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Development of Rapid Curing Process of Reactive Coke Agglomerate

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We commercialized Reactive Coke Agglomerate (RCA), a cement-bonded pellet to decrease the thermal reserve zone temperature for the reduction of the reducing agent rate of blast furnaces. To achieve a high productivity of supplying RCA to large blast furnaces, a rapid curing process of RCA using steam was investigated. We obtained rapid curing of RCA within 18 h by combining primary curing for 12 h and stream curing at 80°C for 5 h subsequently with drying for 1 h. This combination provided sufficient strength to an RCA product when compared with the strength obtained after conventional yard curing, which requires a long curing time of 14 days. Plant trials revealed that a longer primary curing time was required because of the non-homogeneity of thermal conditions. Nevertheless, the curing period could be shortened by 12.5 days with drying and 9 days without drying. Mineralogy and morphology of hardened cement in RCA after rapid curing were investigated. XRD and thermal analysis revealed that the basic mineral composition of cement after rapid curing was comparable with that after conventional yard curing. In plant tests, during rapid curing, hydration and microstructural evolution of cement in RCA were accelerated by steam curing. RCA involving the steam curing process has been implemented in Oita works and it has been helping in a stable operation of two large blast furnaces under a low RAR.

KEY WORDS: cold-bonded pellet; Portland cement; steam curing; crushing strength; hydration; hardening; agglomeration; blast furnace.

1. Introduction

The thermal reserve zone temperature is a factor that controls the reaction efficiency of a blast furnace. Recently, a reduction of the thermal reserve zone temperature has been attempted to achieve an operation with a low reducing agent rate (RAR).[1)] The enhancement of coke reactivity is one effective measure for the reduction of this temperature.[2)] Another measure is a close arrangement between iron ores and carbonaceous materials because of their rapid gasification by a coupling mechanism.[3)] A previous study has developed a new cement (cold) - bonded agglomerate containing carbon above 20 mass%, called Reactive Coke Agglomerate (RCA), for a high reaction rate and a low RAR operation and reported the reduction of the thermal reserve zone temperature in plant tests.[4)]

With regard to the application of cement bonding to burden materials for blast furnaces, many techniques of manufacturing in commercial operation were reported.[5)] Moreover, the influences of these materials on blast furnace operation were reported.[6–10)] In general, cement- bonding agglomerates require a curing period of a few weeks to obtain sufficient strength by the hardening of cement. There are many curing processes such as yard curing,[11,12)] primary curing using storage bins,[13)] autoclave curing under high temperature and high pressure,[14,15)] and high temperature curing in chambers.[16,17)]

Yard curing is the simplest process but requires a large area of a yard, and the autoclave and curing chambers have a limitation of productivity.

A new curing process with a high production capacity is required for RCA production to satisfy a sufficient supplying amount of RCA to a blast furnace because the volume of the blast furnace tends to be enlarged. Hence, a rapid curing process of RCA has been investigated. Steam was selected as the thermal media because steel works generate a large amount of steam. Atmospheric steam curing is widely used to achieve rapid hardening in concrete manufacturing. Furthermore, steam aging and autoclave aging of covert slag are commercialized.[18,19)] However, the information of the continuous rapid curing process using steam for cement-bonded pellet is limited. An example of the commercialization of a material for an electric furnace for silico-manganese production is only reported.[20,21)]

This study provides results of the rapid curing tests in RCA production involving small-scale batch tests, continuous rapid curing tests and plant steam curing tests.

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2. Experimental Procedure

2.1. Small-scale Batch Test

To obtain fundamental parameters such as the holding time and the temperature during the curing of RCA, small-scale batch tests were performed using a single lot of RCA to minimize data dispersion. **Figure 1** shows a schematic of the test procedure.

Crushing strengths of RCA before and after curing were measured on the basis of JIS M8718 except measured numbers of pellet. In this study, an average value of 10 pellets after eliminating the minimum and maximum values in the measurement of 12 pellets was estimated as the crushing strength.

Raw materials and 10 mass% high-early-strength Portland cement (HPC, JIS R5210) were mixed and pelletized using a small drum pelletizer to form RCA. Both T.C and T.Fe of RCA were 30.4 mass%. Mean particle size of RCA was 13.0 mm, ranging between 11 to 15 mm. 50 particles of RCA with approximately 150 g were subjected to each curing condition.

