Paper title: Recent Trend of Refractory for Glass Tank

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Abstract

From the viewpoint of anti-environmental pollution, the oxy/fuel combustion at glass tank furnace becomes more popular in the world. In terms of refractory usage under such circumstance, it faces increasingly harsh conditions due to higher content of hazard materials, such as alkaline materials.

Meanwhile, the requirement for glass quality becomes severer along with increase in the production of flat display glass and/or lighter weight container glass, i.e. thin-thickness bottle.

The above trend in the market makes demands of new refractory. In this report, the following items will be presented.

1. The reaction of refractory with alkaline materials and the suitable material selection.
2. The introduction of new series of AZS fused cast refractory, which have low glass exudation and high creep resistance for super structure.
3. The application of high zirconia fused cast refractory that has good blistering performance. There is no alterative layer between refractory and molten glass. This will be also good for preventing cat-scratches.

Theme 1: Proper refractories for burner block and flue in oxy/fuel combustion

The oxy/fuel combustion has the good points that the amount of NOx and CO2 can be controlled and reduced in respect of environment. Moreover, the good points are the reduction of energy and resources. However, the weak points are that the utility cost of oxygen is expensive, and that the reaction of refractories with alkaline materials and moisture vapor becomes severer. In this report, the suitable refractories for burner block and flue were selected with the alkaline crucible test. Since burner block is used elevated temperature, the alkaline crucible test was carried out at 1500degree-C for 48h with Na2CO3/K2CO3. The test condition for flue was carried out at 1100 degree-C for 24h with Na2CO3/K2CO3. After the alkaline corrosion test, their volume changes, corrosion situations and alterative materials were investigated, and the suitable refractories were selected.

Table-1 shows the properties of tested monolithic samples for burner block. The high alumina 950LP is used now. CA-18U is high alumina monolithic with matrix composed of low SiO2 and low cement. For comparative examination, zirconia and zircon-alumina were also tested. The cutting faces after test are shown in Fig.-1. The linear change of 950LP is 30% and the largest among them,

Table-1 Properties of monolithic test samples for burner block

Material	Brand Name	Chemical Composition /%			Bulk Density	Cold Crushing Strength /Mpa	Apparent Porosity /%
		Al2O3	SiO2	ZrO2			
Alumina	950LP	93	4.7	-	3.30	180	15
	CA-18U	98	0.1	-	3.10	80	19
Alumina-Mullite	CLC-A539	53	40	-	2.40	80	18
Alumina-Baddeleyite	RF-AZS1	44	21	32	3.22	100	19
Alumina-Zircon	CLC-Z310	52	22	20	3.14	110	17
Zircon	CLC-Z900	3	28	63	3.50	80	13

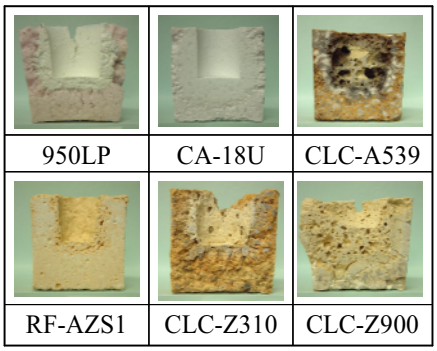

Fig.-1 Cutting faces after corrosion test at 1500degree-C, 48h

and the cause is that SiO2 in the matrix reacted with alkaline and (Na,K)AlSiO4 was formed. On the other hand, the linear change of CA-18U is 4%, and the formation of (Na,K)AlSiO4 was not detected. The alumina-mullite, zirconia and zircon-alumina had their linear change as large as 12 to 23%, and were severely corroded with forming glassy phases. Since CA-18U was most stable among the above samples, the panel test of CA-18U was carried out in the actual furnace. As the result of panel test for one year, CA-18U almost does not have cracks in comparison with 950 LP, and the volume stability was also good. CA-18U is applied as burner block at present.

