Wide Variety in Monolithic Refractories and Precast Block for Coke Oven

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Abstract

Dearing with current demands for coke oven as extending service life, increase in productivity, reduction of internal gas emission, and so on, applications of monolithic refractories and precast block have been suited. In this article, our monolithic refractories and pre-casted blocks for coke oven are introduced in association with current coke oven operation status in Japan.

1. Introduction

Thanks to the developments of refractories and its application technologies associated with operational optimization, coke ovens in Japan have operated more than 40years without stoppage since ignition. Carefully controlled continuous combustion prevents the excessive decrease in temperature which accelerates refractories wear, hence, most of the refractories are used without replacement. However, refractories used for oven exterior where expose to natural air suffer weathering and thermal stress resulted from temperature gradients. Thus, frequent replacement of refractory is carried out. Most of the exterior parts of coke oven are consist of monolithic refractries and precast block.

Since summer in Japan is so hot and humid, work on oven roof should be eliminated in summer. Thus, high stability is required for roof refractories. Furthermore, current tight operation status of coke oven as reduction in coking time intensifies refractories wear severely. It requires durable material as well as suitable repair. In addition, environmental issues are not negligible for coke oven operation. Corresponding to the changes in oven operation status, we have developed and improved many kinds of monolithic refractories and precast blocks for coke oven.

2. Monolithic Refractory and Precast Block for Coking / Combustion Chamber

2. 1 End flue gunning material

End flues of the coking chambers are repeatedly damaged severely by thermal and mechanical shock according to door opening and coke pushing out. Particularly in coke discharging side, serious cracking and joint wear of silica bricks worsen sealability, resulting in promotion of silica brick deterioration or black smoke emission. Therefore, durable gunning materials for end flue repairs are necessary. In addition, hot gunning repair with heavy work load has to be finished in the short time that door is opened. Hence, we developed CN-140-45G which show excellent adhesion in wide temperature range.

Table 1 and Fig.1 show typical property and gunning configuration in commercially operated coking chamber of CN-140-45G, respectively. The excellent adhesiveness of CN-140-45G in temperature range between 200 and 800℃ is attributable to optimization of adhering agent. Additionally, suited grain size distribution and ultra fine powder arrangement achieve wide tolerance range in mixing water amount. Because of easiness in gunning repair operation and durable repaired layer, CN-140-45G is favorable to repair end flues of coking chamber.

Table 1 Properties of gunning material

Properties \ Brand name		CN-140-45G
Chemical composition (mass%)	SiO_2 Al_2O_3	47 44
Permanent liner change (%)	110℃-24h 1000℃-3h	-0.12 -1.02
Cold crushing strength (MPa)	110℃-24h 1000℃-3h	25.0 20.1

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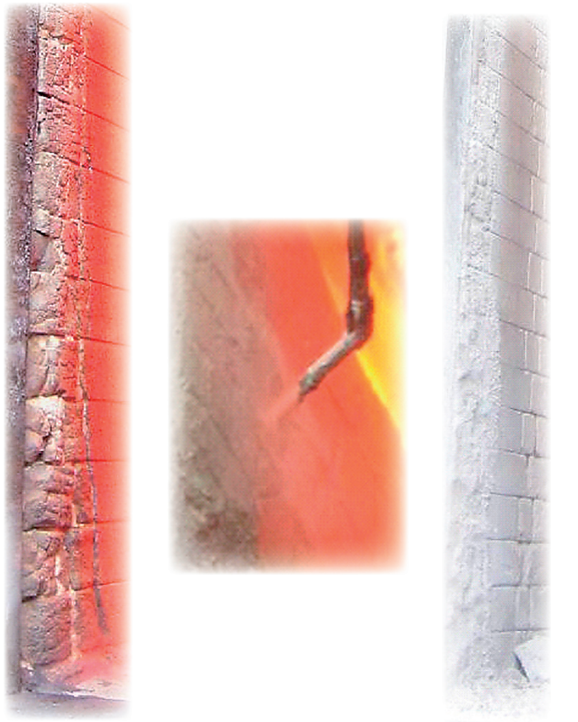


Fig.1 Using situation of gunning material.

