Effect of Alkali Metal Compounds on Limestone Calcination in Desulfurization Process: Molecular Dynamics Simulations

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脱硫プロセスにおける石灰石焼成のアルカリ金属化合物の効果： 分子動力学シミュレーション

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In this study, the change in the desulfurization characteristics of limestone induced by adding some alkali metal compounds and chlorides to limestone was investigated by thermobalance experiments. In addition, molecular dynamics (MD) simulations were performed to elucidate the effect of alkali-metal chloride additions on the CaO calcination for the desulfurization process. The experimental results obtained show that the addition of NaCl into the limestone is the most effective in improving the desulfurization efficiency. The X-ray diffraction analyses of the calcined seashell, limestone and NaCl-doped limestone found that the calcined seashell, as well as the calcined NaCl-doped limestone, have a similar structure as the CaO crystal. These two materials also show a high desulfurization efficiency. The MD simulations show that NaCl doping into the CaO contributes to the crystallization of CaO, while KCl and LiCl dopings have a small contribution. Therefore, the NaCl doping has a predominant effect on the CaO crystallization leading to a high desulfurization efficiency.

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1. Introduction

Recently, acid rain has been recognized as one of the most serious global environmental problems. Sulfur oxides (SO_x) are one of the main sources of acid rain. In a bubbling and circulating fluidized bed coal combustors, limestone is directly supplied into the combustors as a desulfurizer in order to decrease the emissions of SO_x from coal. Those combustors are operated at temperatures ranging from 1073 to 1173 K. The limestone is calcined and sulfurized optimally under this temperature condition. In practical boilers however, limestone, which mainly consists of CaCO_3 , is fed excessively to improve the contact efficiency between the CaO produced and the SO_2 emitted. When accomplishing more than 90% of the desulfurization efficiency, or burning coal with a sulfur content of more than 1 mass%, it is necessary to add limestone more than four times as much as Ca to S mole ratio. Otherwise, the particle size of the limestone should be fine.^(1,2) This is because pores inside the CaO particles ought to be plugged as a result of CaSO_4 formation.⁽³⁾ As the main component of the limestone is CaCO_3 , which is similar to that of seashells, it is possible to use wasted seashells as a desulfurizer. In this case, the CO_2 produced during the calcination of the seashells is fixed again to the seashells and recycled naturally. Naruse et al.,⁽⁴⁾ reported that the desulfurization efficiency of the seashells was over twice as high as that of the limestone. This suggests that the seashells could be used as an effective desulfurizer. To explain the mechanisms and reasons for the high desulfurization efficiency of the seashells, the chemical compositions and the mean pore size of the seashell and the limestone were analyzed. As a result, the seashell was found to

contain more sodium, potassium and chlorine than the limestone. The mean pore size of calcined seashell is over six times as large as that of calcined limestone.⁽⁵⁾ Other researchers have also studied the effect of NaCl on the desulfurization characteristics. They qualitatively suggested that the NaCl-doped limestone could enhance the desulfurization efficiency.^{(6)–(9)} However, the reason of the high desulfurization efficiency of NaCl-doped seashell has not always been explained at an atomic level yet.

This study evaluates the change in the desulfurization characteristics of limestone induced by the addition of some alkali metal compounds and chlorides, by using a thermobalance experiment. The crystal structures of calcined seashell, limestone and NaCl-doped limestone are also analyzed using an X-ray diffraction (XRD) analyzer. Furthermore, the molecular dynamics (MD) simulations are performed for both the pure CaO and NaCl-doped CaO to elucidate the effect of the addition of NaCl on the CaO calcination process. The MD results obtained are discussed in terms of electrostatic interaction energies between Ca–O, Na–O, Ca–Cl and Na–Cl. The effect of other alkali metal chlorides (KCl and LiCl) on the CaO crystallization is also examined and compared with the results for the NaCl-doped CaO. Finally, the MD results obtained are compared with the desulfurization result.

