http://dx.doi.org/10.17159/2411-9717/2016/v116n12a10

Investigation of the reactivity and grain size of lime calcined at extra-high temperatures by flash heating

by X.Y. Wang*, Z.L. Xue*, and J.L. Li*

Synopsis

In low-carbon energy-efficient basic oxygen furnace (BOF) steelmaking processes, limestone partly or completely replaces the active lime. The effects of limestone calcination temperature (1200–1500°C) and time (5–15 minutes) on lime reactivity and CaO grain size were investigated. The reactivity was evaluated by titration with hydrochloric acid, and the CaO grain size was analysed using scanning electron microscopy. The results revealed that for calcination temperatures higher than 1300°C, the reactivity reached a maximum and then decreased . The higher the temperature, the earlier the peak of reactivity appears. The CaO grains grow with increasing temperature and time, which leads to the decrease of reactivity. Notably, the effects of temperature on CaO grain size and reactivity are more marked than that of time. To obtain active lime calcined at ultra-high temperature by flash heating, the calcination conditions should be 1300–1400°C for 10–15 minutes, or 1400–1500°C for 8–10 minutes.

Keywords

limestone, calcination, reactivity of lime, flash heating, ultra-high temperature.

Introduction

Lime is one of the most important slag-making materials for dephosphorization and desulphurization in the basic oxygen furnace (BOF) steelmaking process. The reactivity of lime is a measure of its capability to take part in slag-making. Lime having a reactivity of more than 300.0 mL (4 N HCl), determined by hydrochloric acid titration is generally referred to as active lime (Rusjan *et al.*, 2007; Zeman, 2008). At present, the active lime used for BOF processes comes primarily from a kiln or shaft kiln, where limestone is preheated at 700–900°C, and then calcined at 1050–1200°C (Drenhaus *et al.*, 2010; Oates, 2007).

After cooling to room temperature, the lime is delivered to the steelmaking plant as a slag-making material. In this transfer process, the physical heat of the hot lime is lost. Furthermore, the calcination of lime requires the burning of gas, which leads to the emission of greenhouse gases such as CO_2 (Benhelal *et al.*, 2013). Therefore, the traditional steelmaking process involving the calcination of limestone and transfer of the lime cannot meet the current requirements for low-carbon and energy-efficient steelmaking. The direct replacement of the active lime with limestone in the BOF has been considered and explored by many researchers (Deng *et al.*, 2013; Aziz *et al.*, 2014; Iacobescu *et al.*, 2011). Since the temperature in the converter (1300–1600°C) is much higher than the optimum calcination temperature (1050–1200°C) for the traditional calcination processes, there is concern that the lime calcined at the converter temperature will not have sufficient reactivity to participate in slag-making.

In the present study, the effects of the calcination temperature and calcination time on the reactivity of lime and the CaO grain size, as well as the relationship between these two properties, were investigated for limestone that was flash-heated at high temperatures much greater than the optimum calcination temperature for active lime. The results will provide theoretical guidance for using limestone instead of active lime in converter steelmaking.

Experimental

Physical and chemical properties of the raw materials

Limestone was obtained from the Wulongquan Mine of Wuhan Iron and Steel Corp., which is located in Wuhan City, Hubei Province, China. The chemical composition is listed in Table I. The $CaCO_3$ content was 99.02 wt%, and the limestone contained minor amounts of impurity components, including SiO_2, MgO, Al_2O_3,and deleterious components such as S and P. The X-ray diffraction (XRD) patterns of

---

* *The State Key Laboratories of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China.*

ISSN 2225-6253. Paper received Aug. 2015.

Table I

Chemical composition of the limestone used in the study, wt%

$CaCO_3$	SiO_2	MgO	Al_2O_3	Fe_2O_3	S	P
99.02	0.29	0.29	0.09	0.06	0.013	0.002

the limestone, shown in Figure 1, revealed that it mainly comprised $CaCO_3$. The microstructure of the limestone observed using the scanning electron microscope (SEM) is shown in Figure 2. The grain size of the calcium carbonate ranges from 3 μm to 5 μm.

