Impact of Reducing Atmosphere on the Corrosion of Refractories in Regenerators of Glass Melting Tanks

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1 - Introduction

Because of the increasing strength of environment prediction, the glass producing industry is obliged to reduce their emissions. A particular problem is the emission of nitrogen oxides (NO_x). The nitrogen oxides contribute to the "acid rain", are harmful for the ozone layer in the atmosphere and can damage the human health.

The waste gases of glass melting tanks contain NO_x in values between 1000 and 4000 mg/m³ depended on the type of furnace and the heating medium. The administrations tolerate different values with the lowest rate in Germany being 500 mg/m³. Therefore it is necessary to develop measurements to decrease the NO_x content in the waste gases.

Two types of measurements exist:

- Primary measurements to reduce NO_x in the tank
- Secondary measurements to reduce NO_x in or behind the regenerator.

Primary measurements consists normally to reduce the combustion air flow to nearly stoechiometric or even under stoechiometric conditions, or to apply the 3R system. Hereby natural gas is introduced into the waste gas stream before entering the regenerator. Thereby CO and H_2 are formed, that react with NO to form N_2, CO_2 and H_2O.

Using primary measurements, the glass producer has to be aware of reducing atmosphere in the regenerator. It is well known, that refractories show different behaviour when used in oxidising or reducing atmosphere.

In our laboratory an extensive test work has been conducted to simulate the influence of reducing atmosphere on different refractories in the regenerator. This paper will describe the test work and present the most important results.

2 - Testing method

To determinate the difference of behaviour of refractories in a regenerator with traditional atmosphere on one side and with slightly reducing atmosphere during the exhaust cycle on the other side, a number of tests have been conducted in the "checker function test". Thereby, the specimen are placed into a modified rotary kiln.

Within the test apparatus it is possible to simulate exactly the stresses in a regenerator packing. The temperature as well as the variation can be adjusted to the temperatures in different checker zones. By means of regulation of the flow of oxygen and propane, the oxidising and reducing atmosphere can be simulated. It is also possible to introduce corrosive agents into the gas stream as soda ash or glass raw material.

The most critical zone in the checkers are:

- the upper layers because of high temperature stress and the attack of glass raw material

- the temperature range between 1100°C and 800°C because of the attack of condensing alkali sulphates and oxides.

Therefore the following tests have been conducted:
Test No.1: temperature range 1550 – 1300°C; oxidising atmosphere
Test No.2: temperature range 1550 – 1300°C; reducing atmosphere
Test No.3: temperature range 1100 – 800°C; oxidising atmosphere
Test No.4: temperature range 1100 – 800°C; reducing atmosphere
The following tables show the parameter of the four tests

High temperature tests (1550 – 1300°C)

Cycle time	30 min heating – 30 min cooling
Atmosphere heating	Oxidising: $\lambda = 1.15$ – $O_2 = 3\%$ Reducing: 2 – 8% CO
Atmosphere cooling	$O_2 = 18\%$
Corrosive agent	Heating: $NaHCO_3/Na_2SO_4 = 3:1$ Glass composition
Quantity of corrosive	250g Alkali and Sulphate/cycle 250g composition /cycle
Number cycles	64
Total time	66 hours

Low temperature tests (1100 – 800°C)

Cycle time	30 min heating – 30 min cooling
Atmosphere heating	Oxidising: $\lambda = 1.15$ – $O_2 = 3\%$ Reducing: 2 – 8% CO
Atmosphere cooling	$O_2 = 18\%$
Corrosive agent	Heating: $NaHCO_3/Na_2SO_4 = 3:1$
Quantity of corrosive	250g Alkali and Sulphate/cycle
Number cycles	96
Total time	99 hours

The following brick grades have been tested:

High temperature test:	Stella GGS	Silica for crown and sidewalls
	Fused cast AZS	for target walls
	Fused cast β'''-Alumina	upper checker layers
	Rubinal VZ	Magnesia Zircon for walls and checkers
	Anker DG1	pure Magnesia 96% MgO for checkers
	Anker DG11	pure Magnesia 96% MgO for checkers
Low temperature test:	Fused cast AZS	
	Rubinal EZ	Magnesia Zirkon
	Ankrom B65	Magnesia Chrome direct bonded
	Maxial 300	Super Duty Fireclay

Because of the different place of installation of the different material within the test checker, a comparisation between the different grades is difficult. Because of the same place of installation of one grade during the tests with oxidising and reducing atmosphere, the different behaviour in the two tests is of primary interest. It can be assumed, that the glass melting industry is aware of the behaviour of the different grades in a traditional fired regenerator. The purpose of this paper is to describe the behaviour that can be expected, when reducing atmosphere is present in the regenerator during the exhaust cycle.

3 - High temperature tests

3.1 Stella GGS

Silica is still widely used in Europe in the upper part of the regenerator walls and the crowns. Experience has shown, that under heavy alkali attack and temperatures of below 1500°C, Silica shows severe softening and dripping. This has been confirmed by the test.

