Improving CO2 Absorption Performance of Ca-Based By Different Additives

Luhan Chen¹, Zhiguo Sun¹,*, Jinqiu Xu², Shichao Jia¹, Menglu Wang¹

¹School of Environmental and Materials Engineering
²School of Science Shanghai Polytechnic University, Shanghai 201209, China

*Corresponding author e-mail: zgsun@sspu.edu.cn

Abstract. In this work, different additives (sodium citrate, sodium acetate and KCl) are used to solve the problem that the CO2 absorption capacity of limestone decreases rapidly with the increase of cyclic calcination/carbonation reactions times. The results reflected that after adding 0.5% sodium acetate, the absorption rate and decomposition rate of CO2 in CaO are 1.01 times and 2.08 times higher than that without adding, and the absorption rate and decomposition rate are 2.65 times higher than those without adding after 10 cycles, and the decomposition rate is increased by 95.8%. After the addition of 1.0% sodium citrate, the first absorption rate increased by 28%, the 10 cycles increased by 38%, and the decomposition rate of the first calcium carbonate increased by 2.4 times. After adding 0.8% KCl, although the first absorption rate decreased by 36%, the decomposition rate of CaCO3 increased by 2.08 times after 10 cycles, and by 95.1% after 10 cycles. Therefore the use of additives improves obviously the CO2 absorption of CaO.

1. Introduction

Global warming is mainly due to the use of fossil fuels and other fossil fuels in the past century, the emission of a large number of greenhouse gas CO2, resulting in the greenhouse effect [1-3]. CO2 control in coal-fired power plants is urgent. At present, there are many researches on high temperature CO2 solid absorber [4]. High temperature CO2 solid adsorbent is a promising Ca-based sorbent. Ca-based has low price and wide distribution, so it is worth studying [5-6].

CaO has high CO2 absorption capacity, low preparation cost, long life cycle and good wear resistance. Therefore, CaO is the preferred CO2 absorber. However, CaO as high temperature CO2 remover has some disadvantages [7]. When CaO reacts with CO2 to form CaCO3, the CaO surface product layer will prevent further reaction of CO2 molecule CaO, resulting in decreased adsorption effect [8-11]. When the calcination temperature exceeds 900°C, the absorbent particles are easy to sintering, reducing the ability to absorb CO2. Therefore, many researchers have conducted extensive and in-depth studies on the shortcomings of improved calcium-based absorbents.

In this study, CaO adsorbent is taken as the research object. The additives include sodium citrate, sodium acetate and KCl to study the effect of different additives on CO2 absorption ability during multi-cycle calcination/carbonation [12].
2. Experimental Section

Additive/CaO sorbent is a mixture of CaO and additives containing 0.5%, 0.8% and 1.0%, respectively. Pour the weighed additive into a 200ml beaker, add distilled water, stir for 1h, and mix thoroughly. Then place the mixture in a 120°C oven and bake for 8 hours. After cooling the sample to room temperature, grind it into powder, and then pour it into a dry dish for sealing. The atmospheric Ca-based sorbents CCCR system, as shown in the figure 1. The calcining conditions at 850°C (15 min with 100 vol% N₂) and carbonation condition at 650°C (20 min with 85 vol% N₂, 15 vol% CO₂).

![Diagram of Atmospheric Ca-based sorbents CCCR system](image)

**Figure 1.** Atmospheric Ca-based sorbents CCCR system

First, the sample is completely carbonized in a carbonizing furnace, and its atmosphere is pure N₂ to eliminate the air in the quartz glass tube or other gases that affect the reaction. When the temperature stabilizes, it is converted to a carbonated atmosphere, the reaction is completed, cooled, and then weighed in the balance. The reaction temperature is then raised to change the atmosphere to that of calcining. When the reaction reaches the specified time and cools, the balance is weighed again and the data is recorded. The absorption rate and decomposition rate of CO₂ after reaction are calculated according to equation (1-2):

\[
X_i = \frac{m_1 - m_2}{m_1} \times 100\%
\]

\[
Y_i = \frac{m_2 - m_3}{m_2} \times 100\%
\]

Where, \(X_i\) is the decomposition rate of the reaction, \(Y_i\) is the absorption rate of the reaction, \(m_1\) is initial sample mass of the reaction, \(m_2\) is mass after decomposition by heating in the reaction, \(m_3\) is the mass of carbon dioxide absorbed by the reaction.

