

REDUCTION OF CO₂ EMISSION FROM CEMENT MANUFACTURING PROCESS BY PARTLY SUBSTITUTING SILICATE FOR LIMESTONE

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ABSTRACT

The cement manufacturing industry is one of the major energy intensive industries, and furthermore, plenty amount of carbon dioxide is released from the calcination of limestone, CaCO₃. In Japan, four percent of total carbon dioxide emission is come from cement manufacturing plants. In the previous study, the possibilities of utilization of weathering of alkaline or alkaline earth silicate rocks were demonstrated as a measure for carbon dioxide problem. The amount of the silicate resources was also discussed that silicates are abundant in the crust. In the present paper, the possibilities of utilization of calcium silicate rocks, wollastonite, CaSiO₃ as a substitute for limestone in cement manufacturing plants are discussed.

First of all, the maximum amount of wollastonite substitutively used was determined to be 440 kg and reduced amount of limestone to be 365 kg (30%) for 1 ton production of cement clinker, by adjusting the amounts of main components of cement product from wollastonite with JIS (Japan Industrial Standard). In case of the cement from wollastonite, most of the silica, ca. 220 kg/t-cement was supplied from wollastonite. In the course of evaluation, silica from coal ash was not taken into account. Thus the carbon dioxide from limestone calcination was reduced by 150 kg/t-cement (30%), from 510 to 360 kg/t-cement.

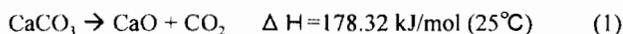
Secondly the process heat balance was evaluated. Necessary amount of process heat is to be supplied from coal combustion. It was also assumed that the coal contained no ash. In the standard cement manufacturing process, the heat for limestone calcination is necessary in addition to the heat for temperature increase from room temperature to flue gas temperature of 359°C or clinker temperature of 1450°C. The reaction heat from wollastonite to clinker is thought to be small because of similar chemical structure to each other. Thus the calcination heat is reduced in case of the cement production using wollastonite, leading to the reduction of amount of coal needed. The reduction of carbon dioxide emission also reduces the sensible heat of gas. Thus the carbon dioxide emission is further reduced by more than 40 kg/t-cement.

Totally, the carbon dioxide from the cement process was reduced by 190 kg/t-cement (24%) at least from 800 to 610 kg/t-cement by substituting wollastonite for 30% of limestone.

Finally, the quality of the produced cement from wollastonite was experimentally evaluated. In the most of analytical results, no remarkable difference was observed between wollastonite substituted alternative cement and conventional cement. Rather, the strength test, texture analysis and free lime analysis for the wollastonite substitute showed better results than the conventional sample. The present results indicated that the sufficient clinker formation reaction is expected even when wollastonite is partly substituted for limestone.

INTRODUCTION

The cement manufacturing industry is one of the major energy intensive industries. In Japan, four percent of total carbon dioxide emission is attributed to the cement manufacturing plants. The calcination reaction of limestone, CaCO₃ given as follows,



releases large amounts of carbon dioxide chemically, and furthermore, this reaction requires appreciable amounts of energy, which also contributes the release of carbon dioxide. In the cement manufacture process, the following clinker formation reaction takes place immediately after the above.



The formed clinker is a kind of silicates.

In the previous study, the possibilities of utilization of weathering of alkaline or alkaline earth silicate rocks were demonstrated as a measure for carbon dioxide problem. In this case, bicarbonate ion is produced from silicate, carbon

dioxide and water. The amount of the silicate resources was also discussed that silicates are abundant in the crust [1]. In other researches[2, 3], the possibilities of carbon dioxide fixation in the form of the carbonates with silicates were discussed.

This process [2, 3] is thought to be the reverse process of the above cement formation reaction. Thus the possibilities of utilization of calcium silicate rocks, wollastonite, CaSiO_3 and other substitutes for limestone are suggested for the mitigation of carbon dioxide release in the cement manufacturing plants. If it is realized, the carbon dioxide emission will be reduced. In the present study, wollastonite was used as a substitute of limestone. From the material balance, maximum content of wollastonite was determined and reduction effect of carbon dioxide emission by its substitution were evaluated from mass and energy balances. Furthermore, the quality of the alternative cement product (obtained by partly substituting wollastonite for limestone) was evaluated experimentally.