2. Experimental and simulation method

2.1 Experimental method

In the desulfurization experiments, a thermobalance experiment was used with samples of scallop and Tsukumi limestone

Table 1. Conditions of Molecular Dynamics Simulations

Number of atoms	864 (Ca) and 864 (O)		
Temperature pattern [K]	298	6900 - 7100	298
Simulation time [ps]	10	10	10
Pressure [MPa]	0.1		
Parameters in potential functions	Kawamura model		
Charge of atoms	Ca=2.0, O=-2.0		
	Na, K, Li=1.0, Cl=-1.0		

of particle diameters ranging from 297 to 420 μm . The calcination and desulfurization of the samples were carried out at 1123 K, which is similar to the operating condition of the fluidized bed combustion. A small amount of alkali metal compound powders were physically mixed with the limestone particles. Agents of chlorides, carbonates and hydroxides were individually added to it in amounts ranging from 0.5 to 3.0 mass%.

2.2 Simulation method

In the MD simulation, the program package Win-MASPHYC Pro1.0 was used.¹⁰⁾ The potential parameters developed by Kawamura^{10),11)} were adopted in this simulation. The conditions of the MD simulations are shown in Table 1. First, a cubic cell composed of 864 molecules of the CaO is made as a unit cell, in which the structure of CaO is constructed, based on the NaCl-like crystal structure.¹²⁾ This unit cell is periodically arranged three-dimensionally to construct the CaO crystal structure. The MD simulations are carried out under the condition of a constant number of atoms and pressure. The initial calculation temperature is set to be 298 K to obtain the crystal structure of CaO. Then, the temperature is changed to from 6900 to 7100 K. Finally, the temperature is reduced to 298 K in order to anneal the CaO structure. It is noted that the MD simulation temperature does not correspond to the actual temperature of calcination, because the temperature based on Kawamura's potential parameters is much higher than the actual temperature. Therefore, the temperature condition of the simulation is given as the decomposed temperature of the crystal structure after the temperature increases rapidly.^{11),13)} The simulation time at each temperature is about 10 ps, and the time step of simulation is 30 ps. In order to discuss the effect of the NaCl doping into CaO, one molecule of CaO in the initial CaO crystal structure is substituted by one molecule of NaCl. The MD simulations for the substituted compound are also carried out under the same MD conditions as those for the pure CaO.

The interaction energy between the atoms is modeled by the potential energy parameters developed by Kawamura.^{10),11)} The energy (E) between the i th and the j th atom is described as

$$E = \frac{Z_i Z_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8} \quad (1)$$

In this equation, the first term in the right hand side represents the Coulomb interaction, the second indicates the repulsion interaction, and the third and fourth terms indicate the van der Waals interaction between the atoms. Here, Z_i and Z_j stand for the charges of the i th and the j th atom, respectively. The distance between the i th and the j th atom is represented by r_{ij} , while A_{ij} , B_{ij} , C_{ij} and D_{ij} indicates the potential parameters between the i th and the j th atom.¹⁰⁾ As the main purpose in this study is to elucidate the effect of NaCl doping into the CaO on the crystal structure qualitatively, Kawamura's model is adopted for the MD simulation. Although the compressibility of ionic crystal evaluated by this model is relatively smaller, compared to the experimental

Fig. 1. Effect of the addition of alkali metal compounds and chlorides into the Tsukumi limestone on the desulfurization efficiency.

one,^{10),11)} the simulated lattice constant agrees well with the theoretical value. The results obtained are discussed in terms of the change of potential energy induced by the NaCl substitution. Additionally, the effects of KCl and LiCl substitutions are also studied under the same MD conditions.

