제철공정의 석회석 세척 과정에서 발생하는 슬러지로부터의 탄산칼슘 합성

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Calcium Carbonate Synthesization from the Sludge Occurring at Limestone Washing Stage in Steel Making Process

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INTRODUCTION

Limestone washing process sludge generated in the process of limestone calcination is mixed sludge produced after processing sludge using drum filter, which is generated when raw limestone is washed in order to make quick lime for steel manufacture. Limestone washing process sludge has been reclaimed for a long time, but at present it is used through development and application which are fit for domestic condition and pilot test. According to the high quality standard for quick lime which is needed in calcination process of limestone, limestone washing process sludge is high quality(CaO 51%) fine particle calcite, different from general toxic sludge in inorganic system. With the exception of the problem of water containing rate (about 20~30%), limestone washing process sludge has a property of regular calcium carbonate which is processed in the physical method using raw stone, and has a value added many times as much as raw stone. Therefore in this research, the experiment was made on the various properties of limestone washing process sludge, especially on the special qualities of manufacture and hydration reaction of limestone washing process sludge.

EXPERIMENT EQUIPMENT AND METHOD

Limestone washing process sludge was not expected to change by several sample ore pickings. But second dust and mist collection sludge is expected to change into the state of quick lime, because dust and mist are collected in the entrance of calcining furnace and sludge is pyrolyzed partially due to the variable temperature of that place.

Second dust and mist collection sludge is produced at the ratio of two to eight, compared with washing process sludge, and it is so hard to pick in the process that mixed sample ore as limestone washing process sludge was used as a subject of experiment. In the case of producing quick lime by calcining limestone, there is a way to test activity that can decide if there is contaminant and reaction is excessive

or not. And in order to find calcination condition to form amount of 56% of limestone, calcination temperature, size of sample ores, and the time of calcination were changed and the changes of each weight were checked. The rate of weight decrease was checked when the diameter of limestone washing process sludge was changed to 3, 5, 8cm, the temperature to 950, 1000, 1100, 1200, 1300℃, and the time of calcination to 1, 2, 3, 4, 5hours.

The analysis of the particle size(Malvern instrument Co. master sizer MS20 zeta sizer) was conducted by picking sample ores, using X-ray power diffractometry to grasp composition minerals according to the kinds of sludge and using SEM(Philips SEM 505) to examine the qualities. In order to grasp the properties of hydration reaction, which form the basis of the grip of the qualities of basic carbonic acid system of limestone washing process sludge, quick lime powders as sample ores were produced by calcining them for 2 hours at 1200℃and by pulverizing them with pulverizer(8 inch disc-dia, 900rpm). And purchased limestone was calcined and pulverized on the same conditions to produce quick lime for steel making, in this way sample ores were made and were compared with those of limestone washing process sludge.

RESULT AND DISCUSSIONS

Mineral Composition and Pyrolysis Property

Calcite, aragonite, and vaterite are heteromorphism of main structure minerals of limestone which is produced in nature. Calcite is that Ca^{2+}ion and CO_3^{2-}ion are configurated by six oxygen ions. Mineral structure of carbonate of M^{2+} is decided by radius of cation and oxygen ion, and if it is 0.99Å and less, it belongs to calcite structure, and if it is more than that it belongs to aragonite structure. Besides calcite crystal, accompanied minerals are different respectively, which are quartz, clay minerals(kaolinite, illite), and mica(muscovite, biotite). Not only limestone washing process sludge but also second dust and mist collection sludge can not confirm the peak of contaminant minerals, and because requisites for quality are high qualities(52% CaO and more), limestone washing process sludge, produced when it is washed, is high quality(52% CaO and more) as well. In order to grasp the pyrolysis properties of limestone washing process sludge, DTA was carried out and the result is as in Fig. 1.

As a result of thermal analysis, endorthermic peak was found at around 667~773℃in the case of sample ore A which is limestone washing process sludge, and at around 676~777℃in the case of sample ore B which is second dust and mist collection sludge. Generally pyrolysis of limestone was started at around 550℃and completed at 1100℃. The reason that pyrolysis temperature of sample ore B is a little higher than that of sample of A is that second dust and mist collection sludge has accompanied minerals such as quartz compared to limestone washing process sludge.

Calcination Property

Degradation process of limestoneis consist of two steps, one step is to decide reaction rate by density and formation energy of CaO which is product from degradation formation, and the other is to decide degradation rate by discharge rate of CaO and CO_2 gas surrounding limestone which is not degraded. The degradation rate increases as the energy of degradation activation increases when the degree of

crystallization of limestone is perfect, and decreases when the degradation rate is rapid and the size of crystal particle is big. The degree of crystallization is the crystal size of calcite which is the structure minerals in the form of limestone, and it is related with calcination process and pulverization process. Crystalline structure limestone has a property to become active in the calcination process of limestone because of the number of crystal, heat conduction rate of crystal, etc., and therefore is hard to calcine and is accelerated to become active. The expense for calcination fuel of crystalline structure limestone is very heavy compared with compact structure limestone, it is not calcined in many cases, and hydration of it is not good generally. Crystalline structure limestone is not suitable for calcination, while pulverization is easy. Compact structure limestone is fit for calcination because heat conduction of it is rapid and it does not become active in calcination process.