Experimental procedure

The rapid calcination of limestone was performed in a 25 kW carbon tube furnace, as shown in Figure 3, with a maximum working temperature of 1700°C. Nitrogen gas was pumped through a hole in the furnace to protect the tube from oxidation. The calcination temperature was set at 1200, 1250, 1300, 1350, 1400, 1450, or 1500°C. Limestone particles (approx. 160 g) with a grain size of 12.5–15 mm were placed in a molybdenum basket. After the set temperature was reached, the basket was placed in the isothermal zone of the carbon tube for 5, 8, 10, 12, or 15 minutes. The basket was then immediately removed from the tube and the samples were transferred to a metal plate for cooling in air. The cooled lime was crushed with a hammer and lime particles with diameters of 1–5 mm were obtained by screening for the evaluation of their reactivity.

The reactivity of the lime was determined according to the YB/T 105-2005 standard procedure, using the device schematically shown in Figure 4. Deionized water (2000 ml) was poured into a 3000 ml beaker and heated to 42–45°C. The water was then agitated and when the temperature fell to 40±1°C, 8 droplets of phenolphthalein indicator with a concentration of 5 g/L were added into the beaker. The lime sample (50 g) was poured into the beaker and the time was set to zero. At the beginning of lime digestion, the water in the beaker was red. The solution was then titrated using 4 mol/L hydrochloric acid at a titration rate designed to ensure that the red colour of the solution only faded. The consumption of hydrochloric acid was accurately recorded when the titration time was 10 minutes and represents the reactivity of the lime. This method was typically used to measure relatively low lime reactivity. For samples with relatively high lime reactivity, the phenolphthalein addition was increased (Garau *et al.*, 2007) to ensure more accurate