2. 2 Precast block for coking / combustion chamber wall repair

For many decades, silica brick has been widely applied to coke oven and hot stove due to its desirable properties as (1) high refractoriness, (2) extremely low thermal expansion coefficient above 700℃, and (3) high creep resistance. Since enormous kinds of complex shape bricks are used for construction, skilled masonries are necessary for accurate brick working. To deal with continuously decreasing population of skilled masonry, steel making plant in Japan had promoted monolithic refractory application. However in the case of silica refractory, brick laying is the dominant method for installation. Regarding the situation, we developed the silica castable CST-K57 for precast block for chamber wall repair.

As indicated in Table 2, CST-K57 shows dense property with sufficient strength. Comparison of thermal expansion curve of CST-K57 after dried at 110℃ and silica brick is shown in Fig.2. Since small thermal expansion of CST-K53 ensures high thermal spalling resistance, it is applicable to hot exchange repair. As shown in Fig.3, complex shape large block excluding cracks can be obtained with high accuracy in geomertical dimension.

Table 2 Typical properties of CST-K57

Brand name		CST-K57
Chemical composition (mass%)	SiO_2 Al_2O_3 CaO	96 0.2 2.2
Permanent linear change (%)	110℃-24h 1000℃-3h 1500℃-3h	-0.03 +0.06 -0.87
Bulk density (g/cm^3)	110℃-24h 1000℃-3h 1500℃-3h	1.87 1.85 1.90
Modulus of rupture (MPa)	110℃-24h 1000℃-3h 1500℃-3h	5.9 3.5 6.7
Cold crushing strength (MPa)	110℃-24h 1000℃-3h 1500℃-3h	25 29 61
Apparent porosity (%)	110℃-24h 1000℃-3h 1500℃-3h	16 18 19
Thermal conductivity (W/m・K)	600℃ 800℃ 1000℃	0.96 1.15 1.36
Water requirement (%)		8.0

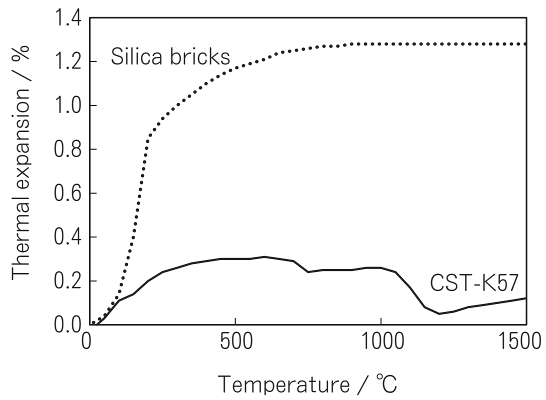


Fig.2 Thermal expansion curves of CST-K57 comparing to silica brick.

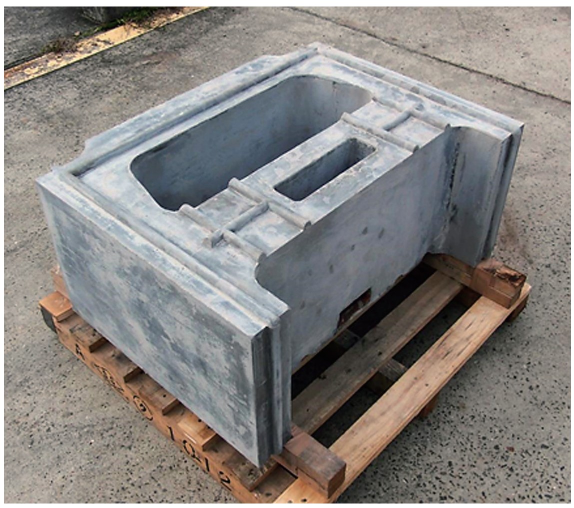


Fig.3 Appearance of precast block.

2. 3 Silica mortar

For brick working of silica brick which exhibits extremely low thermal expansion above 700℃, silica mortar is applied. Mortar is important material for constructing rigid chamber wall with high credibility. For instance, excessively large dry shrinkage of mortar tends to cause interstices between brick, or, inadequate volume change of mortar in high temperature extrudes brick wall. Hence, German standard (DIN: Deutsches Institut für Normung) strictly normalizes high temptarure properties of silica mortar for coke oven construction. In addition, good installabiliy is neccesary so as to reduce the workload of masonry. Therefore, we provide following two silica mortars; MK-95D-7 for construction satisfying DIN requirement and low thermal expansion MK-95D-8 for hot exchange repair.