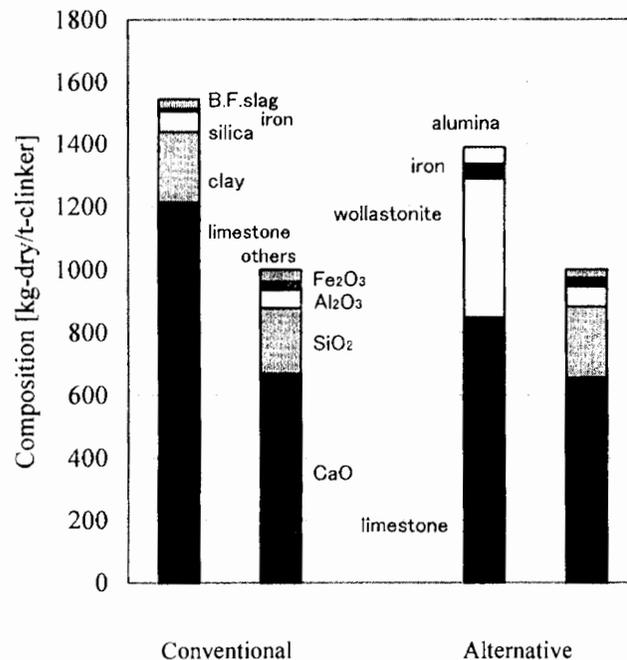


Fig. 1 Blending ratio of raw materials (left bar) and expected chemical contents (right bar) of 1t clinker

MATERIAL BALANCE

Raw Materials and Product Composition

In the conventional Portland cement process, first of all, cement clinker, the main chemical species of which is calcium silicate, is produced from limestone and silica, and then it is pulverized with small amount of gypsum added to get final cement product. In the present study, first of all, we mixed raw materials in order to get the similar chemical composition to the conventional cement clinker. Experimentally, we prepare the raw materials in two ways; from only conventional raw materials and from those with maximum content of wollastonite substitutively used. Conventional blending ratio for Portland cement clinker, are shown in Fig. 1. Standard raw materials are limestone, clay, silica sand, iron source and blast furnace slag, used in the commercial plants of Mitsubishi Material Co. Ltd. Wollastonite, containing CaO , 45.06%; SiO_2 , 46.83%; Al_2O_3 , 0.36%; Fe_2O_3 , 0.30%; others, 1.58% with ignition loss of 5.87% was supplied from Yoshioka Co. Pure alumina (aluminum oxide, >99.9%) was also used to adjust the alumina content in the alternative cement clinker production. In the course of evaluation, silica and other minor components in the coal ash from coal which is used for process heat were not taken into account.

First, the maximum content of wollastonite was determined from silica content in wollastonite and chemical content of silica in the conventional cement clinker. The shortage in iron content in expected alternative cement clinker was supplied from standard raw materials of iron source. The shortage in aluminum content was supplied from pure aluminum oxides. The calculated blending ratio for alternative cement clinker is also shown in Fig. 1. The expected chemical contents of clinkers are also shown in Fig. 1 for both of the conventional and alternative cement clinkers.

It can be seen that the expected chemical content in the alternative cement is roughly same as that in the conventional

cement clinker, though some more better blending ratios may exist. It was determined that the maximum amount of wollastonite substitutively used is 440 kg and reduced amount of limestone is 365 kg (30.1%) for 1 t production of cement clinker, by adjusting the amounts of main components of cement product from wollastonite under JIS (Japan Industrial Standard)[4]. In case of the alternative cement from wollastonite, most of the silica, ca. 220 kg/t-clinker was supplied from the wollastonite.

