OCCURANCES OF AMBER STREAK & BUBBLES IN FLINT GLASS

A CASE STUDY

HIGH QUALITY EXPECTATION EVEN IN SAME INDUSTRY SEGMENT

MARKET COMPETITIONS

CUSTOMER EXPECTATIONS

Introduction

Problem:

Bubbles in Glass

As the glass batch melted, the glass became filled with bubbles of entrapped gas(CO_2,SO_2,O_2,N_2,H_2O(vapor)). The chief source was the chemical release of carbon dioxide from the carbonates in the batch - the soda-ash, potash and lime. The second source was the gas entrapped in the spaces between the particles of batch materials. During the later stages of the melting, usually called the "fining" or refining, the gas bubbles rose to the top, burst, and disappeared.

Reference:
http://www.sha.org/bottle/body.htm

Introduction

Problem:

Amber streak in Glass

Presumably, a long term contact of iron with molten glass results in it's dissolution and gradual oxidation. A change in glass color like yellow/brown can be observed.

It may be occurred because of glass oxidation fluctuation by contaminated cullet, melting foaming, color change, drilling of metal droplets through melting end bottom. This effect could originate in local occurring reducing condition in feeder and working end

Reference:
1. Glass Defects by **Milloslav Barotuska and Co-authors**, Published by Glass Service Inc, Czech Republic
2. Recycling of post-consumer glass: energy savings, co2, emission, reduction, effects on glass quality and glass quality melting by TNO glass group, Eindhoven,NL
3. Test Report by Zentrum fur glass-and Umweltanalytik.

Introduction

What is Bubbles-Seed and Blister ?

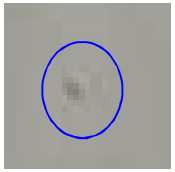
Glass often contains bubbles of gas which ,according to their size, are designated as blisters or seeds. The distinction is a purely arbitrary one and the limiting size differs according to the judgment of the selectors and the kind of ware being produced.

“Bubbles" are air or gas filled cavities within the glass.

In the glass making industry, small bubbles were referred to as "seeds" and larger bubbles as "blisters."

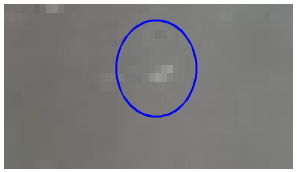
Seeds are not likely more than 1/16 inch in diameter which is lesser than bubble diameter.

Both blisters and seeds are flattened, elongated or otherwise distorted during the process of shaping a piece of ware.



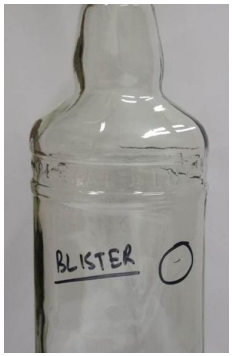
Magnified images of Bubble

Bubble



Magnified images of Seed

Seed



Magnified images of Blister

Blister

Reference:

Modern glass practice by Samuel Ray Scholes, Charles H Greene)

AN APPROACH TO RESOLVE AMBER STREAK AND BUBBLES IN GLASS BOTTLES

CLASSIFICATION & IDENTIFICATION OF BUBBLES

1. **Classification by Appearances(sizes & shapes)**

2. **Classification by mechanism of bubble origin**.

A. Bubbles generated by the decomposition and other reactions of raw materials(PRIMARY BUBBLES).

B. Bubbles generated by the nucleation or by growth of the nuclei as a result of the melt oversaturation.

C. Bubbles produced by chemical reactions with solid impurities.

D. Bubbles produced by chemical reactions of molten glass with liquid impurities.

E. Bubbles generated by electrochemical reactions.

F. Bubbles generated in mechanical way.

Referred: Glass Defects by **Milloslav Barotuska and Co-authors**, Published by Glass Service Inc, Czech Republic

A VIEW ON RELATIVE QUALITY REQUIREMENT OF SEEDS GLASS MARKET SEGMENT WISE

Financial Impact

GLASS MARKET	SEED/OZ	RELATIVE SEED QUALITY
LCD Display		10X better than TV Panel glass
TV Panel		10X better than Float glass
Float / Flat		1000 to 10000X better than container glass
Textile Fiber		100x better than container glass
Tableware	< 2	10x better than container glass
Lighting Glass	~ 25	2x better than container glass
Container	10 ~ 20	10x better than funnel glass
TV Funnel	~ 200	2x better than wool insulation fiber glass
Insulation Fiber	~ 400	

- Fewer defects especially fewer remaining bubbles has become a major requirement in new quality standards for many commercial glasses.
- For example, in the TV glass production, a rate of six bubbles per ton of glass results in 10% rejection rate of the final product, and for new products such as High Definition Television, the quality standards are even more stringent.
- For automobile glass, the most demanding specification requires that gas bubbles be less than 0.5 mm in diameter for transparency purposes.
- Moreover, for windshield glass, reducing by half the defect density would increase the profitability by more than 2 millions dollars per year.
- Consequently, understanding the behavior of gases and bubbles in the glass melt and its identification of sources ,a systematic approach to resolve are of great interest to the glass industry, both from a technological and an economical viewpoints.

Reference: " Bubble transport in three-dimensional laminar gravity-driven flow – mathematical formulation "

Laurent Pilon a,*, Andrei G. Fedorov b, D. Ramkrishna c, Raymond Viskanta

AN APPROACH TO RESOLVE AMBER STREAK IN GLASS BOTTLES

❖ Case Study: First occurrence.

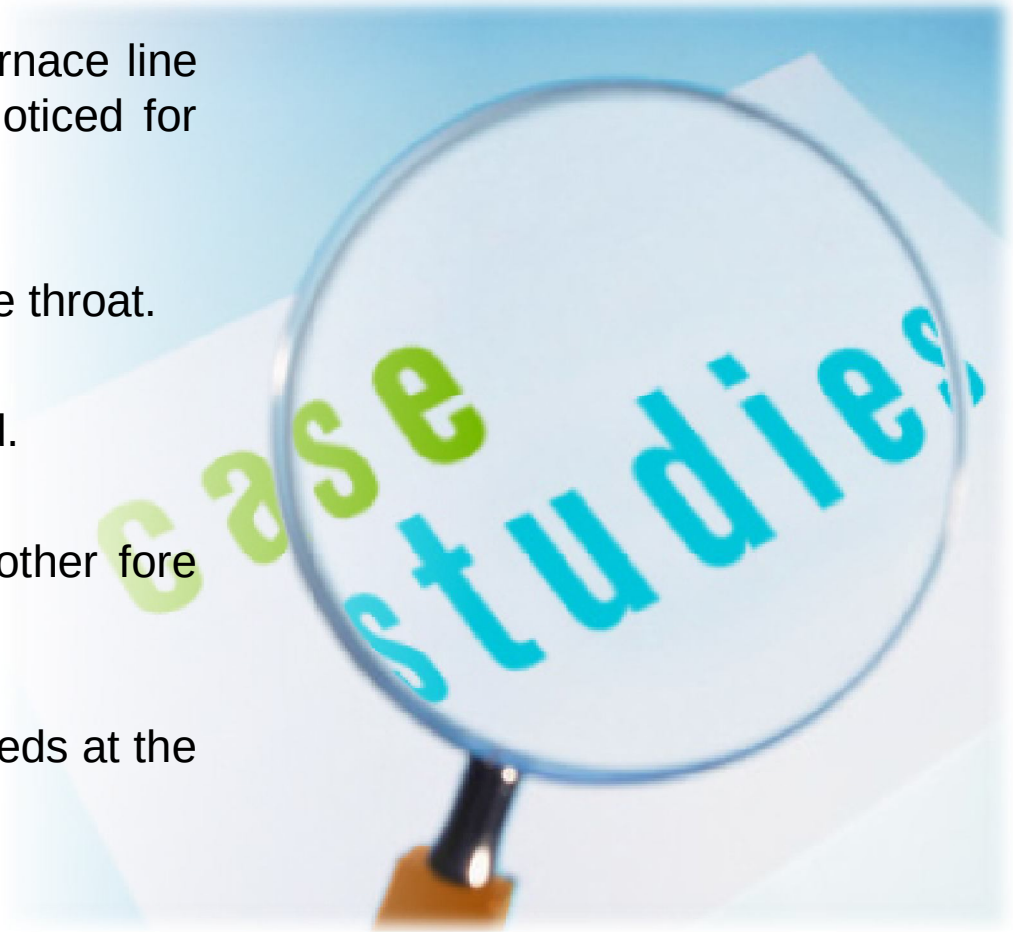
1. In Hyderabad factory in flint glass furnace line No.27, amber streak problem was noticed for 15 days intermittently in Oct-2010.

2. This fore hearth is located close to the throat.

3. Fore hearth No.27 was drawing 68tpd.

4. The problem was not appearing in other fore hearths.

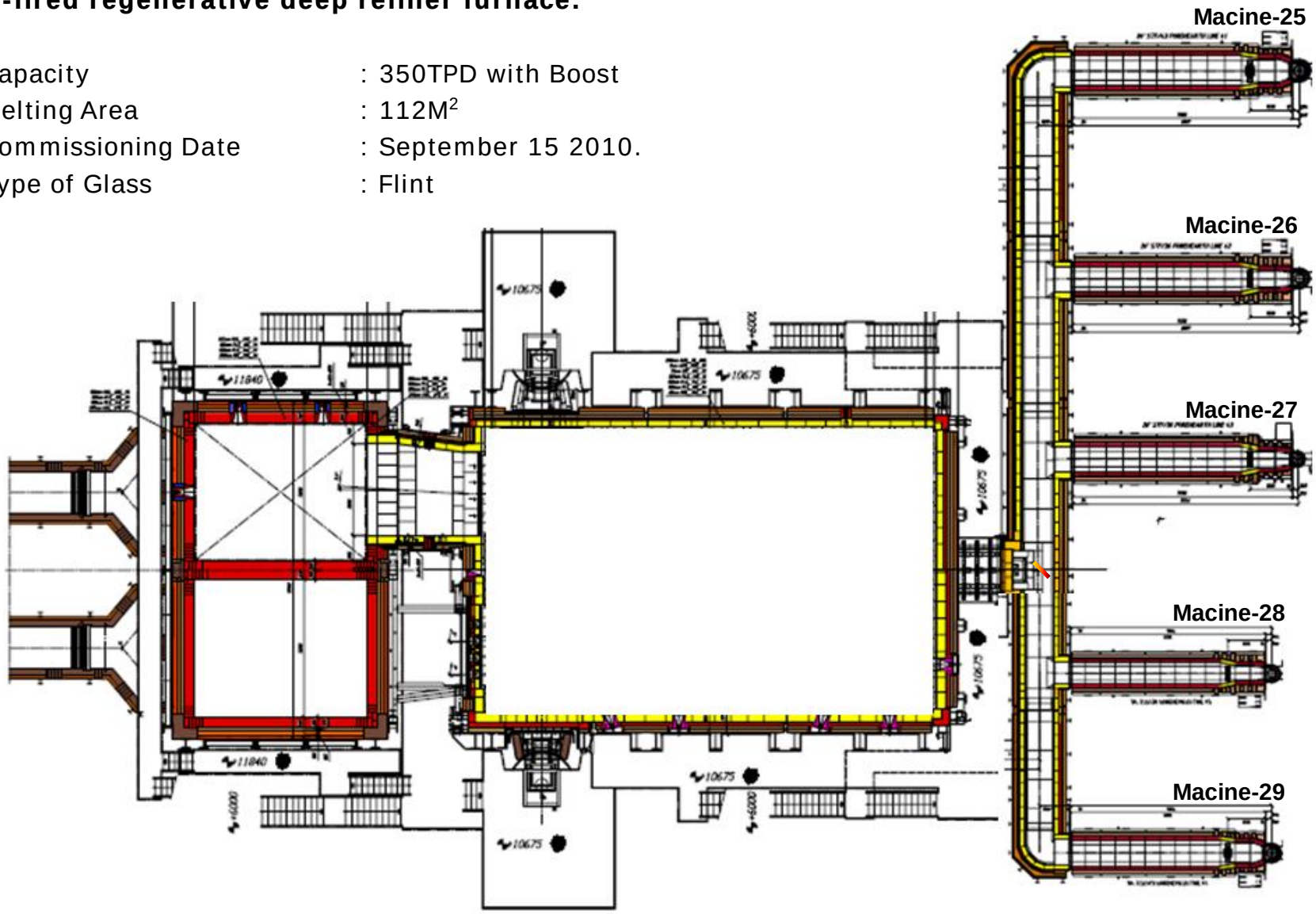
5. The amber streak didn't show any seeds at the edge.



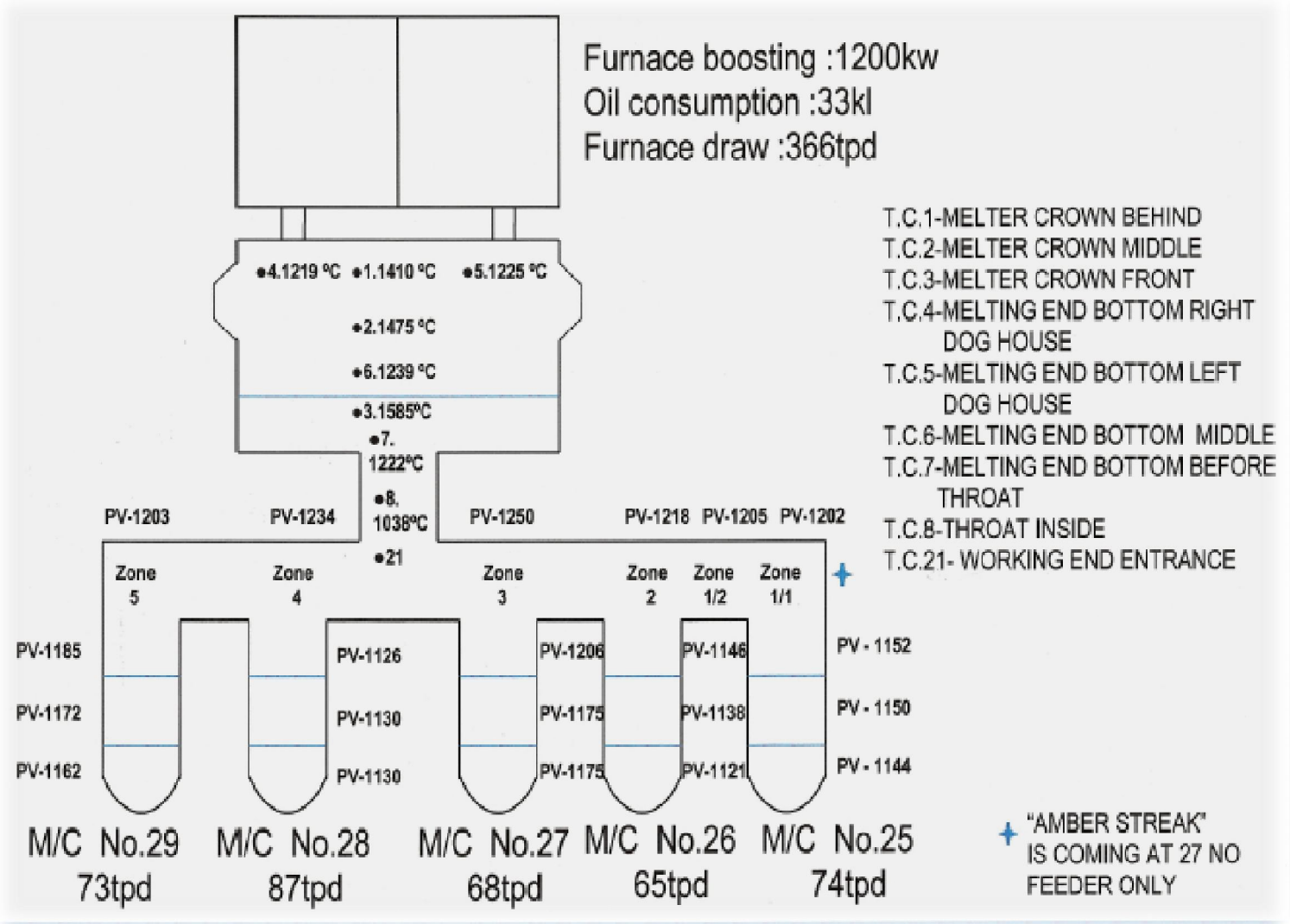
AN APPROACH TO RESOLVE AMBER STREAK IN GLASS BOTTLES

An end-fired regenerative deep refiner furnace:

