

Corrosion Behaviour of Refractory Materials in the Systems Cr_2O_3 and $\text{Cr}_2\text{O}_3 - \text{Al}_2\text{O}_3$ against Glass Melts in Subject to their Composition and the Thermal Conditions*

M. Freund

Traditionally continuous glass filament is made of E-glass and is used for glass-fibre reinforced plastic, whereas the insulation fibres are produced from basalt glass or C-glass. In Central and Western Europe basalt glass for health reasons was melted no longer. Instead of it so-called basalt-substitute glasses are produced. It concerns here short glasses with high ferric oxide content. In order to melt these fibreglasses, special refractories based on chromium oxide (mineral name: eskolaite) for the glass tank's lining are needed. So the aim of this paper is to give a review over refractories of the system $\text{Cr}_2\text{O}_3-\text{Al}_2\text{O}_3$ with chromium oxide content from 15 % up to 95 % for typical fibreglass melts. The first part of the paper is engaged in the characteristics of the refractory bricks due to their production procedure, and also the characteristics of the attacking glasses, which cause the corrosion, are succinctly discussed. The experimental part of the paper depicts the applied corrosion tests, the results of which are discussed and summarized in the last part of this paper.

1 Introduction

More and more durable and specific products are needed for industrial applications. Therefore the demand on fibre glass as a construction and insulating material exploded during the last years.

Nowadays the most important types of fibre glass are on the one hand continuous filaments and on the other hand insulation fibres, since they are age- and weather-proof, chemically resistant, non-flammable and they also possess a high modulus of elasticity. Traditionally the continuous filament is made of E-glass and is used for glass-fibre reinforced plastic, whereas the insulation fibres are produced from basalt glass or C-glass. In Central and Western Europe basalt glass for health reasons was melted no longer. Instead of it so-called basalt-substitute glasses are produced. It concerns here short glasses with high ferric oxide content. In order to melt these fibre-glasses, you need special refractories based on chromium ox-

ide (mineral name: eskolaite) for the glass tank's lining. Due to its low solubility in the glass melt, the corrosion resistance of the fireproof material is remarkably improved. Though, a high commodity price and an extensive preparation and processing causes a high price. That condition poses the question, how high or low the eskolaite content has to be, depending on its position in the glass tank, to achieve the best results. At the same time it's also necessary to examine the corundum content. It is known, that the binder phase is foremost attacked by the aggressive glass melt, which results in a destabilisation of the brick's texture.

In the last years a few studies were published about this subject, but there was, to our knowledge, no diversified publication. So the aim of this paper is to give a review over refractories of the system $\text{Cr}_2\text{O}_3-\text{Al}_2\text{O}_3$ with chromium oxide content from 15 % up to 95 % for typical fibreglass melts.

The corrosion proceeds – superficially regarded – in different stages:

- The so-called starting reaction, which is accompanied with the soaking of the pores of the refractory by the attacking glass melt
- The following diffusion-conditioned reaction of the penetrating substances from the glass melt, the development of diffusion layers and at last
- The convection-conditioned erosion of this layer.

One must consider that a multiplicity of factors influences the described mechanisms. Therefore an accurate knowledge of the "reaction partners" refractory and glass is absolutely necessary. For this reason the author would like to go a little bit in detail on the analyzed refractories and glasses. So the first

Mareike Freund
P-D refractories Dyko Glass
Labor
40549 Düsseldorf
Germany

E-mail: Mareike.Freund@pd-group.com

Keywords: corrosion, Cr_2O_3
refractories, $\text{Cr}_3\text{O}_3-\text{Al}_2\text{O}_3$ refractories,

Received: 10.07.2010

*) The paper presents part of results of M. Freund's diploma thesis which is supported by P-D Refractories DYKO Glass

part of the paper ("state of the art") is engaged in the characteristics of the refractory bricks due to their production procedure. And also the characteristics of the attacking glasses, which cause the corrosion, are succinctly discussed. „The experimental part“ depicts the applied corrosion tests, the results of which are discussed and summarized in the last part of this paper.

2 State of the art

2.1 Refractories based on chromium oxide

Refractories based on Cr_2O_3 are made of highly pure chromium oxide and different additives. The content of eskolaite can vary thereby. The shaping takes place via vibro-casting, hydraulic compaction or isostatic pressing.