Base pattern of curing has three steps: primary curing, curing at high temperatures, and subsequent drying, referring to previous studies.[20,21] The holding time and the temperature in individual steps were varied as shown in **Fig. 2**. Results of preliminary tests indicated the significant influence of the holding time after pelletizing before curing on the crushing strength of an RCA product after drying. Therefore, the holding time was maintained within 1 h in all tests.

2.2. Continuous Rapid Curing Test

Figure 3 shows a schematic of the test apparatus for the continuous rapid curing process. The apparatus comprised a curing room, a blower having 0.4 Nm^3/min flow rate at the maximum value, a hot-air generator having 250°C at the maximum value, and a boiler. The curing room had 13 cm inner diameter and 3 300 cm^3 volume; thus, the room can cure 1.5 kg of RCA at each test. The curing room and steaming pipes were covered by a heater to maintain the temperature between 80°C and 100°C to prevent the condensation of moisture during the tests. In primary curing, RCA was charged in a sealed container and heated at 50°C in a heating chamber similarly to small-scale batch tests. Thereafter, RCA was moved to the curing room to start steam curing and subsequent drying. In steam curing, the supplying amount of steam was controlled to maintain saturated water vapor in the curing room at high temperatures. The drying process using cold air was performed for 2 h to attain a sufficient drying condition of RCA bulk layers. Gas flow rate during the steaming and drying steps was maintained at 0.08 Nm^3/min, equivalently at 0.10 Nm/s in a superficial gas velocity.

Table 1 shows the chemical composition of RCA used in the continuous rapid curing tests. RCA having a mean diameter of 12.4 mm (ranging between 11.2 and 15.3 mm), weight of 1.2 wet-kg, moisture of 12.4%, and bulk density of 1.48 wet-g/cm^3, was used.

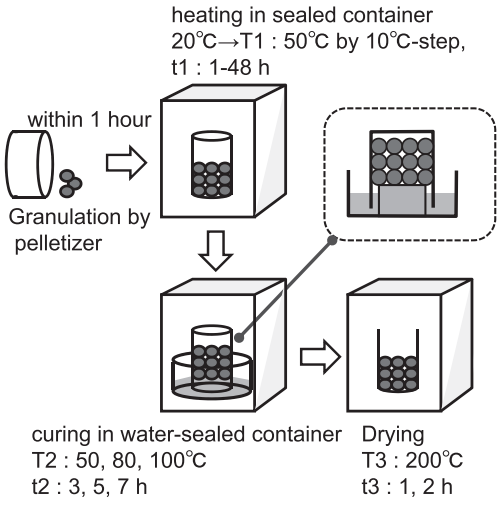

Fig. 1. Batch test procedure of rapid curing of RCA.

2.3. Plant Trial

Plant trials of the rapid curing of RCA were performed.

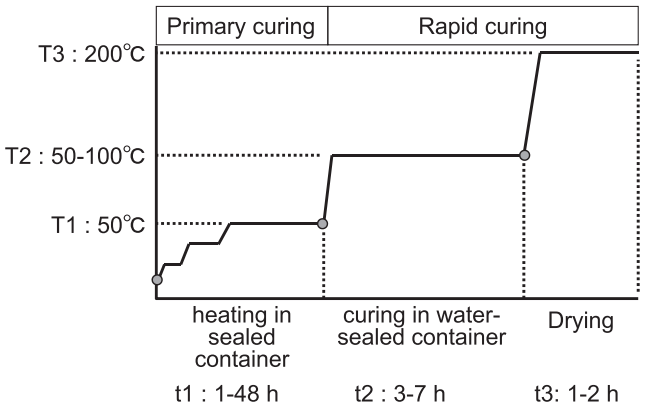

Fig. 2. Conditions and parameters of rapid curing test in small-scale batch.

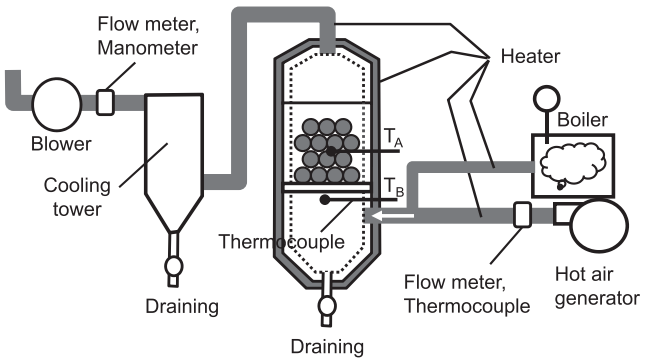

Fig. 3. Schematic of test apparatus of continuous rapid curing process.

