

Utilization of Limestone Concrete Waste as Fluxing Materials of Iron Ore Sintering Process

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The effects of utilization of waste concrete as fluxing material of iron making process on amount of solid disposal, mining operation and CO₂ emission are investigated by developing a system model. It was found that the use of lime stone sand and ballast as osteodentins of concrete would be promising to reduce such environmental burdens. The experimental study was conducted to investigate the capability as fluxing agent of iron ore sintering process.

Key words: Limestone, Cement, Concrete, Iron making, Recycling

1. INTRODUCTION

The treatment of huge mass of waste concrete structure, which is made from limestone, is serious urban problem. Cement or iron and steel making produce CO₂ by calcining limestone. Furthermore, mining of limestone will not be desirable from environmental preservation point of view. Therefore, it is expected to develop new circulating use of waste concrete.

One of the possible routes is utilization of the concrete waste as fluxing materials of iron ore sintering process. Although it is anticipated that the use of ordinal waste concrete may create negative effect, because the concrete contains various oxides, as well as Ca compounds. To solve this problem, the circulating use of the limestone concrete, which is produced by limestone-sand and ballast as osteodentis, was investigated by a system model to evaluate the comprehensive effects, as well as experimentally.

2. SYSTEM MODEL

2-1. Frame work of model

As mentioned above, it is necessary to evaluate the effects of the entrained oxides in the waste concrete on the amount of solid waste disposal, mined stone and sand, and CO₂ emission associated with production of steel and cement and their.

In this work, a steady state model has been developed to calculate materials flow in a system consisted with production of concrete and steel, as shown in Fig.1. The boundary conditions are production of steel and cement, osteodentis to cement ratio, and composition of iron making slag and cement. The amounts of the limestone supply, the waste concrete and slag generation are calculated as a function of the amount of recycling waste concrete to iron making. The change in CO₂ emission in the system was calculated, as well. The estimation of CO₂ emission was made for that generated by the calcination of limestone and the consumption of fossil fuel including electric power generation for

the cement and iron making, taking the effect of slag volume on fuel rate. Those in the mining operation and transportation were not included.

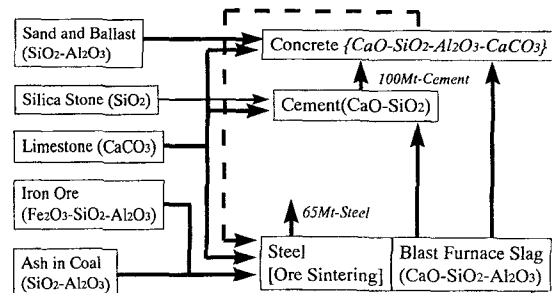


Fig.1 Schematic diagram of Calcium resource circulating use system

2-2. Model calculation result

The mined minerals, solid waste and CO₂ emission increase with the recycling of waste concrete, when ordinary sand and stones are used for concrete osteodentis, as shown in Fig.2, assuming the iron produced by blast furnace process was 65 million tons, cement production was 100 million tons, the osteodentis/cement ratio was 6.0. The entrained oxide such as SiO₂ or Al₂O₃, in the concrete requires additional CaO to maintain the slag composition constant. It leads the increase in the mass of slag and fuel consumption in iron making process.

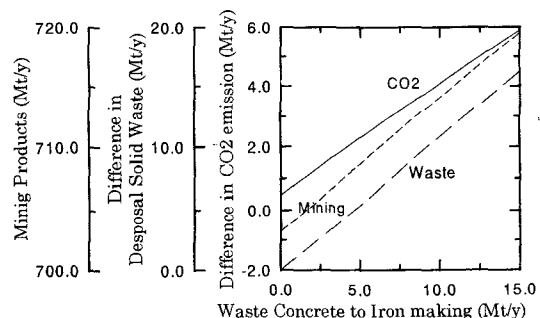


Fig.2 The effects of the ordinal concrete recycling to iron making

On the other hand, the recycling the limestone concrete to iron making process can reduce the mining and solid waste, as shown in Fig.3. Although the reduction of CO₂ emission was expected with the use of waste concrete which are containing de-carbonized calcium, slight increase in CO₂ emission is inevitable, because of the entrained oxides. It can be expected that the energy consumption and CO₂ emission associated with mining operation will be reduced significantly, but the quantitative analysis was not available in this work.