In oxidising atmosphere, the bricks were totally overloaded chemothermically. On the hot end the brick exhibited heavy corrosion and material loss. The structure shows softening and degeneration.

In reducing atmosphere the corrosion phenomena were very similar, the specimen was even stronger effected. In both tests, Silica showed the poorest corrosion resistance. It can be concluded, that Silica can only be used in oxidising atmosphere under well controlled condition, in reducing atmosphere the use should be excluded.

It has to be underlined, that the test is not completely comparable to the praxis, because the lack of a temperature gradient, that exists in the regenerator wall.

3.2 Fused cast AZS

Fused cast AZS is used in target walls in the first ports of cross fired furnaces and in the upper wall parts in end fired furnaces. The corrosion mechanisms observed in practise is an exudation of the glassy phase and formation of nepheline by alkali attack. The formation of nepheline has mainly be observed in gas heated tanks. It can be assumed, that in oil fired tanks, alkali are bound as sulphates and thereby are less reactive. If they are existing as oxides, they are able to attack the Silica containing glassy phase in fused cast AZS bricks.

The sample tested in oxidising atmosphere showed material loss of 3mm as well as edge rounding. The structure of the brick confirmed practical experience. The brick structure exposes recrystallisation at the hot end under formation of bubbly pores and nepheline. It can be supposed, that part of the alkalis is not bonded as sulphate.

The corrosion of the specimen in reducing atmosphere was significantly stronger. The wear at the surface was 13mm more. The modification of the structure was not only visible at the surface, but nearly in the total length of the brick.
The use of fused cast AZS is only recommended in fuel fired furnaces at lower temperatures. It should be excluded in regenerators, where reducing atmosphere is to be expected.

3.3 - Fused Cast β'''- Alumina

Fused Cast β'''- Alumina is used as upper checker layers. In practise, there is only small corrosion to be observed making this material a save solution. The only known corrosion mechanism is the formation of β – Alumina under influence of alkalis.

The test specimen after the test in oxidising atmosphere confirms the practical experience. Besides an infiltration of alkalis, no corrosion or recrystallisation is visible. The brick has still its original length.

Under reducing atmosphere a stronger deterioration of the specimen is obvious. The brick is corroded by 4mm length, the structure is strongly infiltrated. One observes formation of β – Alumina and an increased part of glassy phase. This may result in cracking and softening.

It can be concluded, that the good behaviour of fused cast β'"- Alumina under oxidising atmosphere will change if reducing atmosphere is existing. For this reason the use of this material is not be recommended under reducing condition.

3.4 - Magnesia-Zircon Rubinal VZ

Rubinal VZ is used in the upper chamber part and checker layers, where strong attack of sand carry over or vanadium oxide has to be expected. The Forsterite bonding phase as well as the Forsterite protection shell around the Periclase grain protects against silica attack and the "Forsterite spalling". Practise has shown, that the grade behaves better than pure magnesite in this condition.

The sample tested under oxidising as well as under reducing atmosphere show nearly the same result. There is a corrosion visible at the hot end with material loss of about 3mm. Corrosion takes place in the bonding matrix. The reason of the corrosion is the high amount of glass raw material introduced into the test. CaO in the glass is reacting with Forsterite to form Monticelite. The test result confirms practical experience, when Rubinal VZ is used in regenerators of furnaces, where filter particles are used. In this case, formation of Monticelite is observed resulting in spalling and softening.

In spite of the strong stresses in the test regenerator, Rubinal VZ does not comport worse under reducing atmosphere. The result indicates, that the behaviour of this grade does not depend upon the atmosphere in the regenerator.

3.5 - Pure Magnesite – Anker DG1 and Anker DG11

Pure Magnesite is widely used in the upper part of regenerators, where no Silica and Vanadium attack must be considered or in such cases, where lime attack can take place. The principle corrosion mechanism is the attack of SiO2 on Periclase with formation of Forsterite and on the lime containing bonding phase with formation of low melting Monticelite.

As in the previous case, the samples after the test under reducing and oxidising atmosphere do not differ to a large extend from each other. The corrosion mechanism corresponds to the practical experience. The high SiO2 contend introduced by the glass batch leads to formation of Forsterite and Monticelite. Further tests without batch do not show this type of corrosion, the samples are nearly unaffected.

The test results indicate, that the behaviour of pure Magnesite bricks does not depend upon the atmosphere in the regenerator.

3.6 - Summary

The comparisation of the tests under different atmosphere show, that all bricks containing a certain amount of Silica in the bonding matrix, behave worse under reducing atmosphere. It seems, that the higher amount of reactive Alkalis is resulting in elevated corrosion. If Silica is existing as Forsterite, the atmosphere does not effect the degree of corrosion. Chrome – Magnesia bricks are effected because of the reduction of Iron oxide in the bonding matrix.

Pure Magnesia bricks as well as Magnesia – Zircon bricks are corroded similar to the practical experience, but the atmosphere has no substantial influence on the degree of corrosion.