Table 1. Chemical composition of RCA used in continuous rapid curing test (mass%).

T.Fe	M.Fe	FeO	CaO	SiO_2	Al_2O_3	MgO	CW	T.C	Na_2O+K_2O	P	S	ZnO
33.99	0.35	1.80	12.22	7.37	2.81	0.83	2.59	20.70	0.108	0.067	0.338	0.021

Five tons of RCA having 16 mm diameter were piled on a punching metal equipped with nozzles for supplying steam underneath the pile. The RCA pile was covered by a sheet, cured for a certain time and subsequently steamed. After steaming for a certain time, partial RCA was subjected to conventional yard curing and another partial RCA was dried.

3. Experimental Results

3.1. Small-scale Batch Test

With regard to the temperature of primary curing (T1), the crushing strength of the product was 52 daN/p at T1 = 18°C and 144 daN/p at T1 = 50°C, indicating the importance of T1 as a factor determining the strength of the product. However, in this study, T1 was set at 50°C because it naturally rises up to 50°C in the plant piling condition without any heat treatment because of the latent heat of water vapor, the reaction heat of the hydration of cement, and the frictional heat during granulation.

Conventional yard curing for 12 days was also performed after primary curing (t1 = 48 h, T1 = 50°C). The strength of RCA after conventional yard curing was 144 daN/p. Empirically, 100 daN/p was a lower limit of the strength of RCA for use in a blast furnace.

Figure 4 shows the influence of the holding time (t1) at 50°C in primary curing on the crushing strength of RCA. The crushing strength increased with increasing t1. In particular, the influence was significant in the range of t1 = 1–12 h. In the case of t1 = 1 h, the crushing strength was limited even after steam curing at high temperatures for long holding times.

Figure 5 shows the influences of the holding time (t2) and the curing temperature (T2) in rapid curing at high temperatures on the crushing strength. The crushing strength increased with increasing t2. The influence of t2 was smaller in the case of t1 = 12 h when compared with that in the case of t1 = 1 h.

The influence of T2 varied with t1. In the case of t1 above 24 h, the required temperature of T2 was 50°C. On the other hand, in the case of t1 below 24 h, the required temperature of T2 was above 80°C. A similar phenomenon is observed in the steam curing of cement[22,23] mostly because of a morphological change of hardened cement after hydration. The influence of the drying time (t3) was insignificant in all cases, *i.e.*, 1 h was sufficient for t3.

From these results, we can conclude that the minimum curing time to obtain 120 daN/p strength was 18 h, which is inclusive of drying for 1 h; t1 = 12 h, t2 = 5 h, and T2 = 80°C.

3.2. Continuous Rapid Curing Test

Based on the above findings, the continuous rapid curing tests were performed to demonstrate the minimum curing time. **Figure 6** shows results of the continuous curing tests. T_A and T_B in the figure indicate temperatures at which thermocouples were set as shown in Fig. 3. The crushing strength reached 67 daN/p before drying and increased up to 105 daN/p after drying, almost reaching 122 daN/p, which was the crushing strength after conventional yard curing using the same raw pellets.

3.3. Plant Trial

Large-scale plant tests using pilot-plant made RCA with

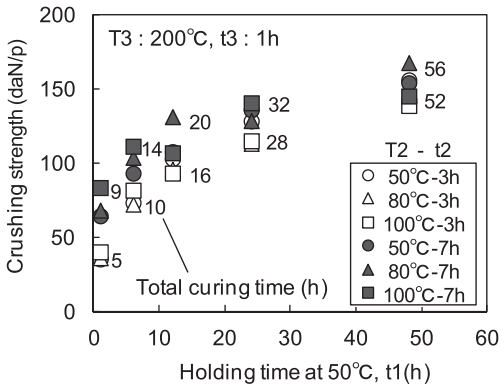

Fig. 4. Influence of the holding time at 50°C in primary curing on the crushing strength of RCA.

