COMERCIAL QUIMICA MASSO S.A.

Headquarters in Barcelona (Spain)
Offices in France (Lyon), Guangzhou (China) & Lima (Peru)

HOW TO REDUCE GLASS DEFECTS

GENERATED BY FUSED-CAST AZS

Lecture presented first time at the:

16th Conference on the Electric Glass Melting
Czech Glass Society
September 14, 2016 - Prague - Czech Republic

Under the tittle: "How to reduce corrosion on fused-cast AZS"

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ABSTRACT:

A global approach coupling laboratory experiments and glass producers' experience about glass defects generated by fused-cast AZS has been implemented by the refractory engineering department from the Spanish distribution company COMERCIAL QUIMICA MASSO and the refractory tests laboratory from German speciality glass producer SCHOTT.

Glass furnaces suffer permanent infiltrations of the alkali compounds, vapours and liquid, within the fused-cast AZS reaction layer, thus pushing out the glassy phase, source of various glass defects as blisters, inclusions, cords, scratches, stones etc. Based on destructive controls of fused-cast AZS samples, the role of impurities found in their raw materials as a source of glass defects has been demonstrated. The results have been found in line with glass producers' experience, illustrated by many glass defects analysis over the time.

A proposal for a strict 3-step quality control procedure has eventually been proposed to glass industry to optimize resources (Zircon sand), reduce glass defects generated by fused-cast AZS and improve furnace running.

SUMMARY

PART 1

PRESENTATION OF MASSO

PART N°1: Presentation of MASSO

Comercial Quimica Masso S.A. has been founded in 1960, formulating and distributing industrial materials & solutions, and chemical ingredients for various industrial applications, among others: Ceramics, Cosmetics, Glass, Electronics, Petroleum, Pharmaceutical, Rubber…

Company yearly turnover is 150 Million euros,
With the precious support of our 320 direct collaborators,
Located in 8 countries: Spain, France, Italy, Hungary, Poland, Turkey China & Peru.

"Refractory Solution" for glass is one of the 15 specialities of Masso. It is active in the field of glass since 1998. Its focus is to select refractory grades with the LOWEST DEFECT POTENTIAL.

For almost 20 years, we are specialized in engineering and contracting refractory sets for glass furnaces. Main contracts refer to fused-cast AZS & sintered Magnesia, but also Silica, Chromium, Alumina & Zircon refractory grades.
Engineered parts like boosting, bubblers, modelling, softwares for furnaces and forehearths are also proposed together with flue gas treatments and heat recovery systems.
Trainings and audits are available under request.

Yearly turnover generated by our department is between 4 to 8 Million euros in the most recent period 2007 – 2016, with one R&D centre and employing 12 persons. After 150 major inspections of refractory sets, Masso has updated the quality and the uniformity of fused-cast materials by proceeding several chemical & physical tests in **Schott refractory laboratory**. Same tests repeated over the years give Masso the necessary feedback to become a trustable partner for glass industry.

Defects generated by fused-cast AZS refractories:

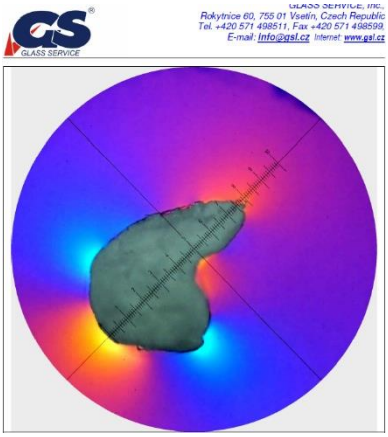


Fig.1: Typical cord

Many glass factories complain about the high rate of defects generated, mainly from the melter, and mainly below the glass level. Considering a 180 T/d end-port furnace, producing 100 g glass-wares, the surface of a 70 m2 tank (10x7), 1,6 m high tank block, including the paving and the weir wall corresponds to a surface of 140,4 m² of fused-cast AZS.

Considering only 2 cm average corrosion after one year, the glass melting tank must digest 2,8 m3 of AZS refractories, among which 40% is highly insoluble ZrO2 crystals. If one cord occupies 25 mm3, we can easily calculate that, after one year, there are 112.000.000 cords generated into the articles.

At the end of the first year, 657.000.000 articles have been produced. In the case cords are separated from each other, we simply conclude that 17% of articles have a visible cord (100x0,5x0,5 mm).

And the calculation does not consider volume of slag exudated from the superstructure, but corrosion of the tank only. Recently, some glass producers have reached 50% second choice (cord was accepted by end-user but cannot be accepted as first choice) and 50% going to produce cullet, for more than 18 months. So, what to do to avoid such situation?

PART 2

EXUDATION / CORROSION

WHICH DIFFERENCES?

PART N°2: Exudation / corrosion of fused-cast AZS, which differences?

That picture illustrates the visual differences between exudation and corrosions.

Exudation concerns the furnace superstructure

Corrosion at the glass level

Corrosion beneath the glass level

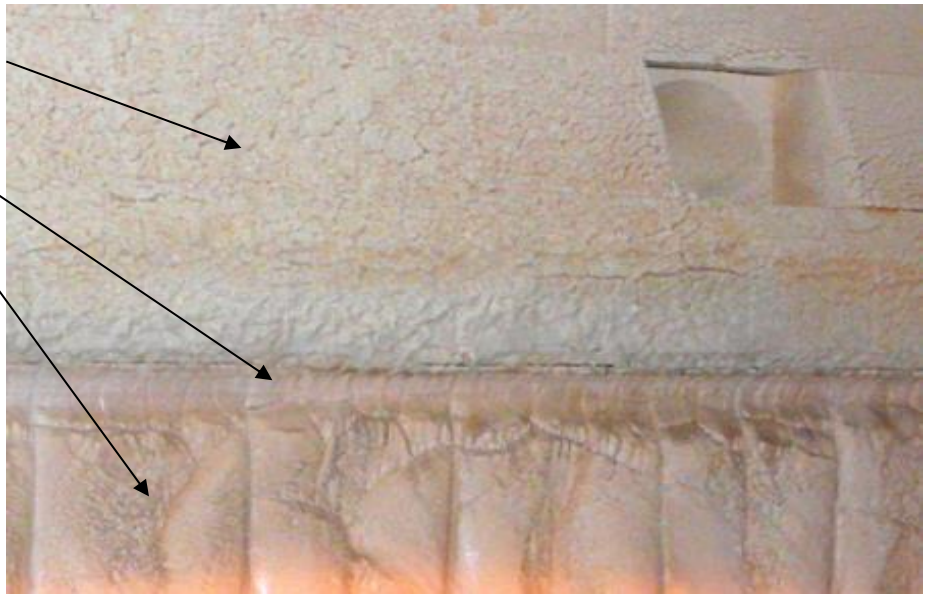


Fig.2: End of life soda-lime glass furnace

Corrosion concerns the molten glass tank.

CONSEQUENCES FOR THE USER:

All corroded AZS parts, both from exudation and corrosion, will flow down to the molten bath tank and **create glass defects**, as ZrO2 crystals cannot be dissolved into the glass, see a picture on the figure 3. The analysed polished cut of a "**zirconia stone**" from final product is shown under electron microscope.

Zone D is the vitreous phase of the stone. Zone A is the core of the stone, that contains the ZrO2 dendrites, here in white. Zone 1 is the dendritic Baddeleyite (ZrO2) crystal.

So, the glass quality is strongly influenced by the exudation/corrosion rate of fused-cast AZS refractories.