The firing must proceed under purposeful atmospheric conditions. The material is surface-machined in principle after burning and may be only dry installed into the glass tank [1].

Though the application of chromic oxide refractories is limited. On the one hand the colouring potential of the eskolaite terminates the use in container glass tanks. In literature the colouring potential is reported in detail by e.g. Weyl [2, 3]. But newer studies [4] show that the colouring potential of Cr_2O_3 is not so high, so that also for container glass chromic oxide blocks can be recommended for highly stressed areas of the melting tank. On the other hand the electrical conductivity increases with rising temperatures, so the application for electro-fuel furnaces is also limited.

Tab. 1 Overview testing samples

	Cr_2O_3 [mass-%]	Al_2O_3 [mass-%]	Open porosity [Vol.-%]
Hydraulic compaction	> 15	< 72	19,2
	30	60	22,2
	50	38	17,1
	77	10	18
Isostatic pressing	30	55	16,7
	50	32	18,3
	60	30	18,5
	95	-	14,5
Vibro-casting	30	42	16,4
	53	27	15,6
	62	17	14,9

Tab. 2 Composition of the test glasses

Fe_2O_3	CaO	MgO	Na_2O	K_2O	B_2O_3
< 1	6	4	14	1	6
10	20	5	5	< 1	0
< 1	8	3	16	< 1	5

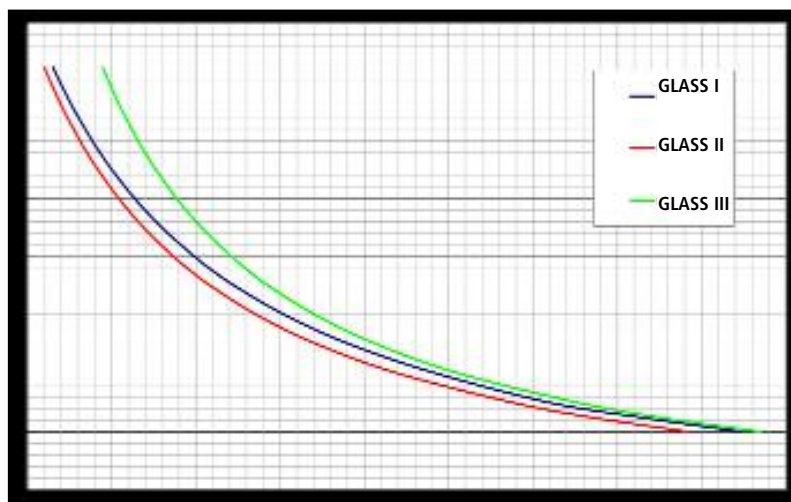


Fig. 1 Viscosity-temperature diagramme of the different glasses

ommended for highly stressed areas of the melting tank. On the other hand the electrical conductivity increases with rising temperatures, so the application for electro-fuel furnaces is also limited.

A further problem represents the evaporation of chromic oxide. This is also discussed in literature in detail [5, 6]. For these reasons chrome oxide material is preferentially used for the production of fibreglasses.

2.2 Manufacturing process

Collectively 11 refractory qualities with chromium oxide content from 15 % to 95 % were under examination. The refractory materials differ by a different content of chromium oxide and their different production methods. Tab. 1 gives an overview over the testing samples.

The several manufacturing procedures are in detail described in the literature [7, 8] and will not be discussed here. The comparison of the manufacturing methods shows that the isostatic pressing results in a very compact and dense structure. The pores of this material possess a very small diameter and are equally distributed.

The structure of the hydraulic compacted brick shows a less homogeneous, but still close appearance.

In the comparison to the isostatically pressed brick the pores of this material have already a larger pore diameter. The material shows pores, which are visible to the naked eye, and exhibits a clearly heterogeneous structure.

2.3 Glasses

After the refractories, also the assigned glasses are to be discussed. For the corrosion tests three different glasses were selected.

Glass I: Alumo-borosilicate glass (C-glass)

Glass II: Basalt-substitute glass

Glass III: Borosilicate glass (C-glass)

Tab. 2 gives the composition of those glasses.