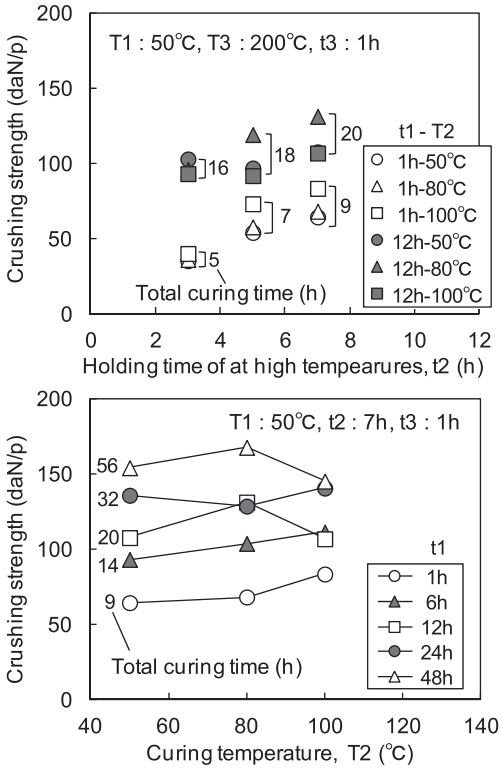

Fig. 5. Influences of the holding time, t2 (A) and the curing temperature, T2 (B) in rapid curing at high temperatures on the crushing strength.

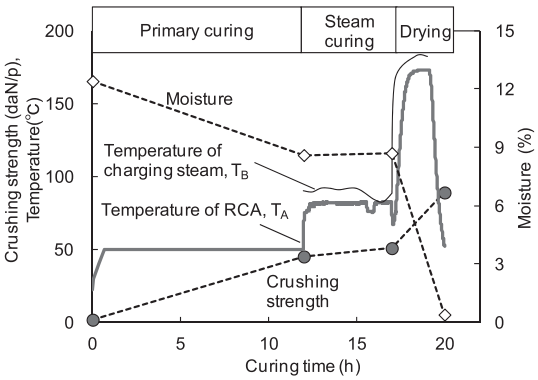

Fig. 6. Results of continuous curing test.

10 mass% HPC were conducted. During these trials, the crushing strength of RCA after conventional yard curing for 14 days was 108 daN/p without drying.

Table 2 shows the conditions and results of the tests. The influences of the holding time of primary curing (t1, Runs 1–3), the temperature of steam curing (T2, Runs 4, 5), and the holding time of steam curing (t2, Runs 6–8) were investigated. To evaluate the influence of drying, a small amount of partial RCA after steam curing was dried in a heating chamber.

The influence of the holding time of primary curing was significant. A low crushing strength was obtained without primary curing even after steaming and drying, whereas the highest crushing strength was obtained by primary curing for 24 h. With regard to the curing temperature, a higher crushing strength was obtained by a lower temperature (60°C). The crushing strength decreased with the shortening of t2.

From these plant results, we can confirm that sufficient strength can be obtained in the condition when t1 = 24 h, T2 = 60°C, t2 = 12 h. Note that it was difficult to maintain a constant temperature and constant steam condition during primary curing within a large pile. This resulted in (1) different results between the same condition, represented as □ and ◇ in Table 2, and (2) longer required curing time when compared with results of offline continuous rapid curing tests.

The reduction of the curing time of RCA with only steaming without drying was investigated. The influence of steam curing for 12 h after primary curing for 48 h was estimated by comparing the strengthening behavior after steam curing and conventional yard curing.

Table 2. Results of plant rapid curing tests of RCA in Oita works.

Run No.		T1 °C	t1 h	T2 °C	t2 h	Crushing strength after drying daN/p
1		38–58	0			19.9
2			12	80	12	133.6
3	□		24			165.0
4	□		24	80	12	110.7
5	◇			60		158.0
6	◇				12	133.8
7			24	60	8	90.6
8					4	79.4

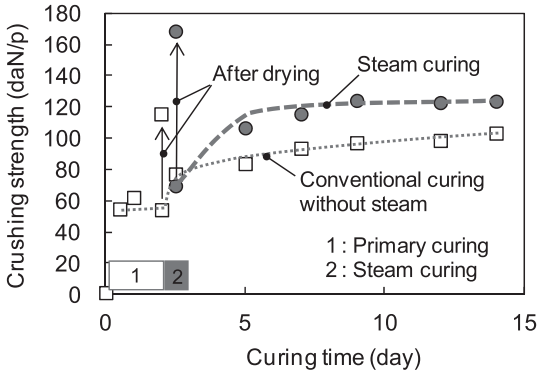

Fig. 7. Curing behavior of RCA after stream curing for 12 h.