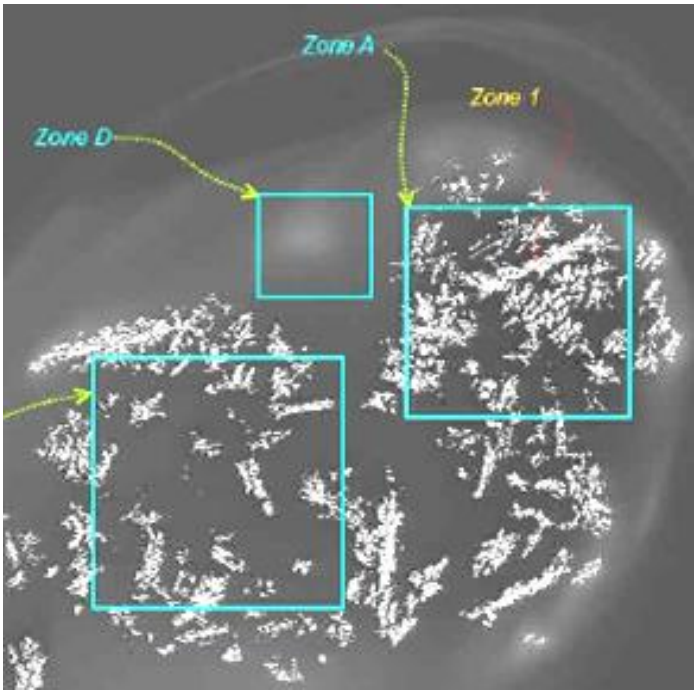


Fig.3: Zirconia stone under electron microscope

Exudation of fused-cast AZS in the alkaline atmosphere

Fig.4: Dog-house arch with AZS

Fig.5: Alkali-aluminosilicate slag enriched with ZrO2

HOW THE EXUDATION TAKES PLACE?

In the superstructure, due to permanent infiltrations of the alkali compounds vapours (Na, K, Ca, Mg) within fused-cast AZS reaction layer, the glassy phase is pushed out from blocks, creating a slag containing ZrO2, see Fig.5.
That type of corrosion is stronger as the time goes by.

As a second step, alkali species diffuse in the viscous matrix, and create different phases, with different thermal expansion, leading to continuous fragmentation of the healthy part of blocks (see previous page).
Typically, the corrosion of the superstructure due to exudation reaches 150 mm at the end of a float furnace life.

WHAT ARE THE CONSEQUENCES OF THE EXUDATION ON THE GLASS BATH?

Due to the glassy phase pushing out of the block, slag enriched with highly insoluble ZrO2 is flowing out and different kinds of heterogeneities like stones, knots, cords and bubbles are generated.

Glass sheet with bubbles larger than 0,5 mm will be rejected. All visible knots, cords and stones will also lead to rejection.

WHAT MASSO IS DOING TO REDUCE EXUDATION?

The exudation is strongly dependant of the dissolution of the glassy phase, the binder between Al2O3 and ZrO2 grains. Two parameters must be under very strict control:

1/ the percentage of the glassy phase
2/ the content in impurities of the glassy phase

1/ The glassy phase should be reduced at a low level, typically below 19% in AZS 33.

2/ The more impurities in the raw materials (Fe2O3, TiO2), the stronger the exudation potential. The content of polyvalent ions (Fe3+/Fe2+, Ti4+/Ti2+) should be as low as possible to avoid redox reactions and gas formation. Presence of flux like B2O3 and high content of Carbon from electrodes will also ease AZS dissolution. Presence of Nitrides impurities should also be avoided.
After 18 years learning from AZS producers and users, Masso has defined some strict limits to AZS producer about percentage of impurities. Masso organizes with the producer a total traceability so that all delivered blocks get high, uniform characteristics.

As result, exudation is daily measured within the producer's labor by volume expansion during high temperature test (1500°C – 16h) on corner samples cut from a cast test plate. The limit for volume expansion due to glassy phase exudation is fixed at 2,5% after one cycle. From another test done within Schott labor, called simplified exudation test, the limit for volume expansion is fixed at 10% after 6 thermal cycles (at 1550°C, see more details in annexe 2).

Testing Report

Test Sample	Fused Cast AZS	Test Series No.	2012-33-5
Brand Name	SJ – 33 WS	Condition of Sample	Block
Customer	ARC	Date of Issue	December 14, 2012

Criteria: JC493-2001

Chemical Analysis (%)

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	ZrO_2
12.62	54.40	0.10	0.06	0.09	0.01	0.01	1.33	33.15

Test Item.	Test Condition	Sampling Position	Test Result			
			Single Value			Average Value
Bulk Density (g/cm^3)	—	Dense Part	3.84	3.84	3.86	3.85
Apparent Porosity (%)	—	Dense Part	1.1	1.2	1.3	1.2
Exudation of Glass Phrase (%)	1500℃ × 16h	Dense Part	1.76	1.88	1.85	1.83

Operator: [illegible] [illegible] Yuan Youheng

Fig. 6: Testing report made by the producer with chemistry and physical values including exudation

External laboratories are regularly checking the uniformity of exudation results. Schott is one of the **laboratory checking chemistry, exudation and corrosion levels** from randomly chosen fused-cast AZS samples, see in the document annexe 2.

Schott verifies that exudation values from our selected grades are conform to our specifications.

Corrosion of fused-cast AZS in the molten glass

HOW THE CORROSION TAKES PLACE?

The glassy phase is the binder between ZrO_2 & Al_2O_3 crystals. Alkalis from the glass corrode refractory due to electrochemical reactions that dissolve in priority the glassy phase.

When the surface of the block is corroded, some porosities will appear (see figure 7) because of glassy phase exudation, releasing zirconia & alumina based defects (inclusions, cords, stones…) in the glass melt.

The weakest elements of the glassy phase are oxides of polyvalent ions: Fe_2O_3 & TiO_2.

Fig.7: AZS cut after a corrosion test

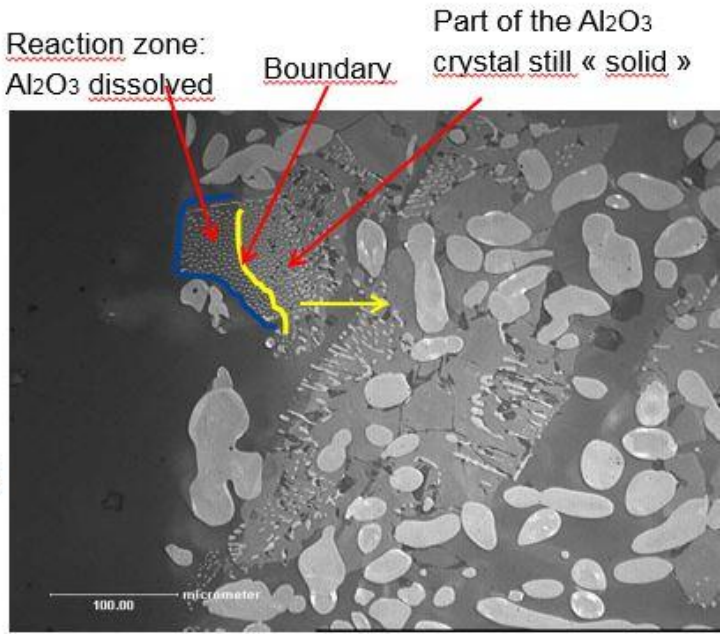


Fig.8: Selective dissolution of Al2O3 and glassy phase during a corrosion test

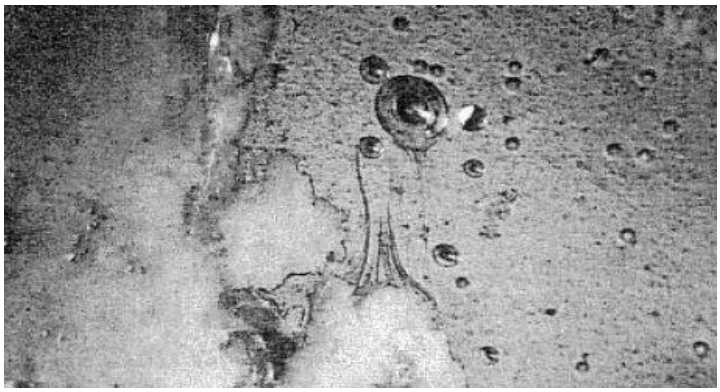


Fig.9: Bubble generation, giving birth to a cord

HOW DEFECTS ARE CREATED?