On the other hand, the alumina - mullite Hi-Al brick is used for flue now. The repairs of this brick are required because of the trouble that the volume expansion occurs by the reaction with alkaline materials. Table-2 shows the composition of bonded refractory samples used for alkaline corrosion test. The linear changes and penetrated depths after alkaline corrosion test are shown in Fig-2. The photographs of cutting faces after alkaline corrosion test are also shown in Fig-3. About 10% or more of linear change was occurred in the alumina-mullite Hi-Al brick. Although the basic bricks had a little linear change, it was confirmed that their penetrated depths are large. Non-oxidized AZS-33 and mullite-silica RG-35 were excellent in volume stability, and their penetrated depths are also little. Based on these results, non-oxidized AZS-33 is used for the high temperature side, and RG-35 is used for the low temperature side in new construction of flue.

Table-2 Chemical compositions of test samples for flue

Material	Brand Name	Chemical Composition /%				
		MgO	Cr2O3	Al2O3	SiO2	ZrO2
Basic	P-B98G	99	-	-	-	-
	BD-70	73	10	-	2	-
Fused Cast	Non-oxidized AZS-33	-	-	46	17	32
Alumina-Silica	Hi-Al	-	-	83	16	-
	CWK-3	-	-	70	26	-
	RG-35	-	-	43	52	-

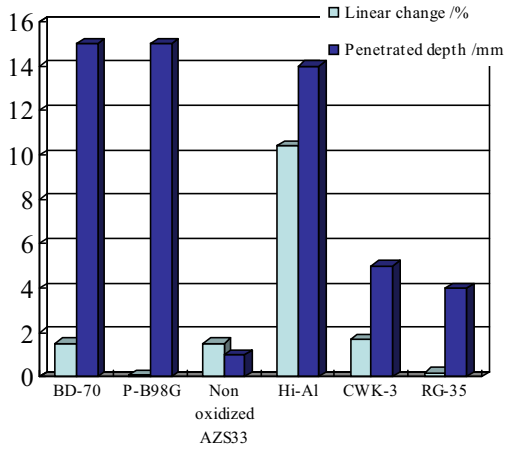

Fig.-2 Linear change and penetrated depth after corrosion test at 1100degree-C,24h

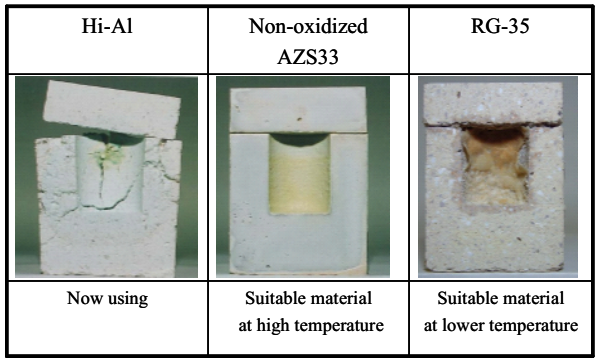

Fig.-3 Cutting faces after corrosion test at 1100degree-C,24h

Theme 2: The introduction of new series of AZS fused cast refractory

The typical properties of AZS are shown in Table-3. The SiO2/Na2O ratio of the new product, ZB-1691X, is higher than that of ZB-1691 with the reduction of Na2O. Since the matrix glass consists of high viscous glassy phase, the various characteristics are improved. The glass exudation of ZB-1691X is 1.65%, and the blister number of ZB-1691X is far less than that of ZB-1691. The corrosion resistance of ZB-1691X is 20% stronger than that of ZB-1691. It is confirmed that the stones generating from ZB-1691X in molten glass are far less than that of ZB-1691. With the application of ZB-1691X, it is expected that glass defects, stones, cat scratches will be reduced.

Table-3 Typical properties of AZS

	33%AZS	35%AZS		41%AZS
	ZB-1681	ZB-1691	ZB-1691X	ZB-1711
Chemical Composition /%				
SiO2	13.5	12	12.8	12
Al2O3	52	50	50	45.8
ZrO2	33	36	35.6	41
Na2O	1.3	1.8	1.4	1.0
SiO2/Na2O	10.4	6.7	9.1	12
Amount of glassy phase /%	19.5	18	18	17
Glass exudation / vol% at 1500degree-C,16h	1.8	2.0	1.65	1.5
Blister number /cm^{-3} at 1400degree-C, 48h, CP glass	-	9.9	4.6	-
Corrosion resistance index at 1500degree-C, 48h Soda-lime-glass	0.87	1.00	1.21	1.31

The typical properties of AZS are shown in Table-4 about ZB-1681, which is the conventional product of 33% AZS, and ZB-H350, which is new product.