Figure 7 shows the results of the curing behavior of RCA with and without steam curing. Steam curing can accelerate the strengthening of RCA. The crushing strength of 100 daN/p was obtained only for a curing time of 5 days with steam curing, whereas it was obtained for a curing time of 14 days after conventional yard curing. Furthermore, drying enhanced the crushing strength up to 169 daN/p after steam curing.

4. Discussion

4.1. Mineralogy of Rapidly Hardened Cement

The mechanism of the development of strength by HPC is the setting and subsequent hardening of a cement paste due to a formation of nearly amorphous calcium silicate hydrate (C-S-H) with the properties of a rigid gel, as a result of the hydration of alite ($3CaO{\cdot}SiO_2$) accounting for 63 mass% as the main component of HPC.[24,25] Although the hydration of HPC is a multi-component reaction and thus has various temperatures, pressures and moisture, it can be simply summarized based on the results in past investigations as follows.[23,24] The dominant minerals in HPC, *i.e.*, alite and belite ($2CaO{\cdot}SiO_2$) form C-S-H and calcium hydroxide (CH, $Ca(OH)_2$) after hydration. The addition of gypsum ($CaSO_4{\cdot}2H_2O$) to a clinker helps to form ettringite (AFt, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) and subsequently to form monosulphate (AFm, $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$) after the hydration of $3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$.

Thus, the mineral components in hardened cement can be classified into un-hydrated cement and reaction product involving CH, C-S-H, AFt, and AFm.

At the early stage of curing, acicular ettringite and fibrous C-S-H are observed as a typical microstructure, and subsequently the formation of massive C-S-H, laminating structure growth of CH, and the formation of monosulphate hydrate occur during curing.[24–27]

A pure HPC was mixed with water and shaped as a spherical sample by hand rolling and subsequently supplied for the rapid curing test in a similar condition explained in subsection 2.2. **Figure 8** shows the result of X-ray diffraction analysis of pure HPC before and after rapid curing. For reference, the result of pure HPC after conventional yard curing is also shown. The difference of X-ray diffraction peak was insignificant between samples after rapid curing and after conventional yard curing. The peaks of CH as a byproduct of cement hydration, and C_3S and C_3A as un-hydrated cement were identified for both samples.

A thermogravimetric and MASS analysis of hardened cement after rapid curing was performed at a heating rate of 5°C/min in He atmosphere (**Fig. 9**). Results revealed that weight loss started at a low temperature below 400°C indicating the dehydration of C-S-H, and subsequently, large endothermic dehydration occurred at 400°C, indicating the dehydration of CH. At 600°C, weight loss and CO_2 generation were observed, indicating the decarburization of $CaCO_3$ mostly formed from CH or C-S-H.

These results concluded that the mineral components of hardened HPC by rapid curing was un-hydrated cement, C-S-H, CH, and $CaCO_3$ and similar to that by conventional

yard curing.

Figure 10 shows analysis results of morphological evolution during the rapid curing of HPC in the similar condition of the continuous rapid curing test reported in subsection 2.2. The identification of mineral phases was performed by their morphology from SEM and chemistry from EDS.[24–27] At the early stage of steam curing (after 12 h at 50°C), acicular ettringite (A1, A2) and monosulphate hydrate having a card-house structure (A1) were previously observed as the typical microstructure. During the subsequent stage involving steaming at 80°C for 5 h and drying, these microstructures disappeared. The amount of C-S-H was increased and the aggregate structure of CH, observed at the later stage of hardening in conventional yard curing for 14 days (D1–D3), was visible within one day (B, C). These observations conclude that the mutual morphology of hardened cement, requiring a few weeks in conventional yard curing, can be obtained by rapid curing within a short period.