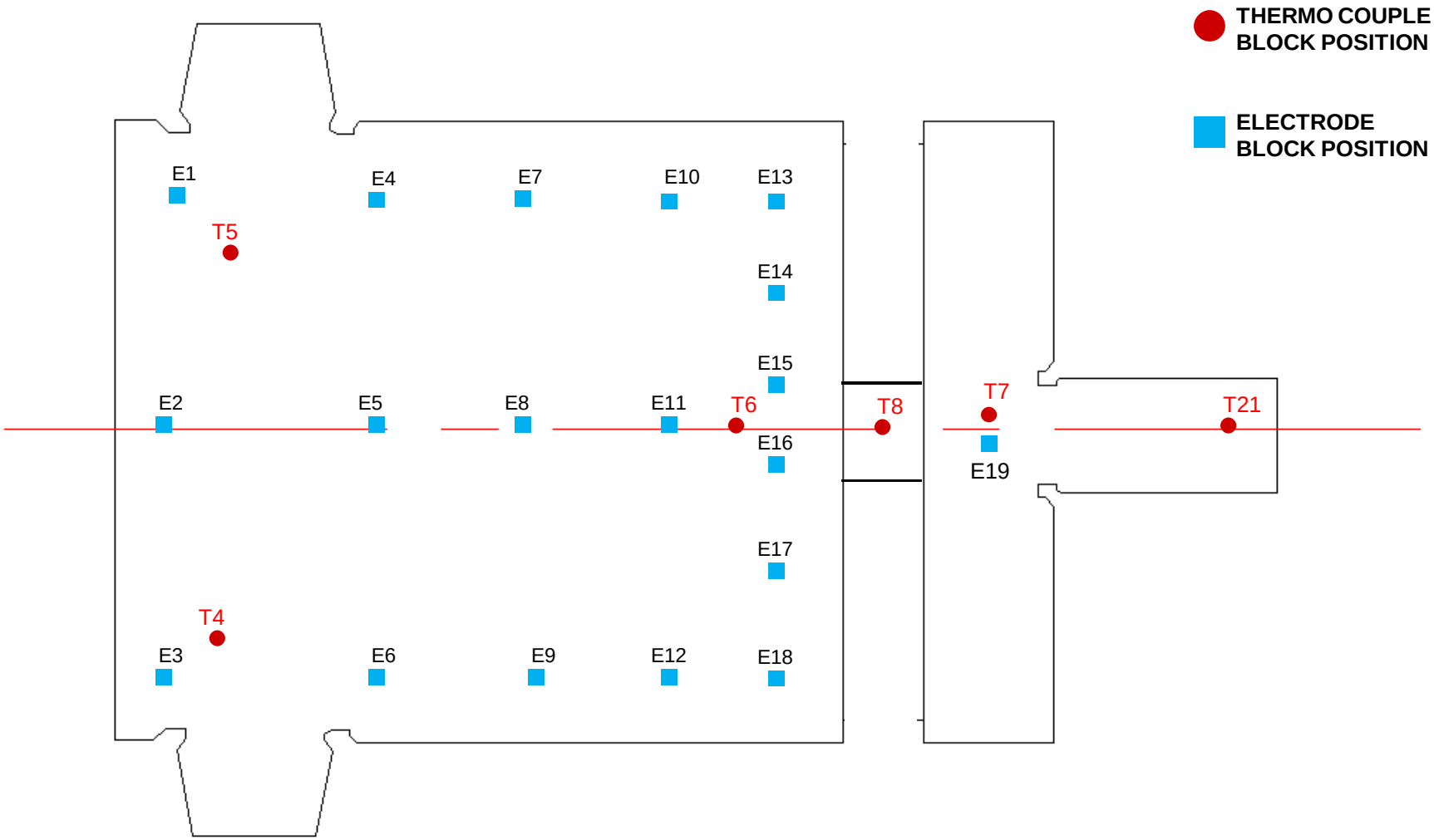
- Capacity : 350TPD with Boost
- Melting Area : 112M^2
- Commissioning Date : September 15 2010.
- Type of Glass : Flint



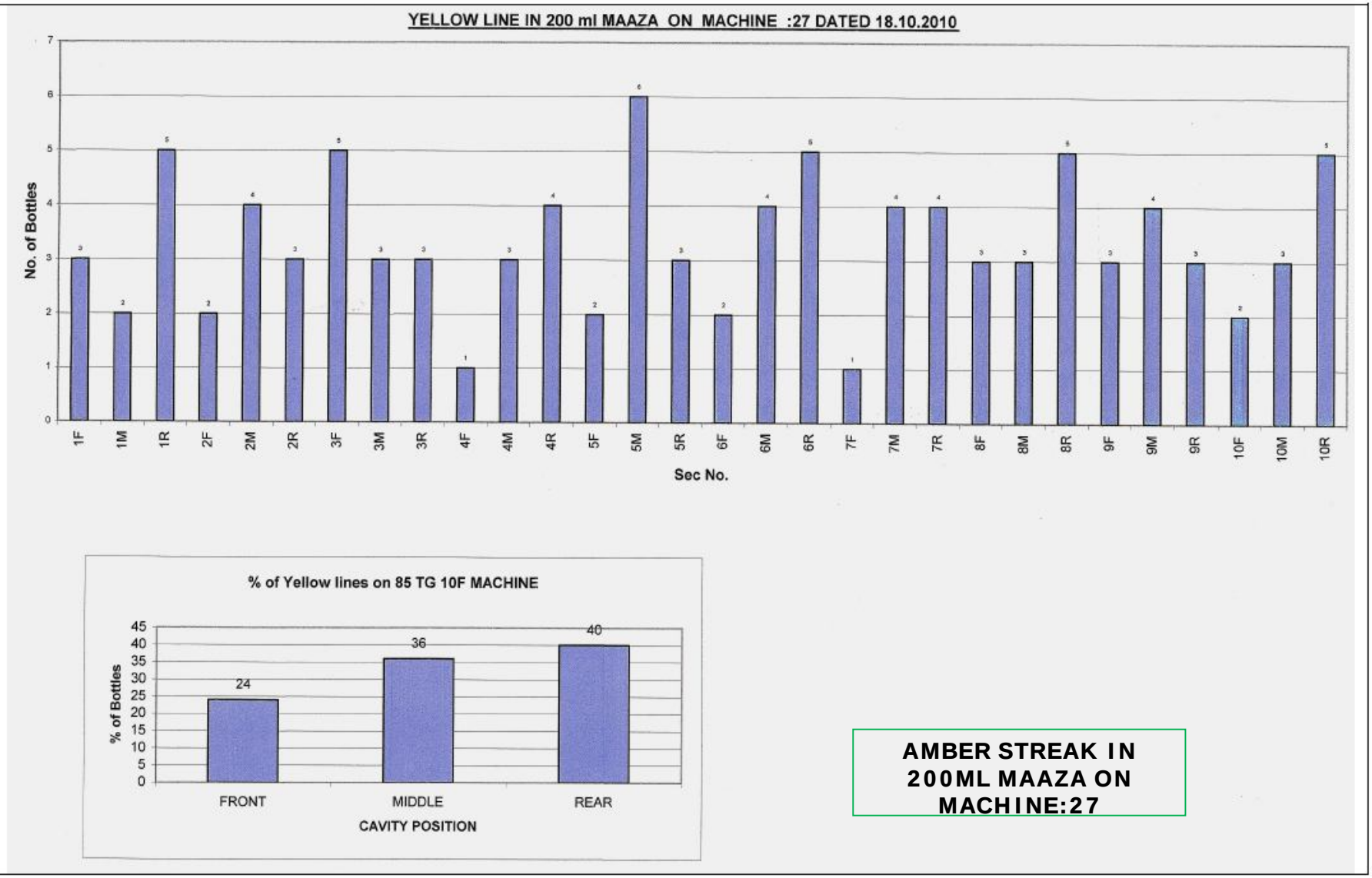
OUT LINE OF FURNACE AND FOREHEARTH / FEEDERS



FURNACE BOOSTER ELECTRODES BLOCKS AND THERMOCOUPLES BLOCKS POSITIONING LAYOUT



AMBER STREAK IN 200ML MAAZA ON MACHINE:27



AMBER STREAK IN 200ML MAAZA ON MACHINE:27

CORRECTIVE ACTION TAKEN

Having assumed some foreign material was lying inside the fore-hearth no:27, at first, we did heavy draining of glass of that particular fore-hearth several times: though it offered a temporary relief but problem resumed soon afterwards.

We also investigated the entire fore -hearths and working end area especially line 27fore-hearth gas heating system as well as the radiation cooling damper area and found no abnormality.

Presuming that amber streak was generated due to some foreign materials contact with the glass in fore hearth / working end. This assumption was based on the fact that sometimes when there was variation in the draw pattern on line 27, Amber streak were observed on fore hearths location on both sides of line27 i.e. fore-heatrth26 and fore -hearth 28. these Amber streaks occurred on these fore hearth for very short duration varying from about half an hour to two hours and subsequently it disappeared when the flow of glass in line27 restored to normal level.

We therefore provided a cooling arrangement at the bottom of the working end and close to the line 27 connection block on 27.10.2010. The size of the wind box was 2150mm(length)x850mm(width)x330mm depth extending equally on either side of the fore- hearth 27. Subsequent to this, we had noticed considerable reduction of almost 95% Amber steaks, and we were continuing the same cooling arrangement. However, we did keep noticing Amber streaks on the adjacent lines periodically for about one hour or two hours once in two days or so.

On 18.11.2010 we started throat boosting on continuous basis. After few days Amber streak problem gradually disappeared.

RESULTS OF EDX- MICROSCOPIC INVESTIGATION AMBER STREAK - BODY

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RESULTS OF MICROSCOPIC INVESTIGATION

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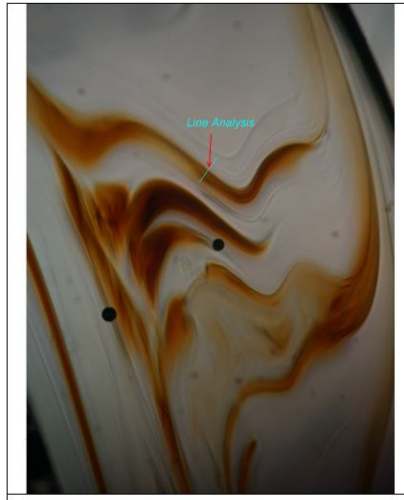

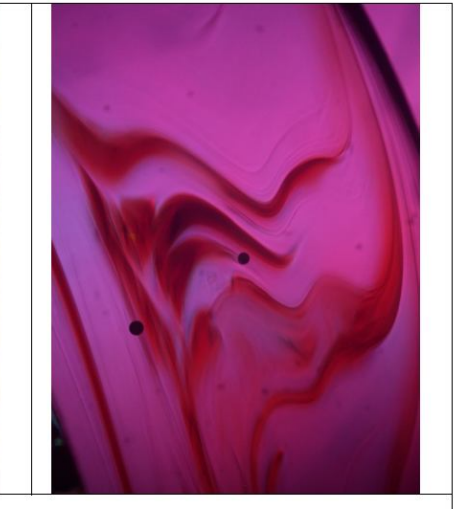

The defect from Sample Amber streak – Body in polished cross-section under stereomicroscope

The defect from the Sample Amber streak Body in polished cut in passing through light and in passing through polarized light between crosses polars with interference wafer of the first order

NOTE:

- **Energy-dispersive X-ray spectroscopy** (EDS, EDX, or XEDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on the investigation of an interaction of some source of X-ray excitation and a sample.
- **The stereo or stereoscopic** or dissecting microscope is an optical microscope variant designed for low magnification observation of a sample, typically using light reflected from the surface of an object rather than transmitted through it.

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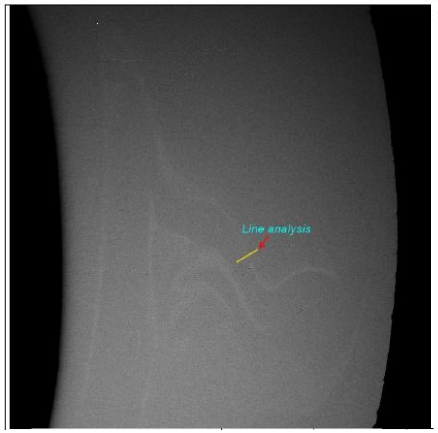

The defect from the Sample „ Amber streak Body “ in polished cut under electron microscope – BSE detector

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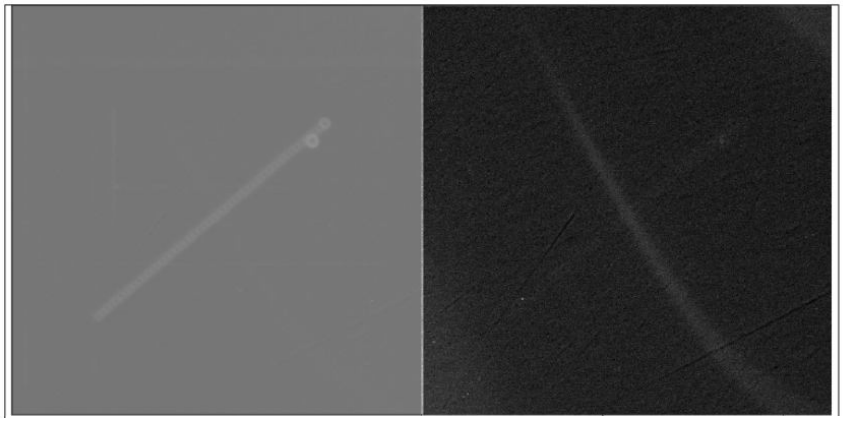

The analyzed part of the defect from the Sample„ Amber streak Body “ in polished cut under electron microscope – SE and BSE detector – with traces originating from line analyses

NOTE:

An electron microscope (EM) is a type of microscope that uses an electron beam to illuminate a specimen and produce a magnified image. An EM has greater resolving power than a light microscope and can reveal the structure of smaller objects because electrons have wavelengths about 100,000 times shorter than visible light photons.

Back-scattered electrons (BSE),
In physics, backscatter (or backscattering) is the reflection of waves, particles, or signals back to the direction from which they came. It is a diffuse reflection

Secondary electrons (SE),
Secondary electrons are electrons generated as ionization products. They are called 'secondary' because they are generated by other radiation (the primary radiation). This radiation can be in the form of ions, electrons, or photons with sufficiently high energy,

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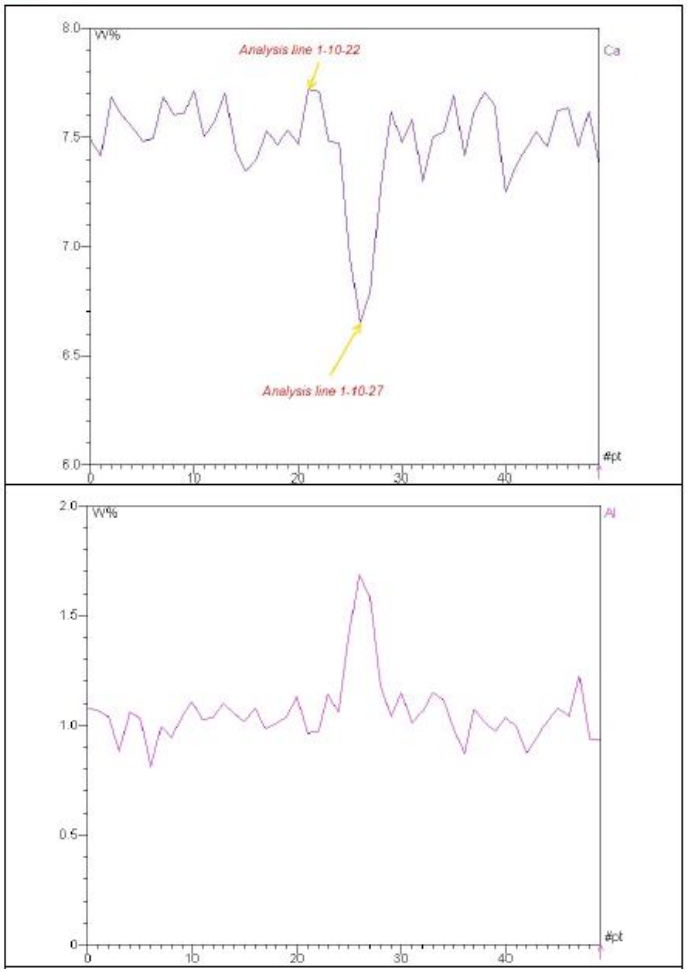

Results of presence of Ca and of Al in marked area from the Sample Amber streak Body

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« Sample „ Amber streak Body »

Analysis line 1-10-22

Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.07	59.19		0.00
Na	Ka	148.1	12.1695	9.33	8.53	Na2O	12.58
Mg	Ka	10.6	3.2511	0.52	0.45	MgO	0.86
Al	Ka	24.6	4.9577	0.96	0.75	Al2O3	1.82
Si	Ka	1025.3	32.0199	35.49	26.55	SiO2	75.93
K	Ka	18.5	4.2969	0.90	0.49	K2O	1.08
Ca	Ka	152.0	12.3282	7.72	4.05	Ca0	7.72
Σ				100.00	100.00		100.00

« Sample „ Amber streak Body »

Analysis line 1-10-27

Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.45	59.37		0.00
Na	Ka	154.3	12.4202	9.73	8.85	Na2O	13.12
Mg	Ka	7.4	2.7267	0.37	0.32	MgO	0.61
Al	Ka	42.7	6.5359	1.69	1.31	Al2O3	3.19
Si	Ka	1001.7	31.6495	35.23	26.22	SiO2	75.37
K	Ka	17.9	4.2343	0.88	0.47	K2O	1.06
Ca	Ka	129.8	11.3921	6.65	3.47	Ca0	6.65
Σ				100.00	100.00		100.00