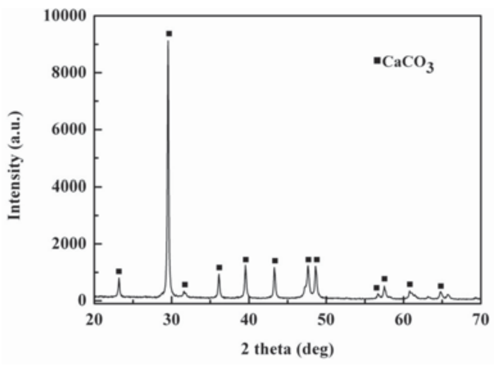

Figure 1—XRD pattern of the limestone

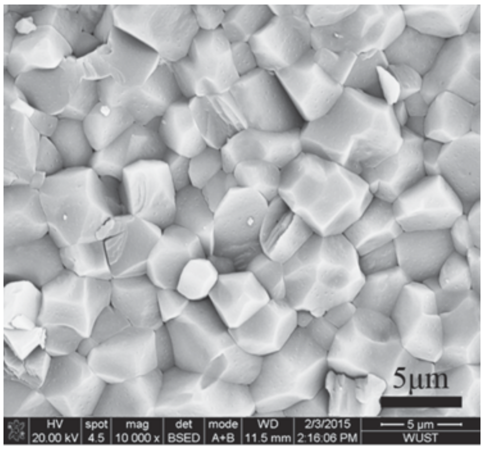

Figure 2—SEM micrograph of calcium carbonate

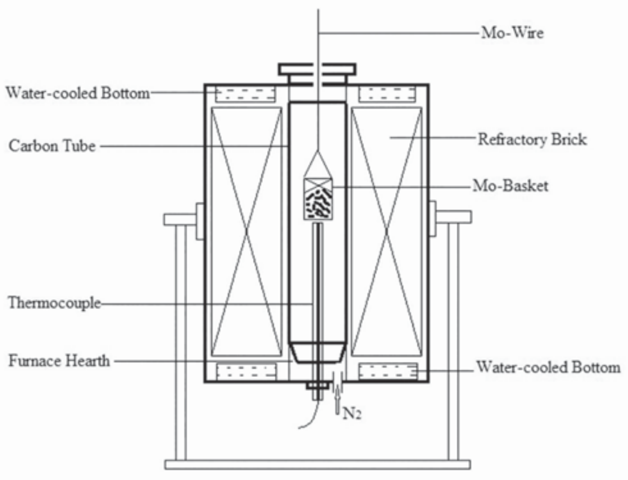

Figure 3—Carbon tube furnace used for lime calcination

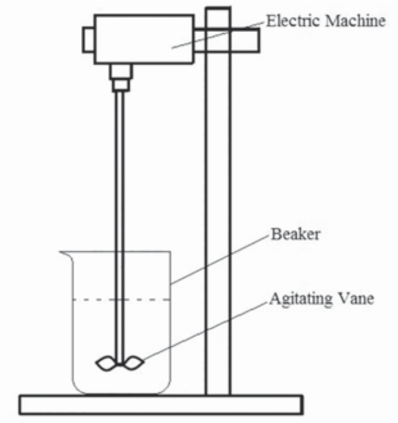

Figure 4—Device used for evaluating lime reactivity

results. Two drops of 5 g/L phenolphthalein were added into the solution at 6 minutes, and an additional 2 drops were added at 8 minutes.

Results

Effect of calcination time on lime reactivity

The effect of calcination time on the reactivity of the prepared lime varied according to the calcination temperature employed (Figure 5). At calcination temperatures between 1200°C and 1300°C, the reactivity of the lime gradually increased as the calcination time was prolonged and surpassed 300.0 mL after 15 minutes of calcination. At temperatures >1300°C, the reactivity of the lime initially increased and then decreased as the calcination time increased. The higher the calcination temperature, the sooner the maximum reactivity was reached. When the lime was calcined at 1500°C, the reactivity reached a maximum value of 393.5 mL after 8 minutes, and then decreased with further increases in calcination time, falling to below 300.0 mL after 15 minutes. Furthermore, when the calcination temperature was 1450°C, the reactivity reached a maximum of 436.2 mL after 10 minutes and decreased to 342.1 mL after 15 minutes.

Effect of calcination temperature on lime reactivity

The effect of the calcination temperature on the reactivity of the lime is shown in Figure 6. As can be seen, the influence of the calcination temperature on the reactivity of lime varied with the calcination time. After 5 minutes of calcination, the reactivity of the calcined product gradually increased as the temperature increased to 1400°C and remained constant at approximately 280.0 mL, which suggests that the decomposition of the internal limestone particles was incomplete, while the external CaO grains grew at higher temperature. In addition, when the temperature was between 1400°C and 1500°C, the reactivity of the lime was between 340.0 mL and 400.0 mL after 8 minutes of calcination. On the other hand, at a calcination time of 10 minutes, the reactivity of the lime exceeded 300.0 mL when the temperature was greater than 1250°C, and a maximum value of 436.2 mL was obtained at 1450°C. The peak reactivity was also observed at 1450°C when the calcination time was 12 minutes; however, it was lower than the peak value at 10 minutes, indicating that the grains of lime grew more rapidly at the same temperature when the holding time was greater than 10 minutes. When the calcination time was 15 minutes, the peak value of reactivity was reached at 1300°C. Therefore, for calcination temperatures of 1250–1350°C, the appropriate calcination time was 10–15 minutes, and for calcination temperatures above 1400°C, the appropriate calcination time ranged from 8 minutes to 10 minutes.

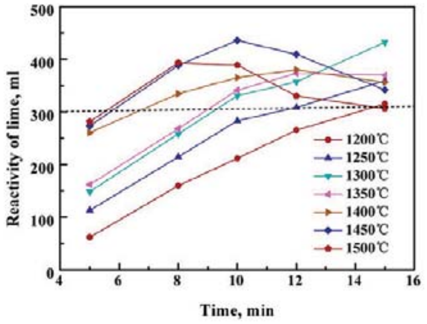

Figure 5—Effect of calcination time on lime reactivity

Discussion

Limestone calcined at high temperature via flash heating decomposes into lime. The degree of decomposition and the growth behaviour of the CaO grains directly affect the reactivity of the calcined products.