Fig.4 and 5 demonstrate smoothness and extendibility of MK-95D-7, respectively. Mortar with poor extendibility increases the load of masonry, resulting in reduction in brick laying work efficiency. Both MK-95D-7 and MK-95D-8 exhibit superior extendibility by optimizing grain size distribution, dispersant and flocculent.

Table 3 summarizes evaluated results according to DIN 1089 Part 3 and JIS. Obviously, MK-95D-7 perfectly satisfies DIN requirements. Fig.6 shows creep curves evaluated by DIN method. Creep curves of MK-95D-7 and MK-95D-8 shown in Fig.6 are those of the brick/mortar compound body. Good agreement of three creep curves ensures inhibition of gas emission caused by wall structure deterioration.

Fig.7 shows thermal expansion behaviors of MK-95D-7 and MK-95D-8. In spite of steep expansion above 1200℃ of MK-95D-7, it is applicable to practical construction since suitable creep deformation shown in Fig.6 compensate the expansion. In fact, there is no description about thermal expansion in DIN which regards thermal

Fig.4 Comparison of mortar paste smoothness.

Fig.5 Difference in extendibility of mortar paste.

Table 3 Properties of silica mortars

Properties		DIN requirements for KS94	MK-95D-7	MK-95D-8
Chemical composition (mass%)	SiO_2	≧94	95	94
	Al_2O_3+TiO_2	≦5.5	1.9	1.9
	Foreign oxides	≦1.5	1.0	2.0
Grain size spread (mass%)	>2mm	0	0	0
	1-2mm	≦2	0	0
Consistency <DIN>	Mixing water (%)	≦34	27	27
	Consistency	-	20	17
Permanent linear change after drying at 110℃ evaluated by DIN method	Mixing water (%)	≦34	27	27
	PLC(%)	≧-4	-2.78	-2.04
Modulus of rupture (MPa)	110℃	≧0.1	0.5	0.8
	1100℃	≧0.7	1.1	4.6
Thermal creep (%) <DIN>	ΔD_{25}	≧-0.3	-0.033	-0.223

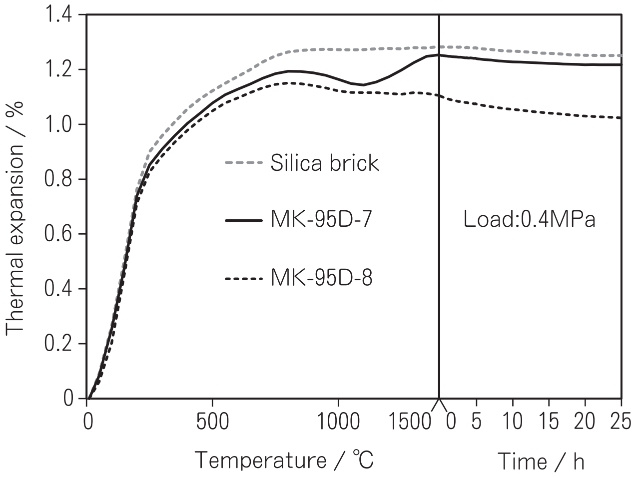


Fig.6 Thermal creep behavior of silica bricks with and without horizontal mortar joint.

Table 4 Properties of precast blocks

Properties \ Brand name		CST-N48	CST-N418
Chemical composition (mass%)	SiO_2	40	43
	Al_2O_3	49	47
	MgO	6	6
Permanent liner change (%)	110℃-24h	-0.01	-0.04
	1000℃-3h	-0.03	-0.06
	1200℃-3h	+0.02	-0.08
Modulus of rupture (MPa)	110℃-24h	11.8	11.0
	1000℃-3h	10.2	9.6
	1200℃-3h	12.1	8.3
Cold crushing strength (MPa)	110℃-24h	42.5	57.9
	1000℃-3h	60.3	61.0
	1200℃-3h	67.1	50.8
Apparent porosity (%)	110℃-24h	14.3	18.8
	1000℃-3h	18.5	25.5
	1200℃-3h	22.5	26.7