3. Result and Discussion

3.1. Effect of KCl content on CO₂ cyclic absorption property

As can be seen in figure 2, the absorption rate of the first time is 36% lower than that of CaO, when the amount of KCl added is 0.5% and 0.8%. After 10 cycles, the absorption rate of 0.8% is 2.4 times that of CaO. KCl as an additive has been proved effective in this experiment. After the addition of KCl, the CO₂ absorption capacity of Ca-based sorbent was increased by 2.4 times. Meanwhile, this effect was maintained in the subsequent cycle, with only 41% attenuation. Figure 3 shows the decomposition rate of absorbent with 0.8% KCl was 95.1% higher than that of CaO after 10 cycles. The cyclic reaction was stable, when the optimal addition of KCl was 0.8%. But the carbonation reaction was
inhibited when the addition was increased to 1.0%. From the perspective of overall circulation, KCl promotes CO₂ absorption by CaO.

![Figure 2. Absorption rate of absorbent with KCl added](image)

![Figure 3. Decomposition rate of absorbent with KCl added](image)

3.2. Effect of Sodium acetate content on CO₂ cyclic absorption property

The absorption rate of CaO absorbent with sodium acetate is obviously higher than that without CaO absorbent. As shown in figure 4. When sodium acetate was added at 1.0%, the single absorption rate was 23% higher than that without sodium acetate. After three cycles, the stability of the absorption rate is better than CaO when the addition amount is 0.5% and 0.8%. After 10 cycles, when sodium acetate was added 0.5%, the absorption effect was better, 95.8% higher than that of CaO. In terms of decomposition rate (figure 5), the trend is basically the same as KCl, but the effect is better than KCl. The higher the content of sodium acetate, the lower the decomposition rate. The optimal addition of sodium chelate is 0.5%. During calcination, sodium acetate will release organic matter and CO₂, and CaO will form a more developed pore structure. After calcination of calcium acetate, it has a developed pore structure and a higher specific surface area, which is conducive to carbonation reaction and diffusion of CO₂ in pores.
3.3. Effect of Sodium citrate content on CO$_2$ cyclic absorption property

It can be seen figure 6 and figure 7. The absorptivity and decomposition rate values are not well compared with those without addition, when sodium citrate is added. With the addition of 1.0%, the single absorption rate was higher than that without addition of 28%. The absorption rate of sodium citrate added was little different from that of the unadded after four cycles. From the decomposition rate, the role of sodium citrate is very small. After the 10 cycles, the decomposition rates of the four samples were basically the same. The decomposition rate after sodium citrate was 2.4 times higher than that before sodium citrate was added, and 11.9% higher after 10 cycles. It indicates that sodium citrate has little effect on CO$_2$ absorption by CaO when it is used as additive.
3.4. Effect of different additive content on CO2 cyclic absorption property

The absorption and decomposition rates of the three additives were compared as shown in the figure 8. Although the absorption rate of sodium citrate was 20% higher than that of sodium acetate during the first cycle, the absorption rate of sodium citrate after 10 cycles was 15% lower than that of sodium acetate. Among the three additives, 0.5% sodium acetate has the best absorption effect. The addition of 0.5% sodium acetate not only improved the absorption capacity of the absorbent, but also made the whole reaction process more stable. From the perspective of decomposition rate (figure 9), adding 0.5% sodium acetate decomposition rate is relatively stable. The absorption of sodium acetate is not only good, but also less than the other two additives. In practical application, sodium acetate has higher transportation safety and lower cost than KCl, so it is worth studying as a CO2 absorption additive.
4. Conclusion