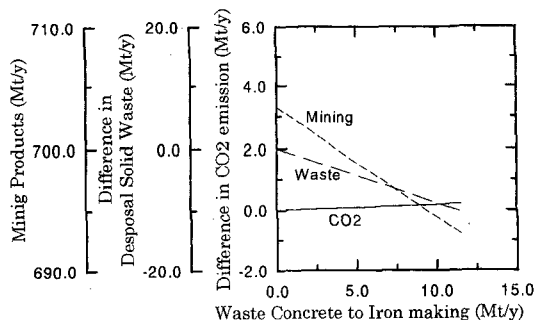


Fig.3 The effects of limestone concrete recycling to iron making

3. EXPERIMENT

Feasibility of the limestone concrete waste, which was prepared using limestone-sand and ballast as osteodentins, for iron ore sintering process as fluxing materials was fundamentally examined by thermo-gravimetric and differential thermal analysis (TG-DTA).

3. 1. Sample Preparation

Two kind of limestone concrete (A and B) were prepared by varying the ratios of limestone sand (-5mm in particle size), limestone ballast (10 to 20mm), portland cement. The mixing ratios of [limestone sand : limestone ballast : portland cement] in mass basis are [1.5 : 3.0 : 0.5] and [1.0 : 2.0 : 0.5] for concrete A and B, respectively. These materials were mixed well with adding water and left to harden for several days. The concrete were crushed to have particle size smaller than 10mm. Practical limestone (-3.0 mm) for iron making was also used for comparison. Chemical composition of these samples are listed in Table I. Although Al₂O₃ content of the concrete A and B is slightly higher than the limestone, large differences in chemical composition are not found between the concrete and limestone. Chemical composition of two kinds of iron ores used for experiments are listed in Table II. Ore C is hard hematite ore from Brazil and R is pisolitic goethite ore from Australia. Both ores are typical iron ores currently used in the Japanese steel industry. These materials are subjected to further crushing by a blade mill and sieved into particle

ranges: -0.25, 0.25-0.50, 0.50-1.00, 1.00-1.20, and +1.20mm.

Table I Chemical composition of limestone and concretes (mass%) LOI: Loss On Ignition

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	LOI
limestone	54.27	2.21	0.30	0.79	0.46	41.20
Concrete A	53.58	2.26	0.75	0.33	1.20	40.76
Concrete B	55.29	2.01	0.58	0.33	1.29	39.57

Table II Chemical composition of Iron ores (mass%)

	T-Fe	CaO	SiO ₂	Al ₂ O ₃	LOI
Ore C	67.4	0.01	0.06	0.94	1.54
Ore R	57.9	0.04	5.46	2.63	7.96

3. 2. TG-DTA

Pure-dense alumina pans of 4mm inside diameter and 5mm height was used in the experiments. Sample mass was 10mg for the individual measurement of the concrete or limestone sample, and 35mg for their mixture sample with the ores. The mixture samples are prepared by well mixing the ore and the fluxing material with the addition of ethanol and then dries completely. The CaO concentration of the mixture is set as 20mass% on the basis after calcination. Weigh out 35mg of the sample and is press-shaped into a disk of 3.8mm diameter and about 1mm thickness. Reference material was α -Al₂O₃ and heating rate was fixed as 20K/min

3. 3. Individual Sample Analysis

Figs. 4 to 6 show TG curves obtained for the limestone, concrete A and B, respectively, with different particle size ranges, i.e., -0.25, 0.5-1.00 and 1.00-1.20mm. For samples of -0.25mm, shown in Fig.4, masses of the concrete samples gradually decreases from 373 to 873K. The changes are comparably significant at about 710K and these can be ascribed to the decomposition of hydroxyl group (dehydration) in the cement. Decreasing rate of masses from 980 to 1100K, attributed to decomposition of CaCO₃, are almost same for all the samples. However, the order of decreased mass is limestone > concrete A > concrete B. The concrete and limestone samples give similar TG curves, as shown in Fig. 6. This phenomena suggests that cement components tend to be concentrated in the fine particles after crushing.