RESULTS OF EDX- MICROSCOPIC INVESTIGATION AMBER STREAK - BODY

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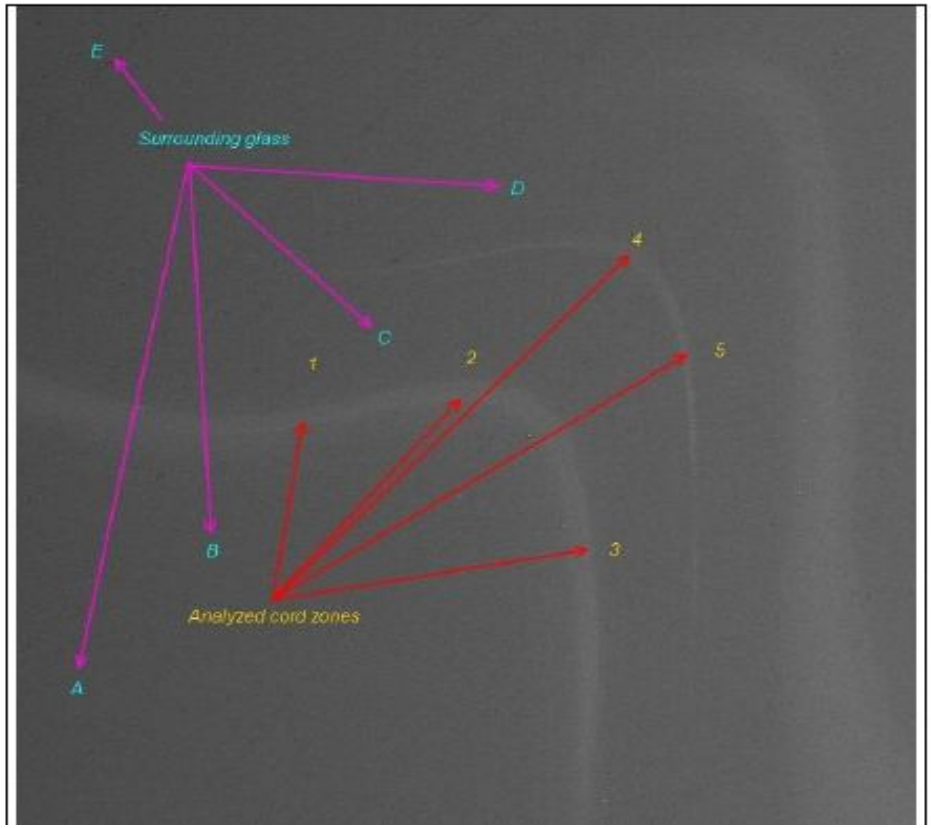

The analyzed part of the defect from the Sample „ Amber streak Body “ in polished cut under electron microscope – BSE detector – with marks of analyzed zones

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« Sample „ Amber streak Body »

Analyzed cord zones

1 Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.38	59.32		0.00
Na	Ka	176.8	13.2959	9.75	8.87	Na2O	13.14
Mg	Ka	9.4	3.0688	0.41	0.35	MgO	0.68
Al	Ka	47.3	6.8769	1.63	1.27	Al2O3	3.09
Si	Ka	1145.2	33.8410	35.20	26.21	SiO2	75.29
K	Ka	19.1	4.3723	0.82	0.44	K2O	0.99
Ca	Ka	152.1	12.3348	6.81	3.55	Ca0	6.81
Σ				100.00	100.00		100.00

2. Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.61	59.48		0.00
Na	Ka	179.3	13.3901	9.87	8.95	Na2O	13.30
Mg	Ka	6.4	2.5282	0.28	0.24	MgO	0.46
Al	Ka	46.8	6.8432	1.62	1.25	Al2O3	3.05
Si	Ka	1156.2	34.0029	35.48	26.35	SiO2	75.90
K	Ka	16.0	4.0014	0.69	0.37	K2O	0.83
Ca	Ka	144.5	12.0189	6.46	3.36	Ca0	6.46
Σ				100.00	100.00		100.00

3. Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.31	59.22		0.00
Na	Ka	184.2	13.5738	9.90	9.01	Na2O	13.35
Mg	Ka	12.1	3.4834	0.52	0.44	MgO	0.86
Al	Ka	49.0	7.0031	1.66	1.29	Al2O3	3.13
Si	Ka	1165.0	34.1321	35.02	26.07	SiO2	74.92
K	Ka	17.5	4.1824	0.73	0.39	K2O	0.88
Ca	Ka	157.1	12.5356	6.86	3.58	Ca0	6.86
Σ				100.00	100.00		100.00

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« Sample „ Amber streak Body »

Analyzed cord zones

4. Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.21	59.18		0.00
Na	Ka	186.7	13.6641	10.00	9.11	Na2O	13.48
Mg	Ka	8.7	2.9505	0.37	0.32	MgO	0.61
Al	Ka	51.1	7.1493	1.72	1.33	Al2O3	3.24
Si	Ka	1167.2	34.1648	34.85	25.99	SiO2	74.56
K	Ka	18.8	4.3412	0.78	0.42	K2O	0.94
Ca	Ka	155.8	12.4828	6.74	3.52	Ca0	6.74
Fe	Ka	3.6	1.9023	0.32	0.12	FeO	0.41
Σ				100.00	100.00		100.00

5. Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.21	59.16		0.00
Na	Ka	186.7	13.6635	10.07	9.17	Na2O	13.58
Mg	Ka	9.0	2.9966	0.38	0.33	MgO	0.64
Al	Ka	49.8	7.0583	1.69	1.31	Al2O3	3.19
Si	Ka	1156.2	34.0029	34.83	25.96	SiO2	74.50
K	Ka	22.7	4.7693	0.95	0.51	K2O	1.15
Ca	Ka	151.1	12.2913	6.60	3.45	Ca0	6.60
Fe	Ka	3.0	1.7291	0.27	0.10	FeO	0.34
Σ				100.00	100.00		100.00

RESULTS OF EDX- MICROSCOPIC INVESTIGATION AMBER STREAK - BODY

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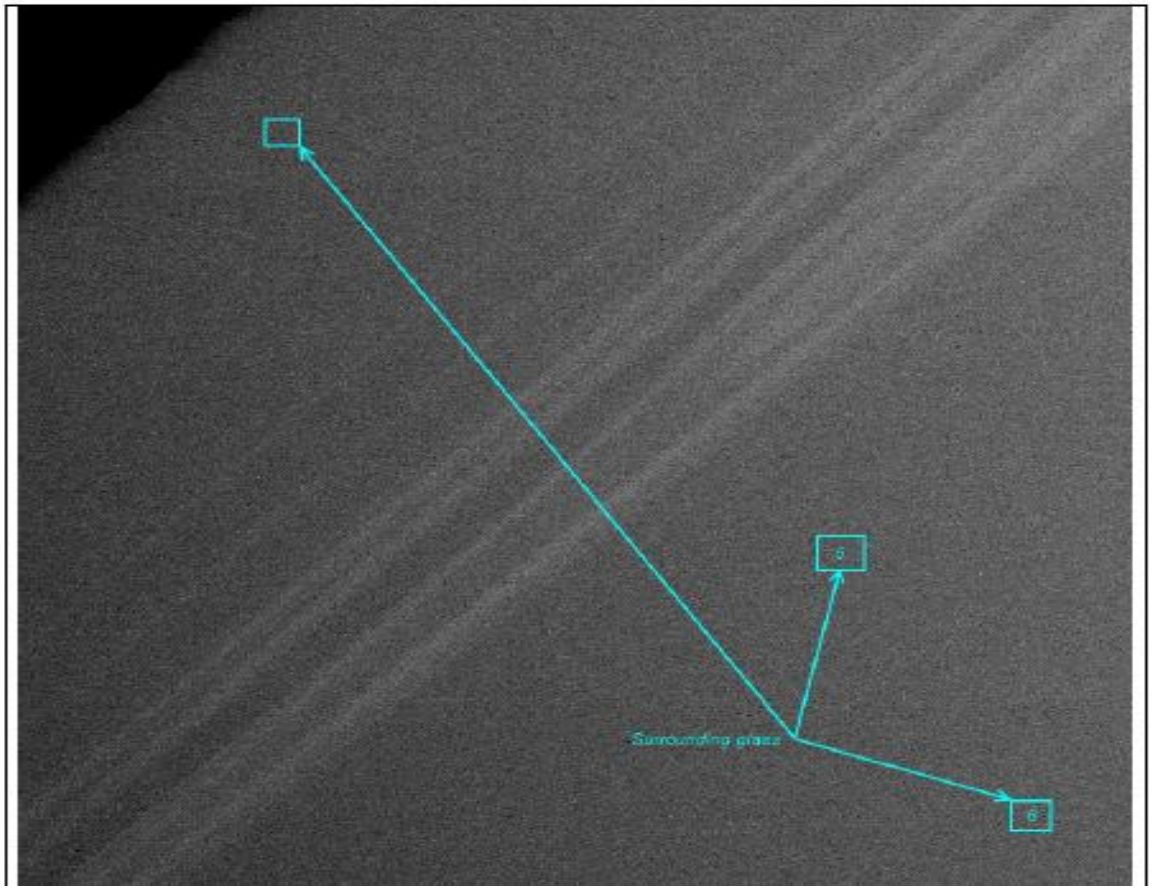

The defect from the Sample „ Amber streak Body “ in polished cut under electron microscope – BSE detector

RESULTS OF EDX- MICROSCOPIC INVESTIGATION AMBER STREAK - BODY

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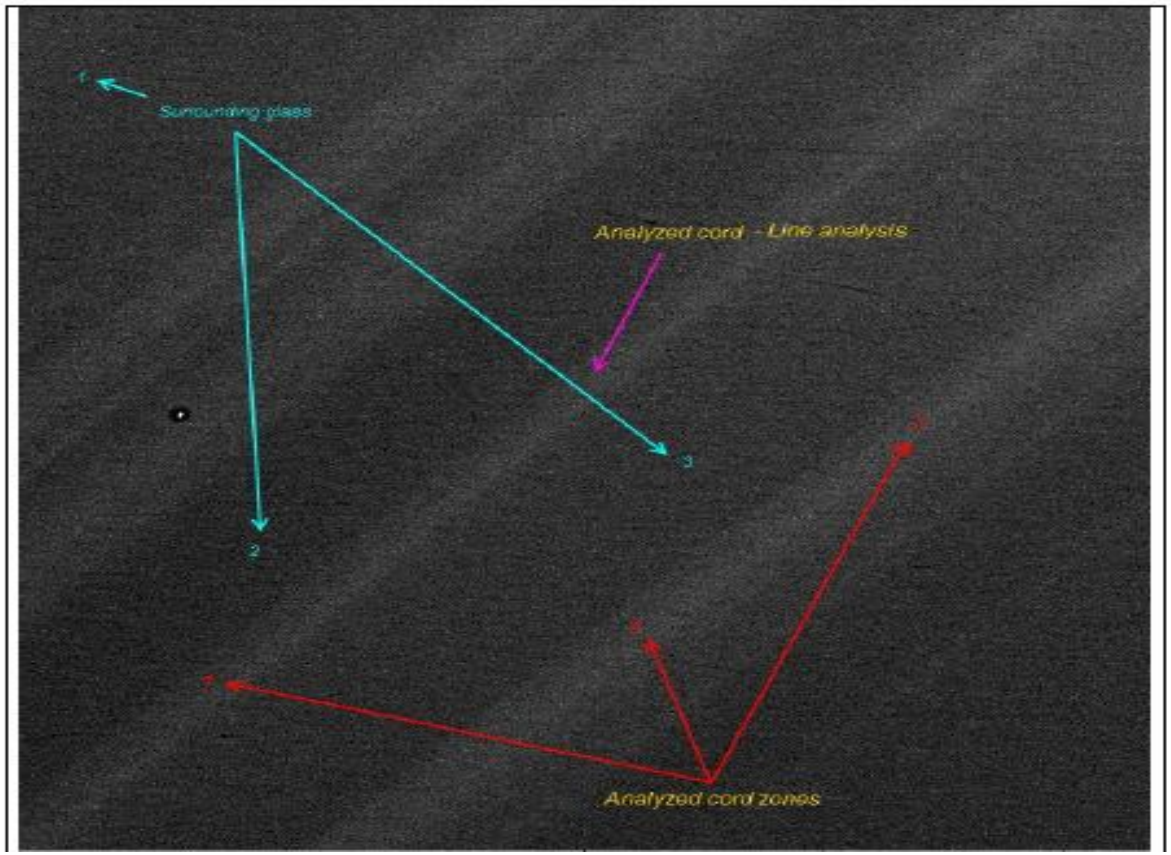

The defect from the Sample „ Amber streak Body “ in polished cut under electron microscope – BSE detector – with marks of analyzed zones

RESULTS OF EDX- MICROSCOPIC INVESTIGATION AMBER STREAK - BODY

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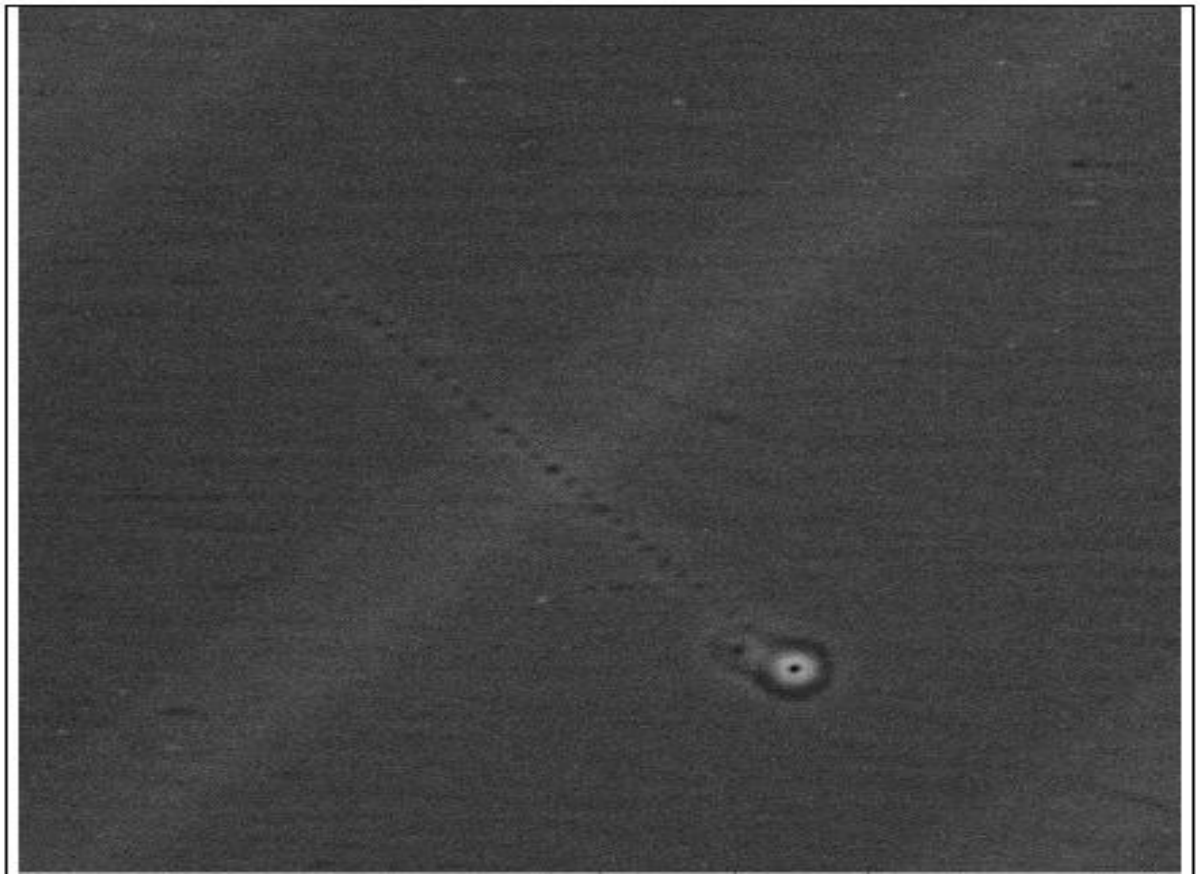
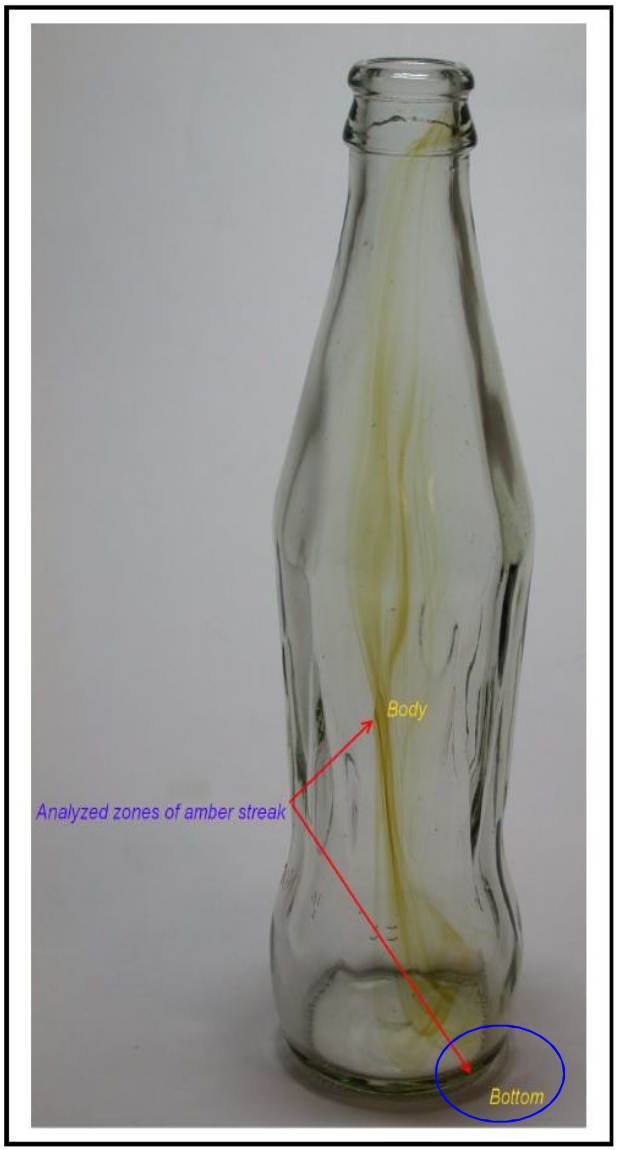


The analyzed part of the defect from the Sample „ Amber streak Body “ in polished cut under electron microscope – BSE detector – with traces originating from line analyses