The experiment compared the absorption with CaO reagents as raw materials, sodium citrate, KCl and sodium acetate as additives, made into a variety of cyclic calcination/carbonation reaction of adsorbent, by comparing the same calcination temperature, melt temperature, reaction time carbonate reaction under the circular curve, to explore the influence of additives for CaO adsorbent carbonation rate. Sodium citrate, KCl and sodium acetate have the ability to improve the reaction effect. And the lifting effect varies greatly. The absorption rate of 0.5% sodium acetate was 2.5 times higher than that of 1.0% sodium citrate, and the decomposition rate was 2.08 times higher. There are different additives have different optimum amounts. Excessive additives not only greatly reduce the CO$_2$ absorption capacity of CaO, but also increase the production cost. Considering the above two aspects, sodium acetate makes the most suitable additive choice. When sodium acetate is added at 0.5%, the absorption of CO$_2$ is the best, the absorption rate is more than 3 times that of CaO, and the decomposition rate is 2.65times that of CaO.

Acknowledgments

The authors gratefully acknowledge financial support by National Natural Science Foundation of China (No. 21806101), Natural Science Foundation of Shanghai (No.16ZR1412600), Research Center of Resource Recycling Science and Engineering, Shanghai Polytechnic University and Gaoyuan Discipline of Shanghai – Environmental Science and Engineering (Resource Recycling Science and Engineering), Cultivate discipline fund of Shanghai Polytechnic University (No.XXKPY1601), and Postgraduate Foundation of Shanghai Polytechnic University (EGD17YJ0026, EGD18YJ0059, EGD18YJ0062).

References

[1] Erickson P, Lazarus M. Would constraining US fossil fuel production affect global CO2 emissions A case study of US leasing policy [J]. Climatic Change, 2018(150): 29-42.
[2] Ahmed K, Ahmed S. A predictive analysis of CO2 emissions, environmental policy stringency, and economic growth in China [J]. Environmental Science and Pollution Research, 2018, 25(16): 16091-16100.
[3] Boothandford M E, Abanades J C, Anthony E J, et al. Carbon capture and storage update [J]. Energy and Environmental Science, 2014, 7(1): 130-189.
[4] Bui M, Adjiman C S, Bardow A, et al. Carbon capture and storage (CCS): the way forward [J]. Energy and Environmental Science, 2018, 11(5): 1062-1176.
[5] Yan F, Jiang J, Zhao M, et al. A green and scalable synthesis of highly stable Ca-based sorbents for CO2 capture [J]. Journal of Materials Chemistry, 2015, 3(15): 7966-7973.
[6] Han L, Zhang Y, Lin K, et al. Developing a Novel CaO-Based Sorbent for Promoted CO2 Capture and Tar Reduction [J]. Energy & Fuels, 2017, 31(5): 5306-5317.
[7] J. Blamey, E.J. Anthony, J. Wang, P.S. Fennell. The calcium looping cycle for large-scale CO2 capture [J]. Progress in Energy and Combustion Science, 2009,36(2).
[8] Zhang Y, He L, Ma A, et al. CaO-based sorbent derived from lime mud and bauxite tailings for cyclic CO2 capture [J]. Environmental Science and Pollution Research, 2018, 25(28): 28015-28024.
[9] Luo C, Zheng Y, Guo J, et al. Effect of sulfation on CO2 capture of CaO-based sorbents during calcium looping cycle [J]. Fuel, 2014(127): 124-130.
[10] Dinca C, Slavu N, Badea A, et al. Benchmarking of the pre/post-combustion chemical absorption for the CO2 capture [J]. Journal of The Energy Institute, 2017, 91(3): 445-456.
[11] Antzara A, Heracleous E, Lemonidou A A, et al. Improving the stability of synthetic CaO-based CO2 sorbents by structural promoters [J]. Applied Energy, 2015: 331-343.
[12] Bui M, Adjiman C S, Bardow A, et al. Carbon capture and storage (CCS): The way forward [J]. Energy and Environmental Science, 2018, 11(5): 1062-1176