DTA curves are shown in Figs. 7 to 9. Endothermic peaks at about 710K are observed for -0.25mm samples of the concrete A and B, which are observed as mass decreases in their TG curves. Endothermic peaks of the concrete A and B at about 1100K attributed to the decomposition of CaCO₃ is comparably smaller than the limestone. The peaks at 710K almost disappear for the samples of 0.50-1.00mm, as

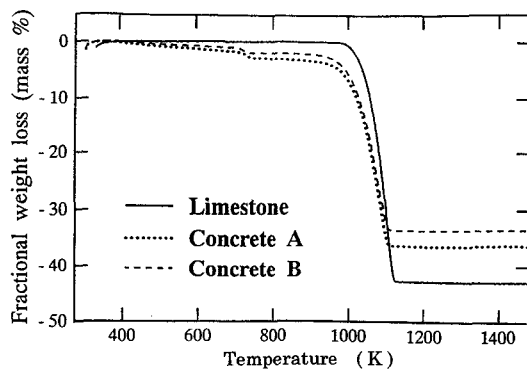


Fig. 4 TG curves of limestone and concretes A and B during heating (Particle size: -0.25mm, in Ar)

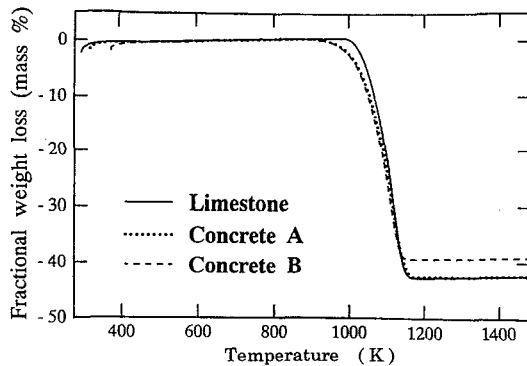


Fig. 5 TG curve of limestone and concretes A & B during heating (Particle size 0.50-1.00 mm, in Ar)

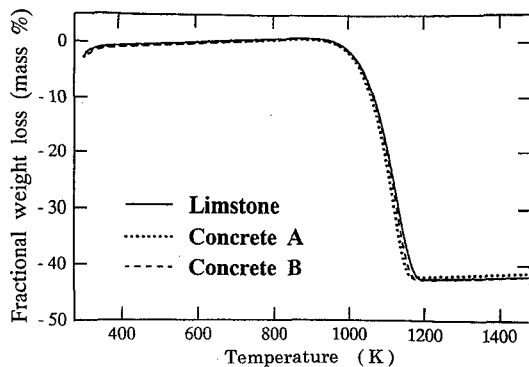


Fig. 6 TG curve of limestone and concretes A & B during heating (Particle size 1.00-1.20 mm, in Ar)

shown in Fig. 8, and the peaks of CaCO_3 decomposition become broad with increase in the particle size.

The thermal analyses above gives a result that there is no difference of the concrete samples and limestone having particle size over 0.5 mm.

