Energy Proc, 2009, 1: 4867–4871
- 18 O'connor W C, Dahlin D C, Rush G E, et al. Carbon dioxide sequestration by direct mineral carbonation: Process mineralogy of feed and products. Miner Metall Process, 2002, 19: 95–101
- 19 Huijgen W J J, Witkamp G J, Comans R N J. Mineral CO₂ sequestration by steel slag carbonation. Environ Sci Technol, 2005, 39: 9676–9682
- 20 Hernandez G M, Lopez R P, Renard F, et al. Mineral sequestration of CO₂ by aqueous carbonation of coal combustion fly-ash. J Hazard Mater, 2009, 161: 1347–1354
- 21 Huntzinger D N, Gierke J S, Sutter L L, et al. Mineral carbonation for carbon sequestration in cement kiln dust from waste piles. J Hazard Mater, 2009, 168: 31–37
- 22 Rendek E, Ducom G, Germain P. Carbon dioxide sequestration in municipal solid waste incinerator (MSWI) bottom ash. J Hazard Mater, 2006, 128: 73–79
- 23 Iizuka A, Fujii M, Yamasaki A, et al. Development of a new CO₂ sequestration process utilizing the carbonation of waste cement. Ind Eng Chem Res, 2004, 43: 7880–7887
- 24 IEA. CO₂ emission from fuel combustion highlights. France: OECD/IEA, 2011
- 25 Xu T, Apps J A, Pruess K. Mineral sequestration of carbon dioxide in a sandstone–shale system. Chem Geol, 2005, 217: 295–318
- 26 Fu Q, Lu P, Konishi H, et al. Coupled alkali-feldspar dissolution and secondary mineral precipitation in batch systems: 1. New experiments at 200°C and 300 bars. Chem Geol, 2009, 258: 125–135
- 27 Ma H W. Potassic Rocks in China (in Chinese). Beijing: Chem Industry Press, 2010
- 28 Liu J, Han Y, Wang Y. Potassium extraction from Potassium-rich shale by high pressure hydrothermal method. Min Metall, 2008, 4: 31–37
- 29 Casey W H, Westrich R, Arnold G W. Surface chemistry of labradorite feldspar reacted with aqueous solutions at pH = 2, 3, and 12. Geochim Cosmochim Acta, 1988, 52: 2795–2806
- 30 Berg A, Banwart S A. Carbon dioxide mediated dissolution of Ca-feldspar: Implications for silicate weathering. Chem Geol, 2000, 163: 25–42
- 31 Oelkers E H, Schott J. Does organic acid adsorption affect alkali-feldspar dissolution rates? Chem Geol, 1998, 151: 235–245
- 32 Blake R E, Walter L M. Effects of organic acids on the dissolution of orthoclase at 80°C and pH 6. Chem Geol, 1996, 132: 91–102