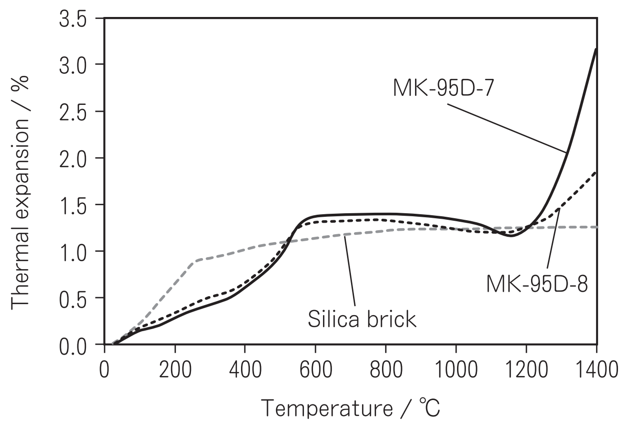


Fig.7 Thermal expansion curves of silica mortars.

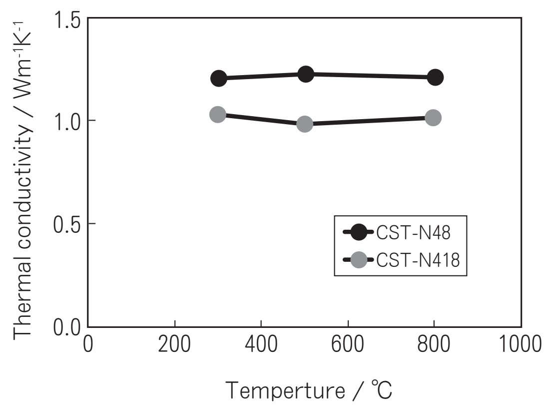


Fig.8 Thermal conductivity of precast blocks.

creep as the top priority. Low thermal expansion of MK-95D-8 is attributed to low expansion silica contained as raw materials. It is suitable to short heating up schedule as hot exchange repair.

2. 4 Door block

While unique properties and excellent stability in practical operation of graze coated door block is described as the other article in this booklet, unburnt door blocks are introduced in this report.

During the coal coking, which usually requires 20 to 24h, both end of the coking chamber are shut by doors on which several numbers of precast blocks are installed. Subsequent to the coking completion, the doors are opened in order to discharge the coke. Therefore, door block repeatedly suffers one thermal shock in a range between 1000℃ and room temperature everyday. Thus, CST-N48 which shows high thermal shock resistance as well as high strength has been widely applied for precast block of chamber door. In addition, lo thermal conductivity castable, CST-N48, was recently developed in terms of environmental influence.

Table 4 and Fig.8 show typical properties and thermal conductivity of CST-N48 and CST-N418, respectively. Approximately 10% decrease in thermal conductivity is attributable to increase in porosity. Conservation of high strength is achieved by optimization of grain size distribution and small quantity additives.

2. 5 Sole (hearth) repair throwing materials

Sole (hearth) of discharging side of coking chamber tends to be damaged by thermal and mechanical shock along with coke discharging. Since excessively rough surface of this area results in high pushing out load that deteriorates in-chamber status, elimination of void defects in this part is appreciated. In order to repair the damage, two types of repair materials are available.

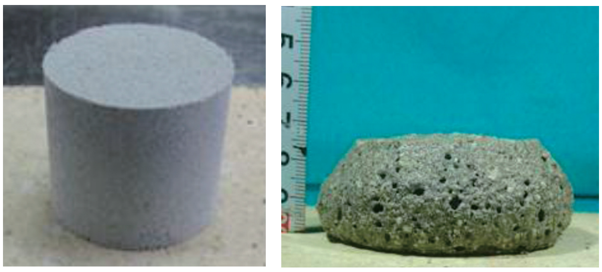
The one is water mixing type SCOAT-A29 which shows high abrasion resistance. 5kg of this product is packed in a plastic bag. 1 little of water is directly poured in the plastic bag followed by mixing by hand shaking to make slurry. The slurry including plastic bag is thrown onto the damaged area. Because of high adhesive strength and abrasion resistance, repaired layer remains after 1year commercial operation.

The other one is dry scattering SCOAT-A34 which permits easy leveling. Tight adhesion of this product is achieved by adequate melting at lower temperature range as shown in Fig.9. Fig.10 exhibits both products on brick after heated for 1hour in practically operated coking chamber. It is obvious that good contacts are obtained for both materials.