After a short corrosion test, it is possible to observe the evolution of the reaction zone, a highly viscous glass, that will generate inclusions, also called devitrified or knots by glass makers, see figure 8.

Oxygen bubble formation in the reaction zone is the consequence of an electro-chemical reaction between a residual gas (closed porosity) and the viscous reaction zone. Those gases can only escape through the reaction zone.

They push out not only the vitreous phase of the reaction layer in the glass melt (birth of inclusions), but also, time to time, ZrO2 dendrites which are the source of cords & stones, see figure 9.

WHAT MASSO IS DOING TO LIMIT CORROSION RATE?

In accordance with the more severe glass producers, Masso has specified some strict parameters in the chemical composition of selected fused-cast AZS grades. It is to reduce as much as possible the corrosion of blocks during their life, thus generating as less glass defects as possible. Of course, the filling and the homogeneity of blocks must be checked so that the correct density can be reach. More over the generation of such defects also depends on the running conditions of the furnace and the type of glass.
Schott has validated that corrosion rate of our selected grade is comparable with the best supplier in the world, see annexe 1.

MASSO GUARANTEES THAT THE SELECTED GRADES WILL RESPECT THE FOLLOWING LIMITS:

About our EM-33 grade (AZS 33%), here is the agreed specification :

	Typical Value	Unit	Guaranteed value
ZrO2	33,0	%	> 32,5
Al2O3	Rest	%	Rest
SiO2	13,2	%	< 14,0
Na2O	1,35	%	< 1,40
Fe2O3 + TiO2	0,20	%	< 0,25
CaO	0,10	%	< 0,12
MgO	0,01	%	< 0,02
K2O	0,01	%	< 0,02
B2O3	No addition	%	No addition

Fig.10: Guarantee given by Masso to end-user for EM-33

Schott has also verified the chemistry of our EM-33, see annexe 2. About EM-41 (AZS 41%), here is the agreed specification :

	Typical Value	Unit	Guaranteed value
ZrO2	40,5	%	> 39,7
Al2O3	Rest	%	Rest
SiO2	11,5	%	< 12,0
Na2O	1,10	%	< 1,20
Fe2O3 + TiO2	0,16	%	< 0,20
CaO	0,09	%	< 0,11
MgO	0,01	%	< 0,02
K2O	0,01	%	< 0,02
B2O3	No addition	%	No addition

Fig.11: Guarantee given by Masso to end-user for EM-41

MASSO HAS ESTABLISHED A 3-STEP QUALITY CONTROL PROCEDURE TO REDUCE RISKS OF GENERATED DEFECTS, see figure 13 next page

Step 1: Pour spout samples

Masso will control that the producer is using very pure raw materials, necessary to fit with the above specifications. The annexe 0 explains the pour spout sampling procedure and the figure 12 shows the melting analysis report accordingly.

Melting Analysis Report - PC/47

Item No.	Batch No.	Brand Name	Chemical Composition (%)									
			SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	ZrO_2	K_2O	Na_2O	Amount
1	2016-3-354	SJ-33	13.49	51.76	0.11	0.09	0.08	0.01	32.85	0.01	1.36	99.76
2	2016-3-355	SJ-33	13.41	51.76	0.09	0.08	0.07	0.01	32.95	0.01	1.36	99.74
3	2016-3-356	SJ-33	13.44	51.86	0.12	0.09	0.08	0.01	32.82	0.01	1.37	99.80
4	2016-3-361	SJ-33	13.54	51.86	0.10	0.08	0.08	0.01	32.82	0.01	1.27	99.77
5	2016-3-366	SJ-33	13.56	51.77	0.10	0.09	0.07	0.01	32.85	0.01	1.29	99.75
6	2016-3-371	SJ-33	13.46	51.96	0.11	0.09	0.07	0.01	32.82	0.01	1.23	99.76
7	2016-3-376	SJ-33	13.50	51.97	0.10	0.09	0.08	0.01	32.71	0.01	1.28	99.75
8	2016-3-381	SJ-33	13.43	51.90	0.10	0.09	0.07	0.01	32.79	0.01	1.24	99.64
9	2016-3-386	SJ-33	13.66	51.21	0.11	0.09	0.07	0.01	33.24	0.01	1.35	99.75
10	2016-3-389	SJ-33	13.75	51.48	0.11	0.09	0.05	0.01	32.98	0.01	1.28	99.76
11	2016-3-390	SJ-33	13.90	51.45	0.11	0.10	0.05	0.01	32.85	0.01	1.28	99.76
12	2016-3-391	SJ-33	13.32	51.59	0.10	0.09	0.06	0.01	33.23	0.01	1.31	99.72
13	2016-3-396	SJ-33	13.56	51.50	0.10	0.09	0.07	0.01	33.16	0.01	1.34	99.84
14	2016-3-401	SJ-33	13.60	51.82	0.10	0.09	0.09	0.01	32.87	0.01	1.32	99.91
15	2016-3-406	SJ-33	13.45	52.02	0.09	0.08	0.09	0.01	32.71	0.01	1.33	99.79
16	2016-3-411	SJ-33	13.73	51.45	0.08	0.08	0.07	0.01	32.96	0.01	1.33	99.72

Fig.12: Melting analysis report about EM-33, on pour spout samples

Step 2: Chemical and physical tests on plates

During the production, each 20 Tons of cast product, the producer is testing chemistry and physical properties of standardized plate (600x400x300) to evaluate their evolution in the time. The figure 13 shows the location of corner samples used for tests according to a strict procedure. The testing report from corner sample has been shown previously at the figure 6. **Measurements done at the producer are double-checked by Schott laboratories following the sampling procedure defined between Masso, the producer and the end-user.**

As a conclusion, the checking of pour spout samples **combined with** the checking of corner samples (chemical + physical) is the **safest procedure to get a uniform, high quality set of AZS blocks, leading to the lowest possible rate of defects originated from refractory wear** during the furnace life.

Step 3: Traceability list:

The full traceability of all blocks is effective through a blocks list, indicating weight and batch number of each block.