For optimal performance of the corrosion the viscosity-temperature behaviour of the glasses must be defined, in order to specify the optimal temperature for the test. Fig. 1 shows the viscosity-temperature behaviour of the three glasses mentioned before.

The comparison of the viscosity curves shows that glass I and glass III own nearly the same characteristics. Glass II is according to the calculations the shortest. Within the range of the test temperatures of 1450 °C all glasses possess low viscosity. Due to these values one must anticipate an intensive corrosion reaction, since the melt can penetrate very fast into the pores because of its very low viscosity. How important the viscosity-temperature behaviour is, can be taken also from the literature. In the dissertation of Schaefer-Rolffs [9] the viscosity behaviour of basalt glass is discussed in detail. Also Tooley [10] postulates, that an increase of the temperature of around 50 °C causes a duplication of the corrosion rate. A further aspect that must be considered is the surface tension of the glasses. G.W. Morey [11] shows, that the surface tension decreases starting from a temperature of 1200 °C until 1500 °C only moderately,

while the viscosity in this temperature range drops rapidly. Because of a constant surface tension the capillary mobility of the low-viscosity glass melt increases. Therefore the pores of the refractory material fill faster and more deeply.

3 Experimental procedures

To examine the corrosion effects, the samples mentioned above were submitted to two different testing methods: the static plate corrosion test and the crucible corrosion test.

For the static plate [12] test the refractory material was shaped into plates with the dimension of 25 x 13 x 100 mm³. These plates were cemented in a special mounting, and this was attached over a crucible within the testing glass. After the inspection temperature is reached, the plates were dipped into the glass melt with the help of a mechanism and remain there up to the end of the preservation time (in this case to 240 h). After the test the plates were halved and the corrosion was measured. Via mathematical equations the influence of the corrosion can now be represented.

For the crucible corrosion test, a crucible was cut out of the refractories with the dimension 100 x 100 x 50 mm³, and it was furnished with a central bore with a drilling depth of 50 mm. After the pre-melting the test crucibles were exposed to a temperature of 1450 °C for duration of 240 h. After cooling the crucibles were cut perpendicularly and the surface was examined visually. For further investigations samples were taken at the ground and at the flux line of the crucible, embedded, polished carefully and analyzed microscopically. The glass, which remained after the test in the crucible, was also analysed to clarify its mineral (XRD) and elemental (XRF) composition.

4 Results and discussion

Introductory it must be mentioned that the results of the tests are valid only for the applied temperature of 1450 °C. At this temperature particularly the qualities with low chrome oxide content show rather bad corrosion resistance. However these qualities are used in practice in thermally less loaded ranges of the glass tank. On the basis of the statement of Tooley, that a temperature degradation by 50 °C results in half the corrosion rate, has to be concluded that refrac-

tories with lower chromium oxide content would probably supply satisfying results at the actual application temperatures.

The evaluation of the static plate test leads to the following conclusions:

- With rising chrome oxide content the corrosion resistance increases. Glasses with a low alumina and high alkali content possess a better corrosion effect than glasses with higher Al₂O₃ content and lower alkali content. Isostatically pressed bricks show a better corrosion resistance than hydraulic compacted or vibrocast qualities. As a further result of this work it was found that not only the oxide composition of the refractories plays an important role for the corrosion resistance. An exact knowledge of the texture and the mineralogy of the materials is much more important, to give a good application recommendation.

The investigations were carried out on different structure types. The following microscopic pictures show, using as example a refractory with 30 % Cr₂O₃, the importance of the texture. Fig. 2 presents the virgin texture of a vibrocast refractory with a chromium oxide content of 30 %.

This refractory consists of fused alumina-zirconium-silica (AZS) grains in a chrome-rich matrix. The oblong corundum bars typical for the recycled fused-cast AZS are visible over the whole structure. Altogether the virgin material seems irregularly and porously. The recycled material was already used in melting tanks and therefore it contains impurities and other mineral structures compared to the virgin material.

The corrosion test shows that this type of structure was most strongly damaged by the glass melt. The AZS grains were totally dissolved by the glass, so that a porous skeleton from eskolaite and baddeleyite remained (Fig. 3).