3. Results and discussion

3.1 Effect of doping of alkali metal compounds into limestone on desulfurization characteristics

In order to study the effect of the presence of some alkali metal compounds in the limestone on the desulfurization characteristics, some traces of chlorides, carbonates and hydroxides are added into the limestone. The desulfurization experiments for each sample are conducted using a thermobalance. Figure 1 shows the relationship between the desulfurization efficiency and alkali metal fraction added to the Tsukumi limestone. The results show that the desulfurization efficiency enhances for all of those additives. The addition of NaCl into the limestone is the most effective agent on improving the desulfurization efficiency. The desulfurization efficiency for the limestone with 1 mass% of NaCl was almost the same as that for the wasted seashell.^{4),5)} The mean pore size of about 0.39 μm for the NaCl-doped limestone after calcination was found to be comparable to that for the calcined seashell, but for the calcined limestone without NaCl doping, the mean pore size was about 0.07 μm . In order to elucidate in detail the effect of the NaCl doping on the CaO structure, crystal structures of the calcined seashell, the limestone and the NaCl-doped limestone were analyzed by XRD. The spectra shown in Fig. 2 indicate that CaO in both the calcined seashell and the NaCl-doped limestone is well crystallized, whereas the CaO in the calcined limestone is disordered. Therefore, this result suggests that NaCl doping can contribute to the crystallization of CaO.

3.2 MD simulations on structures of CaO and NaCl-doped CaO

The experimental results for the above-mentioned indicated that NaCl doping into the limestone can enlarge the pore size inside the CaO particles to enhance the CaO crystallization. To make clear the reason for this phenomenon, the change in CaO structures induced by the NaCl doping was calculated using the MD simulations. Figure 3 shows the changes of volume (V), pressure (P) and temperature (T) for pure CaO and NaCl-doped CaO. The temperature of 6900 K corresponds to the minimum temperature for the formation of

Fig. 2. XRD spectra of the calcined particles.

Fig. 3. Changes of volume (V), pressure (P) and temperature (T) for (1) pure CaO and (2) NaCl-doped CaO.

the melted CaO structure in the present MD simulation using the Kawamura model. Although the simulated temperature is too high and not realistic, compared with the experimental

melting temperature of the CaO species, the lattice constant of the CaO crystal could be simulated correctly, as shown in our previous study.¹⁴⁾ Additionally, the Kawamura model includes all parameters for Ca, O, Na, K, Li and Cl in the potential function shown in Eq. (1). Therefore, we adopted the potential function based on Kawamura's model and qualitatively discussed the change of the CaO structure induced by NaCl doping.

As shown in Fig. 3, the changes of volume and pressure at 298 K are quite small. The calculated mean bond length between Ca and O atoms is 2.30×10^{-10} m (1×10^{-10} m = 1 Å), which is a little shorter than the theoretical length of 2.41×10^{-10} m.^{11),12)} At 6900 K (10–20 ps), the CaO structure is largely deformed due to the thermal vibrations of the Ca and O atoms, resulting in a volume expansion of 1.59 times as large as that of the initial CaO crystal structure at 298 K. The structure at the high temperature is likely to be amorphous. By annealing this amorphous structure at 298 K, the volume of CaO decreases rapidly. However, the volume of the annealed structure at 30 ps is 1.13 times as large as that of the initial crystal structure. These results suggest that the amorphous CaO structure formed at 6900 K is too largely deformed to return to its initial crystal structure. Conversely, the NaCl-doped CaO can return to the initial crystal structure since the volume at 30 ps is almost the same as that at 10 ps. This result indicates that the NaCl doping may affect the crystallization of the CaO. During the early stage of the high temperature, the volume of NaCl-doped CaO also expands to 1.35 times as large as that of the initial structure. However, the volume rapidly decreases after about 12 ps. After annealing, the volume is the same as that of the initial crystal structure at 298 K. Consequently, the NaCl-doped CaO seems to regain its initial crystal structure even after annealing. The temperature of 7100 K corresponds to the minimum temperature for the formation of melted NaCl-doped CaO structure in this simulation.