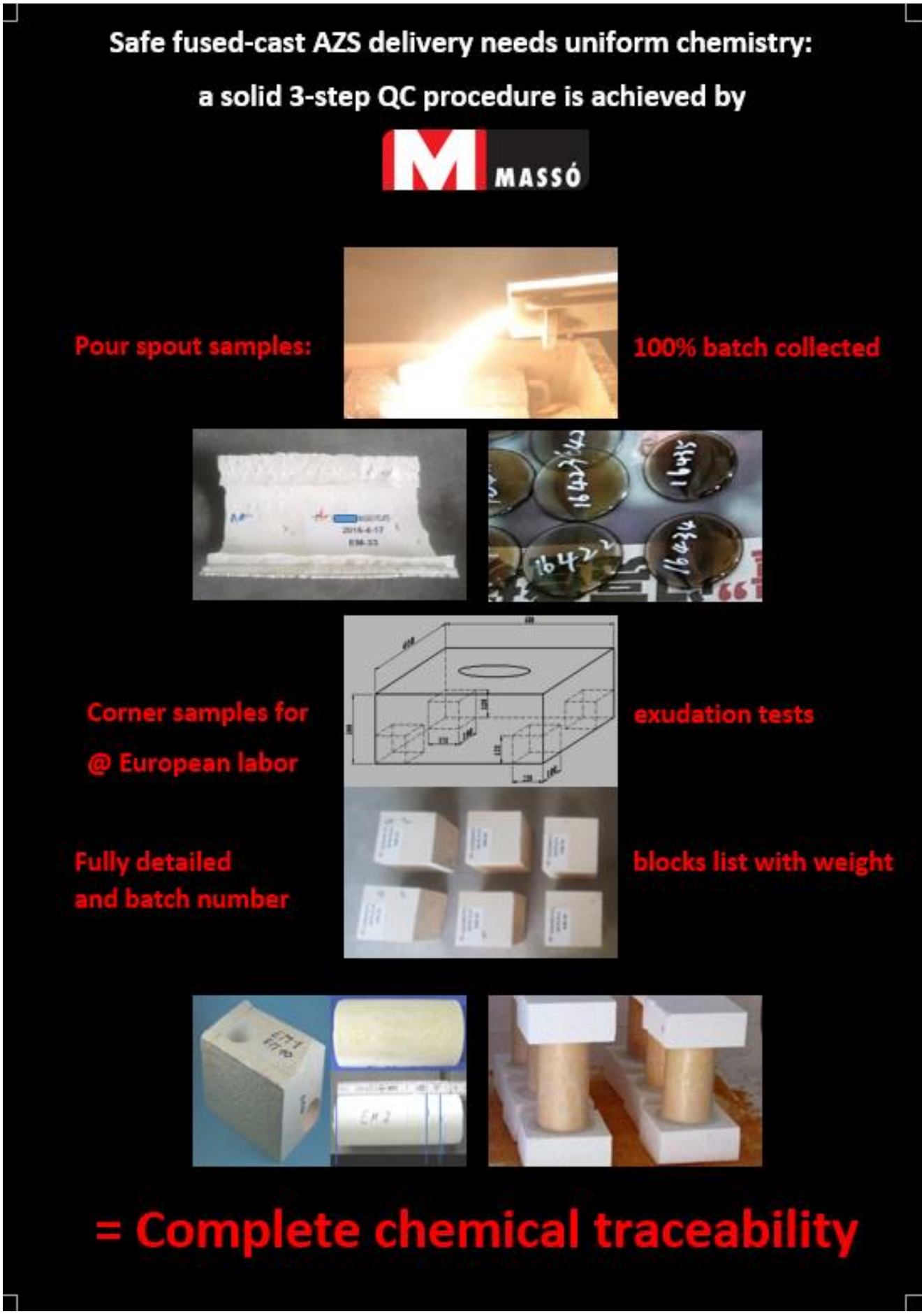


Fig. 13 : 3-step quality control procedure (3SQC)

PART 3:

ANNEXES

ANNEXE 0:

POUR SPOUT SAMPLING PROCEDURE

Annex 0: The pour spout sampling procedure

That annexe describes the procedure about pour spout samples, collected after that a batch of electro-fused AZS is casted into transfer mold. At the beginning of a raw materials silo, the first three AZS batches of the day are XRF-analyzed by the producer's lab, by collecting the pour spout sample, grinding it and heating it at 1100°C in Pt crucible before the analyze within the X-ray fluorescence spectrophotometer. Then one analysis is made every 5 AZS batches.

Pour spout samples of all other non-analyzed batches are kept. Schott will perform some chemical analysis among them to confirm the measurement of the producer. For 212 Tons, there are 284 batchs of fused-cast AZS, among which 65 have been XRF-checked at the producer's lab, and 12 double-checked at Schott's lab, see figures 13 and 14.

Fig 13: Pour spout samples randomly selected for Schott analysis

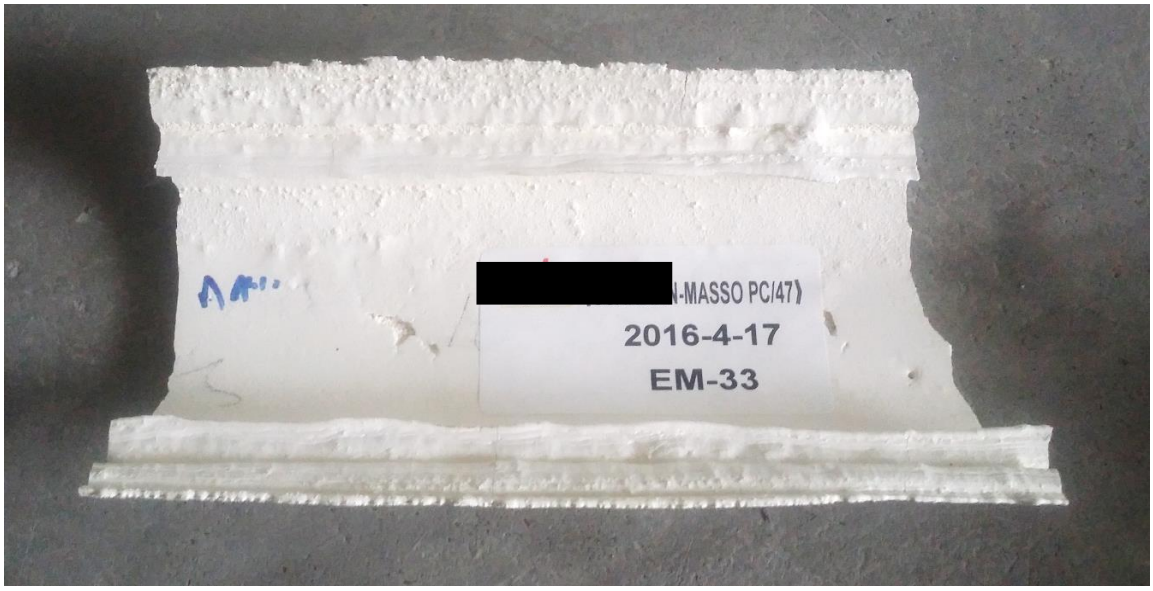


Fig 14: Pour spout sample with identification – detail

According to statistical approach, the risk of missing a batch out of specification is < 4%. If we need to reduce the risk, we have to increase the number of samples XRF-checked. It is a question of cost !

The pour spout samples of all other non-analyzed batches are kept by the producer, see figures 15 and 16.

Fig 15: Storage of 100 pour spout samples in EM-33

Fig 16: Storage of 107 pour spout samples in EM-36

ANNEXE 1:

TESTS REPORT BY SCHOTT

CORROSION

Annex 1: Corrosion tests report by Schott

The following pages show the corrosion tests made by SCHOTT on our selected grades of fused-cast AZS in comparison with the 3 other approved suppliers used by Schott, with soda-lime glass, through commonly accepted static plate corrosion tests.