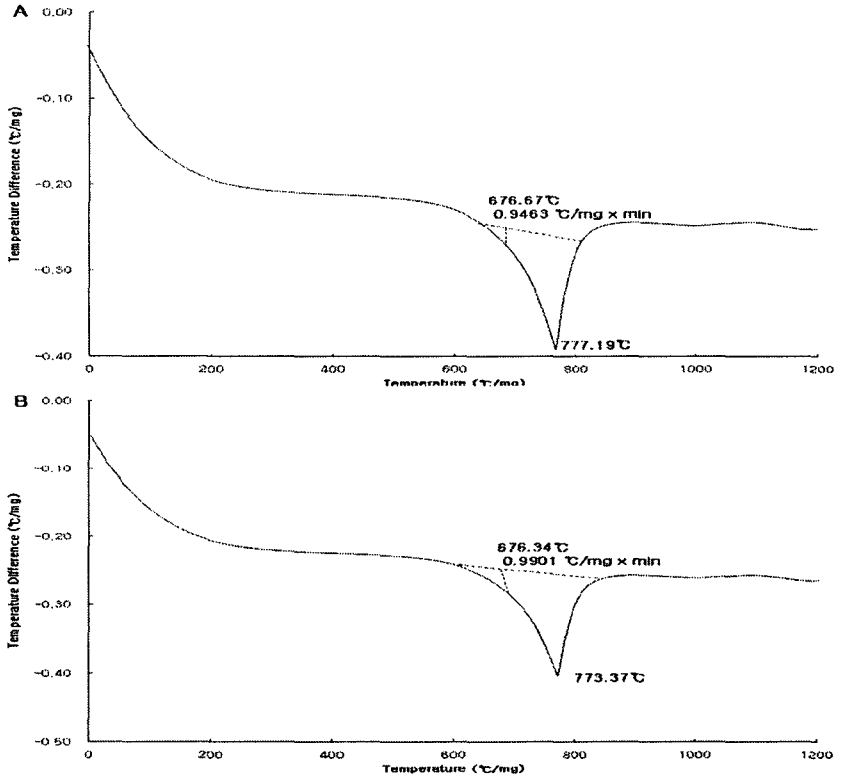

Figure 1. DTA curve of limestone washing process sludge (A-limestone washing process sludge. B-wet dust collect or sludge).

Calcite crystals have tetrahedron lattice that belongs to the hexagonal system. They discharge CO_2 and produce CaO crystal grain of unit cubic structure when it is heated, and the degradation reaction is proceeded. When heating is started after degradation, small CaO crystal grains are combined and changed into CaO crystals of three dimensional cubic structure. From this point CaO crystals grow and get compact structure by degrees.

In the case of producing quick lime by calcining limestone, there is a way to test activity that can decide

if there is contaminant and if the reaction is excessive or not. And in order to find calcination condition to form the amount of 56% of limestone, calcination temperature, size of sample ores, and the time of calcination were changed and the changes of each weight were checked. The rate of weight decrease was checked when the diameter of limestone washing process sludge was changed to 3, 5, 8cm, the temperature to 950, 1000, 1100, 1200, 1300℃, and the time of calcination to 1, 2, 3, 4, 5hours.

Hydration Reaction Property

Quick lime powders, which were produced respectively by limestone washing process sludge and natural limestone, were sample ores. In order to grasp properties of change of hydration reactor and liquid concentration, XRD and the size of particles of respective sample ores were examined according to the hydration time. As well, comparative experiment of natural limestone sample ores was made to check the relation of hydration temperature, change of liquid concentration, and the size of particle formation. Magnetic stirrer, shaking incubator, and ultrasonic vibration reactor were used as hydration reactors. The change of liquid concentration was 7wt% and it was checked as the time varies during 30 minutes. Liquid concentration was changed to 5 and 10 wt%, and the hydration reaction time was changed to 5, 10, 30 minutes in the experiment about the effect of hydration reaction time. Right after the reaction, materials of no reaction were checked by XRD through quick filtration and drying, and the examination of the range of particle size of each sample ore was carried out.

In this experiment, liquid concentration of limestone washing process sludge was changed in each hydration reactor for 5 minutes. A sudden exothermic reaction was showed in early hydration of CaO-H_2O system, and the higher the liquid concentration is the higher the reaction temperature is. Hydration was completed when the rise of temperature finished and this was regarded as the point of reaction termination. With this, it is interpreted that the equilibrium of system is maintained because hydration reaction is completed and there is no more quick lime to react.

Generally magnetic stirrer is used in the case of hydration of quick lime, so property comparison with other reaction equipments is needed. When quick lime is stirred in hydration, reaction rate increases and dispersion of particles gets better. In the case of using ultrasonic vibration reactor, hydration temperature is higher than in other reactors, and hydration reaction is not active but continuous, which differs from the fact that hydration is completed within 10 minutes in other reactors.

CONCLUSION

Experiment of the properties of calcination and hydration reaction of limestone washing process sludge and natural limestone was conducted and the conclusion is as below.

1) The mineral composition of limestone washing process sludge is calcite, but there is a chance of it mixing with slaked lime.

2) Compared with the existing hydration methods of magnetic stirrer and shaking incubator, hydration in the ultrasonic vibration reactor produced more homogeneous slacked lime powders than in any other reactors, and formed minute slaked lime powders of even grain size by uniform reaction to the whole sample ore without any violent reaction.

3) Adequate concentration of liquid to make slaked lime in ultra sonic vibration reactor was 10wt% and less.
4) Homogeneous minute powders(1~5㎛) were formed by reaction at normal temperature, because the solubility decreases as the temperature rises, and particles are formed as minute powders by hydration react at a low temperature. While, in the case of natural limestone, heterogeneous particles of 10~20㎛ were formed.

Consequently, hydration of limestone washing process sludge was done better and produced more homogeneous fine slacked lime powder than that of natural limestone. Slaked lime powders, formed from limestone washing process sludge, are very minute and have such a short hydration time that reaction finishes between early 5 minutes and 10 minutes.

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