Reduction in Carbon Dioxide Emission from Calcination

The carbon dioxide from limestone calcination is evaluated under the assumption that 44.01g of carbon dioxide is released with 56.08g of CaO from the limestone, though small error may occur by the small content of CaCO₃ in other raw materials. Taking the CaO content of 53.6 % in the employed limestone into account, the carbon dioxide emission was evaluated to be reduced by 153.5 kg/t-cement (30.1 %), from 509.8 kg /t (=11.58 kmol/t) for conventional cement to 356.3 kg/t (=8.10 kmol/t) for alternative one.

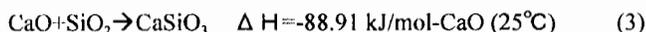
PROCESS HEAT BALANCE

Outline of the Process

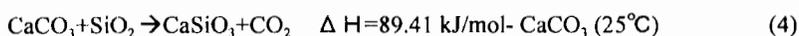
Secondly the process heat balance was evaluated. Necessary amount of process heat is to be supplied from coal combustion. It was also assumed that the coal contained no ash. In the standard cement manufacturing process, the heat for reaction including limestone calcination is necessary in addition to the heat for temperature increase from room temperature to flue gas temperature of 359°C or clinker temperature of 1450 °C. The reaction heat from wollastonite to clinker is thought to be small because of similar chemical structure to each other, and furthermore, the heat is equivalent between conventional and alternative processes. Thus the calcination heat is reduced in case of the cement production using wollastonite, leading to the reduction of amount of coal needed. The reduction of carbon dioxide also reduces the sensible heat of gas.

Heat for Clinker Formation

Heat for clinker formation is evaluated as follows. The reaction heat (or enthalpy change) of the clinker formation at 25°C was assumed to be expressed by

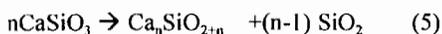


Thus the total reaction heat is evaluated as



Thus the heat to be input for the clinker formation is reduced by 311 MJ/t (30.1 % from 1035 MJ/t to 724 MJ/t for 1 t clinker formation.

In the present evaluation, the reaction heats from CaSiO₃ to Ca_nSiO_{2+n} and other minor reactions, and heat loss from the reactor were not evaluated. Taking the intrinsic composition of clinker, Ca_nSiO_{2+n} into account, the following hypothetical reaction can be considered.



Though the value of ΔH is thought to be positive and additional heat is necessary, this value is thought to be equivalent between conventional and alternative processes and was not considered further, as well as the heat loss from the reactor.

Reduction in Carbon Dioxide Emission from Coal Combustion

The coal composition (without ash) was assumed to be C:72, H:6, O:16, H₂O:6 wt%. The higher heating value was assumed to be 30 MJ/kg-wet. The ΔH of H₂O (from water to steam), CO₂, N₂ from 25°C to 359°C are 55.73, 14.36 and 9.90 kJ/mol respectively. The ΔH of clinker from 25°C to 1450°C was assumed to be 1480 MJ/t taking the heat capacity of CaSiO₃ into account. The air composition was assumed to be N₂:80, O₂:20 mol% and air ratio to be 1.0. From 1 kg of coal burnt, 60 mol of CO₂, 33.3 mol of steam and 280 mol of N₂ are released. Thus the process heat balance in MJ/t-clinker is expressed as follows, when y kg of coal is burnt.

	H ₂ O	CO ₂	N ₂	clinker	reaction	combustion
Conventional;	(55.73)(0.0333y)	+(14.36)(0.060y+11.58)	+(9.90)(0.280y)	+1480	+1035	= 30y
Alternative	;	(55.73)(0.0333y)	+(14.36)(0.060y+8.10)	+(9.90)(0.280y)	+1480	+ 724 = 30y

The resulting amount of coal for alternative process was 94.67kg, reduced by 14.73 kg (13.5%) from 109.40 kg for conventional process. The release of carbon dioxide from coal combustion was also reduced by 38.9 kg (13.5%) from 288.8 kg to 249.9 kg by partly substituting wollastonite for limestone.

Total Reduction in Carbon Dioxide Emission

Finally, the total carbon dioxide emission, the sum of emission from limestone calcination and coal combustion, was evaluated to be reduced by 192.4 kg (24.1 %) from 798.6 kg to 606.2 kg for 1t of cement clinker production by substituting wollastonite for 30.0 % of limestone. This reducible amount corresponds to ca. one % of total emission of carbon dioxide.