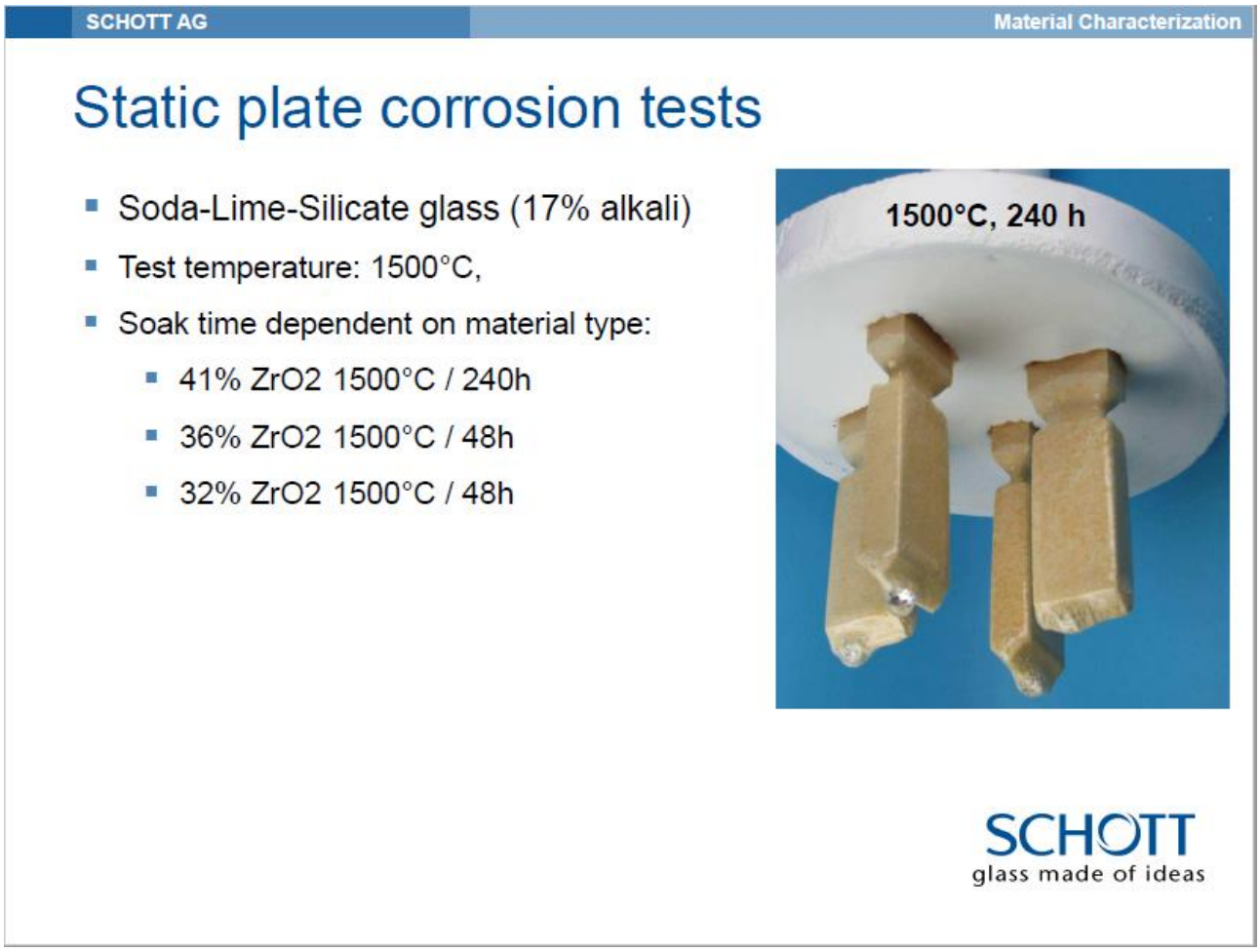


Fig.1: Static plate corrosion test – sample view after soak, before cutting

After soaking time, samples are cut and corrosion rates are measured. The following pages are showing samples picture of our selected fused-cast AZS grades.

EM-33 for AZS 33%
EM-36 for AZS 36%
EM-41 for AZS 41%

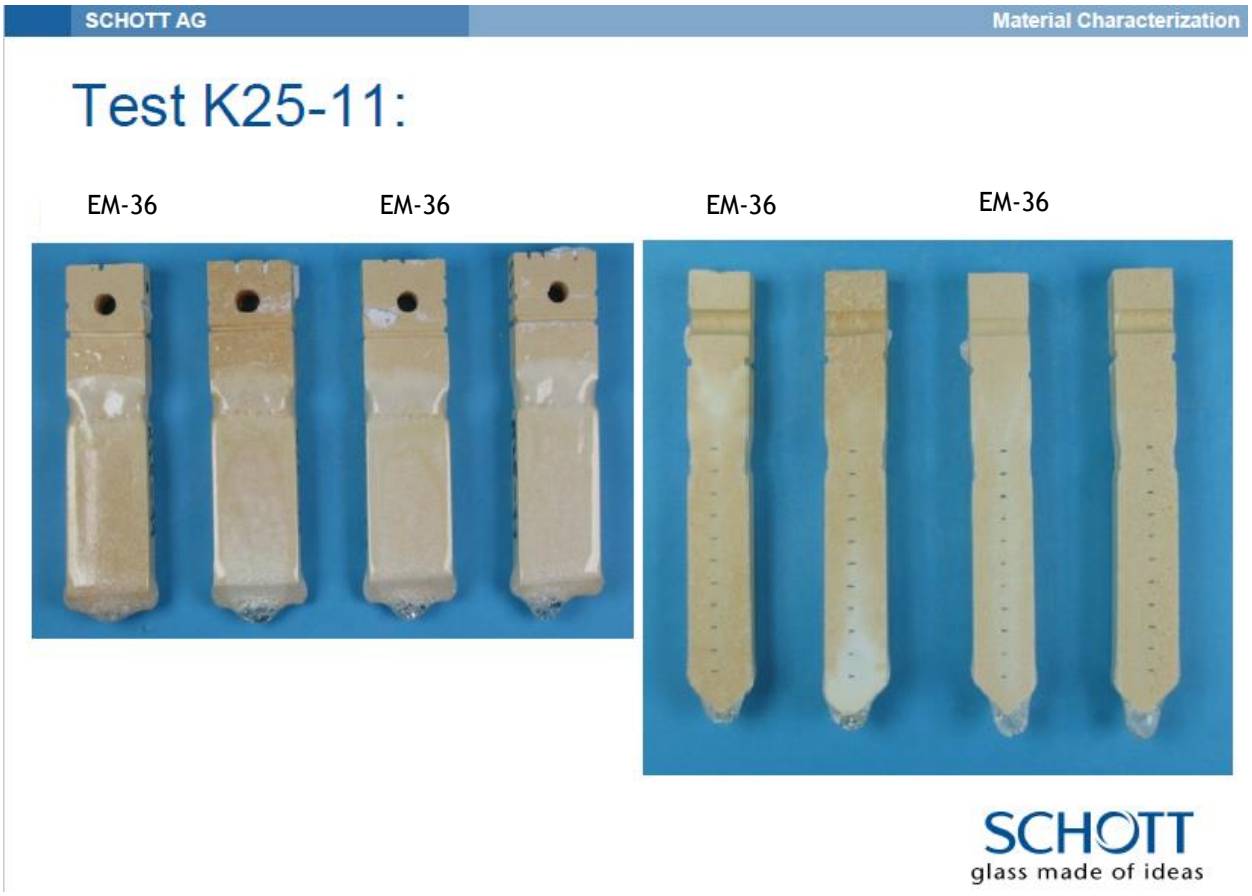


Fig.2: EM-36 samples after cutting

Fig.3: EM-33 samples after cutting

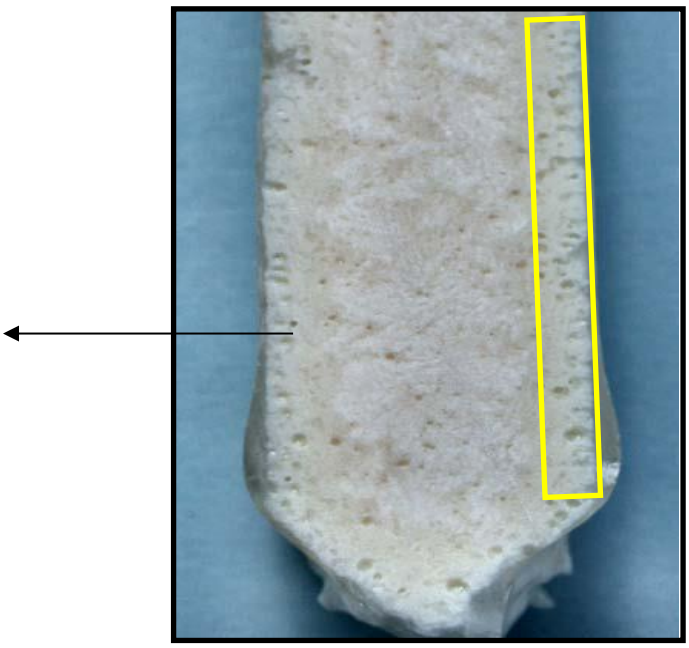
SCHOTT AG Material Characterization

Test K17-11:

EM-41 EM-41 EM-41 EM-41

SCHOTT
glass made of ideas

Fig.4: EM-41 samples after cutting



The figure 5 below is a zoom of corroded sample, beneath the glass level, to see the reaction layer, yellow area. It is the remaining part at the surface of the sample, after the test.
Its color is white whereas the healthy part of the sample, inside, is still light brown.

reaction layer

Fig.5: Reaction layer of sample

The figure 6 at the following page shows all results of static corrosion plate tests.