RESULTS OF EDX- MICROSCOPIC INVESTIGATION
AMBER STREAK - BOTTOM



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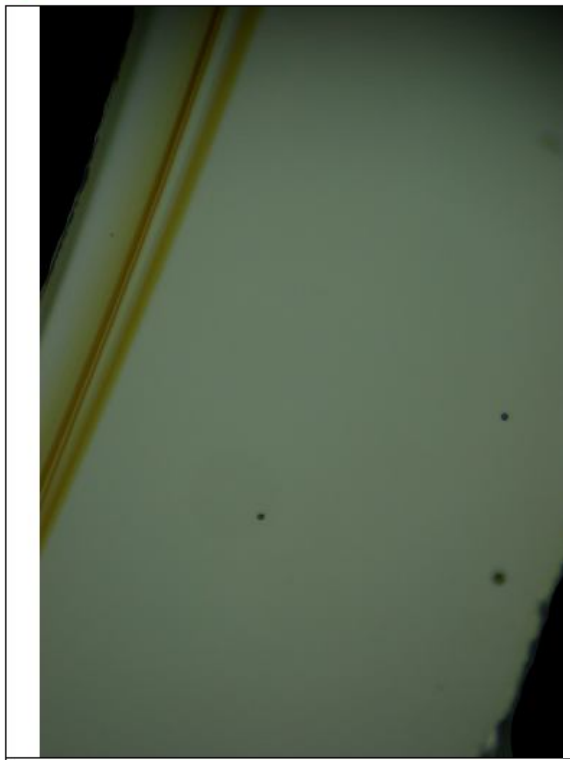

The defect from the Sample „ Amber streak Bottom “ in polished cross section in passing through light

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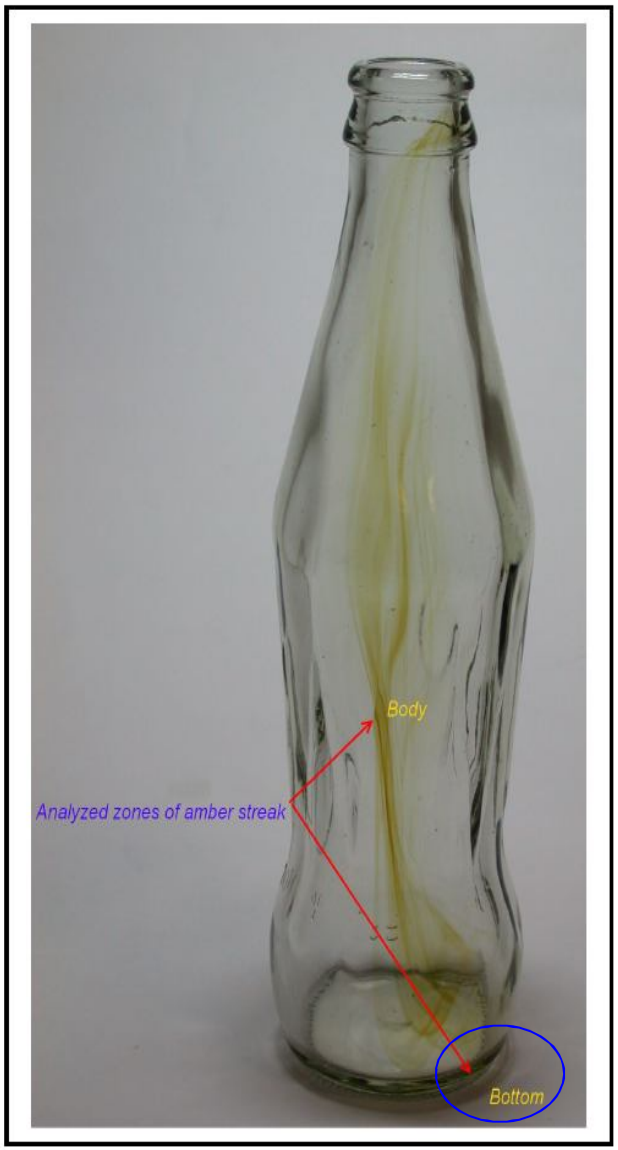
The detail of the defect from the Sample „ Amber streak Bottom “ in polished cut in passing through polarized light between crosses polars with interference wafer of the first order

RESULTS OF EDX- MICROSCOPIC INVESTIGATION
AMBER STREAK - BOTTOM



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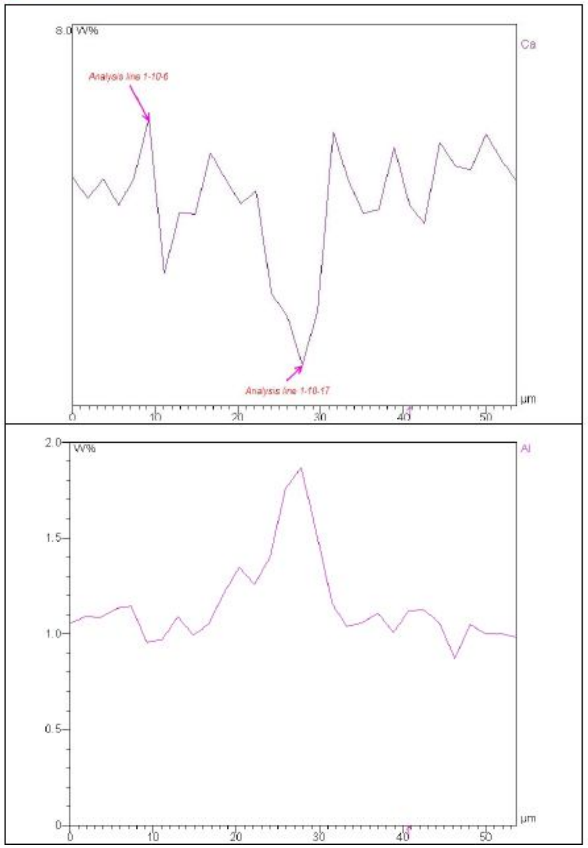

Results of Ca presence and of Al presence in marked area from the Sample Amber streak Bottom

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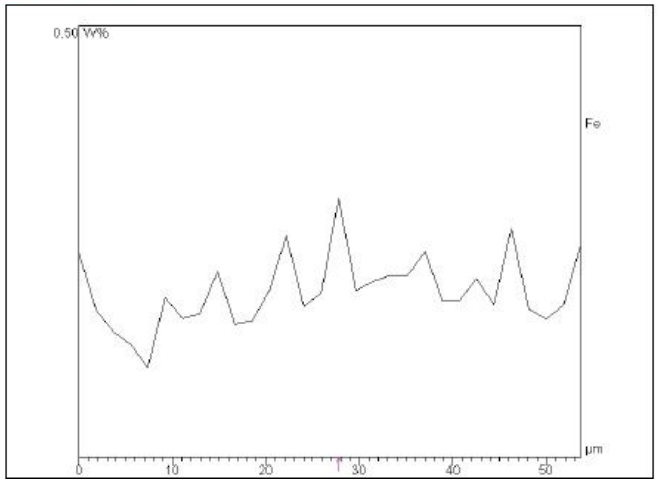

Results of Fe presence in marked area from the Sample „ Amber streak Bottom “

RESULTS OF EDX- MICROSCOPIC INVESTIGATION AMBER STREAK - BODY/BOTTOM

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« Sample „ Amber streak Body »

Analysis line 1-10-6

Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.00	59.13		0.00
Na	Ka	192.8	13.8866	9.56	8.74	Na2O	12.89
Mg	Ka	11.4	3.3711	0.44	0.38	MgO	0.73
Al	Ka	31.0	5.5692	0.96	0.75	Al2O3	1.81
Si	Ka	1299.5	36.0481	35.38	26.49	SiO2	75.69
K	Ka	22.2	4.7081	0.85	0.45	K2O	1.02
Ca	Ka	191.3	13.8310	7.63	4.00	CaO	7.63
Fe	Ka	2.3	1.5028	0.18	0.07	FeO	0.24
Σ				100.00	100.00		100.00

« Sample „ Amber streak Bottom »

Analysis line 1-10-16

Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.35	59.36		0.00
Na	Ka	196.0	14.0011	9.46	8.61	Na2O	12.75
Mg	Ka	13.4	3.6618	0.51	0.44	MgO	0.84
Al	Ka	62.1	7.8805	1.87	1.45	Al2O3	3.53
Si	Ka	1301.6	36.0782	34.92	26.04	SiO2	74.71
K	Ka	24.9	4.9870	0.93	0.50	K2O	1.12
Ca	Ka	171.1	13.0805	6.66	3.48	CaO	6.66
Fe	Ka	3.8	1.9392	0.30	0.11	FeO	0.39
Σ				100.00	100.00		100.00

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« Sample „ Amber streak Bottom »

Analyzed cord zones

1. Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.19	59.10		0.00
Na	Ka	206.2	14.3581	10.37	9.44	Na2O	13.98
Mg	Ka	6.1	2.4677	0.24	0.21	MgO	0.41
Al	Ka	56.0	7.4812	1.77	1.39	Al2O3	3.35
Si	Ka	1233.7	35.1244	34.74	25.89	SiO2	74.32
K	Ka	19.8	4.4510	0.77	0.41	K2O	0.93
Ca	Ka	161.8	12.7183	6.59	3.44	CaO	6.59
Fe	Ka	3.9	1.9718	0.32	0.12	FeO	0.42
				100.00	100.00		100.00

2. Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.28	59.21		0.00
Na	Ka	207.5	14.4048	10.00	9.10	Na2O	13.48
Mg	Ka	12.9	3.5882	0.49	0.42	MgO	0.82
Al	Ka	58.0	7.6140	1.76	1.36	Al2O3	3.32
Si	Ka	1291.5	35.9380	34.81	25.93	SiO2	74.47
K	Ka	23.2	4.8125	0.87	0.46	K2O	1.04
Ca	Ka	167.1	12.9267	6.52	3.40	CaO	6.52
Fe	Ka	3.4	1.8351	0.27	0.10	FeO	0.35
Σ				100.00	100.00		100.00

3. Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.28	59.18		0.00
Na	Ka	206.0	14.3518	10.01	9.10	Na2O	13.49
Mg	Ka	16.8	4.0936	0.65	0.56	MgO	1.07
Al	Ka	61.0	7.8124	1.87	1.45	Al2O3	3.54
Si	Ka	1269.5	35.6301	34.64	25.79	SiO2	74.11
K	Ka	23.5	4.8447	0.89	0.47	K2O	1.07
Ca	Ka	163.5	12.7884	6.45	3.36	CaO	6.45
Fe	Ka	2.6	1.6241	0.21	0.08	FeO	0.27
Σ				100.00	100.00		100.00

RESULTS OF EDX- MICROSCOPIC INVESTIGATION AMBER STREAK - BOTTOM

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« Sample „ Amber streak Bottom »

Surrounding glass

1. Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				44.96	58.97		0.00
Na	Ka	206.7	14.3775	10.08	9.20	Na2O	13.59
Mg	Ka	14.9	3.8555	0.58	0.50	MgO	0.95
Al	Ka	34.2	5.8511	1.05	0.82	Al2O3	1.99
Si	Ka	1294.9	35.9854	35.05	26.19	SiO2	74.98
K	Ka	21.7	4.6544	0.82	0.44	K2O	0.99
Ca	Ka	185.7	13.6285	7.32	3.83	CaO	7.32
Fe	Ka	1.7	1.2985	0.14	0.05	FeO	0.18
Σ				100.00	100.00		100.00

2. Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				45.01	59.05		0.00
Na	Ka	203.9	14.2777	10.02	9.14	Na2O	13.50
Mg	Ka	12.0	3.4698	0.47	0.40	MgO	0.78
Al	Ka	30.6	5.5290	0.94	0.73	Al2O3	1.78
Si	Ka	1298.2	36.0305	35.25	26.34	SiO2	75.41
K	Ka	21.0	4.5785	0.80	0.43	K2O	0.96
Ca	Ka	184.5	13.5829	7.32	3.83	CaO	7.32
Fe	Ka	2.4	1.5625	0.20	0.07	FeO	0.26
Σ				100.00	100.00		100.00

3. Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				44.87	58.95		0.00
Na	Ka	203.4	14.2623	9.84	9.00	Na2O	13.27
Mg	Ka	17.7	4.2033	0.68	0.58	MgO	1.12
Al	Ka	35.8	5.9835	1.09	0.85	Al2O3	2.06
Si	Ka	1303.6	36.1049	34.91	26.13	SiO2	74.67
K	Ka	24.6	4.9608	0.92	0.49	K2O	1.11
Ca	Ka	191.1	13.8231	7.45	3.91	CaO	7.45
Fe	Ka	3.2	1.7774	0.25	0.10	FeO	0.33
Σ				100.00	100.00		100.00

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« Sample Amber streak Bottom »

Surrounding glass – Average composition of the blue marked zone

4 Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				44.95	58.93		0.00
Na	Ka	211.5	14.5414	10.31	9.40	Na2O	13.89
Mg	Ka	14.4	3.7903	0.56	0.48	MgO	0.92
Al	Ka	34.7	5.8938	1.07	0.83	Al2O3	2.02
Si	Ka	1289.0	35.9027	34.95	26.10	SiO2	74.77
K	Ka	22.8	4.7788	0.86	0.46	K2O	1.04
Ca	Ka	180.6	13.4375	7.12	3.73	CaO	7.12
Fe	Ka	2.1	1.4660	0.17	0.07	FeO	0.22
Σ				100.00	100.00		100.00

5. Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				44.87	58.90		0.00
Na	Ka	210.8	14.5180	10.19	9.31	Na2O	13.73
Mg	Ka	13.6	3.6944	0.52	0.45	MgO	0.87
Al	Ka	33.9	5.8239	1.03	0.80	Al2O3	1.95
Si	Ka	1303.8	36.1077	34.95	26.13	SiO2	74.77
K	Ka	24.6	4.9549	0.92	0.49	K2O	1.11
Ca	Ka	187.2	13.6816	7.31	3.83	CaO	7.31
Fe	Ka	2.6	1.6011	0.21	0.08	FeO	0.26
Σ				100.00	100.00		100.00

6. Measures & Results

Elt	XRay	Int	Error	W%	A%	Formula	Ox%
O				44.92	58.92		0.00
Na	Ka	212.5	14.5758	10.25	9.35	Na2O	13.81
Mg	Ka	13.8	3.7129	0.53	0.46	MgO	0.88
Al	Ka	35.9	5.9890	1.09	0.85	Al2O3	2.06
Si	Ka	1303.8	36.1076	34.95	26.11	SiO2	74.76
K	Ka	22.3	4.7268	0.83	0.45	K2O	1.01
Ca	Ka	186.2	13.6462	7.26	3.80	CaO	7.26
Fe	Ka	2.1	1.4528	0.17	0.06	FeO	0.22
Σ				100.00	100.00		100.00

COMMENTS ON AMBER STREAK PROBLEM BY GLASS SERVICE INC, CZECH REPUBLIC

The explicit account of the presence of this defect in glass is very difficult. Our SEM-EDX microanalysis not given account of the problem of coloration of the defect (amounts of iron and of other possible coloring agents are rather under area of detection limit), nevertheless this colored streak has had increased content of Al2O3 with simultaneous decreased content of CaO against the surrounding glass.

The flowing of corrosion products from Aluminosilicate/Alumina refractory caused the rise of this defect.

We estimate that this material is applied rather at zone of glass feeding – plunger/rotation tube/bowl. The coloration of the defect could be caused by its contamination by lubricants used in this zone

NOTE:

- **SEM-EDX michroanalysis ; Scanning Electron Michroscopy with Energy Dispersive Xray spectroscopy**

CONCLUSION

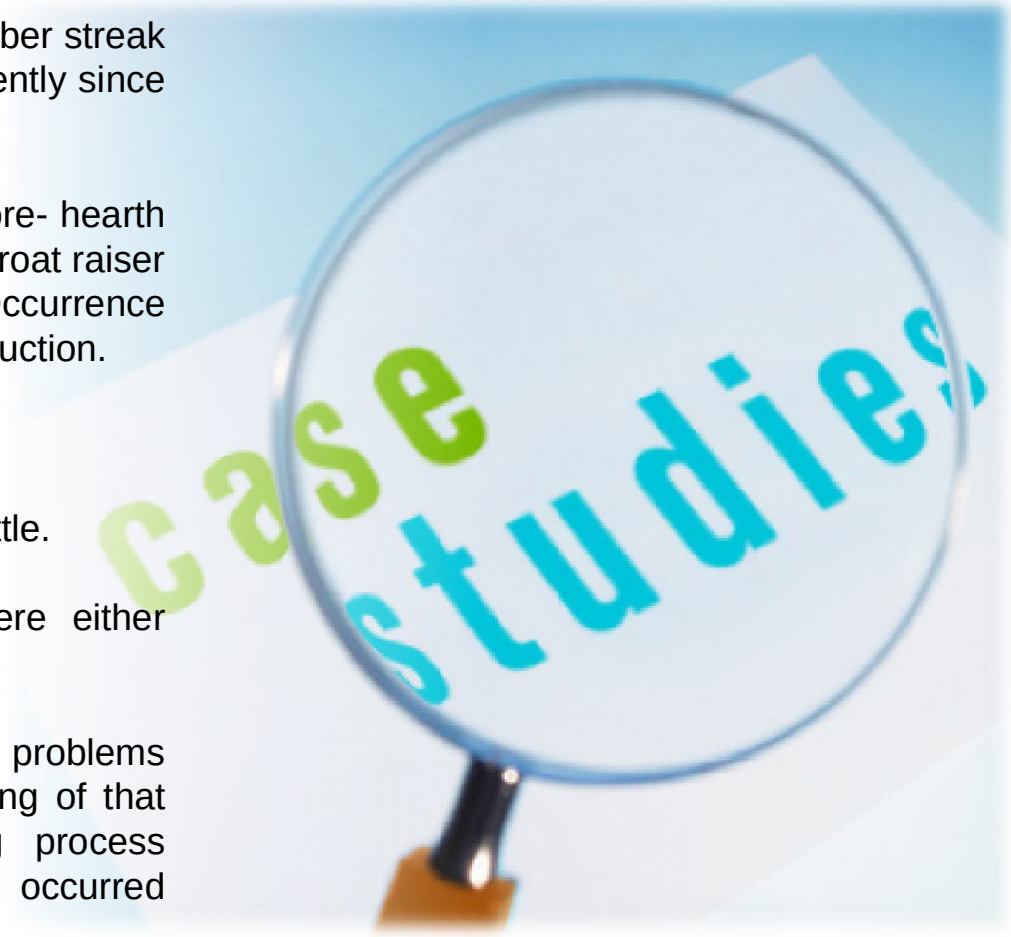
There might be some foreign materials (alumina silicate refractory pieces contaminated with lubricants) was lying near working end entrance and fore hearth 27 entrance causing this amber streak problem.