QUALITY OF THE PRODUCT -EXPERIMENTAL

Procedures

Next, the quality of the produced cement from wollastonite was experimentally evaluated in comparison with that from standard raw materials, and for some test, with that from commercial plants of Mitsubishi Materials Co. Ltd. The raw materials (<1.2 mm), dried at 100 °C for 24 hr, in Fig. 1 for 1 kg of clinker formation were weighed, were mixed for 30 min and the resulting mixture was crashed into fine powder (more than 90% is <0.09 mm). From the resulting fine powder, a part of 100g was weighed and was mixed with 20g of diluted sulfuric acid solution to have 0.55 g of SO₃ in the mixture, and then pressed. A two cm cubic sample was cut and was dried at 110 °C for 20hr. The dried sample was heated at 1000°C for 90 min and then at 1450°C for 90 min. The produced clinker was rapidly cooled down with air to ca. 800°C within 15 min, and then gradually cooled down to the room temperature.

After crushing the produced clinker into <3.4 mm, gypsum dihydrate (<1.2 mm) dried at 40°C for 24 hr was added to have 1.7 wt% of SO₃, and then the mixture was pulverized again to get fine powder cement sample.

Properties of Cement Clinker

All measurements were conducted based on the standard method for cement test. The free-lime (free-calcium oxide) content was measured to examine the progress of clinker formation reaction [5]. SO₃ contents [6] was measured to determine the amount of gypsum to be added. Particle diameter distribution was measured to confirm the negligible difference among the samples by laser diffraction method. Their crystal structure was measured by X-ray diffraction method.

The texture structure of the clinker was observed as follows. The crushed clinker sample was placed in a greased vessel and epoxy resin was filled and cured. After 24 h, the sample was pull out from the vessel, cut with a diamond cutter at the center, and the cross section was polished. The polished surface was treated with acetic acid for five s to get pink color. The surface was observed with a microscope. The compression strength were tested according to JIS[7].

QUALITY OF THE PRODUCT -RESULTS

Particle Diameter

The obtained median particle diameter of alternative cement clinker was 14.8 μm, which is very close to the that for conventional one of 15.1 μm. There was not so obvious difference in particle diameter distribution curve, either.

X-ray Diffraction

From the results of the X-ray diffraction analysis, no remarkable difference was observed between alternative (wollastonite substituted) cement clinker and conventional one. It was found that main crystals were calcium silicates, Ca₃SiO₅ with Ca₂SiO₄ for both.

Chemical Analyses and Texture Analysis by Microscopic Observation

The results on free-lime content and SO₃ contents in both clinkers are shown in Table 1. It is well known that the free lime is the residue which did not reacted with silica. From in Table 1, it was demonstrated that alternative clinker had less free CaO, which indicates the further progress of the clinker formation reaction for the alternative clinker than that of conventional one, though the value for the conventional one satisfied the standard.

The progress of the clinker formation for the alternative cement clinker was also confirmed by the microscopic observation. In case of alternative cement clinker, no obvious free lime was found while small amount of free lime was found for the conventional clinker.

Table 1 Results on chemical analyses of conventional and alternative cement clinkers

Residue [wt%]	Conventional cement clinker	Alternative cement clinker
CaO	0.77	0.20
SO ₃	0.57	0.70

Compression Strength

Finally the results on the compression strength test of the alternative and conventional cements are shown in Table 2. The commercial cement is that produced in the commercial process from the same raw materials as for conventional cement. It was observed that the properties of alternative cement was vary close to the others, or it showed rather larger strength for the results of 28 days.