To precisely illustrate the structural changes of pure CaO and NaCl-doped CaO, 27 atoms around the doped NaCl were picked out from the CaO structures. **Figures 4(a)** and **(b)** show the structures of pure CaO and NaCl-doped CaO at 6900 K, respectively. From Fig. 4(a), it is confirmed that the CaO molecules in pure CaO scatter randomly at 6900 K. On the other hand, Fig. 4(b) shows the NaCl-doped CaO maintains the crystal-like structure even at 6900 K. Therefore, it is expected that the NaCl doping contributes to maintaining the crystal structure even at high temperatures. To elucidate the effect of NaCl doping on the crystallization, the change of the distances of the second nearest neighbor between the Ca and O atoms for pure CaO and NaCl-doped CaO at 6900 K was investigated. In **Figs. 5(a)** and **(b)**, $\text{Ca-O}(m)$ highlights the distance between the Ca and O(m) atom shown in Fig. 4. The distances of the eight second nearest Ca–O bonds are shown in these figures. Figure 5(a) shows that all Ca–O distances for pure CaO are equal before the temperature increases. As time advances, the distances of Ca–O(1), Ca–O(6) and Ca–O(8) increases suddenly, while the distance for Ca–O(5) decreases. However, for the NaCl-doped CaO, the Ca–O distances fluctuate largely at the early steps due to the NaCl doping, as shown in Fig. 5(b). Again, as time advances, the Ca–O distances converge in the region between about 4 and 5×10^{-10} m. In other words, the structure of NaCl-doped CaO transforms to an ordered structure even at 6900 K.

In order to explain the reason for this behavior, the potential energies between the Ca atom and the nearest and the second nearest atoms for the pure CaO and NaCl-doped CaO

Fig. 4. (a) Positions of Ca and O atoms for pure CaO at 6900 K and (b) positions of Ca, O, Na and Cl atoms for NaCl-doped CaO at 6900 K.

are evaluated as shown in Table 2. Generally, more negative potential energy between the atoms means more stable bonding. Comparing the results for the pure CaO with that of the NaCl-doped CaO, both the potential energies of the nearest atoms and the second nearest atoms for the NaCl-doped CaO is negatively larger than those of the pure CaO. This is caused by the difference of atomic charges between the Ca and Na and/or between O and Cl. In the NaCl-doped CaO, the Ca atom neighboring Cl has enough positive charge, since the Ca and Cl charge is +2 and -1, respectively. Therefore, the potential energy of the second nearest Ca-O in the NaCl-doped CaO becomes more negative than that in the pure CaO, as shown in Table 2. This result means that the Ca atom in the NaCl-doped CaO is more stable than that in the pure CaO.

3.3 Comparison of the structures of NaCl, KCl and LiCl-doped to CaOs

In the previous subsections of 3.1 and 3.2, it was confirmed that NaCl was an effective additive to improve the desulfurization efficiency of limestone. Furthermore, the effect of other alkali chlorides of KCl and LiCl on the desulfurization efficiency was tested to elucidate whether those compounds have a similar function to NaCl or not.

The desulfurization experiments for KCl and LiCl-doped limestone were again conducted by using a thermobalance. As shown in Fig. 1, the desulfurization efficiency for the KCl-doped limestone was much lower than that for the NaCl-doped limestone under the condition of a low addition fraction. The desulfurization efficiency became approximately 30% when 1 mass% of KCl was added into the limestone. As for the LiCl addition into the limestone, the desulfurization efficiency became about only 23% when 1 mass% of the LiCl was added into the limestone. From the results for KCl and LiCl dopings, it is concluded that the effect of these compounds on the desulfurization is much smaller than that of

Fig. 5. Changes of distances between Ca and the second nearest O atoms at 6900 K for (a) pure CaO and (b) NaCl-doped CaO.

Table 2. Interaction Energies between the Ca Atom and the Nearest and the Second Nearest Atoms for the Pure CaO and NaCl-Doped CaO

	Potential energy [eV]			
	Pure CaO		NaCl-doped CaO	
	Ca-Ox6 (the nearest atoms)	Ca-Ox8 (the second nearest atoms)	Ca-Cl+Ca-Ox5 (the nearest atoms)	Ca-Ox8 (the second nearest atoms)
6900 K	-123.11	-94.18	-128.61	-103.60

NaCl.