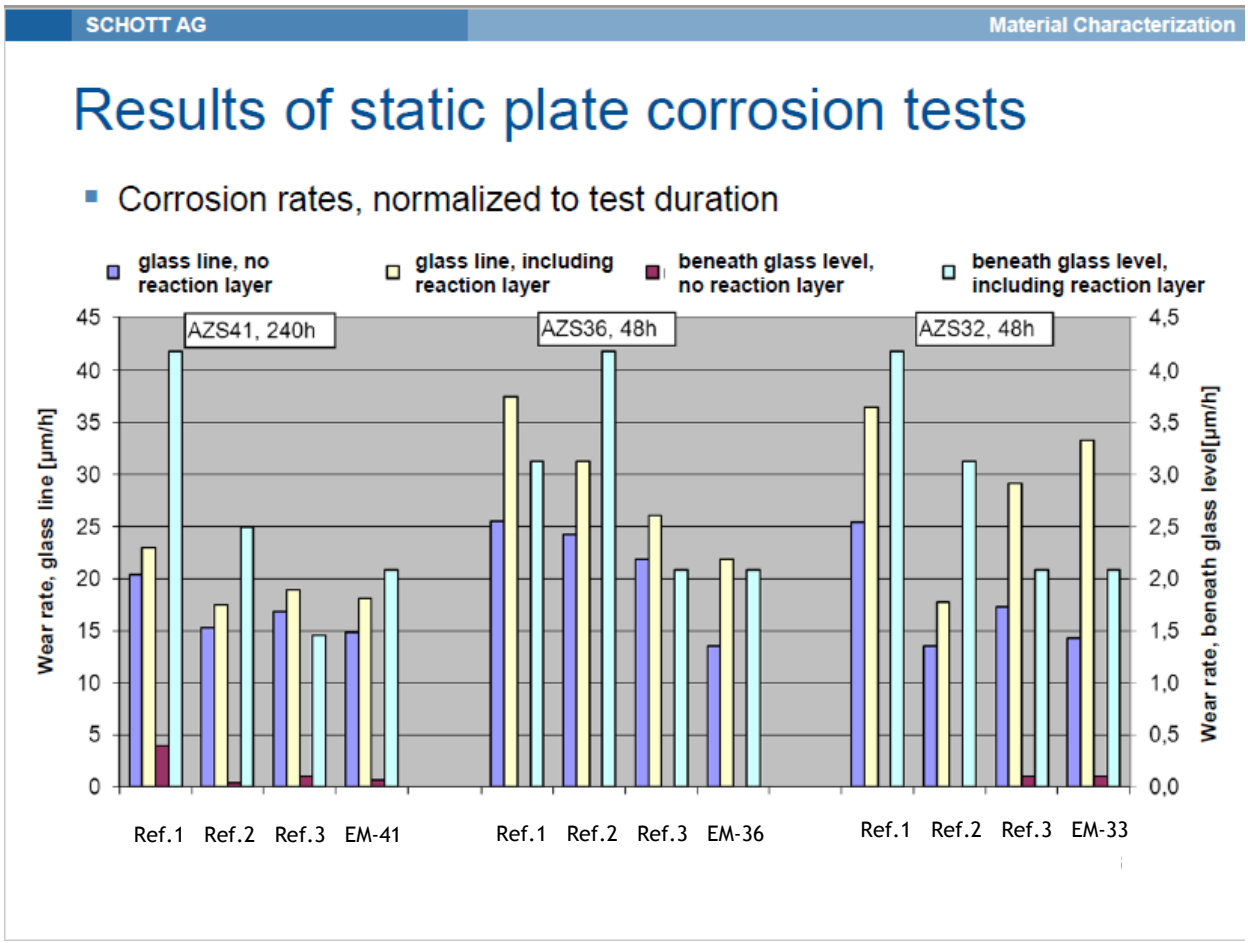


Fig.6: Static corrosion plate tests report

Wear rate on Y-axle are indicated in micrometer/hour.

On the left part, we can observe grade EM-41 and 3 main competitors, duration of the test is longer due to higher resistance of AZS 41%. On the central part, we can observe grade EM-36 and 3 main competitors. On the right part, we can observe grade EM-33 and 3 main competitors.

For each sample, Schott has indicated 4 different types of measurements, subject to different interpretations:

- In blue, **glass line, no reaction layer**. It is the corrosion at the glass level, without considering the corroded part still present at the surface of the sample (the so-called reaction layer).

- In cream, **glass line, including reaction layer**. It is the corrosion at the glass level, considering the corroded part still present at the surface of the sample. Cream values are thus always higher than blue values.

- In purple, **beneath glass level, no reaction layer**. It is the corrosion under the glass level, without considering the corroded part still present at the surface of the sample.

- In blue light, **beneath glass level, including reaction layer**. It is the corrosion under the glass level, considering the corroded part still present at the surface of the sample. Blue light values are thus always higher than purple values.

ANNEXE 2:

TESTS REPORT BY SCHOTT

EXUDATION

SCHOTT

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Our message of:		Facsimile:	+49 (0) 3641/ 28889-117	E-mail:	christian.kunert@schott.com

Exudation of AZS samples

Lab report 25/14

Dear Mr. Canaguier,

Masso ordered two measurements on fused cast AZS material at Schott:

- Simplified exudation tests (our offer no. TSK – 141118 – 475 – Fdg/Kne)
- Semiquantitative XRF-measurement (our offer no. TSK – 141110 – 471 – Fdg)

This report summarizes the results of these tests.

1 Sampling

Masso supplied sections of the following fused cast AZS blocks:

- ·33 PT, batch no. 13-11-449 (for sample EM 1 and EM 10)
- ·33 PT, batch no. 14-1-136 (for sample EM 2)
- ·33 PT, batch no. 14-1-387 (for sample EM 3)

As requested by Masso, three additional samples were investigated:

- ·33D produced 2013, lab ref. 039-2013
- Ref. 1: AZS33-material from European supplier 1, lab ref. 008-2015
- Ref. 2: AZS33-material from European supplier 2, lab ref. 012-2011

As specified by Masso, the samples EM 1, EM 2 and EM 3 were drilled from an outer corner of the 33 blocks with 20mm distance to the casting skin, see Figure 2 in Annex 1. Figure 3 shows how the drilling core (Ø 41mm) was sectioned into the XRF-sample (20-30mm below the casting skin) and exudation sample (30-120mm below the casting skin).

Samples EM 1 and EM 10 were taken from the same S 33 block (batch no. 13-11-449), but with the greatest possible distance between the two samples. Figure 4 shows the positions for the samples EM 1 and EM 10.

The sample from 33D (lab reference 039-2013) could be taken from exactly the same location as samples EM 1 – 3, since the sample block also had one outer corner.

The samples Ref. 1 and Ref. 2 were taken from blocks from two different European refractory suppliers, both qualified for SCHOTT purchases for this kind of material. The samples were also taken in the corner of the blocks, each with 20mm distance to the casting skin.

2 Simplified Exudation Test

2.1 Experimental

During heat-up and thermal cycling, fused cast AZS materials are known to exude a portion of the glassy phase present in the material. The test procedure recommended by TC11 of ICG for exudation tests proposes measuring the volume of exuded glassy phase after each thermal cycle at room temperature to follow the development of exuded volume over the number of heating cycles.

The simplified test performed for the current order measures the volume of exuded glassy phase only after the complete test procedure with 6 thermal cycles.

The samples are treated with the following temperature program:

First cycle:	room temp. ↗ 1550°C, 72h dwell time ↘ 800°C, 5h dwell time
Second to fifth cycle:	800°C ↗ 1550°C, 2h dwell time ↘ 800°C, 5h dwell time
Last cycle:	800°C ↗ 1550°C, 2h dwell time ↘ room temp.