3. 4. Analyses for Samples Mixed with Iron Ore

3. 4. 1 The Case of Ore C

DTA curves obtained for -0.25 mm samples are shown in Fig. 10. A sharp endothermic peaks at about 1470K is caused by the melting and are agreed well with the eutectic temperature (1478K) of mono-calciumferrite and hemi-calciumferrite in the binary system of $\text{CaO-Fe}_2\text{O}_3$. No big differences can be observed in the curves

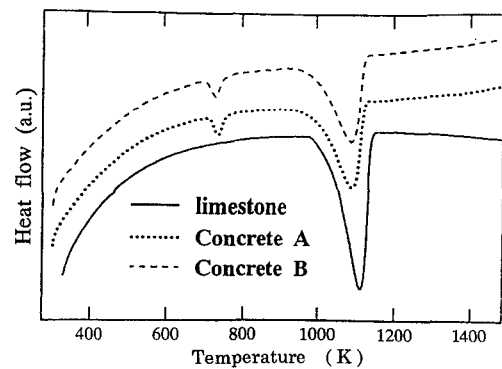


Fig. 7 DTA curves of limestone and concretes A & B during heating (Particle size: -0.25mm, in Ar)

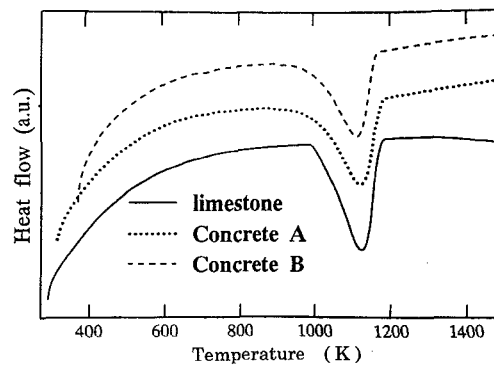


Fig. 8 DTA curves of limestone and concretes A & B during heating (Particle size: 0.50-1.00mm, in Ar)

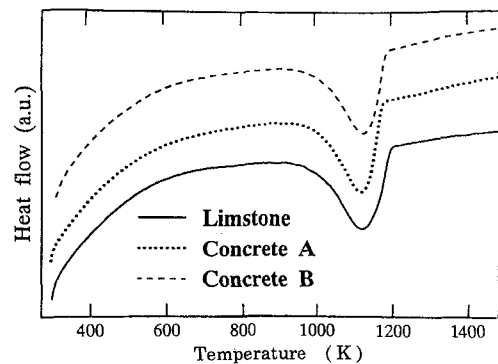


Fig. 9 DTA curves of limestone and concretes A & B during heating (Particle size: 1.00-1.20mm, in Ar)

except for small endothermic peaks at 710 to 730K attributed to dehydration of cement components in the concrete samples. DTA curves obtained for 0.50-1.00mm samples are shown in Fig. 11. Although the endothermic peak of melting for the limestone is comparably broader, all the samples give higher melting temperatures by about 20K. This implies that the rate of reaction between the ore and limestone decreases.

3. 4. 2 The Case of Ore R

DTA curves obtained for -0.25mm and 0.50-1.00 mm samples are shown in Figs. 12 and 13, respectively. The endothermic peaks ascribed to melting are different between the concrete and

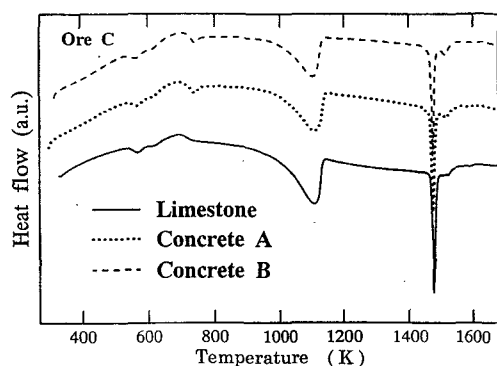


Fig.10 DTA curves of mixtures of ore C and different lime sources during heating (particle size of ore C: -0.25mm, lime sources -0.25m)