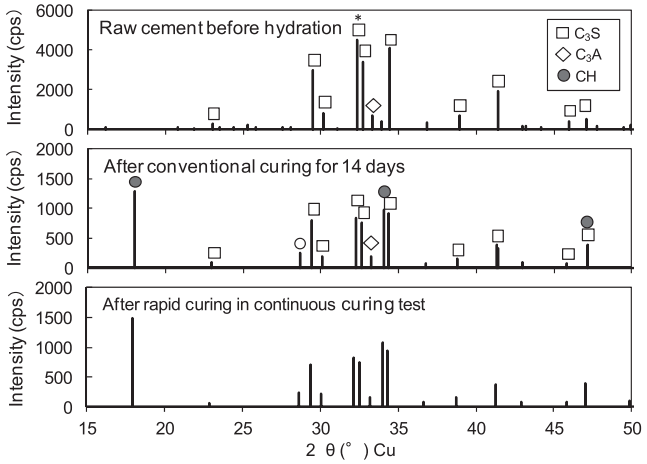

Fig. 8. X-ray diffraction of pure HPC before and after rapid curing. (C_3S: $3CaO{\cdot}SiO_2$, C_3A: $3CaO{\cdot}Al_2O_3$, CH: $Ca(OH)_2$, * represents the peak used for estimation of un-hydrated cement).

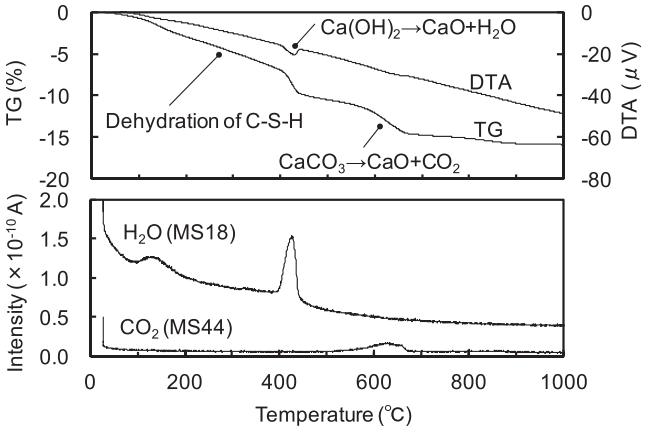

Fig. 9. TG/DTA-MASS analysis result of pure HPC after rapid curing.

4.2. Relation between Crushing Strength and Cement Hydration in RCA Rapid Curing

XRD analysis of RCA was conducted after small-scale batch tests reported in subsection 2.1. To evaluate the amount of un-hydrated cement, we focused on alite (C_3S). The height of the first major peak of $3CaO{\cdot}SiO_2$ (d : 2.7874 Å, showed as * in Fig. 8) was measured against the peak height of Fe_2O_3 as an inner standard. **Figure 11** shows the relation between the crushing strength and peak height of un-hydrated C_3S in RCA after rapid curing. The amount of un-hydrated cement tended to decrease with a longer curing time and a higher curing temperature, yielding a high crushing strength of RCA. Nevertheless, the crushing strength was determined hardly by hydration and was influenced by the microstructure of hardened cement or porosity of RCA depending on curing conditions.

The hydration behavior of cement in RCA during steam curing in plant trials reported in subsection 2.3 was analyzed using XRD and thermogravimetry under a heating rate of

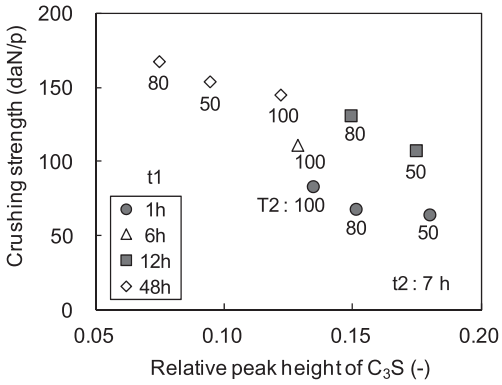

Fig. 11. Relation between the crushing strength and the amount of un-hydrated C_3S in RCA after rapid curing.