The structural constitution of the next type exhibits a high portion of chrome-corundum. In that texture you hardly find pure corundum or eskolaite.

Fig. 4 presents the virgin structure of a refractory material, which contains also 30 % of chromium oxide.

The chromium oxide is finely distributed, so the structure appears more homogeneous and dense than the structure of the vibrocast material. Furthermore, this material contains a variable portion of so-called rebonded ma-

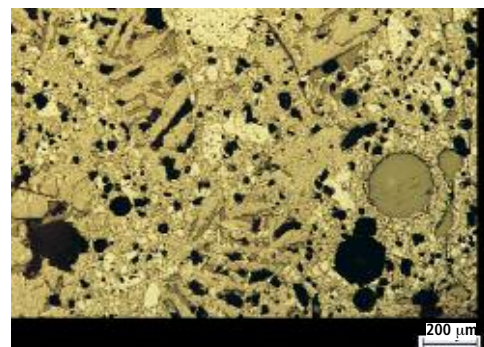


Fig. 2 Virgin texture of vibrocast brick with 30 % Cr₂O₃



Fig. 3 Texture after the corrosion test

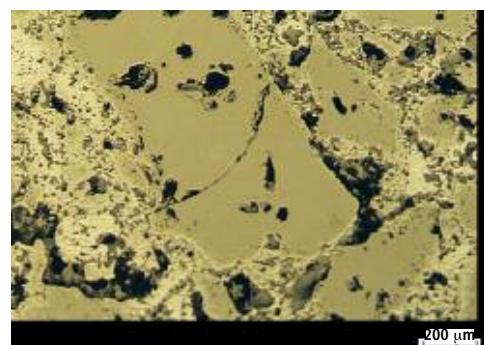


Fig. 4 Virgin texture of a hydraulic compacted brick

terial besides raw materials. In that context the description "rebonded" means a product which has been already once fired. But that material has never been in contact with a glass melt or any other corrosive substances. The mechanical and chemical characteristics of the bricks is changed by those additives since the rebonded material was fired once and shows in contact with the glass another behaviour than the unfired raw material. How much that additive material affects the corrosion resistance is dependent on the quantity and the kind of material added.

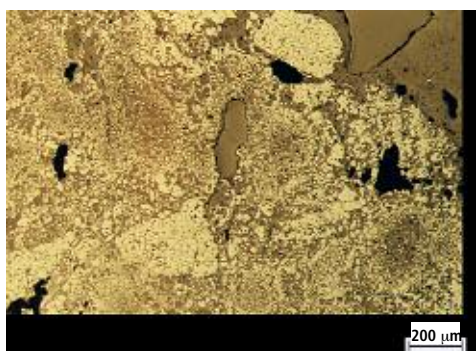


Fig. 5 Texture after the corrosion test

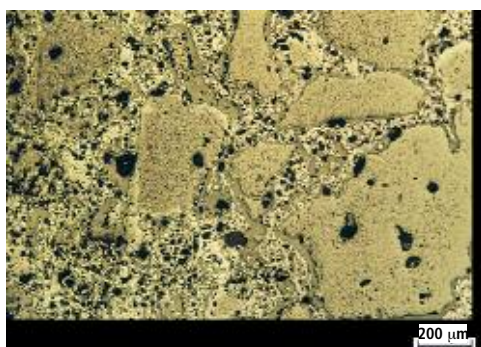


Fig. 6 Virgin texture of an isostatically pressed brick

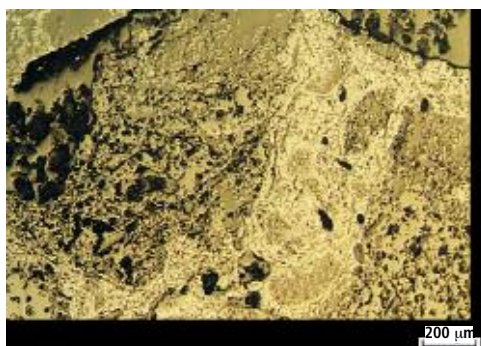


Fig. 7 Texture after the corrosion test

The following Fig. 5 shows the texture of the hydraulic compacted brick after the corrosion test.