2. 6 Slurry gunning for chamber wall coating

As widely accepted, emission of coking chamber gas deteriorates the natural environment. Occasionally, emission of coking chamber gas through inspection hole installed on burning chamber possibly occurs. In this case, emitting gas is supplied from cokimg chamber through cracks or joint defects according to difference in in-chamber pressure. In order to prevent from the emission, we developed slurry gunning material JTM-K-3 to coat the wall surface.

JTM-K-3 is consists of siliceous powder and optimal binder component. As shown in Fig.11 and 12, which show external surfaces of slurry sprayed red hot brick, thick sedimentation layer was formed for slurry made of JTM-K-3. While sedimentation layer of JTM-K-3 shows rapid expansion in high temperature range, thermal expansion behavior of heated layer is agreed with that of

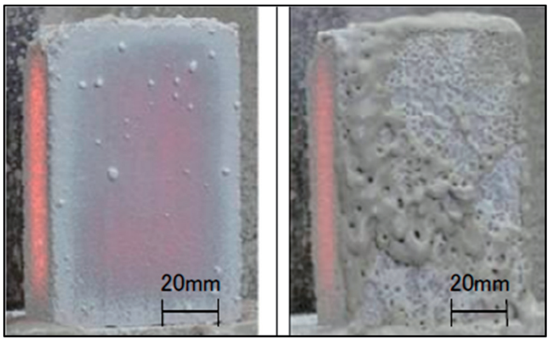


Before heating After heating at 900 for 3h

Fig.9 External appearance of SCOAT-A34 before and after heating.

SCOAT-A29 SCOAT-A34

Fig.10 Adhesion status of SCOAT-A29 and SCOAT-A34 after heated in practical coke oven coking chamber for 1h.



Without binder JTM-K-3

Fig.11 Sedimentation of slurry prepared by JTM-K-3 on the vertical surface of red hot brick.

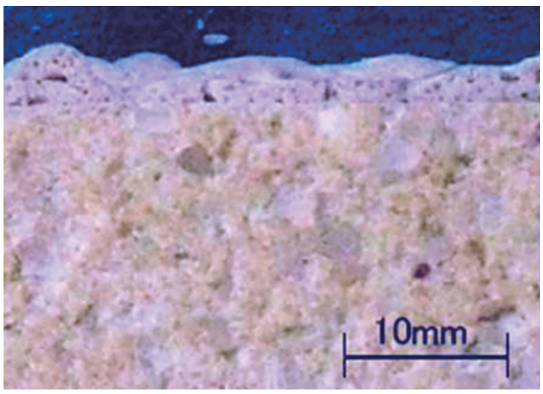


Fig.12 Cut section of JTM-K-3 sedimentation layer.

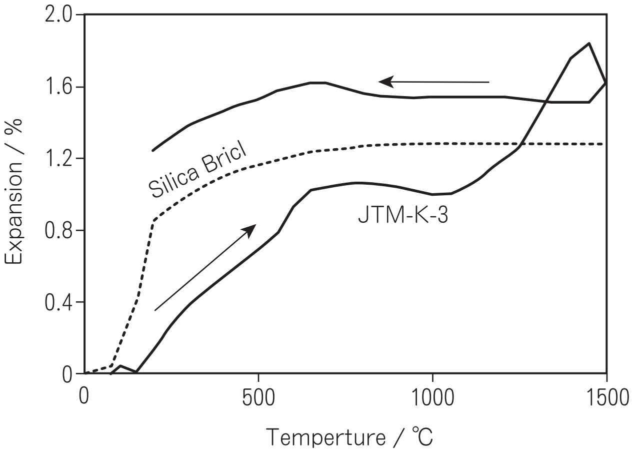


Fig.13 Thermal expansion behavior of JTM-K-3 in comparison with silica brick.

Table 5 Properties of precast blocks

Properties \ Brand name		CST-N413	CST-N415	CST-N417
Chemical composition (mass%)	SiO_2	60	82	60
	Al_2O_3	34	16	31
	MgO	3		3
Permanent liner change (%)	110℃-24h	-0.03	-0.03	-0.05
	1000℃-3h	-0.08	-0.14	-0.17
	1200℃-3h	-0.07	-0.17	-0.02
Modulus of rupture (MPa)	110℃-24h	8.8	9.0	13.9
	1000℃-3h	9.0	10.0	9.6
	1200℃-3h	9.9	12.1	10.4
Cold crushing strength (MPa)	110℃-24h	39.0	42.8	81.5
	1000℃-3h	51.0	60.7	63.2
	1200℃-3h	55.0	58.8	94.3
Apparent porosity (%)	110℃-24h	17.9	12.0	12.1
	1000℃-3h	22.1	15.0	17.9
	1200℃-3h	22.6	15.2	18.9

silica brick as shown in Fig.13. According to tight adhesion and coincidence of thermal expansion of heated layer, long term prevention of gas leakage from coking chamber to combustion chamber is expected.