AN APPROACH TO RESOLVE AMBER STREAK AND BUBBLES IN GLASS BOTTLES

❖ Case Study: Second occurrence

1. In Hyderabad factory in flint glass furnace amber streak and bubbles problems were noticed intermittently since June 2013.

2. These problems were occurring mostly in Fore- hearth 27 which was the closest fore-hearth to the throat raiser and some times in the adjacent line of 28 . Occurrence of the defects are causing sever loss of production.



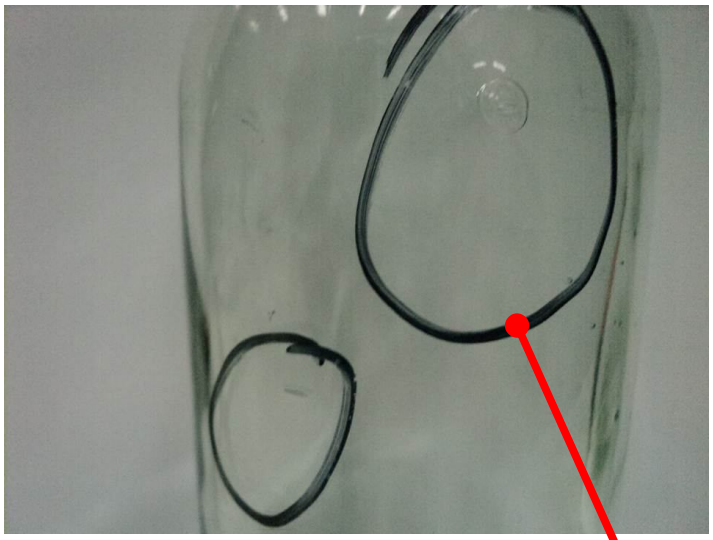
3. Bubbles were having a typical pattern in a bottle.

4. Occurrence of Bubbles and amber streak were either pre or post consecutive to each other.

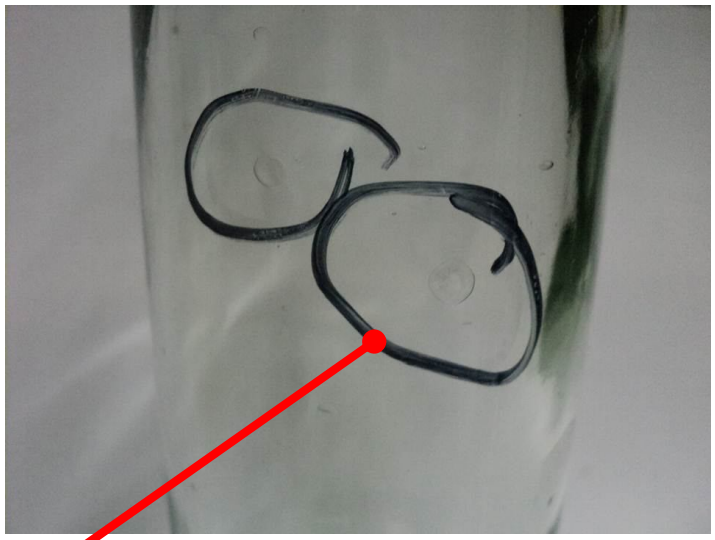
5. Whenever bubbles (and amber streak) problems occurred, we carried out heavy glass draining of that particular forehearth though this draining process offered some temporary relief, but problem occurred soon after.

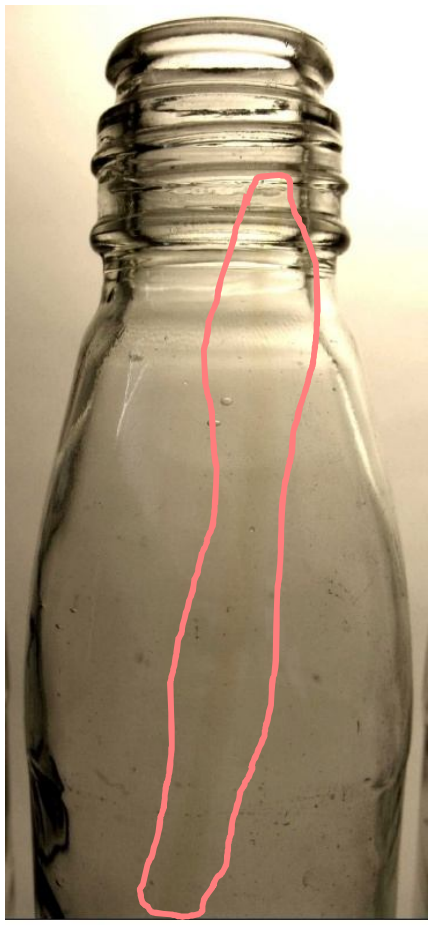
SAMPLES OF BUBBLES AND AMBER STREAK

Bubble -1



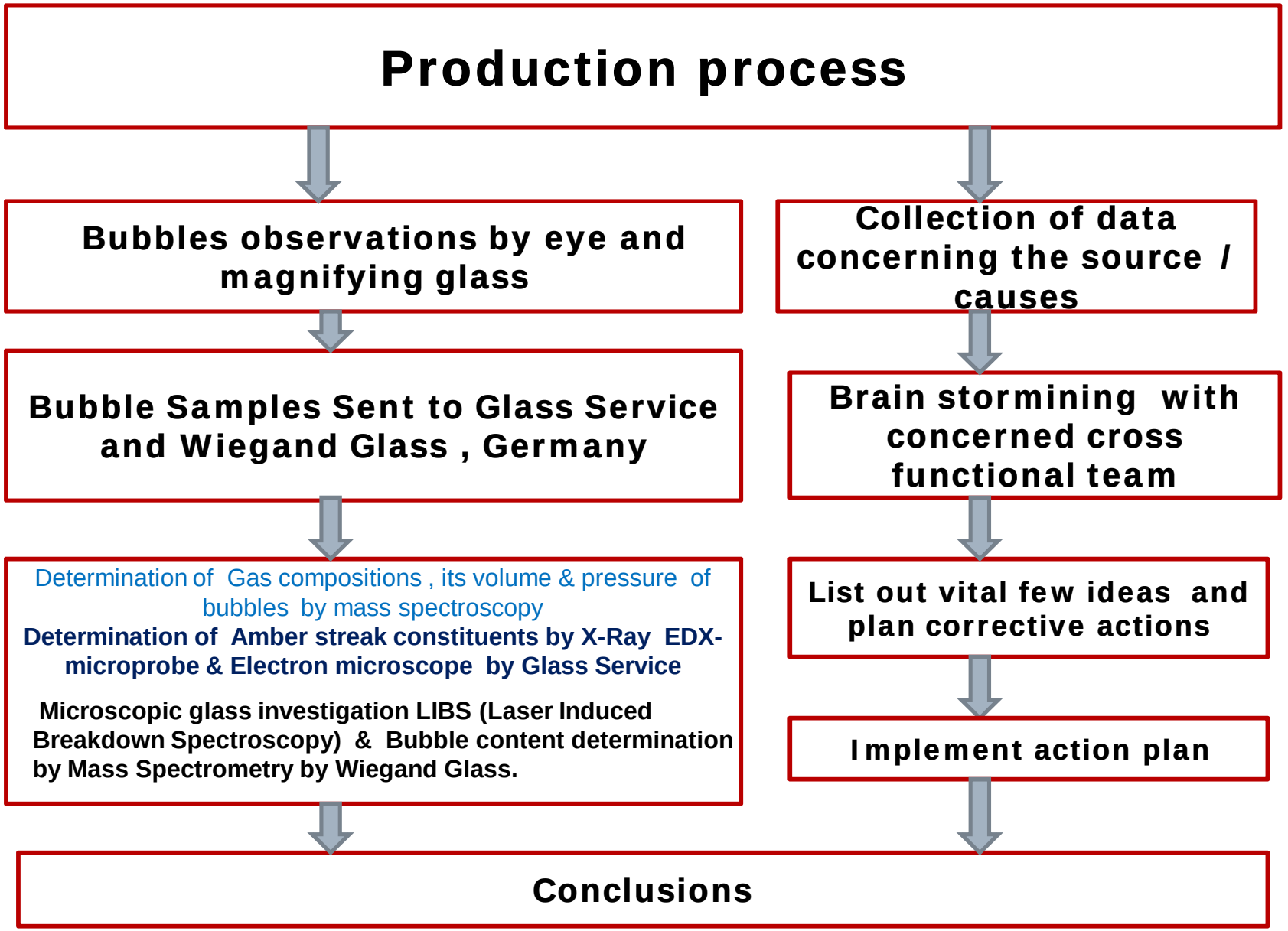
Bubble-2





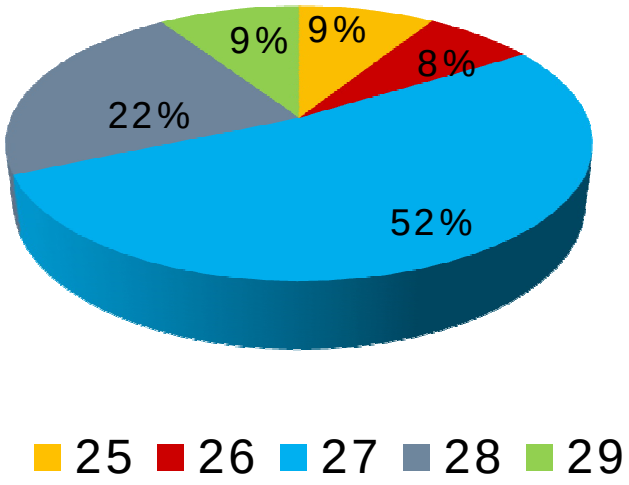
Amber streak

AN APPROACH TO RESOLVE AMBER STREAK AND BUBBLES IN GLASS BOTTLES

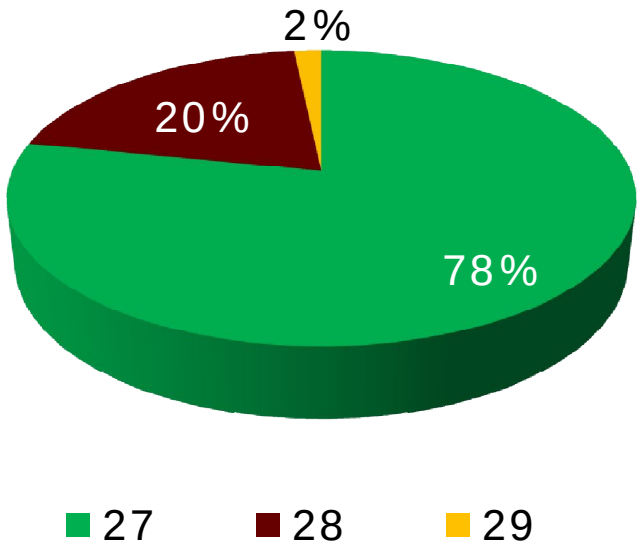


IDENTIFICATION OF MOST PROBLEM PRONE MACHINES IN TERMS OF AMBER STREAK& BUBBLES(JUNE-13 ~ OCT-13)