The heating rates for the first heat up are 100K/h up to 1200°C, then 50K/h up to 1550°C. Cooling to 800°C is done with a cooling rate of 75K/h.

During the second to fifth cycle, the heating rates are 75K/h up to 1540°C, the 10K/h up to 1550°C.

The cylindrical exudation samples were placed on blocks made of insulation fire brick to absorb the exuded glassy phase. Further pieces of insulating fire brick were placed on top of the

samples to absorb glassy phase exuded from the top surface. After the thermal cycling, the adhering blocks of insulating fire brick were removed carefully from the samples without removing any AZS material.

According to the formulae in the Annex 2 the volume of exuded glassy phase was determined for each sample.

2.2 Results

Figure 5 to Figure 11 show the samples after the exudation test. The exuded glassy phase is visible on the surface of all samples in various amounts. Due to crystallization the glassy phase is milky white.

Table 1 summarizes the measured and calculated values for the exudation samples. Figure 1 gives a diagram of the calculated volumes of exuded glassy phase (in vol.-%).

Table 1: Results of the exudation test

Sample	L_{AZ} mm	L_T mm	M_{AZ} g	M_T g	V_{AZ} cm³	V_T cm³	V_{AZcorr} cm³	V_{anhGp} cm³	M_{anhGp} g	M_{Gp} %	V_{Gp} %
33 EM1	83,5	83,9	417,6	399,3	108,4	110,7	109,9	0,8	2,1	4,9	**7,4**
33 EM2	77,5	77,9	389,0	374,8	100,7	102,9	102,3	0,6	1,6	4,0	**6,2**
33 EM3	82,7	83,2	415,6	397,4	107,6	109,9	109,5	0,4	1,0	4,6	**7,0**
33 EM10	75,2	75,7	377,7	358,3	97,6	100,0	99,2	0,8	1,9	5,6	**8,6**
33D	68,7	69,1	349,6	337,2	89,4	91,5	90,9	0,6	1,6	4,0	**6,2**
Ref. 1	81,5	82,1	399,0	372,8	106,0	108,3	108,0	0,3	0,7	6,7	9,9
Ref. 2	81,8	82,4	413,2	403,3	107,3	109,7	109,3	0,4	1,0	2,6	**4,0**

L_{AZ}	Length of sample before the test
L_T	Length of sample after thermal cycling
M_{AZ}	Mass of sample before the test
M_T	Mass of sample after thermal cycling
V_{AZ}	Volume of sample before the test
V_T	Volume of sample after thermal cycling
V_{AZcorr}	Volume of the AZS sample before the test, corrected by the volume change during the exudation test
V_{anhGp}	Volume of adhering glassy phase on the sides of the AZS sample after the exudation experiment
M_{anhGp}	Mass of adhering glassy phase on the sides of the AZS sample after the exudation experiment
M_{Gp}	Exuded glassy phase in mass-%

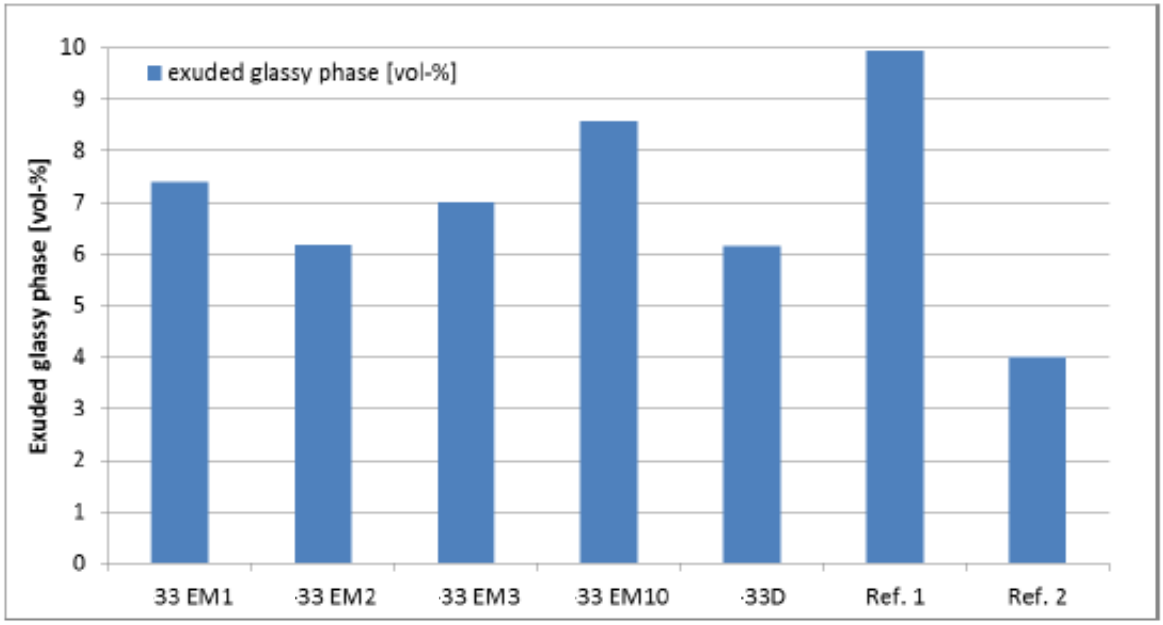

Figure 1: Exuded glassy phase [vol-%] after 1x 72h/1550°C + 5x 2h/1550°C

2.3 Discussion

For the three 33-samples EM 1 – 3 values in the range between 6,2 and 7,4 vol.-% of exuded glassy phase are determined.

The sample 33 EM 10 shows a higher amount of exuded glassy phase (8,6 vol.-%). Sample EM 10 was drilled from the same block as sample EM-1, but further in block with a coarser crystal structure.

The sample 33 D shows a similar result to the 33-samples EM 1 – 3 (6,2 vol.-%). In the current test, the sample from the "low exudation" material 33 D does not perform significantly differently from the standard material 33, although block size and sampling position were equal.

The two samples Ref. 1 and Ref. 2 from two different qualified European suppliers AZS33 materials exhibit remarkably different values for the volume of exuded glassy phase (9,9 and 4,0 vol.-%). These two samples show the range of exudation behavior. The results from the three 33-samples EM 1 – 3 are well within this scattering range of European material of the same class.

3 Semiquantitative XRF measurements

3.1 Experimental

The samples were analyzed with XRF spectrometry according to SOP 3-033[1].

Al_2O_3, Na_2O, HfO_2, SiO_2 and ZrO_2 were determined after sample preparation to a fused bead. Other elements were determined from a compact, polished sample surface.

With XRF spectrometry the determination of Li, B, N, C is not possible.

3.2 Results

Table 2 summarizes the results of the semiquantitative XRF measurements. The analytical results were calculated and normalized as oxides.

Elements/oxides which are not listed are below the determination limit of the method.