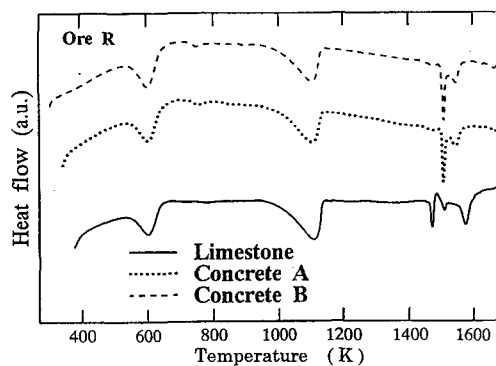


Fig.12 DTA curves of mixtures of ore R and different lime sources during heating (particle size of ore R: -0.25mm, lime sources -0.25m)

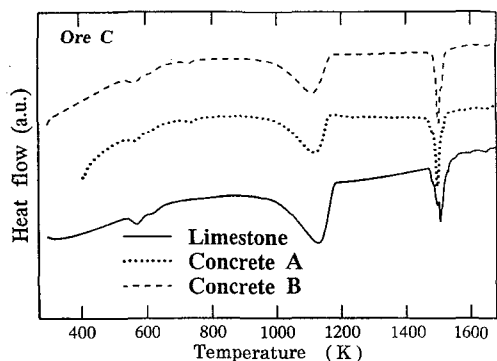


Fig.11 DTA curves of mixtures of ore C and different lime sources during heating (particle size of ore C: 0.50-1.00mm, lime sources 0.50-1.00m)

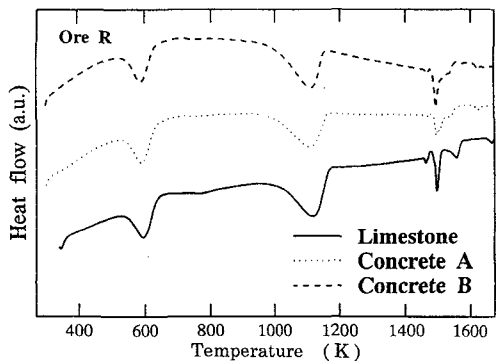


Fig.13 DTA curves of mixtures of ore R and different lime sources during heating (particle size of ore R: 0.50-1.00mm, lime sources 0.50-1.00m)

limestone samples of finer particle size. The shape of peak become resemble each other with increase in particle size, but there is still remarkable difference for 0.50–1.00mm samples. Ore R shows considerably higher gangue contents such as Al_2O_3 and SiO_2 , comparing to ore C (see Table 2). These can result in an increase in the stability of calciumferrite (CF) phase formed during heating, and therefore a rising in the incongruent melting temperature of CF. This is a reason of the differences in the DTA curves between the cases using ores C and R. Although further detailed examination is necessary to clarify the minerals formation and their melting behavior, significant negative effect does not appears in the melt formation process by the use of the concrete samples.

3. 5. Discussions and Conclusions

The thermal properties of the concrete samples are quite similar to that of the limestone for ironmaking except for endothermic peaks found in the -0.25 mm concrete samples at the lower temperature (about 710K) ascribed to dehydration of portland cement components. This is caused by the segregation of the cement components to finer particle sizes in a crushing process. However, such segregation of lime components having hydroxyl groups does not

seem to lead any serious problems in the iron ore sintering process. Considering the fact that slacked lime is sometimes used as a binder for raw materials in the sintering process, this will rather give merits such as improvement of the granulation performance.

On the reaction with ore s and melting properties, the concrete samples are similar to the limestone sample for ore C which is of a hematite with a high iron grade. On the contrary, significant difference was found for ore R which is of goethite containing relatively high SiO_2 and Al_2O_3 , especially when using the finer particles size. This appears to be caused by the difference of reaction behavior before melting. However, since the melting temperature ranges for the concrete samples are limited comparing to the limestone sample, it is possible to bring about a better performance in the sintering process in terms of rapid melt-formation and particles rearrangement in the bed.

4. CONCLUSION

It as proved that the recycling of limestone concrete to iron ore sintering process is beneficial to reduce solid waste disposal, mining of limestone, and CO_2 emission. It was proved that there is no negative effect for melting phenomena in iron ore sintering by TG-DTA.