Degree of limestone decomposition

The decomposition of $CaCO_3$ at high temperature can be expressed as follows:

$$\Delta G^0 = 169120 - 144.60T, J/mol \quad [1]$$

The calcination of limestone can be described by the unreacted core model, which depicts the thermal decomposition of $CaCO_3$ particles via five steps as follows:

(1) Heat transfers from the surrounding environment to the boundary layer of $CaCO_3$
(2) Heat transfers through the porous lime layer to the reaction interface
(3) $CaCO_3$ decomposition
(4) Diffusion of CO_2 produced at the reaction interface to the particle surface through the product layer
(5) CO_2 evaporation from the surface of the particle to the surrounding gas flow.

The five steps essentially comprise three stages, which are the internal heat transfer in the particle, the decomposition of $CaCO_3$ at the reaction interface, and the diffusion of CO_2 in the product layer. The higher the temperature of the surrounding environment, the larger the temperature gradient in the limestone particle; this leads to a higher rate of internal heat transfer and enhances the limestone decomposition rate. The internal heat transfer is related to the thickness of the product layer and the thermal conductivity. The rate of diffusion of CO_2 through the product layer is related to both the thickness and the density of the product layer. The decomposition rate R_D (kg/s·m²) of $CaCO_3$ is expressed follows:

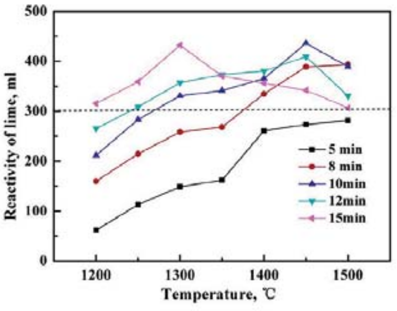

Figure 6—Effect of calcination temperature on lime reactivity

$$R_D = k_D(p_e - p) \qquad [2]$$

where k_D represents the reaction rate constant, $k_D = 0.00122\exp(-4026/T)$; p (Pa) is the partial pressure of CO_2 at the reaction interface; p_e (Pa) is the equilibrium pressure for CO_2 decomposition, $p_e = \exp(17.74 - 0.00108T + 0.332\text{In}T - 22020/T)$;, and T (K) refers to the temperature of the reaction interface. The value of p_e is determined by only the temperature of the reaction interface (Ning, Zhong, and Fu, 2003). The higher the temperature, the larger the value of p_e; this results in a higher decomposition reaction rate at the interface. In addition, a higher rate of CO_2 diffusion from the reaction interface results in a smaller value of p, which also leads to a higher rate of decomposition at the interface.

Equation [2] reveals that the decomposition rate for $CaCO_3$ depends on the calcination temperature and the CO_2 diffusion rate. The decomposition of single spheres (10 mm diameter) of $CaCO_3$ has been investigated by Hill (Hill, 1968; Hill and Winter, 1956), who found that the decomposition rate was controlled by the heat transfer to the reaction boundary through the product layer and the internal diffusion of CO_2 in the product layer.

The mineral composition of the calcination products obtained by the calcination of limestone at different temperatures and times was also evaluated using XRD analysis (Philips Xpertpro). The results are shown in Figure 7. The particle size of the limestone studied in this paper is 12.5–15 mm. The decomposition rate was found to be controlled by the heat transfer to the reaction boundary through the product layer and the internal diffusion of CO_2 in the product layer. As can be seen in Figure 7, when calcination at 1250°C was extended for longer periods, the peak for CaO gradually increased, while the peak for $CaCO_3$ decreased and eventually disappeared at calcination times longer than 12 minutes. However, when the calcination temperature was 1400°C, the peak of $CaCO_3$ basically disappeared after 8 minutes.