The test results prove that the structural constitution of that texture was less damaged by the aggressive glass melts than that of the material containing ZAC-grains. Reason for this is the lower solubility of the chrome-corundum in comparison to the pure corundum. As well one can see that the rebonded

material was hardly attacked by the glass melt.

The following structure owes corundum as a main phase, which is surrounded by the second main phase, eskolaite. The very finely distributed chromium oxide surrounds the large corundum grains. Thereby small chrome-corundum formation arises at the seams of the corundum grains. Fig. 6 gives the texture of an isostatically pressed material also with a chrome content of 30 %, containing a portion of the rebonded material as well.

The isostatically pressed material shows the lowest damage to the structure in the test (Fig. 7).

The reason for this is on the one hand the density of the material, which is created by isostatically pressing. On the other hand, the re-bonded material provides because of its low solubility an improvement of the corrosion behaviour.

Using refractory qualities with Cr_2O_3 content of 30 % as an example, it could be shown, how important the texture of the material is. Thus the bricks possess all 30 % chromium oxide, but show very different behaviour in contact with glass melt. On the one hand, the way of the production is responsible for the corrosion behaviour. Thus the isostatically pressed materials show the best results in the test series. On the other hand, the selection of the raw materials plays a basic role. It could be proven by analysis that particularly the re-bonded material improves the corrosion resistance. Finally, it is not enough to know only the chemical composition of the material. It is absolutely necessary to know also the texture of the refractory. Only this way it is possible to give a good recommendation. The final choice of refractories is dependent on the parameters which apply to glassmaker's specific case.

To find the best solution, it is important to have a discussion between glassmaker and refractory manufacturer to optimize material choices based on the aforementioned perceptions. Therefore, a close working relationship with glassmakers and furnace constructors has to be an emphasis of the refractory industry.

Acknowledgement

The author would like to thank Prof. Dr F. Gebhardt and Dr M. Schilling for the kind support and the very helpful discussions. Sincere thanks are given to all colleagues in laboratory and manufacturing, who have assisted the author during his work.

References

- [1] Kollenberg, W.: Technische Keramik: Grundlagen, Werkstoffe und Verfahrenstechnik, Chapter 5.1.3.2., Vulkan-Verlag, *Jahr ergänzen*, p. 508
- [2] Weyl, W., Thümen, F.: Konstitution und Farbe der Chromgläser. Sprechsaal 66 (1933) [12] 197–199
- [3] Weyl, W., Marboe, E.C.: The constitution of glasses, Vol. 1. Intersci. Publ., 1962, p. 306
- [4] Boymanns, G, Gebhardt F., Goerenz E.: Chromic oxide blocks for use in the container glass industry. *Glastechn. Berichte* 70 (1997) 121–125
- [5] Caplan, D., Cohen, M.: The volatilization of chromium oxide. *J. Electrochem. Soc.* 108 (1961) 438–442
- [6] Graham, H.C., Davis, H.H.: Oxidation/vaporization kinetics of Cr_2O_3 . *J. Am. Ceram. Soc.* 54 (1971) [2] 89–93
- [7] Gebhardt, F.: Werkstoffwissenschaftliche Grundlagen und anlagenspezifische Anforderungen. In: *Feuerfeste Werkstoffe für die Glasindustrie und deren Prüfung*. Hüttentechnische Vereinigung der deutschen Glasindustrie, *Jahr ergänzen*, p. 4
- [8] Salmang, H., Scholze, H.: *Keramik*, Chapter 2.6. Springer Verlag, *Jahr ergänzen*, pp.169–174
- [9] Schaefer-Rolffs, W.: Untersuchungen von magmatischen Gesteinen im Hinblick auf ihre Verwendbarkeit für die Herstellung von Mineralfasern. Diss. Fakultät für Bergbau und Hüttenwesen der RWTH Aachen 1979
- [10] Tooley, F.: *The Handbook of glass manufacture*, Vol. 1. Books for industry, Inc., New York 1974, p. 443
- [11] Morey, G.W.: *Properties of Glass*. Reinhold Publishing Corp., *Jahr ergänzen*, p. 179
- [12] Dunkl, M.: Corrosion tests – a very important investigation method for the selection of refractories for glass tanks. *Glastechn. Ber.* 67 (1994) [12] 325–334