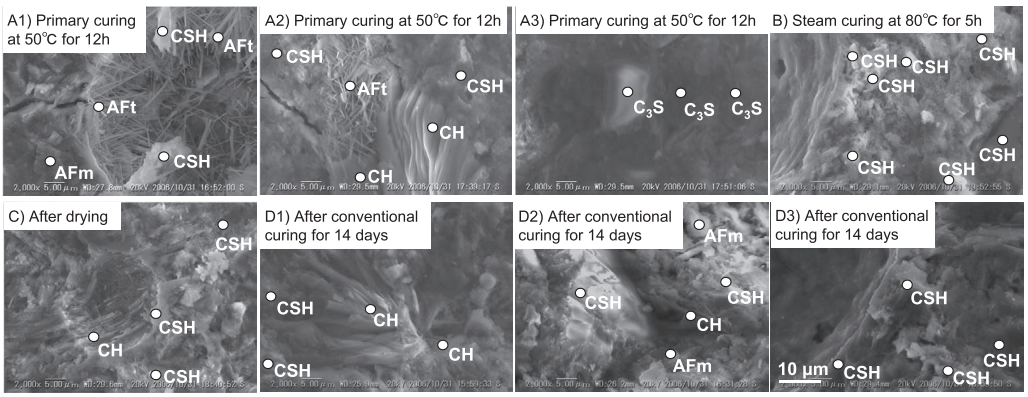

Fig. 10. Morphological changes during rapid curing of HPC (magnification ×2 000). C_3S: alite, AFt: ettringite, CSH: calcium silicate hydrate, AFm: monosulphate, CH: $Ca(OH)_2$.

20°C/min in Ar. TG_{500} was defined as weight loss % until 500°C as an index of the amount of C-S-H and $Ca(OH)_2$, referring the result in Fig. 9. **Figure 12** shows changes in the relative peak height of C_3S and TG_{500} of RCA with stream curing for 12 h. The relative peak height of C_3S decreased and TG_{500} increased after steam curing when compared with those during conventional yard curing. This implies the acceleration of cement hydration by steam curing.

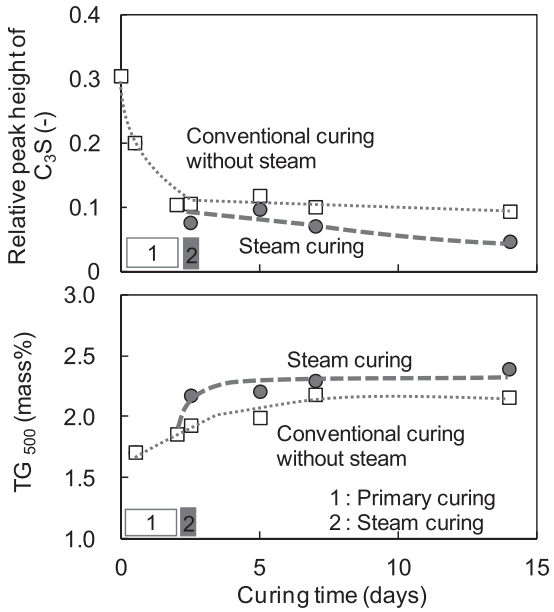

Fig. 12. Changes in the relative peak height of C_3S and TG_{500} of RCA with stream curing for 12 h.

5. Commercialization of RCA

The manufacturing process of RCA was implemented in Oita works in December 2011. **Figure 13** shows an overview of the production flow. Raw materials were roughly crushed and mixed with cement and then pelletized. The raw pellets were subjected to primary curing with steam and transported to yard for secondary curing. **Figure 14** shows operational change of Oita No. 1 blast furnace at the start of using RCA. The production capacity of RCA was approximately 900 t/d supplying to two large blast furnaces having 5 775 m^3 inner volume at 40 kg/tHM RCA consump-

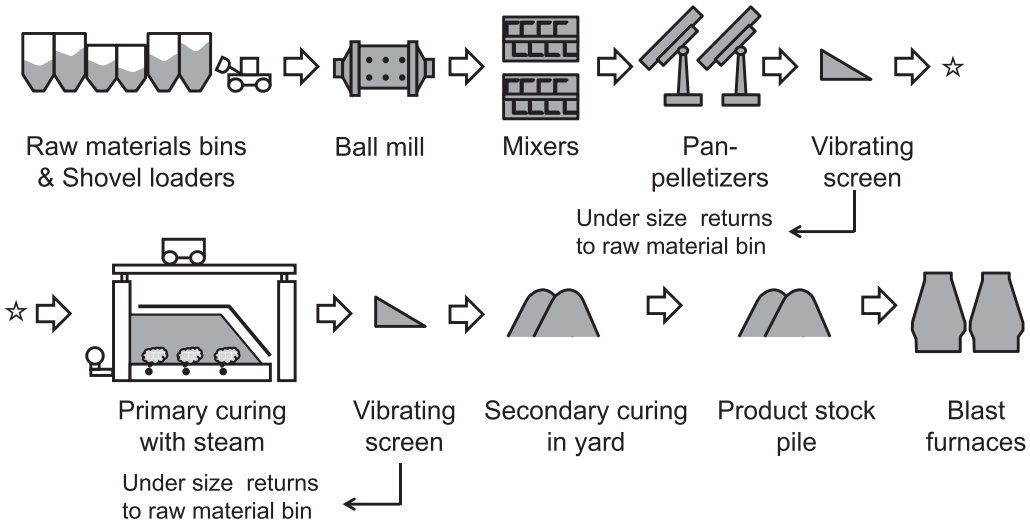

Fig. 13. Production flow sheet of RCA implemented in Oita works.