These XRD analysis results reveal that as the calcination temperature and calcination time increased, the heat transfer rates inside the particle and the internal CO_2 diffusion rate were enhanced, which accelerated the decomposition of $CaCO_3$. Consequently, the reactivity of the products gradually increased.

Characteristics of the CaO grains in products calcined at ultra-high temperatures

Assuming completed decomposition of $CaCO_3$, the reactivity of lime is closely related to the grain size of the product CaO as well as the porosity and the bulk density. It has been previously reported (Sun *et al.*, 2007; Chen *et al.*, 2007; Feng *et al.*, 2004) that the reactivity of lime increases with increasing porosity and decreases with increasing bulk density and grain size. Notably, the CaO grain size as well as the porosity and bulk density of lime are significantly affected by the behaviour of the CaO grains during the calcination.

Since CO_2 is released by limestone particles during calcination at high temperature, the particles become porous. In addition, the product particles comprise a large number of fine CaO grains. Therefore, to minimize the free energy of the system, the fine grains fuse and grow to form a large number of aggregates of various sizes according to the influences of gravity and surface tension. This process is referred to as sintering. Variation of the CaO grain size after calcination at high temperature was observed by SEM (Nova400). Figure 8 shows the micro-morphologies of CaO grains calcined at 1300°C, 1450°C, and 1500°C for 10 minutes. It can be seen

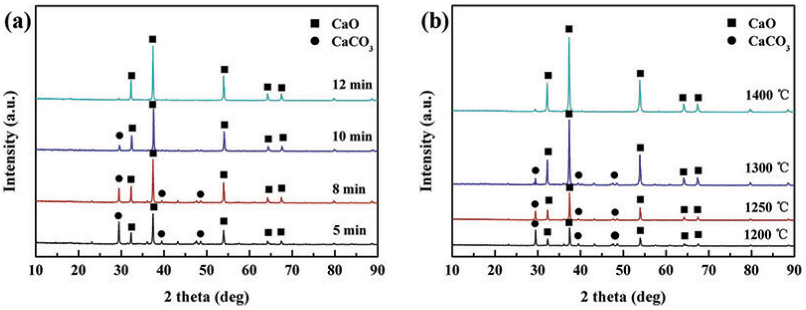

Figure 7—XRD patterns of samples (a) calcined at 1250°C for different times and (b) calcined at different temperatures for 8 minutes

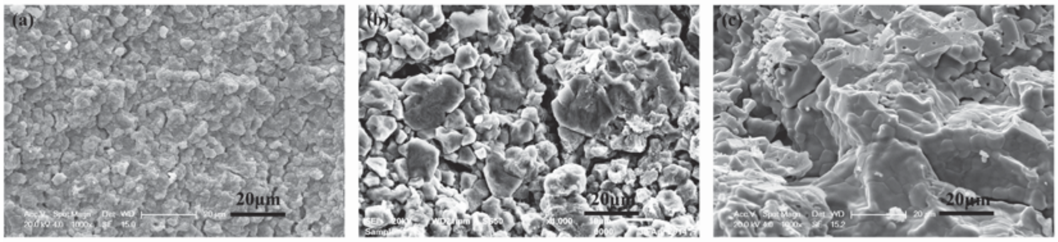

Figure 8—Effects of calcination temperatures on the CaO grain size: (a) 1300°C, 10 min; (b) 1450°C, 10 min; (c) 1500°C, 10 min

that fusion and growth of the CaO grains was more significant as the calcination temperature increased. Thus, the size of the CaO grains calcined at 1300°C was 5–10 minutes and the surfaces of the grains were rough, while at 1450°C a portion of the small particles fused into larger particles with porous structures. The CaO grains calcined at 1500°C were completely fused with a smooth surface, indicating that they were excessively sintered.