3. Monolithic Refractory and Precast Block for Oven Roof

3. 1 Charging hole frame and charging hole lid

Since temperature variations of coal charging hole flame and charging hole lid are large, low expansion castable with high thermal shock resistance is desirable to the precast block. In particular, localized rapid heating around charging hole by radiation and convection causes cracks to charging hole frame. Furthermore, high strength is necessary for charging hole flame since it is ground by charging hole lid which intensively screwed and pushed into the hole of the flame by equipments installed on coal charger. We provide various kinds of materials for charging hole precast block.

Table 5 and Fig.14 show typical properties of castables applied to the charging hole and external appearance of charging hole frame, respectively. CST-N413 and CST-N415 are the castable with excellent thermal spalling resistance suitable to the flame which suffers severe thermal shock. They are appreciated to many commercially operated coke oven. Additionally, CST-N417 is high strength material with superior thermal shock resistance obtained by optimizing binding system.

3. 2 Base block for gas conduit

Generally, it is natural to apply castable of which maximum service temperature is 1400℃ to precast blocks for coke oven roof taking operation temperature into consideration. However, excessively high temperature air occasionally attacks the gas conduit base block by forced combustion, which is the procedure to eliminate carbon deposited on the ceiling of coking chamber. Since the procedure generates air stream from charging hole to gas conduit, considerably hot burning flame concentrates to the gas conduit base block. As a result, surface of gas conduit base block is melted. Thus, we developed the high refractoriness castable CST-A7218 suited for coke oven roof.

Fig.14 Appearance of charging hole frame.

Effectiveness of CST-A7218 was experimentally validated. In order to reproduce the high temperature flame attack, surface of refractory specimens were heated at 1600℃ for 5hours by direct exposure to oxygen-propane

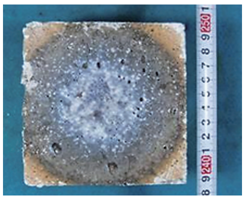
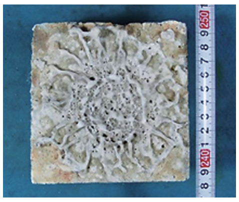
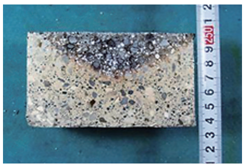
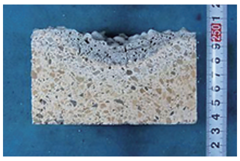
	CST-A7218	CST-N48
Heated surface		
Cut surface		
Melting depth	0 mm	9 mm

Fig.15　Burner heating test results.

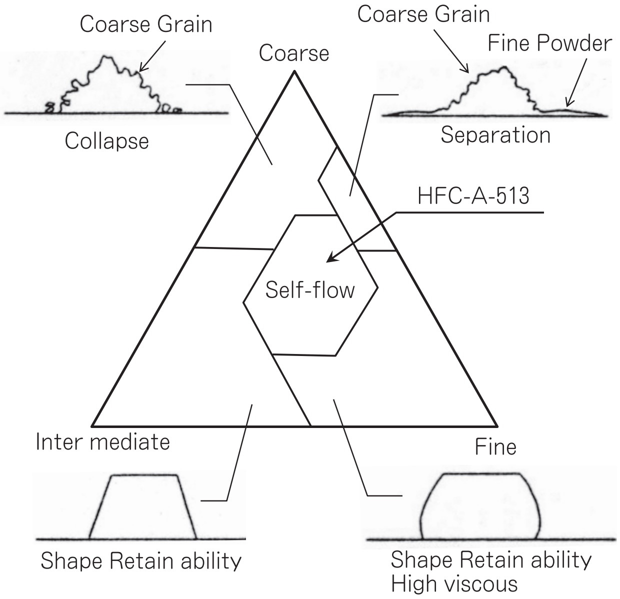
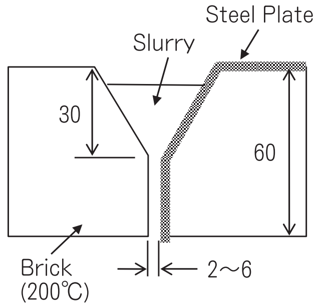


Fig.16　Effect of grain size distribution on flow status of castable mix.