M/C WISE CONTRIBUTION % OF YELLOW LINE

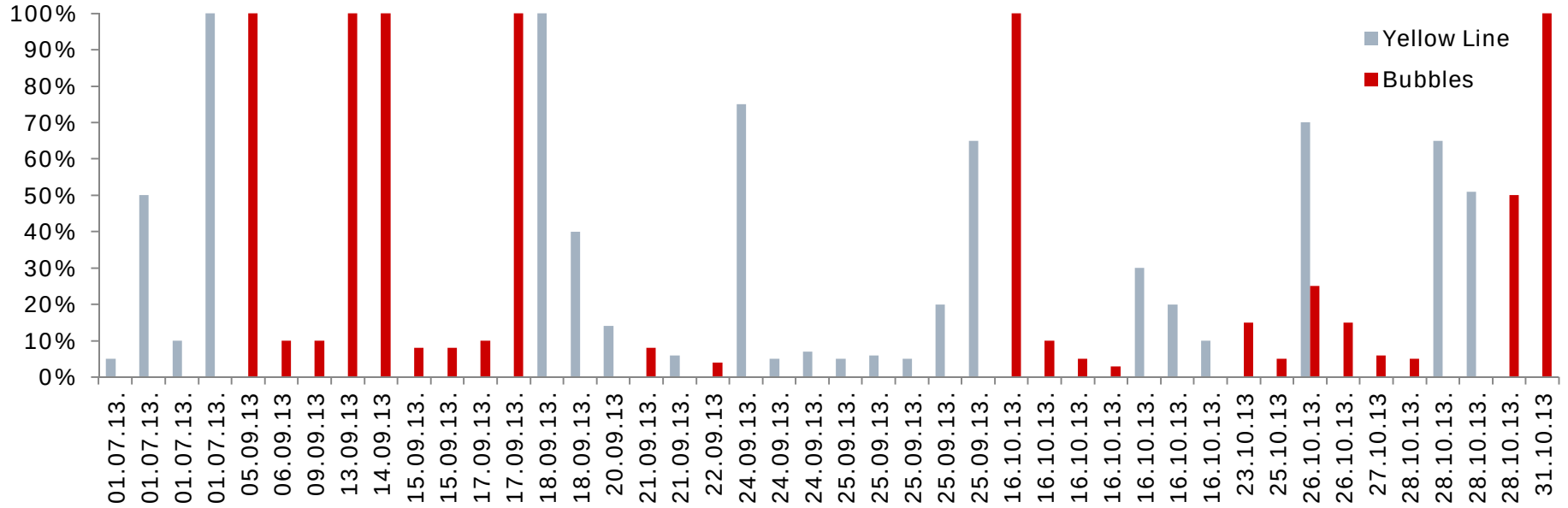


M/C WISE CONTRIBUTION % OF BUBBLES

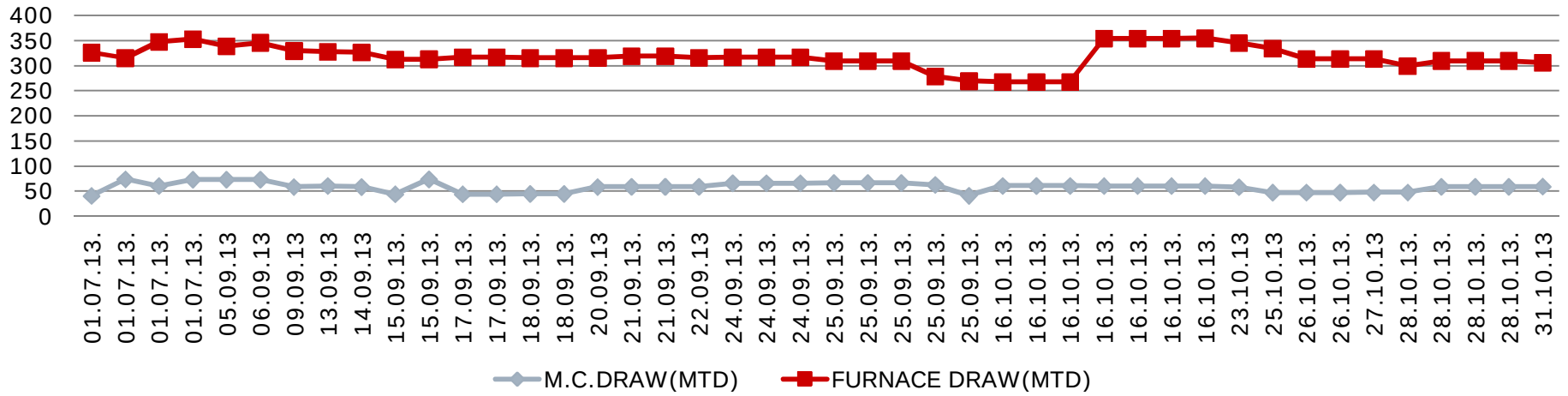


CALCULATION BASED ON OCCURANCES OF AMBER STREAK& BUBBLES IN ALL 5 MACHINES ON DAILY BASIS DURING JUNE-13 TO OCT-13

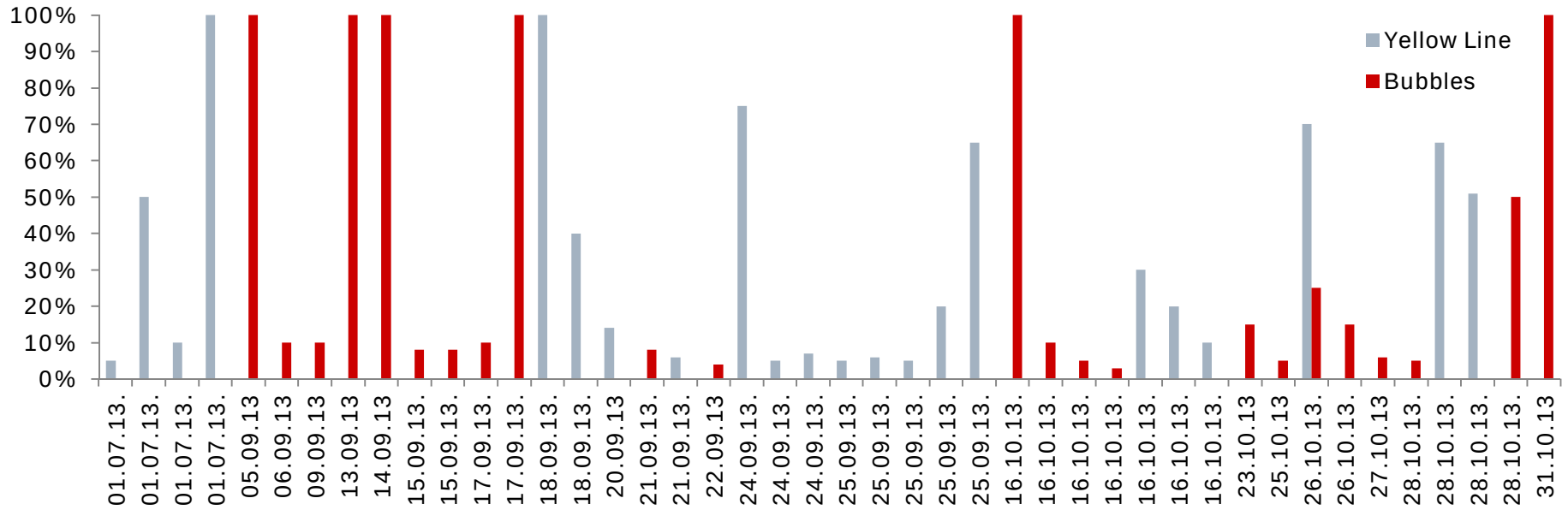
M/C -27 Amber streak Bubbles



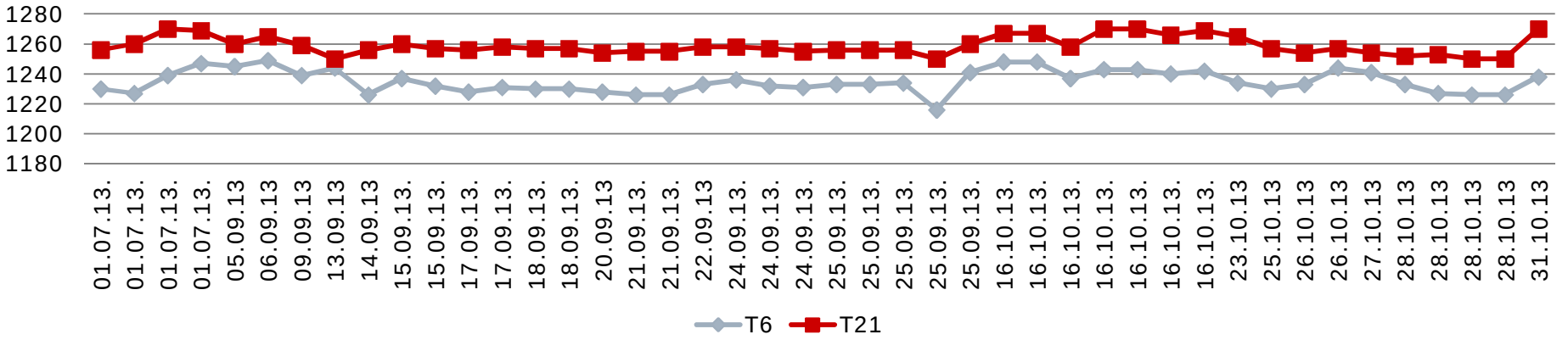
27 M/C DRAW &FURNACE DRAW



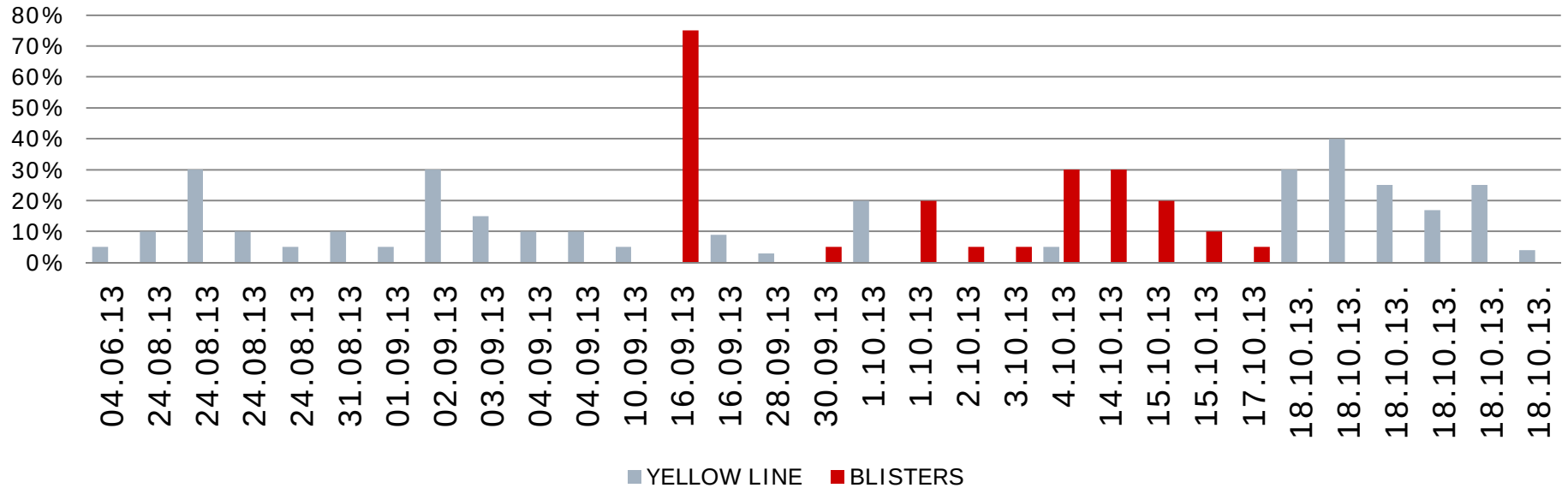
M/C -27 Amber streak and Bubbles



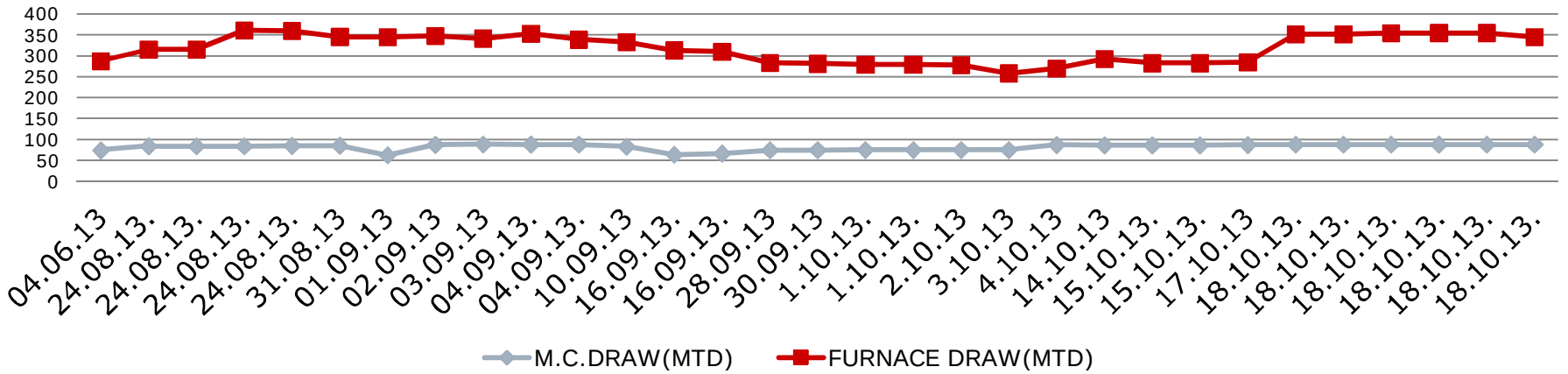
27 M/C FURNACE BOTTOM TEMP(T6)WORKING END(21)



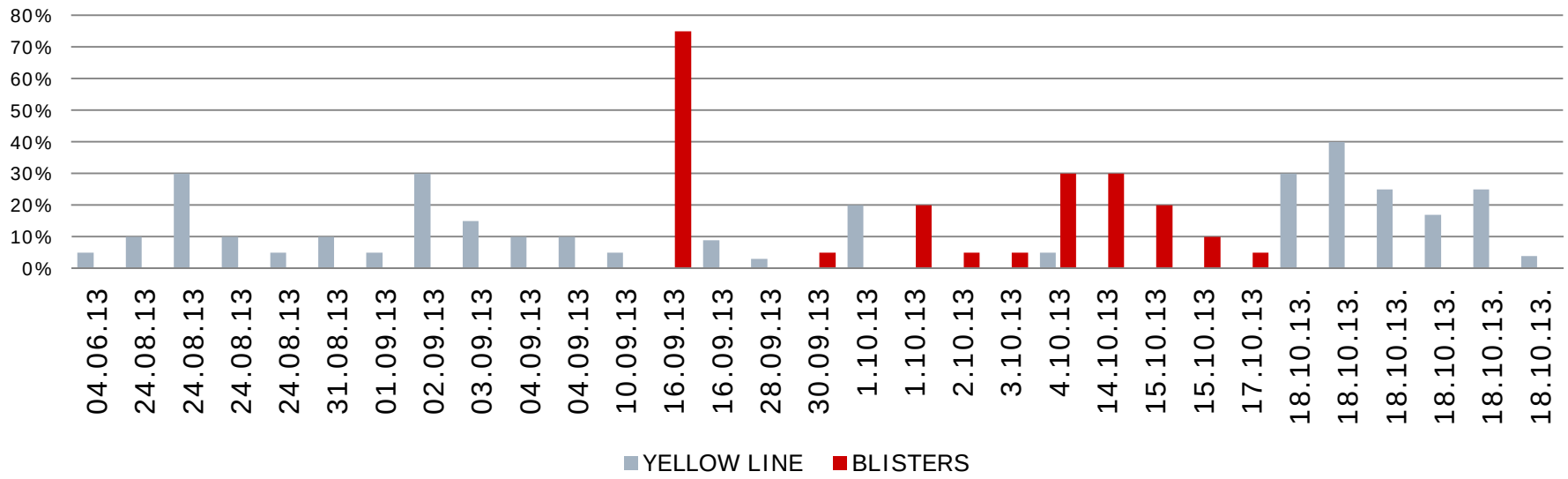
M/C -28Amber streak and Bubbles



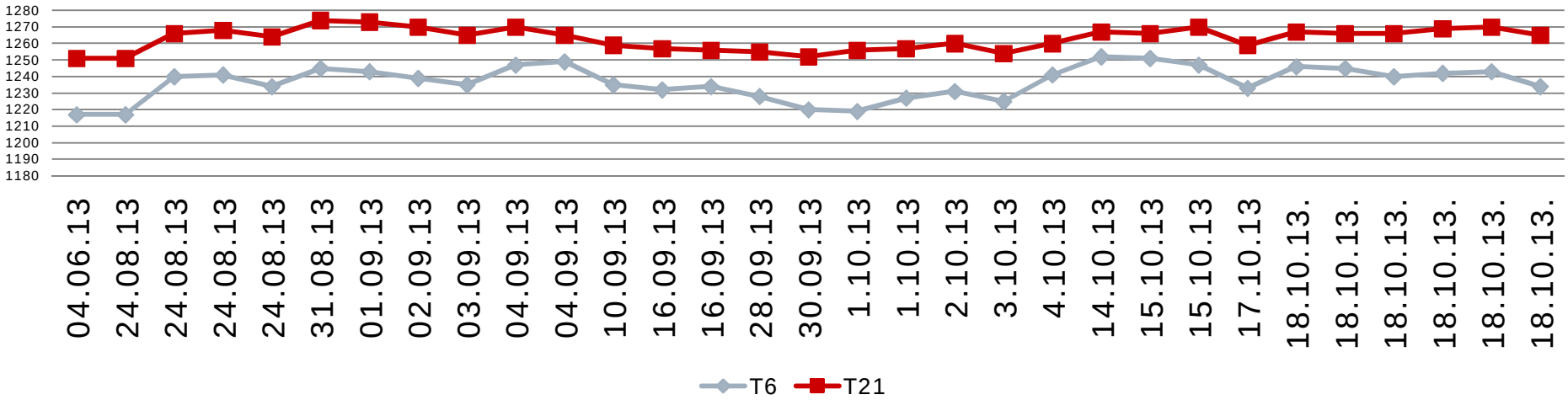
28 M/C DRAW&FURNACE DRAW



M/C -28Amber streak and Bubbles



28 M/C FURNACE BOTTOM TEMP(T6)&WORKING END(T21)



GLASS COMPOSITION BEFORE OCCURRENCE OF AMBER STREAK & BUBBLE

Date	SiO2	Al2O3	Na2O	K2O	R2O	MgO	CaO	RO	SO3	Fe2O3
10-May-13	71.99	1.54	12.84	0.96	13.80	1.60	10.60	12.20	0.24	0.147
13-May-13	71.96	1.58	12.86	0.96	13.82	1.59	10.59	12.18	0.24	0.137
15-May-13	71.86	1.58	12.91	0.98	13.89	1.62	10.58	12.20	0.24	0.135
17-May-13	71.87	1.53	12.88	0.97	13.85	1.74	10.52	12.26	0.24	0.154
20-May-13	71.84	1.56	12.89	0.98	13.87	1.55	10.71	12.26	0.24	0.148
22-May-13	71.75	1.53	12.80	1.00	13.80	1.78	10.67	12.45	0.24	0.153
24-May-13	71.75	1.59	12.86	0.95	13.81	1.71	10.67	12.38	0.24	0.139
27-May-13	71.97	1.58	12.89	0.98	13.87	1.58	10.54	12.12	0.24	0.136
29-May-13	71.89	1.58	12.81	0.96	13.77	1.63	10.64	12.27	0.24	0.138
31-May-13	71.92	1.58	12.73	0.98	13.71	1.54	10.74	12.28	0.27	0.140
3-Jun-13	71.99	1.58	12.68	0.98	13.66	1.50	10.78	12.28	0.27	0.14
5-Jun-13	71.76	1.53	12.85	0.98	13.83	1.62	10.77	12.39	0.27	0.14
7-Jun-13	71.85	1.54	12.81	1.00	13.81	1.67	10.74	12.41	0.27	0.14
10-Jun-13	71.85	1.49	12.76	1.01	13.77	1.71	10.68	12.39	0.27	0.14
12-Jun-13	71.93	1.49	12.71	1.01	13.72	1.65	10.72	12.37	0.27	0.14
14-Jun-13	71.94	1.49	12.76	0.98	13.74	1.68	10.65	12.33	0.27	0.15
17-Jun-13	71.95	1.55	12.70	1.04	13.74	1.67	10.60	12.27	0.27	0.14
19-Jun-13	72.07	1.55	12.64	1.04	13.68	1.67	10.54	12.21	0.27	0.14
21-Jun-13	72.16	1.54	12.64	1.04	13.68	1.58	10.54	12.12	0.27	0.14
24-Jun-13	72.18	1.55	12.57	1.04	13.61	1.63	10.52	12.15	0.27	0.15
26-Jun-13	72.10	1.58	12.66	1.06	13.72	1.56	10.54	12.10	0.27	0.15
28-Jun-13	71.94	1.56	12.81	1.02	13.83	1.60	10.57	12.17	0.27	0.14
1-Jul-13	71.95	1.55	12.82	1.01	13.83	1.63	10.54	12.17	0.27	0.146
3-Jul-13	71.98	1.59	12.74	1.02	13.76	1.72	10.47	12.19	0.25	0.134
5-Jul-13	71.97	1.61	12.77	1.04	13.81	1.60	10.54	12.14	0.25	0.136
8-Jul-13	71.80	1.61	12.82	1.03	13.85	1.79	10.46	12.25	0.25	0.154
10-Jul-13	71.85	1.60	12.81	0.96	13.77	1.74	10.54	12.28	0.25	0.163
12-Jul-13	71.79	1.59	12.90	0.99	13.89	1.65	10.60	12.25	0.25	0.150
15-Jul-13	71.64	1.57	12.93	1.01	13.94	1.72	10.65	12.37	0.25	0.139
17-Jul-13	71.72	1.60	12.94	1.00	13.94	1.62	10.66	12.28	0.25	0.125
19-Jul-13	71.88	1.59	12.88	0.99	13.87	1.53	10.66	12.19	0.25	0.128
22-Jul-13	71.78	1.60	12.97	0.91	13.88	1.62	10.64	12.26	0.25	0.141
Min	**71.64**	**1.49**	**12.57**	**0.91**	**13.61**	**1.50**	**10.46**	**12.10**	**0.24**	**0.125**
Max	**72.18**	**1.61**	**12.97**	**1.06**	**13.94**	**1.79**	**10.78**	**12.45**	**0.27**	**0.163**
Avg	**71.90**	**1.56**	**12.80**	**1.00**	**13.80**	**1.64**	**10.61**	**12.26**	**0.26**	**0.142**