Table-4 Typical properties of ZB-1681 and ZB-H350

	ZB-1681	ZB-H350
Chemical Composition /%		
SiO2	13.5	10
Al2O3	52	57
ZrO2	33	32
Na2O	1.3	0.9
Amount of glassy phase /%	19.5	14.7
Deflection /mm	19	8 Ref. MB-G 13
Glass exudation /vol% at 1500degree-C, 16h	1.8	1.3
Corrosion resistance index at 1500degree-C, 48h Soda-lime-glass	1.0	1.1

MB-G: α/β-alumina

ZB-H350 is zirconia 32% AZS being reduced the amount of Na2O and SiO2 and increased the amount of Al2O3.

The cantilever creep test was carried out under elevated temperature at 1680 degree-C for 24h. Sample size is 20mm width x 2mm thickness x 150mm length, and the amount of creep deformation is measured as the deflection. The deflection of α/β – alumina is 13mm, and that of ZB-1681 is 19mm. The deflection of ZB-H350 is 8mm, and the creep resistance of ZB-H350 equals to that of α/β – alumina. The above phenomenon is recognized as special texture which has the cross section of zirconia and alumina crystals, and higher ratio of SiO2/Na2O in comparison with ZB-1681. It is confirmed that the corrosion resistance of ZB-H350 is good and the glass exudation of ZB-H350 is less than that of ZB-1681.

The new product ZB-H350 is recommended as suitable material for breast wall and crown in oxy/fuel combustion furnace. When the cat scratches have come out by the glass exudation from breast wall, the cat scratches can be reduced with the installation of ZB-H350.

Theme 3: The application of high zirconia fused cast refractory

For the improvement of glass quality and the reduction of glass defect, the optimization of the operation is important. From the viewpoint of furnace design solution, PDW (Permanent Dam Wall system) is recommended as one of new technology. On the other hand, from the viewpoint of furnace material solution, the application of high zirconia fused cast refractory ZB-X9510 gives the excellent effects with the installation as paving blocks.

The properties of ZB-X9510 and ZB-1711 as representative of AZS are shown in Table-5. ZB-X9510 has the texture composed of zirconia crystal and very few glassy phase.

The glass exudation of ZB-X9510 is zero, because it has less glass phase. Fig-4 shows microstructure after corrosion test.

Table-5 Typical properties of ZB-X9510 and ZB-1711

	ZB-X9510 (ZFC)	ZB-1711 (41%AZS)
Chemical Composition /%		
ZrO2	94.5	41
SiO2	4.0	12
Al2O3	0.8	45.8
Na2O	0.4	1.0
Crystallography /%		
Baddeleyite	94	40
Corundum	0	43
Glassy phase	6	17
Glass exudation /vol % at 1500degree-C, 16h	0	1.5