The micro-morphologies of CaO grains calcined at 1350°C and 1450°C for 5–15 minutes are shown in Figure 9. In Figures 9a–c It can be seen that the sizes of the CaO grains calcined at 1350°C for less than 10 minutes were similar, although the morphologies of the grains starts to reconstruct. When the holding time was prolonged to 15 minutes, the size of CaO grains increased to more than 30 μm in diameter. In Figure 9d–f, it can be seen that the neonatal CaO grains calcined for 5 minutes were fine, while a portion of them had fused and increased in size. After heating for 10 minutes, the size of the grains increased and a portion of them fused to form grains with diameters greater than 20 μm. In addition, when the calcination time was 15 minutes, the CaO grains all completely fused and became densified. Furthermore, a comparison of Figures 9a and 9c reveals that the neonatal grains calcined at 1450°C were finer than those calcined at 1350°C, even though the tendency for fusion and growth was greater for the grains calcined at the higher temperature.

Thus, when the calcination temperature was greater than 1300°C, the CaO grains in the product layer gradually fused and grew to form a sintered layer of low reactivity as the temperature and calcination time increased. Moreover, the higher the calcination temperature, the greater the tendency for excessive sintering. The fusion and growth of the CaO grains at high temperature resulted in not only an increase in the grain size and bulk density, but also a decrease in the porosity and specific surface area, which led to the densification of the calcined products. Consequently, the reactivity of the lime decreased.

The temperature in the converter is typically above 1400°C after the operation of slag splashing, which is when the limestone is added into the converter using an overhead bunker. The scrap and hot metal is then charged and the limestone is completely decomposed during this process. Therefore, under the conditions in the convertor for limestone flash heating to an ultra-high temperature, the limestone should be added so that it resides in the convertor for 8–12 minutes to ensure the formation of an initial slag with appropriate properties.

Conclusions

The influence of the calcination temperature and time on lime reactivity and size of the CaO grains was investigated using flash heating to an ultra-high temperature. In addition, the relationship between the size of CaO grains and the reactivity of the lime was studied using the SEM. Several key insights were indentified and are summarized below.

When the calcination temperature was between 1200°C and 1300°C, the reactivity of the lime gradually increased with the calcination time and was greater than 300 mL after 15 minures. In addition, when the calcination temperature was > 1300°C, the reactivity of the lime initially increased and then decreased as the calcination time increased. Furthermore, the time required to reach the maximum lime reactivity decreased as the calcination temperature increased. Notably, the maximum lime reactivities were greater than 300.0 mL.

It was also found that the effect of the calcination temperature on the grain size of CaO and lime reactivity was greater than that of calcination time. At higher calcination temperatures, finer primary grains of CaO were formed that exhibited a greater impetus for fusion and growth. The prolongation of the calcination time at high temperature thus led to rapid CaO grain growth and densification of the lime, which resulted in a decrease in the reactivity. Consequently, calcination times of 10–15 minutes and 8–10 minutes are appropriate for limestone calcination at 1250–1350°C and >1350°C, respectively.

Acknowledgements

The financial support from the National Natural Science Foundation of China (No.51374160) is greatly acknowledged. The authors are also grateful to Dr J.L Lei for technical assistance with SEM operation.

References

Aziz, M.M., Hainin, M.R., Yaacob, H., Ali, Z., Chang, F.L., and Adnan, A.M. 2014. Characterisation and utilisation of steel slag for the construction of roads and highways. *Materials Research Innovations*, vol. 18, no. 2. pp. 255–259.