Table 2 Results on compression strength test for cements

	Compression strength [N/mm ²]		
	3 days	7 days	28days
Alternative	22.9	40.6	63.7
Conventional	23.4	39.5	59.3
Commercial	26.1	41.4	59.8
JIS standard	>12.5	>22.5	>42.5

DISCUSSION

In the present study, wollastonite was used as a representative of calcium silicates. Though silicates are very abundant on the earth, pure wollastonite may not be so abundant. We might consider the use of other silicates as an alternative raw material, where the reduction efficiency may be less than the present evaluation. On the other hand, it is well known that blast furnace slag has already used as a raw materials of cement production process. The blast furnace slag has good properties comparable to wollastonite from the view point of the efficiency in the reduction of carbon dioxide emission. It should be stressed that the blast furnace slag should be recycled into cement production process from the view points of the mitigation of carbon dioxide problem, even if it costs much.

The weathering of alkaline rocks, such as alkaline or alkaline earth silicate is thought to have played a great role in the historical reduction in the atmospheric carbon dioxide of this planet. The initial carbon dioxide pressure on the planet is thought to have been several tens atm, but recently, it is less than several hundreds ppm. After the weathering reaction the formed bicarbonate ion is converted into the carbonates such as limestone. In the course of the process one mol of carbon dioxide is incorporated in the limestone with silicate consumption. Thus, the silicates are thought to be more alkaline than carbonates. To utilize the weathering process artificially, the most important factor is its rate. Here, limestone is often used for acidic gas treatment such as sulfur dioxide and hydrogen chloride removal. In these flue gas treatment processes, carbon dioxide is also emitted. It may possible to substitute silicates for limestone in these processes, though some kinetic evaluation is also essential. Furthermore, substitution with silicates for sodium hydroxide will also contribute the reduction in carbon dioxide emission because sodium hydroxide is produced using much electricity and it can be easily used for absorption of carbon dioxide, if necessary.

It can be suggested that there may be various possibilities to reduce carbon dioxide emission not by direct recovery but by indirect substitution of alkaline materials in carbon dioxide emission processes with alkaline or alkaline earth silicate.

CONCLUSION

The possibilities of utilization of a calcium silicate rock, wollastonite, CaSiO₃, as a substitute for limestone in cement manufacturing plants are discussed. First of all, the maximum amount of wollastonite substitutively used was determined to be 440 kg from silica content in wollastonite and chemical content of silica in the conventional cement clinker. The reduction in carbon dioxide emission was evaluated to be reduced by 153.5 kg/t-cement from 509.8 kg/t (=11.58 kmol/t) to 356.3 kg/t (=8.10 kmol/t)

Secondly the process heat balance was evaluated. Necessary amount of process heat is to be supplied from coal combustion. The resulting amount of coal for alternative process was 94.67kg, reduced by 14.73 kg (13.5%) from

109.40 kg for conventional process. The release of carbon dioxide from coal combustion was also reduced by 38.9 kg (13.5%) from 288.8 kg to 249.9 kg by partly substituting wollastonite for limestone.

Totally, the carbon dioxide emission, the sum of emission from limestone calcination and coal combustion, is evaluated to be reduced by 192.4 kg (24.1 %) from 798.6 kg to 606.2 kg for 1t of cement clinker production by substituting wollastonite for 30 % of limestone. This reducible amount corresponds to ca. one % of total emission of carbon dioxide.

Next, the quality of the produced cement from wollastonite was experimentally evaluated based on the standard method for cement test. In the most of results of analyses, no remarkable difference was observed between wollastonite substituted alternative cement and conventional cement. It was found that main crystals were calcium silicates, Ca_3SiO_5 with Ca_2SiO_4 for both, by the X-ray diffraction analysis. It was demonstrated that alternative clinker had less free CaO, which indicates the further progress of the clinker formation reaction for the alternative clinker than for conventional one. The progress of the clinker formation for the alternative cement clinker was also confirmed by the microscopic observation. In addition, it showed rather larger strength for the results of 28 days. The present results indicate that the sufficient clinker formation reaction is expected even when wollastonite is partly substituted for limestone.

Finally it was concluded in the discussion section that there are other possible alternative resources such as blast furnace slag than wollastonite, and that there are various possibilities to reduce carbon dioxide emission not by direct recovery but by indirect substitution with alkaline or alkaline earth silicate rocks.

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