Interstice	Sealing
3mm	possible
4mm	possible
5mm	possible
6mm	impossible

Fig.17　Evaluation of sealability of S-SEAL-C1.

burner. Fig.15 shows the external appearances and cut sections of post examined CST-A7218 and CST-N48 which is common as castable for coke oven roof blocks. While large molten part was observed for CST-N48, CST-A7218 showed just a thin molten layer. Hence, high refractoriness of CST-A7218 is verified.

3. 3　Gas conduit

On gas conduit base block, gas conduit is installed. It is a large section of which bricks or precast blocks were assembled. Recently, assembly of large size castable blocks is dominant in Japan for the sake of work load saving. In order to obtain large block with homogeneous structure, application of high flow castable is desirable. For the purpose, high flowability low expansion castable HFC-A513 is suitable. Due to its high flowability which is attributed to grain size optimization (Fig.16), no vibration is required to cast. Thus, proper structure can be obtained even if it casted at application site apart from block manufacturing plant.

3. 4　Paving block and inspection hole block

For the paving and/or inspection hole block, high strength low thermal expansion CST-N48 and CST-N418 are desirable because of high stability. Characteristics of these materials, which already described in the section 2.4, are also favorable to roof paving block and/or inspection hole. Especially for the roof application, water repelling treatment is possible.

3. 5　Sealing material for charging hole

In order to prevent coking chamber gas emission through interstices between charging hole flame and lid, slurry filling around lid is effective. While sealability is the top priority required to the powder as is obvious, some additional properties are neccesarry. Slurry is prepared on ground level followed by pumping up to the oven roof. Thus easiness of dispersion, low viscosity, and stability of suspension is the important factors for slurry preparation. On the other hand, adding inadequate dispersant causes forming which disturbs slurry inspection. Moreover, good separabilty is important for easiness in lid removal for coal charging.

S-SEAL-C1 is the particle size and additive optimized powder suited to prepare charging hole sealing slurry. As shown in Fig.17, 50mass% suspension of S-SEAL-C1 can fill 5mm interstices. No precipitation is observed

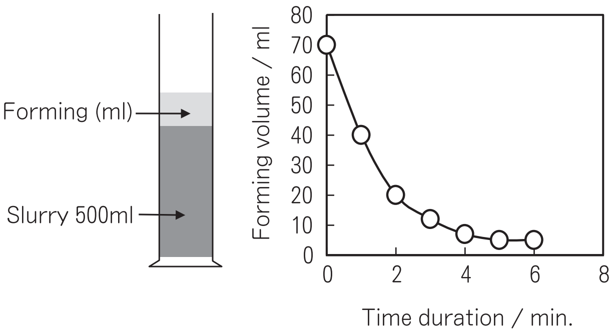


Fig.18 Changes in forming layer volume as a function of time.

for 50mass% suspension more than 3days. Rapid disappearance of forming layer (Fig.18) allows visual inspection of slurry tank just after the slurry preparation.

4. The Other Monolithic Refractories for Coke Oven

For roof paving castable, PVS-145 which can be used for casting, gunning, pumping, and troweling just by adjusting the mixing water amount is suitable. For installation of precast blocks on roof, excellent plasticity mortar MA-50D-11 is useful for underlay material in order to adjust the block level. For convenient formation of thermal insulation layer on roof, application of insulation castable LV-100-3 is recommended since it is used as castable as well as ramming material by adjusting mixing water. SPK-N-2 has many successful results of pressure injection of buckstay. Adding to above, we can provide various kinds of monolithic refractories for coke oven.

5. Conclusion

In this article, monolithic refractories for coke oven are introduced. In order to take measures for recent demands for coke oven operation as prolonging its service life and reduction of environmental load, monolithic refractories and repair materials should play important roles. We will develop and improve not only material but also installation method for stable operation of coke oven.