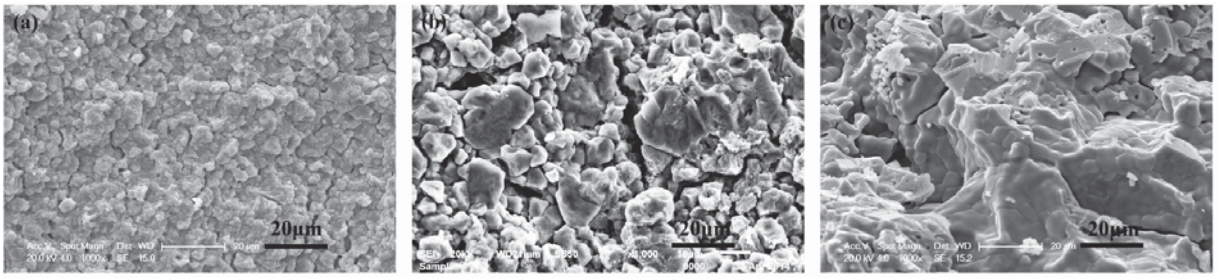

Figure 9—Effects of calcination time on the CaO grain size: (a) 1350°C, 5 min; (b) 1350°C,10 min; (c) 1350°C, 15 min

Benhelal, E., Zahedi, G., Shamsaei, E., and Bahadori, A. 2013. Global strategies and potentials to curb CO_2 emissions in cement industry. *Journal of Cleaner Production*, vol. 51, no. 13. pp.142–161.

Chen, M., Wang, N., Yu, J., Yu, J.K., and Yamaguchi, A. 2007. Effect of porosity on carbonation and hydration resistance of CaO materials. *Journal of the European Ceramic Society*, vol. 27, no. 4. pp.1953–1959.

Deng, T.F., Nortier, P., Mattias, E.K., and Chen, S.C. 2013. Limestone dissolution in converter slag at 1873 K (1600°C). *Metallurgical and Materials Transactions B*, vol. 44, no. 1. pp. 98–105.

Drenhaus, T.B., Simsek, E., Wirtz, S., and Scherer, V. 2010. A coupled fluid dynamic-discrete element simulation of heat and mass transfer in a lime shaft kiln. *Chemical Engineering Science*, vol. 65, no. 9. pp. 2821–2834.

Feng, X.P., Zhou, X.D., Xie, J.L., and Zhang, Z.W. 2004. Effects of calcining technology and microstructure on the activity of lime. *Journal of Wuhan University of Technology*, vol. 26, no. 5. pp.28–30.

Garau, G., Castaldi, P., Santona, L., Santona, L., Deiana, P., and Melis, P. 2007. Influence of red mud, zeolite and lime on heavy metal immobilization, culturable heterotrophic microbial populations and enzyme activities in a contaminated soil. *Geoderma*, vol. 142. no. 11. pp.47–57.

Hill, A. 1968. The mechanism of the thermal decomposition of calcium carbonate. *Chemical Engineering Science*, vol. 23, no. 4. pp. 297–320.

Hill, K.J. and Winter, E.R.S. 1956. Thermal dissociation pressure of calcium carbonate. *Journal of Physical Chemistry*, vol. 60, no. 10. pp.1361–1362.

Iacobescu, R.I., Koumpouri, D., Pontikes, Y., Saban, R., and Angelopoulos, G.N. 2011. Valorisation of electric arc furnace steel slag as raw material for low energy belite cements. *Journal of Hazardous Materials*, vol. 196, no. 1. pp. 287–294.

Ning, J.T., Zhong, B.J., and Fu, W.B. 2003. Study on the calcination of fine limestone power at high temperature. *Journal of Combustion Science and Technology*, vol. 9, no. 6. pp. 205–208 [in Chinese].

Oates, T. 2007. Lime and Limestone. Wiley.

Rusjan, D., Strli , M., Pucko, D.Z., and Koruza, K. 2007. Copper accumulation regardingthe soil characteristics in Sub-Mediterranean vineyards of Slovenia. *Geoderma*, vol. 141, no. 2. pp. 111–118.

Sun, P., Grace, J.R., Lim, C.J., and Anthony, E.J. 2007. The effect of CaO sintering on cyclic CO_2 capture in energy systems. AIChE Journal, vol. 53, no. 9. pp. 2432–2442.

Zeman, F. 2008. Effect of steam hydration on performance of lime sorbent for CO_2 capture. *International Journal of Greenhouse Gas Control*, vol. 2, no. 7. pp.203–209.

◆