GLASS COMPOSITION DURING AMBER STREAK & BUBBLE

Date	SiO2	Al2O3	Na2O	K2O	R2O	MgO	CaO	RO	SO3	Fe2O3
24-Jun-13	72.18	1.55	12.57	1.04	**13.61**	1.63	10.52	**12.15**	0.27	0.151
28-Jun-13	71.94	1.56	12.81	1.02	**13.83**	1.60	10.57	**12.17**	0.27	0.143
1-Jul-13	71.95	1.55	12.82	1.01	**13.83**	1.63	10.54	**12.17**	0.27	0.146
23-Aug	71.86	1.66	12.81	0.98	**13.79**	1.79	10.50	**12.29**	0.24	0.152
25-Aug	71.96	1.69	12.73	0.95	**13.68**	1.72	10.54	**12.26**	0.24	0.150
28-Aug	71.96	1.64	12.8	0.98	**13.78**	1.57	10.64	**12.21**	0.22	0.165
30-Aug	71.95	1.64	12.87	0.9	**13.77**	1.58	10.66	**12.24**	0.22	0.159
2-Sep	72.09	1.62	12.77	0.93	**13.70**	1.52	10.66	**12.18**	0.22	0.170
4-Sep	71.98	1.61	12.79	0.93	**13.72**	1.66	10.61	**12.27**	0.22	0.167
6-Sep	71.99	1.58	12.93	0.91	**13.84**	1.56	10.65	**12.21**	0.17	0.166
9-Sep	71.74	1.59	13.01	0.91	**13.92**	1.79	10.59	**12.38**	0.17	0.158
11-Sep	71.87	1.51	12.94	0.89	**13.83**	1.81	10.62	**12.43**	0.17	0.161
13-Sep	71.88	1.53	12.99	0.86	**13.85**	1.77	10.61	**12.38**	0.17	0.162
16-Sep	71.82	1.56	13.00	0.87	**13.87**	1.57	10.81	**12.38**	0.17	0.157
18-Sep	71.82	1.56	12.98	0.87	**13.85**	1.57	10.84	**12.41**	0.17	0.158
20-Sep	71.95	1.54	12.95	0.90	**13.85**	1.49	10.81	**12.30**	0.18	0.156
23-Sep	71.99	1.53	12.95	0.88	**13.83**	1.45	10.84	**12.29**	0.18	0.156
25-Sep	72.02	1.54	12.87	0.88	**13.75**	1.45	10.87	**12.32**	0.18	0.156
27-Sep	72.01	1.53	12.86	0.86	**13.72**	1.53	10.85	**12.38**	0.18	0.156
30-Sep	72.08	1.53	12.83	0.87	**13.70**	1.51	10.83	**12.34**	0.18	0.159
1-Oct	72.11	1.54	12.92	0.85	**13.77**	1.45	10.75	**12.20**	0.18	0.179
3-Oct	72.14	1.54	12.89	0.84	**13.73**	1.43	10.78	**12.21**	0.18	0.160
7-Oct	72.00	1.53	12.87	0.87	**13.74**	1.53	10.80	**12.33**	0.18	0.162
11-Oct	71.98	1.50	12.99	0.85	**13.84**	1.44	10.86	**12.30**	0.18	0.164
15-Oct	71.86	1.51	13.00	0.85	**13.85**	1.57	10.86	**12.43**	0.18	0.164
17-Oct	71.86	1.50	13.06	0.84	**13.90**	1.56	10.81	**12.37**	0.19	0.161
19-Oct	71.96	1.49	12.96	0.85	**13.81**	1.51	10.86	**12.37**	0.19	0.158
21-Oct	72.02	1.48	12.93	0.85	**13.78**	1.53	10.83	**12.36**	0.19	0.152
22-Oct	72.02	1.56	12.93	0.87	**13.8**	1.6	10.66	**12.26**	0.19	0.150
25-Oct	71.89	1.58	13.05	0.88	**13.93**	1.6	10.64	**12.24**	0.18	0.158
28-Oct	71.97	1.51	13.05	0.81	**13.86**	1.51	10.81	**12.32**	0.17	0.153
30-Oct	72.07	1.51	13.05	0.8	**13.85**	1.5	10.73	**12.23**	0.17	0.152
Min	**71.74**	**1.48**	**12.57**	**0.80**	**13.61**	**1.43**	**10.50**	**12.15**	**0.17**	**0.14**
Max	**72.18**	**1.69**	**13.06**	**1.04**	**13.93**	**1.81**	**10.87**	**12.43**	**0.27**	**0.18**
Mean	**71.97**	**1.56**	**12.91**	**0.89**	**13.80**	**1.58**	**10.72**	**12.29**	**0.20**	**0.16**

Remarks:

Fe2O3% was increased during the period of occurrence of amber streak and bubbles

BRAINSTORMING ON PROBLEMS: FREQUENT OCCURANCE OF AMBER STREAK / BUBBLES IN M / C 27 & 28

S.No.	IDEAS	PROBABILITY (0 to 10SCALE)	REMARKS
1	Low/High Glass Level	0	FOUND OK (153mm)
2	Foreign materials (refractory piece, metal) in working end and fore hearth	8	FOUND PLUNGER PIECES ON 30.09.13 AND 16.10.13, FOUND WELDING ROD ON 23.10.13
3	Worn out running plunger	2	As per PM 20 DAYS before changed
4	Worn out running "O" ring	2	As per PM 10 DAYS before changed
5	Shear mechanism too close to orifice ring	2	As per PM not frequently changed
6	Plunger touching to orifice ring	0	not found
7	Too hot /Too cold blank or mould	0	It is not loading blister
8	Unusual refractory corrosion	0	not found
9	cold glass in forehearth /spout	8	found
10	Reboil in working end and forehearth	5	By appearance it does not looks like reboil blisters, but waiting for GLASS SERVICE REPORT
11	Inproper oxygen ratio in working end and forehearth	2	one week before checked and adjusted
12	carbon deposit /burner cleaning in working end	10	no schedule of cleaning As per PM It is need base

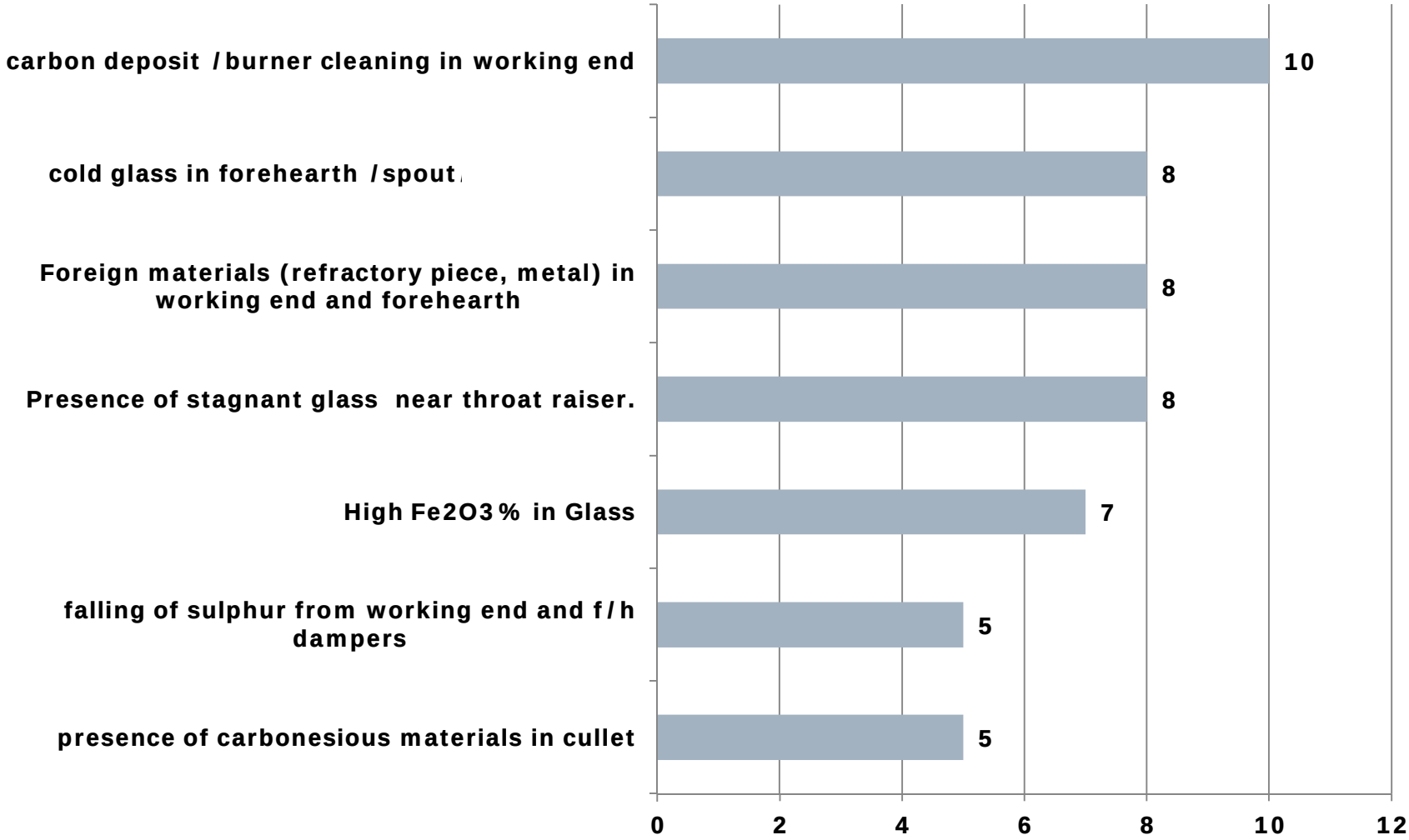
BRAINSTORMING ON PROBLEMS: FREQUENT OCCURANCE OF AMBER STREAK / BUBBLES IN M / C 27 & 28

S.No.	IDEAS	PROBABILITY (0 to 10SCALE)	REMARKS
13	carbon deposit /burner cleaning in forehearth	3	6 months schedule available .Last cleaning done before 45 days
14	Oil dropping in spout	2	
15	Temperature profile in working end and forehearth	5	Improper temperature profile creates reboil blisters .By appearance it does not looks like like reboil blister. Waiting for GLASS SERVICES REPORT
16	in correct size of plunger /orifice ring	2	By appearance and intensity of blisters in bottle it does not looks like due to this reason
17	Water leakages from batch charger ,water jacket of dog house	0	not found
18	Dripping from working end drown	0	Slight dripping visible near chimney of working end raiser BUT not touching glass
19	Leakage of indirect cooling air into forehearths	0	not found (Cooling blower not running)
20	peeling off f/h-27 refractory channel	0	not observed
21	falling of sulphur from working end and f/h dampers	5	some deposits are visible .tobe cleaned in next job change
22	E xcess fines in raw materials	0	not found
23	e xcess fines in cullet	4	occassionally found
24	presence of carbonaceous materials in cullet	5	some times found
25	Damaged spout	0	not found

BRAINSTORMING ON PROBLEMS: FREQUENT OCCURANCE OF AMBER STREAK / BUBBLES IN M / C 27 & 28

S.No.	IDEAS	PROBABILITY (0 to 10SCALE)	REMARKS
26	leakage between orifice ring and spout	0	not found
27	Glass level touches skimmer block	0	not found
28	NO,of times glasslevel checking in f/h by steel rod	0	not found
29	Booster water leakage	0	not found
30	RAISER thermocouple earthing	0	not found (no error reading)
31	Unmelted /un refined glass from melting	0	Not found (since seed level is normal)
32	Batch sagregation	0	Not found (since seed level is normal)
33	low melting temperature	0	Not found (since seed level is normal)
34	Throat area extra water cooling	0	no water cooling
35	LUMP in fine chemicals	0	Not found (since seed level is normal)
36	Redox change in melter	5	Since some times excess carbonesious materials found in cullet
37	closing of working end chimney completely	0	found open
38	Dust falling from EOT crane over head of f/h	3	during operation by PM
39	improper spout firing	2	
40	High Fe2O3% in Glass	7	Very high Fe2O3%rich glass at bottom might be come in contact with mainstream glass causing these sort of problem.
41	Leakage of Compressed air into glass bath from W.E and Forehearths walls since the origin of bubbling seems to be at Working End entrance(near Raiser).	2	Checked and found no blower/compressed line there
42	Presence of stagnant glass near throat raiser.	8	This is the assumption because there is simultaneous

LIST OF VITAL FEW IDEAS
(=,>5 SCALE)



ACTION PLANS ON VITAL FEW IDEAS

S.NO	SOURCES/POSSIBLES REASONS	CORRECTIVE ACTION PLANS	DATE OF COMPLETION	RESPONSIBILTY
1	Carbon deposit / burner cleaning in working end	To clean carbon deposit/burner in working end as per schedule made	Last cleaning done on 1st Nov-13	Prodn. Maintenance
2	Cold glass in forehearth / spout	To clean fore hearth/spout burners and O2% checking as per schedule	Last cleaning 20th Oct-13	Prodn. Maintenance
3	Foreign materials (refractory piece, metal) in working end and fore hearth	To strengthen Cullet washing and sorting	Immediate & on going	Glass Deptt
4	Presence of stagnant glass near throat raiser.	Action of serial no 05 might help to sort out this problem if it is there.	Implemented from 4th Nov-13	Glass Deptt
5	High Fe2O3% in Glass	To reduce Fe2O3% in Glass by doing batch / Raw materials adjustment	Implemented from 4th Nov-13	Glass Deptt
6	Falling of sulphur from W.E and FHT dampers	To clean sulphur from W.E and FHT dampers during the job change period of the relevant machines	Implemented on 5th Nov-13	Glass Deptt & Prodn Maint.
7	Presence of carbonaceous materials in External cullet	To tighten cullet inspection and washing & sorting system	Immediate & on going	Glass Deptt.

GLASS SERVICE REPORT ON BUBBLE ANALYSIS

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E-mail: info@gsl.cz Internet: www.gsl.cz

BUBBLE GAS ANALYSIS

Sample: Clear Glass Bottles
Data file: agi 38863 - 38868

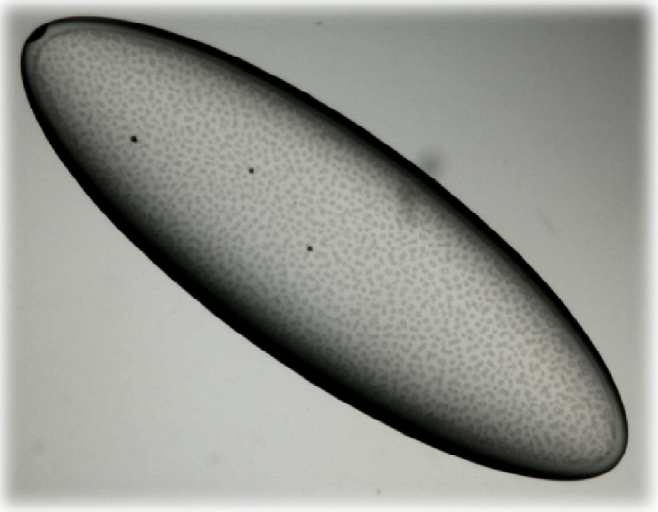
Sample	Dimension [mm]			D.EQ.	Volume	p	Gas composition [vol. %]										Note
ID	a	b	c	[mm]	[ml]	[kPa]	N_2	CO_2	O_2	Ar	SO_2	H_2S	COS	CO	CH_4	H_2	
1	3,20	1,00	0,13	0,75	2,18E-04	6,0	0,3	5,2			94,5						Deposits
3	2,80	0,60	0,17	0,66	1,50E-04	1,5	1,8	7,9			90,3						Deposits
5	2,50	0,57	0,22	0,68	1,64E-04	2,0	0,5	5,2			94,3						Deposits
6	2,80	1,03	0,10	0,66	1,51E-04	1,0	0,7	7,0			92,3						Deposits

D.EQ. - Calculated diameter of sphere shape bubble
TR. - Traces

Sample Bottles

Comments:

- Medium size bubbles containing outstandingly high levels of sulfur dioxide; there was observed a large amount of bubbles in the delivered bottles, often located in straps along the bottles.
- High content of sulfur dioxide indicates that the bubbles were most probably formed by the temperature reboil caused by the local glass reheating or glass temperature instability in the low temperature zone – distributor, forehearth, and/or feeder. The glass melt is sensitive to any increase of temperature. The SO2 solubility in the melt decreases significantly with increasing temperature, therefore excessive SO2 is separated into bubbles.
- The bubble appearance in the stripes could show evidence of the local problem more downstream of the process in the low temperature zone – for instance the burner flames may touch the glass level, causing the local glass reheating.
- The high SO2 levels present in bubbles as well as comparably larger bubble sizes may also indicate some contamination of the glass melt e.g. by dropping of the sulfur containing deposits which may settle at the colder corners or zones of the superstructure, the possible source location could be also at the lower temperatures – distributor, forehearth, and/or feeder.