Table 2: Results of XRF analysis [% (m/m)]

Oxide	33-PT EM01	33-PT EM02	33-PT EM03	33-PT EM10	33-D (039-2013)	Ref. 1 (008-2015)	Ref. 2 (012-2011)	Relative MU [%]
Al_2O_3	52,5	50,8	49,9	51,9	52,5	50,4	48,5	3
CaO	0,057	0,065	0,067	0,059	0,072	0,13	0,064	30
Fe_2O_3	0,087	0,085	0,079	0,091	0,074	0,088	0,079	25
HfO_2	0,66	0,68	0,72	0,67	0,71	0,65	0,74	15
K_2O	0,014	<0,010	0,010	<0,010	<0,010	0,032	0,014	40
Na_2O	1,1	1,0	1,1	1,1	0,9	1,0	0,8	20
P_2O_5	<0,05	<0,05	<0,05	<0,05	<0,05	0,075	0,075	20
SiO_2	13,0	13,3	12,6	12,5	11,8	16,2	13,7	8
ThO_2	0,013	0,016	0,012	0,015	<0,010	<0,010	<0,010	40
TiO_2	0,047	0,057	0,053	0,061	0,033	0,08	0,095	30
U_3O_8	0,017	0,013	0,015	0,015	0,010	0,013	0,015	40
Y_2O_3	0,062	0,064	0,064	0,063	0,068	0,076	0,083	30
Yb_2O_3	0,013	0,015	0,017	0,015	0,014	0,016	0,018	40
ZrO_2	32,4	33,9	35,4	33,5	33,7	31,5	36,1	5
MnO	<0,010	<0,010	<0,010	<0,010	<0,010	0,011	0,011	40

Relative MU: relative measurement uncertainty

Mainz, 30.03.2015 Christian Kunert

[1] Analysis report no. 3-2014-03393 and 3-2015-00424

Annex 1

Figure 2: Sampling position

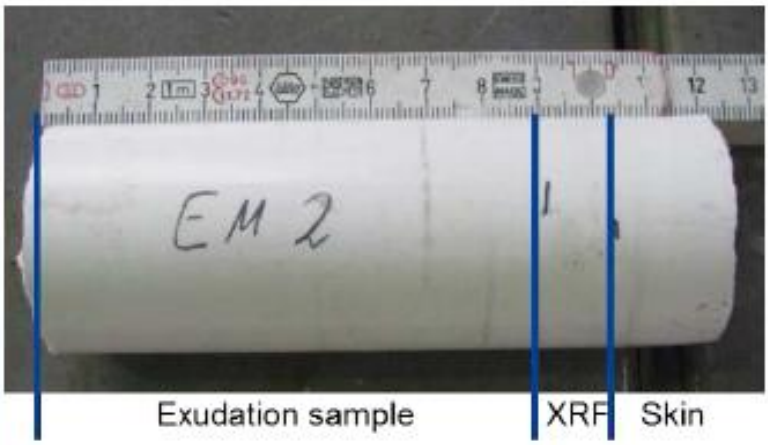

Figure 3: Division of drilling core into samples

Figure 4: Sampling position for samples EM 1 and EM 10

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Figure 5: Sample 33 EM 1 after the test

Figure 6: Sample 33 EM 10 after the test

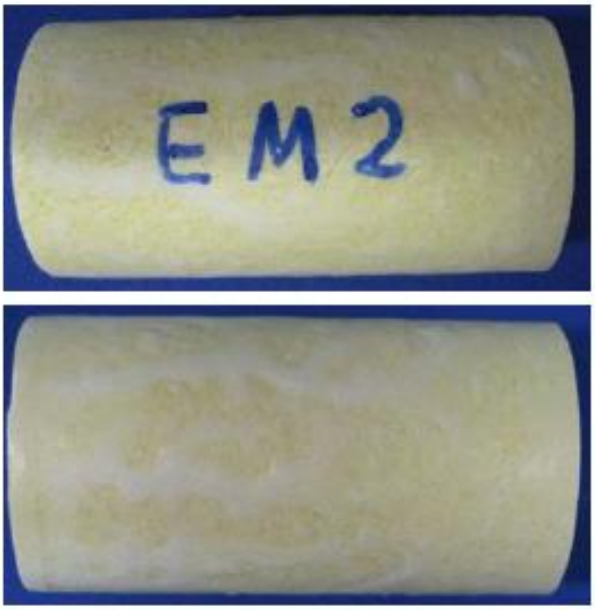

Figure 7: Sample 33 EM 2 after the test

Figure 8: Sample 33 EM 3 after the test

SCHOTT

Figure 9: Sample 33 D after the test

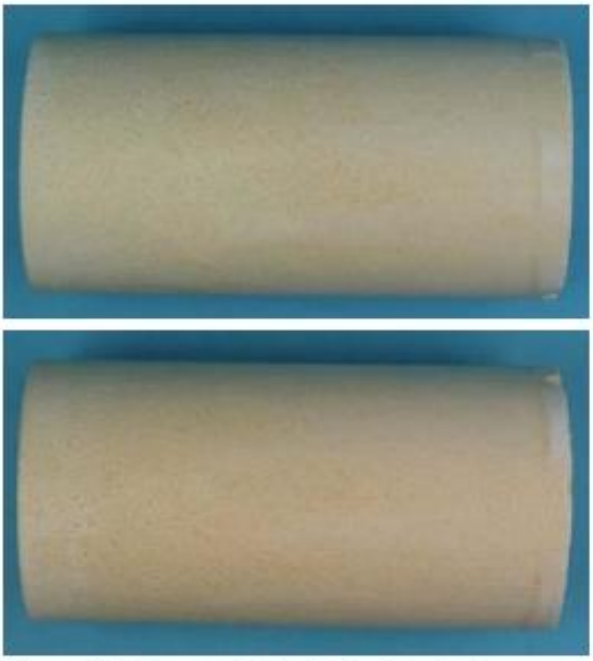

Figure 10: Sample Ref. 1 after the test

Figure 11: Sample Ref. 2 after the test

Annex 2

Determination of the amount of exuded glassy phase after AZS exudation test:

During the exudation test, the AZS samples are placed on plates made of insulating fire bricks, which absorb the exuded glassy phase. After the experiment, the adhering insulating fire bricks are removed carefully without removing anything from the AZS samples.

The amount of exuded glassy phase is calculated from the mass and volume of the samples prior and after the test according to the following formulae:

Determination of the amount of exuded glassy phase in mass-%:

M_{Gp} = Exuded glassy phase in mass-%

$$= \frac{M_{AZ} - M_T + M_{anhGp}}{M_{AZ}} \cdot 100\%$$

Determination of the amount of exuded glassy phase in volume-%:

V_{Gp} = Exuded glassy phase in volume-%

$$= \frac{M_{AZ} - M_T + M_{anhGp}}{\rho_{Gp} \cdot V_{AZ}^{corr}} \cdot 100\%$$

M_{anhGp} = $V_{anhGp} * \rho_{Gp}$

V_{anhGp} = $V_{AZcorr} - V_T$

M_{AZ} = mass of AZS sample as delivered (in grams)

M_T = mass of AZS sample after exudation test (in grams)

M_{anhGp} = mass of adhering glassy phase on the sides of the AZS sample after the exudation experiment (in grams)

V_T = volume of the AZS sample after the exudation test, including the adhering glassy phase (in cm³)

V_{anhGp} = volume of adhering glassy phase on the sides of the AZS sample after the exudation experiment (in cm³)

V_{AZcorr} = volume of the AZS sample as delivered, corrected by the volume change during the exudation test (in cm³)

$$= V_{AZ} \cdot \left(1 + \frac{3 \cdot (L_T - L_{AZ})}{L_{AZ}}\right)$$

V_{AZ} = volume of AZS sample as delivered (in cm³)

L_{AZ} = length of AZS sample as delivered (in cm)

L_T = length of AZS sample after exudation test (in cm)

ρ_{Gp} = density of exuded glassy phase (2,50 g/cm³)

NOTES:

MASSO TARGET IS

100% OF BLOCKS FIT WITH THE BEST SPECIFICATION TO REDUCE THE RISK OF DEFECTS GENERATED BY AZS

TO RESUME:

- **Define best specifications (chemistry, visual defects, tolerances, joints) in accordance with the needs of the end-user**

- **Define the level of the sampling procedure depending on quality requirements:**
  - ► **strict (**), very strict (***), extremely strict (****)**
  - ► **always with the 2 steps of checking:**

  Pour spout samples and corner samples from cast AZS block

- **Follow-up closely the project with the AZS producer and get traceability lists of all blocks to complete the 3SQC procedure**

- **Do inspections every three weeks to the producer to avoid any deviation, including GPR Scan to check location of cavities**

- **Send samples to recognized laboratory, like Schott (or others)**

- **Remit a solid two-year guarantee (or more) against defective refractory blocks**

- **"There is no trust, but only proves of trust!"**

"If you don't want to finish with empty pockets,
pay attention before choosing your jacket !"