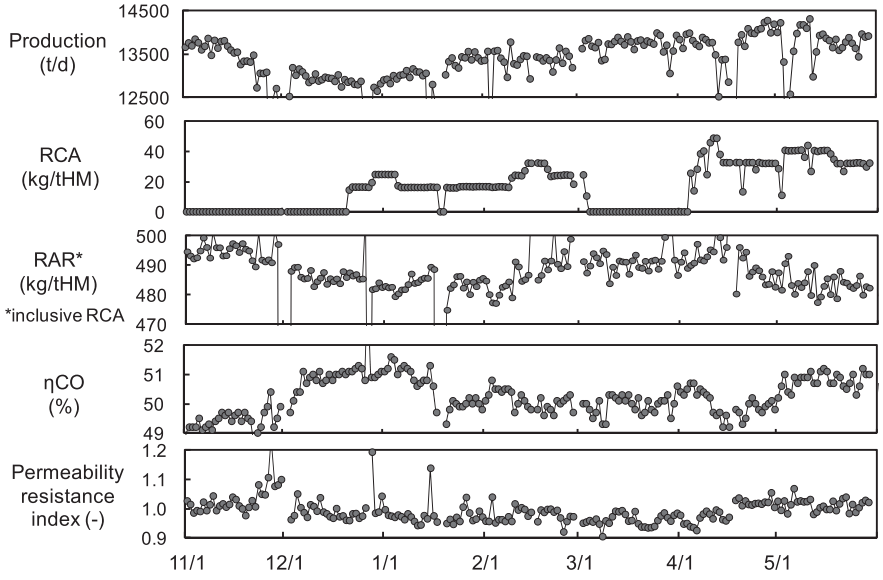

Fig. 14. Operational data of RCA use in Oita No. 1 blast furnace.

Table 3. Operational change of Oita No. 1 blast furnace between before and after RCA use. *RAR includes carbon in RCA.

		Without RCA	With RCA	difference
Production	t/d	13 554	13 815	+261
Reducing agent rate*		490.2	487.6	−2.6
Coke rate	kg/tHM	338.7	324.7	−14.0
PCR	kg/tHM	151.5	162.8	+11.3
Ore composition				
Sinter	%	82.8	76.5	−6.3
Pellet	%	1.7	4.9	+3.2
RCA	%	0	2.1	+2.1
Hot metal temperature	°C	1 530	1 537	+7
Horizontal shaft probe data				
Temperature	°C	687	672	−15
$CO_2/(CO+CO_2)\cdot 100$	%	37.1	38.8	1.7

tion at the maximum value. **Table 3** shows the operational change of Oita No. 1 blast furnace before and after RCA use.[28] Charged Fe content was maintained by changing the amount of the use of sinter, and hot metal temperature was mainteined by changing RAR during the evaluation period of operation with RCA. The reduction of RAR in a similar extent to a previous estimation[4] was observed. The measurement data of a horizontal shaft probe set above 15.225 m from tuyeres showed an enhancement of gas utilization indicating the improvement of reduction efficiency due to a coupling effect of RCA.[29]

The rapid curing process was also implemented and helped to shorten the curing period by 4 days to attain a crushing strength of 100 daN/p, yielding an improvement of RCA quality and stable material flow in the works.

6. Conclusions

We commercialized RCA, a cement-bonded pellet, to decrease the thermal reserve zone temperature for the reduction of the RAR of blast furnaces. The rapid curing process of RCA using steam was investigated.

(1) RCA can be cured to attain sufficient strength within 18 h, which is the shortest period, by combining primary curing for 12 h and stream curing at 80°C for 5 h subsequently with drying for 1 h. Plant trials revealed that curing period can be shortened by 12.5 days with drying and by 9 days without drying.

(2) Mineralogy and morphology of hardened cement within RCA after rapid curing were comparable with those after conventional yard curing. The cement hydration in RCA was accelerated by steam curing in plant trials.

(3) RCA involving the steam curing process has been implemented in Oita works and it has been helping in a stable operation of two large blast furnaces under a low RAR.

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