4 - Low temperature tests

4.1 - Fused Cast AZS

This material is widely used in checkers in the sulphate condensation zone. In practical use, the following behaviour has been observed:

- If Alkali Sulphates are predominant, no noticeable corrosion is visible. The brick are in certain cases able to survive two furnace campaigns.
- If Alkali Oxides are predominant, often volume increase and spalling are observed. The corrosion may lead to checker collapse in certain cases.

The specimen after the test in oxidising atmosphere has been affected by the following corrosion mechanism:

- Brick growth at the "hot end", due to formation of nepheline
- Fissures in the brick structure
- Infiltration on the "hot end" with softening of the bonding phase
- At the cold end, the corrosion phenomena are visible only to a very small extend.

The corrosion under reducing atmosphere is much more severe and pronounced. The brick structure is destroyed in the whole specimen. The sample is completely fissured and broken into single pieces held together by reaction products. The original brick structure is not more to identify. Corrosion is visible throughout the whole sample.
As pointed out above, the use of fused cast AZS is only possible under oxidising atmosphere in furnaces heated by heavy fuel oil. Under reducing condition, the corrosion is that strong, that the use of fused cast AZS should be excluded.

4.2 - Ankrom B65

As described above, Chrome – Magnesia has been used widely in the condensation zone of regenerators. Due to the disposal problems, the use has decrease in the last years.

The sample tested under oxidising condition shows at the "hot end" corrosion of sulphur on the magnesia part of the brick. The corrosion does not lead to a destruction of the sample.

The sample tested under reducing condition shows a much higher degree of corrosion. Besides the attack of sulphates on the Magnesia, the bonding phase is practically destroyed. The whole specimen is brittle The reason is the Redox effect on the iron oxide in the bonding matrix. $Fe2O3$ is transformed into FeO and absorbed into the Magnesia grain leaving an open structure, where corrosives can infiltrate and weaken the structure. Under reducing atmosphere, even Chrome Oxide is corroded.

It must be concluded, that Chrome – Magnesia can not be used under reducing condition.

4.3 - Rubinal EZ

Rubinal EZ is a Magnesia – Zircon brick used as standard in the condensation zone in many regenerators. Its structure consists out of periclase grains protected by a shell of forsterite and zirconia, and a bonding phase consisting as well out of forsterite and zirconia. The bonding matrix and the protection shell are normally not effected by the attack of alkalis and sulphates.

The sample after the test at oxidising atmosphere confirms the practical experience. The sample is deeply infiltrated, but the bonding matrix is nearly unaffected. Only a small part of pure periclase in the matrix as well as not protected grains show a sulphate attack. This attack leads to formation of a small amount of fissures in the microstructure. The formation of cracks may also be caused by the change of modification at the test temperatures. In practical use, cracking has not be observed until today.

The samples after the test in reducing atmosphere show an increase of the described corrosion. It is obvious, that also the forsterite in the bonding phase and the protection shell is attacked. Cracking of the sample is visible to a larger extend than at the sample tested under oxidising atmosphere.

It can be concluded, that the use of Rubinal EZ under reducing atmosphere has to considered as more dangerous than the use under standard condition. The life time will be decreasing, if reducing condition is possible.

4.4 - Maxial 300

Fireclay is still used widely in the lower part of the checkers in a temperature range below 800°C as well as in the chamber walls under 1,000°C. In practise, softening is visible, if the bricks are overheated, especially after alkali infiltration has occurred.

The sample tested under oxidising atmosphere shows the behaviour of practical use. The "hot end" shows a corrosion of the corrosives on the bonding phase with a material loss of a few millimetres. The surface shows a compact reaction zone and as consequence the typical appearance of overheating.

The specimen tested under reducing atmosphere shows the same type of behaviour, but to a much larger extend. The surface shows a thicker reaction zone and a material loss of about 15mm. As above, the sample is compact and does not show cracks. The appearance of the sample is that of a brick loaded at higher temperatures than the test temperatures.

It can be concluded, that fireclay should not be used under reducing atmosphere in the checkers, in the walls, the temperature limit of fireclay should be lowered to 800°C.

4.5 - Summary

The test shows, that all material containing SiO2, are affected under reducing atmosphere. The reason can be the reduction of SiO2 to SiO, followed by a vaporisation of SiO. This assumption has not be confirmed yet. With increasing SiO2 content in the bonding phase, the softening temperature of the bonding phase decreases, leading to softening and cracking of this bonding phase and the total brick. The use of all these types has to be considered as potentially dangerous for the life time of the checkers. The use of fused cast AZS, Fireclay and also sillimanite should be excluded under this severe condition.

All bricks containing Fe2O3 are effected by the reduction to FeO and the loss of bonding. The use of these bricks should be excluded under reducing atmosphere.

5 - Conclusion

A test apparatus has been presented to compare the behaviour of different refractories under oxidising and reducing atmosphere in simulating the condition existing in the regenerator. Base on the results of four tests, recommendation has been given for the choose of the appropriate type of material, if reducing atmosphere exists in the regenerator.