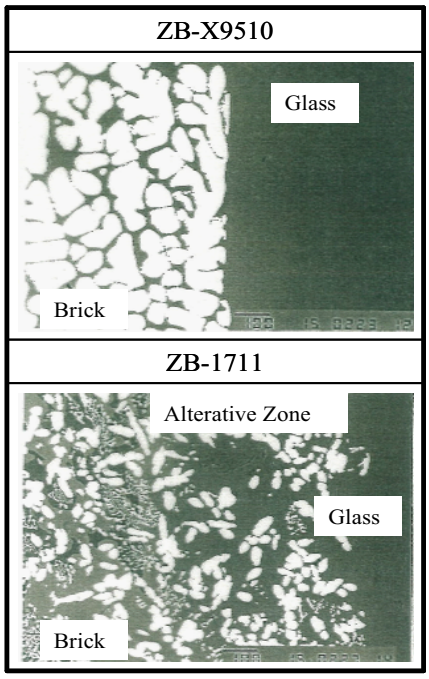

Fig.-4 Comparison of microstructure after corrosion test

A remarkable difference can be observed between the microstructures of the corroded surfaces of ZB-X9510 and that of ZB-1711. In case of ZB-X9510, the surface is clear and smooth, and no alterative layer can be seen. Therefore, it is considered that the rate of corrosion is governed simply by the diffusion rate of baddeleyite into the glass. In contrast, in case of ZB-1711, the corundum in the interface are melted and lost. It is also observed that a part of this alterative layer would be taken by the glass. The alterative layer is melted gradually into the glass through the interface with the glass. This is considered as the corrosion mechanism of ZB-1711. The generation of stones in the glass can be recognized as the peeling off phenomena of the alterative layer into the glass.

We have the equipment which can carry out observation of blisters continuously in the laboratory. As the result of using this equipment and carrying out comparative evaluation of blistering rates between ZB-X9510 and ZB-1711, the blistering rate of ZB-X9510 is less about 1/5 of that of ZB-1711 at 1400 degree-C. It is confirmed that ZB-X9510 is excellent in anti-blistering characteristics. ZB-X9510 is installed as paving blocks in many furnaces for high quality glass.

Fig.-5 shows the cutting faces of ZB-X9510 and AZS after the campaign. There are many blisters in the glass on AZS and the alterative layer is formed in the boundary of glass on AZS. However, the glass on ZB-X9510 is transparent, and does not have blisters. The glass on ZB-X9510 was removed easily. This is because the alterative layer does not exist between ZB-X9510 and the glass.

On the other hand, the glass on AZS could not be removed. It is clear that the alterative layer exists in the interface on AZS. It is considered that the alterative layer may become the origin of generating stones and cat scratches. From the application result, ZB-X9510 is confirmed to be effective for the reduction of glass defects.

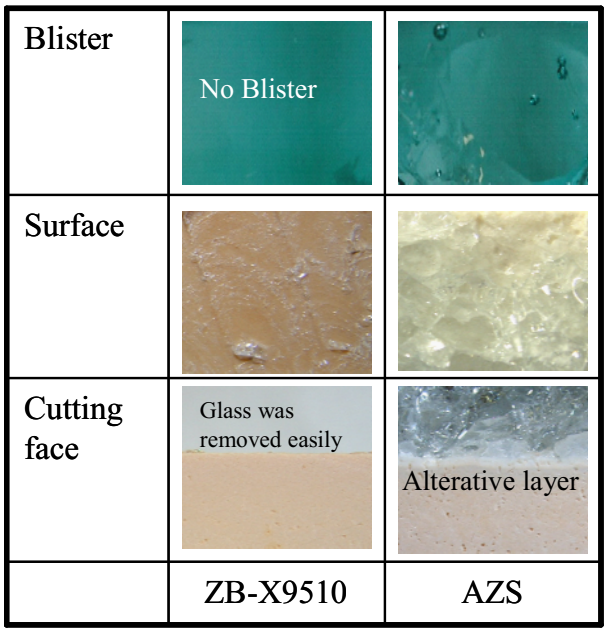

Fig.-5 Comparison with appearance of ZB-X9510 and AZS after the campaign

Conclusion

1) From the alkaline test, CA-18U which has low silica and low cement in their matrix is suitable refractory for burner block, and had good performance in the actual furnace. Regarding flue, non-oxidized fused cast brick AZS-33 and mullite-silica bonded brick RG-35 are suitable refractories.
2) As new products, ZB-1691X is suitable for side wall and paving blocks, ZB-H350 is suitable for super structure. These products have low exudation and good corrosion resistance properties, and are effective in the reduction of glass defects.
3) High zirconia fused cast refractory ZB-X9510 has the texture composed of zirconia crystal and very few glassy phase. The glass exudation of ZB-X9510 is zero. From the application result, ZB-X9510 is confirmed to be extremely effective for the reduction of glass defects, and gives excellent cost performances.