The MD simulations were also performed for the KCl and LiCl-doped to CaO to understand the effect of these doping on the CaO structure. Figures 6(a), (b) and (c) show the structures of the NaCl-doped CaO, the KCl-doped CaO and the LiCl-doped CaO at 7000 K, respectively. At this temperature, the crystal structure was kept in all conditions. In the KCl-doped CaO, the K and the Cl atoms are further apart from each other, as shown in Fig. 6(b). This means that the interaction energy between the K and the Cl atoms is weaker than that between the Na and the Cl atoms. As a result, the structure around the Cl atom is more deformed from the crystal structure than Fig. 6(a) for the NaCl-doped CaO. In the LiCl-doped CaO at high temperature, the Li can move freely inside the CaO crystal lattice, as shown in Fig. 6(c). This result may be due to the small ion radius (0.90×10^{-10} m) of the Li, compared with that (1.16×10^{-10} m) for the Na. Therefore, it is not expected that the LiCl doping into lime-

Fig. 6. (a) Positions of Ca, O, Na and Cl atoms for NaCl-doped CaO, (b) Positions of Ca, O, K and Cl atoms for KCl-doped CaO and (c) Positions of Ca, O, Li and Cl atoms for LiCl-doped CaO at 7000 K.

Fig. 7. Schematic picture showing the change in the pore size of pure CaO and NaCl-doped CaO.

stone can contribute to the CaO crystallization.

From the experimental and MD studies, it is confirmed that the NaCl doping into the limestone is more effective to enhance the desulfurization efficiency than those of KCl and LiCl. Among the Na, K and Li ions, Na is found to be the most appropriate for the substitute of Ca in a CaO crystal because the ion radius of Na is similar to that of Ca (1.14×10^{-10} m). **Figure 7** is a schematic picture showing the change of the CaO structure. The mean pore size of the calcined NaCl-doped CaO was over six times as large as that of the calcined pure CaO. This result can be attributed from the fact that NaCl-doped CaO can retain the crystal structure at the calcination temperature. As a result, the desulfurization reaction can be produced over the whole of a particle for the NaCl-doped CaO, so that the desulfurization efficiency of the NaCl-doped CaO is higher than that of the pure CaO.

4. Conclusions

The effect of the doping of alkali metal compounds (NaCl, KCl and LiCl) into limestone on the desulfurization charac-

teristics was studied by both experiments and MD simulations. The desulfurization experiments showed that the pore size of the calcined NaCl-doped limestone was almost the same as that of the calcined seashell and much larger than that of the calcined limestone without the NaCl addition. The XRD analysis indicated the CaO in both seashell and the NaCl-doped limestone was crystallized, whereas CaO in the calcined limestone was in a disordered form. The desulfurization efficiency of limestone was enhanced largely by the NaCl addition when compared to the KCl and LiCl additions.

The change of structure of the CaO induced by the NaCl, KCl and LiCl substitutions was calculated by the MD simulations based on the potential parameters developed by Kawamura. The results indicated that the addition of NaCl into the limestone was the most effective for improving the CaO crystallization. The structure of the NaCl-doped CaO was stable even at high temperatures, while the pure CaO was unstable at the same temperature. On the other hand, the KCl and LiCl dopings into the CaO had a smaller effect on the CaO crystallization than the NaCl doping. Consequently, from the results of the experiments and the MD simulations, it can be concluded that the NaCl doping into the limestone was the most effective for improving the desulfurization efficiency.

Notation

A : potential parameter
 B : potential parameter
 C : potential parameter
 D : potential parameter
 E : potential energy
 e : electron
 g : pair correlation functions
 i : number of atom
 j : number of atom
 r : interatomic distance
 Z : charge

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