The Deposits inside the bubble in passing through light

GLASS SERVICE REPORT ON AMBER STREAK ANALYSIS

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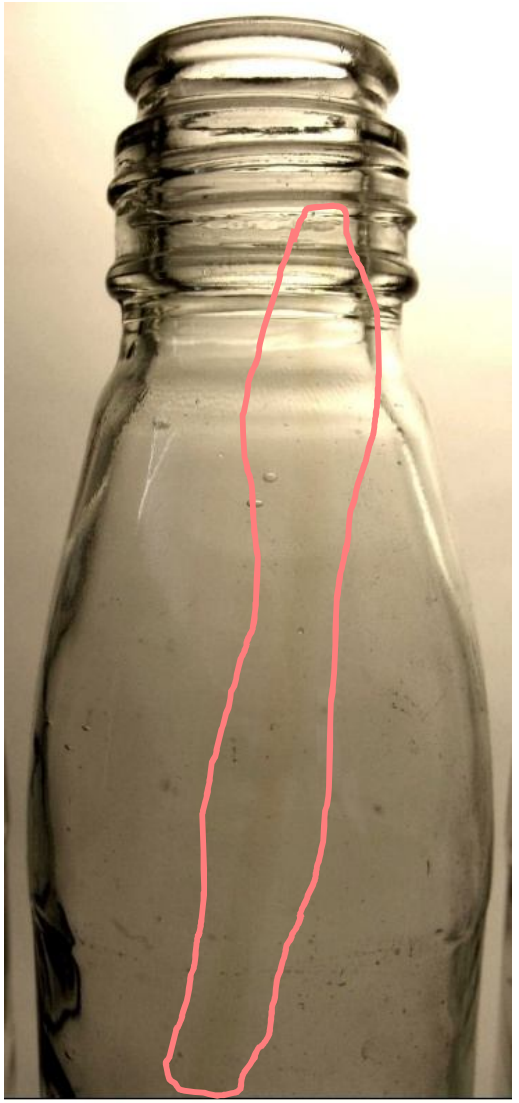
Comments:

There was observed a distinct amber streak in the Bottle. There should be a possibility of the bubble appearance due to potential melting issues as namely temperature variations and/or pull change, initiating the release of the dead zones containing the stagnant glass having the different redox state.



Amber streak bottle

WIEGAND GLASS REPORT ON AMBER STREAK AND BUBBLE ANALYSIS

Laboratory report for Contract No. 1801/2013

ZENTRUM FÜR GLAS- und UMWELTANALYTIK GmbH

Samples received on:	13.11.2013
Test period:	From 14.11.2013 till 15.11.2013
Sampling:	By AGI
Sample description:	Big Bottle with amber stripes
Applied method:	Microscopic glass investigation LIBS (Laser Induced Breakdown Spectroscopy) bubble content determination by mass spectrometry.

Results:

In the object to be examined is a bottle with amber stripes. Along the strip are round inclusions at a size of about 300-600 microns and the color of them are black. At the right angle, the inclusions appear shiny metallic.

With LIBS there could be detected a high content of iron, manganese and vanadium at the position of the black inclusions. Moreover, there are still small amounts of chromium and nickel. Furthermore, an increased iron oxide content in a measurement can be compared to the smear determine glass.

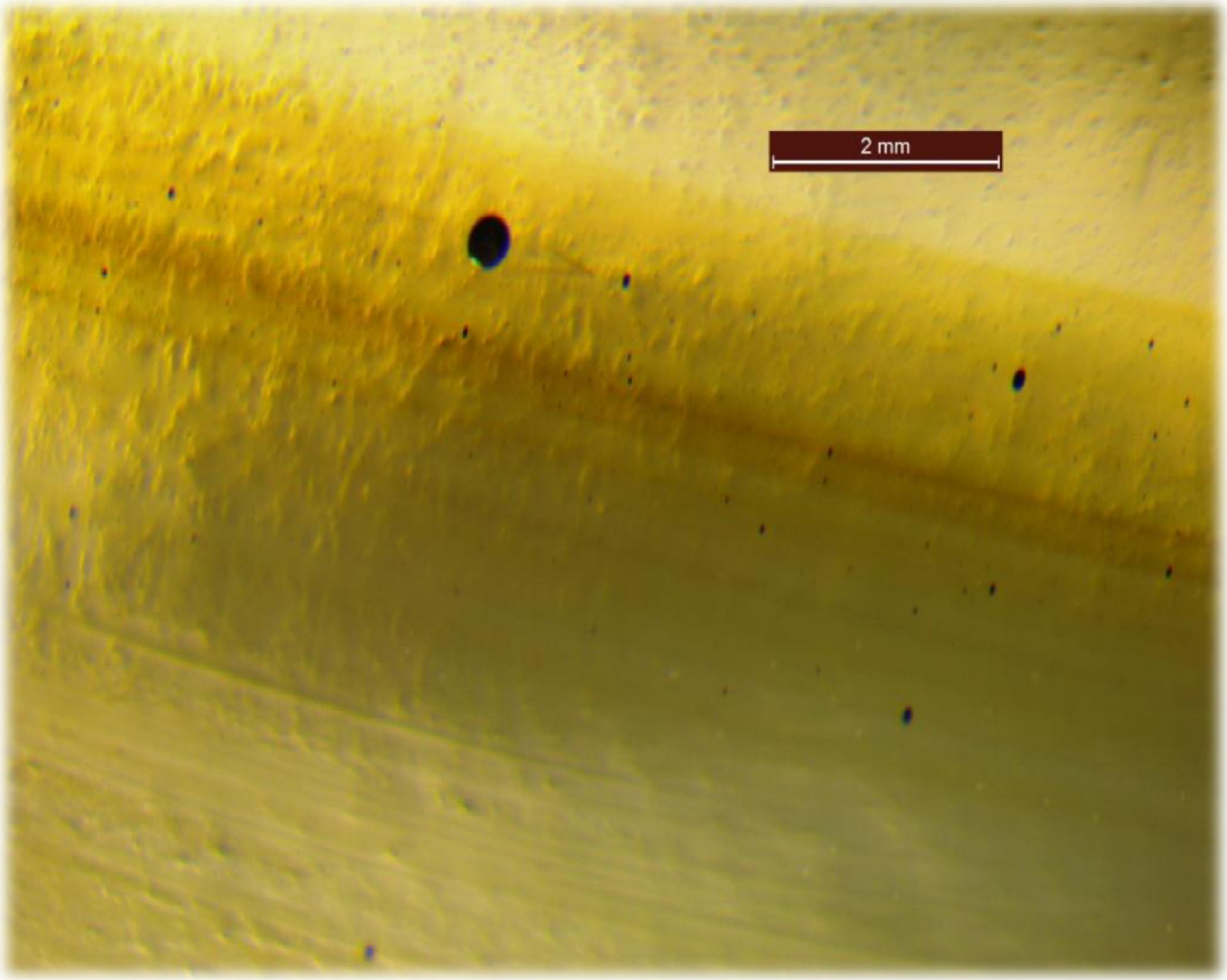
The investigation shows that the black inclusion probably residues of a steel with alloying elements manganese, chromium, nickel and Vanadium.

NOTE:
Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy which uses a highly energetic laser pulse as the excitation source. In principle, LIBS can analyse any matter regardless of its physical state,

WIEGAND GLASS REPORT ON AMBER STREAK AND BUBBLE ANALYSIS

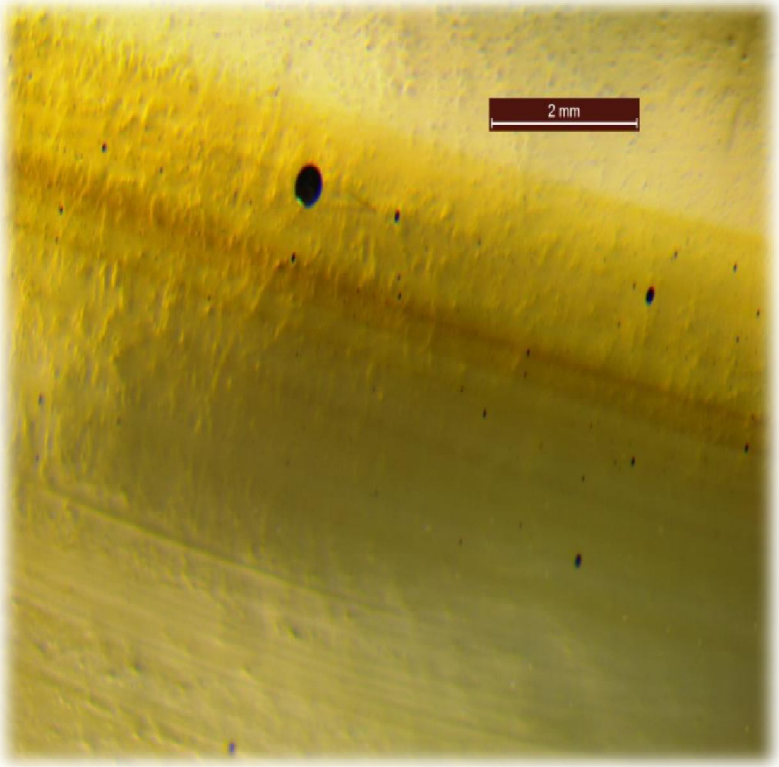
Photographic recording of the glass bottle with amber stripes. The right figure shows two of the larger inclusions are highlighted.

WIEGAND GLASS REPORT ON AMBER STREAK AND BUBBLE ANALYSIS

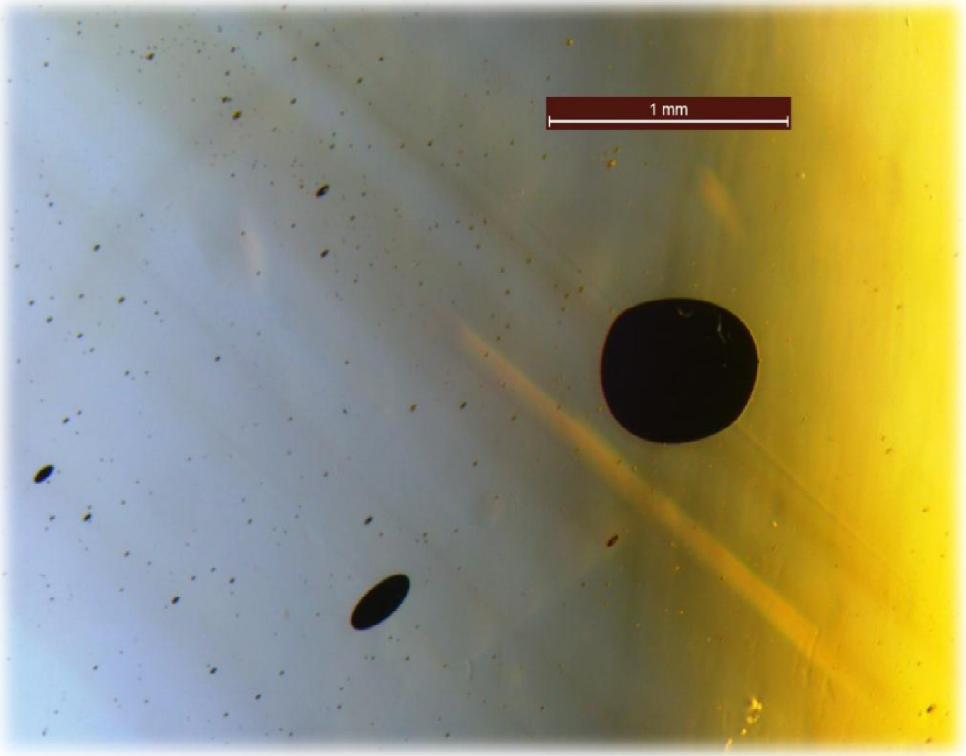


Micrograph of inclusions

WIEGAND GLASS REPORT ON AMBER STREAK AND BUBBLE ANALYSIS



Micrograph of inclusions



Further Detail of black inclusions.

WIEGAND GLASS REPORT ON AMBER STREAK AND BUBBLE ANALYSIS

Laboratory report for Contract No. 1802/2013

ZENTRUM FÜR GLAS- und UMWELTANALYTIK GmbH

Samples received on:	: 13.11.2013
Test period:	: From 14.11.2013 till 15.11.2013
Sampling:	: By AGI
Sample description:	: Small bottles of bubbles, glass defects
Applied method:	: Microscopic glass investigation LIBS (Laser Induced Breakdown Spectroscopy) bubble content determination by mass spectrometry.

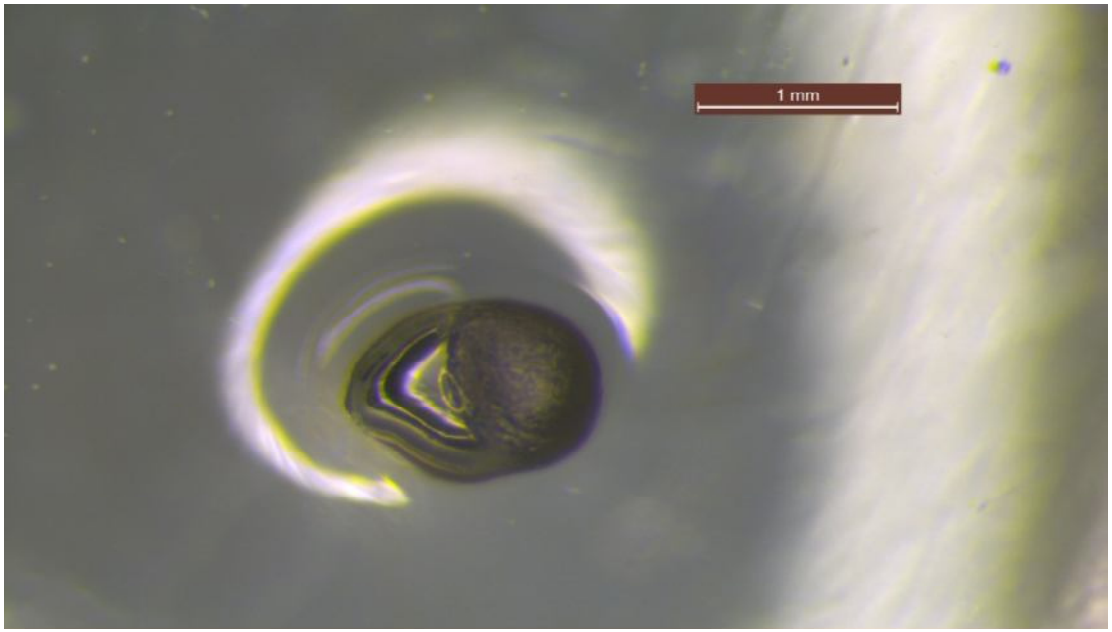
Results:

The object to be examined is two small bottles of bubbles and a black enclosure with a size of about 500 microns.

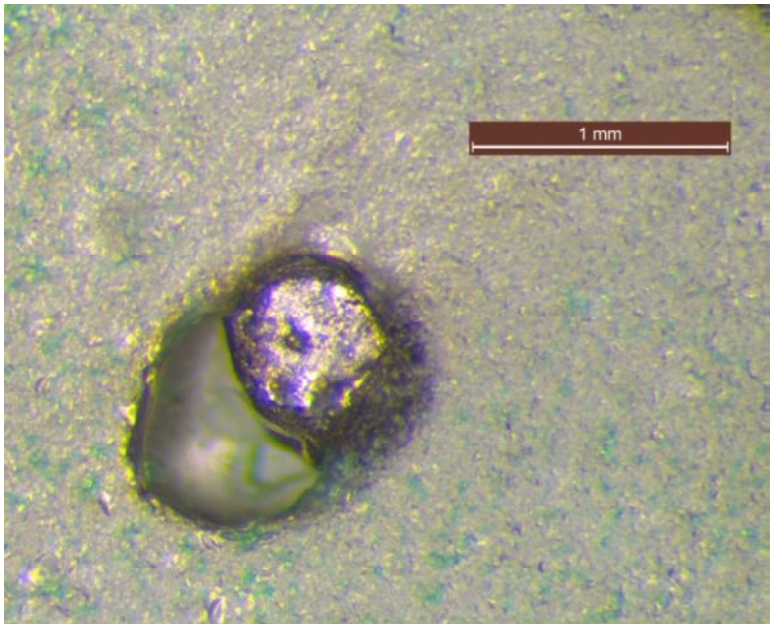
The inclusion has been sanded. The included foreign body is shining metallic. With LIBS, a high content of iron and manganese could be detected at this point. It also the elements copper, vanadium, molybdenum, and chromium are found.

The investigation shows that trapped debris is probably residues of a steel alloy with the above ingredients. This for an example can be reached during the batching process or cullet.

WIEGAND GLASS REPORT ON AMBER STREAK AND BUBBLE ANALYSIS



Micrograph of black inclusion



Micrograph of sanded foreign body

WIEGAND GLASS REPORT ON AMBER STREAK AND BUBBLE ANALYSIS

ANALYSIS RESULTS OF BUBBLE CONTENT DETERMINATION

CONTENT	BLISTER/ BUBBLE A	BLISTER/ BUBBLE B	BLISTER/ BUBBLE C
[%]			
H2	-	-	-
H2O	-	-	-
He	-	-	-
CO2	6,0	1,6	6,6
CO	-	-	-
O2	-	-	-
N2	(1,1)	-	-
SO2	93	98	93
Ar	-	-	-
Volumen [nl]	70	459	45
Pressure [mbar]	127	225	84
Size [mm]	2,250 × 0,368 × 0,144	3,280 × 0,880 × 0,304	0,688 × 0,432 × 0,288

Components below the detection limit are not listed. The percentage content of disclosures relate to the sum of the analyzed components.

The sums of content differ due to rounding part of 100%. The values in parentheses are not sure they are at the limits of detection.

WIEGAND GLASS - CONCLUSION

It may be concluded as follows:

- The possible source location could be near feeder 27 and feeder 28 entrance in Working End since all bubbles contain High level of SO2 and larger in size indicating contamination of the glass melt by dropping of sulphur containing deposits.

or

- The bubble appearance in the stripes with condensate could show evidence of the local problem more downstream of the process in the low temperature zone especially near feeder 27 and feeder 28 entrance in Working End– for instance the burner flames may touch the glass level, causing the local glass reheating.

- There might be some trapped debris is probably residues of a steel alloy with high content of iron and manganese lying at the bottom most probably near feeder 27 and feeder 28 entrance in Working End since those two feeders were the most problem driven areas. The amber streak and bubbles might be the result of this trapped debris.

THANK YOU