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## Metallurgy

# Microscopy inspection of white residue found on different samples from CMS RPC gas system

### Summary:

SEM inspection and EDS analysis were performed on various provided samples from different locations of the CMS RPC gas system.

Presence of chlorine was confirmed in a significant amount (up to 60 wt. % in some cases) until the chambers (locations from A to D both included). Chlorine was not detected on the sector E and it was not detected or considered punctual contamination (not generalized) on the samples from the purifiers (location G and F).

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## TABLE OF CONTENTS

Microscopy inspection of white residue found on different samples from CMS RPC gas system .	1
1. Introduction .....	4
1.1 Aim of the study .....	4
1.2 Key words .....	4
2. Protocol.....	4
2.1 Samples .....	4
2.2 Equipment.....	6
3. Results and discussion .....	7
3.1 Ball floats .....	7
3.2 Residue from the inner surface of the quick supply connector #26 .....	8
3.3 Resistance type PT100 of the flowcells .....	9
3.4 Additional material.....	9
3.5 Needle valve .....	10
4. Summary of observations .....	14

## LIST OF FIGURES AND TABLES

Figure 1 - Samples information and schema of their location.....	5
Figure 2 - Some of the samples under study .....	6
Figure 3 - Comparison of ball's surface aspect (200x and 1 kx) and EDS (at 5keV) on the residue present in ball #1 .....	8
Figure 4 - Needle valve surface at the location where the residue accunulated and FIB cut to estimate the residue thickness (23x, 50x, 200x and 1kx) .....	11
Figure 5 - Needle valve surface A (23x, 50x, 200x and 1kx) .....	12
Figure 6 - Needle valve surface B (50x, 200x, 1kx and 5kx) .....	13
Table 1 - EDS semi-quantitative results (at 5 keV) on the residue present on the float balls surface (values in wt. %).....	7
Table 2 - EDS semi-quantitative results (at 5 keV) on the residue from the inner surface of the quick supply connector #26 on a C sticker (values in wt. %).....	9
Table 3 - EDS semi-quantitative results (at 5 keV) on PT100 (values in wt. %).....	9
Table 4 - EDS semi-quantitative results (at 5 keV) on additional materials (values in wt. %) .....	10
Table 5 - EDS semi-quantitative results (at 5 keV) on the needle valve surface and FIB cross section (values in wt. %) .....	13
Table 6 - Summary of Cl detected presence on the samples.....	14



## 1. Introduction

The present study describes the microscopic examination by Scanning Electron Microscopy (SEM) and microanalysis performed by Energy Dispersive X-Ray Spectroscopy (EDS) on various samples from different locations of the CMS RPC gas system.

### 1.1 Aim of the study

The goal is to characterize the observed residues during visual inspection and better understand their origin.

### 1.2 Key words

SEM, FIB, EDS, CMS, RPC, gas system, flowcell, PT100, needle valve, chlorine

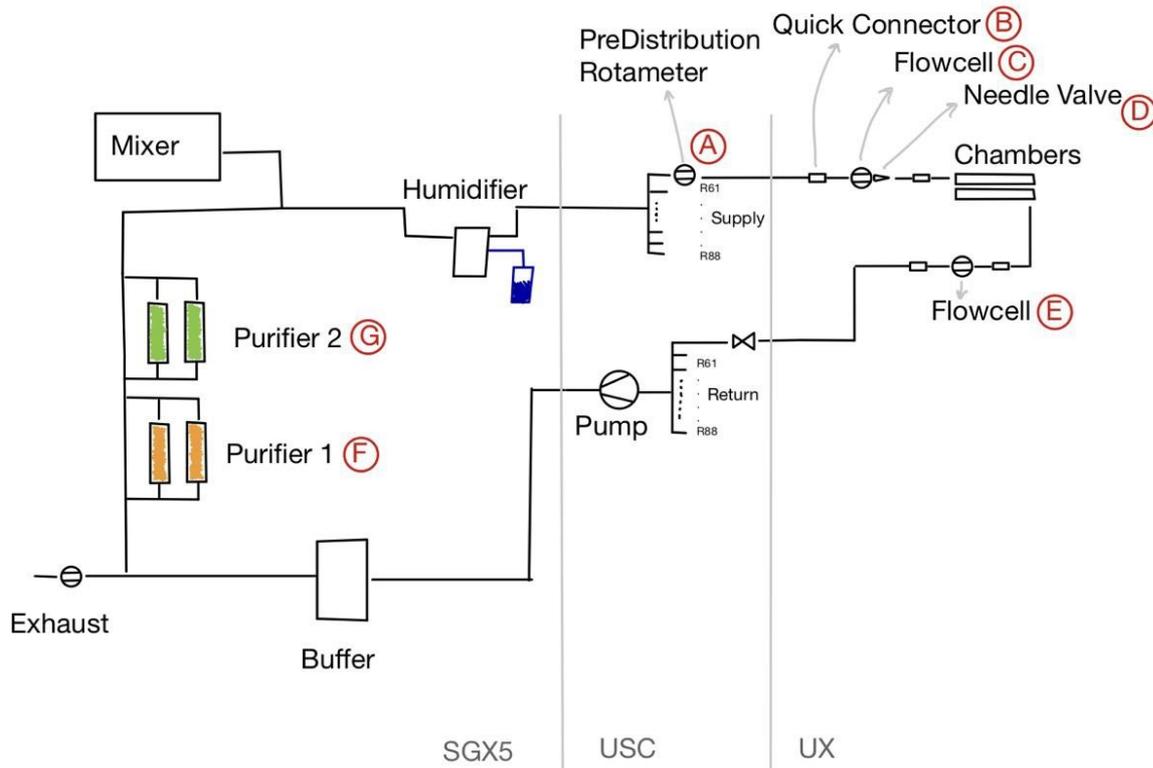
## 2. Protocol

### 2.1 Samples

The samples under study were collected from different locations and their information is detailed in Figure 1. Representative images are displayed in Figure 2.

The samples correspond to:

- The metallic ball floats from two different rotameters (ball #1 and ball #2) used to regulate flow at pre-distribution of CMS RPC gas system;
- Residue collected from ball #1 and from the inner surface of the quick supply connector #26. To collect the particles on a carbon sticker of known composition was employed (84.6 wt. % C, 14.6 wt. % O, 0.4 wt. % Na and 0.4 wt. % S);
- Resistance type PT100 of the flowcells used to read the flow in different sectors of the gas line for the CMS RPC gas system and a reference;
- Additional material from different locations (24MS, R3 11, R3 15, Al Ni 65);
- Needle valve from supply #26 that presents a region with a whitish residue.



Sample	ID	Information	Location
<b>Rotameter float ball</b>	Ball #1 after use	PreDistribution Rotameter #64	A
	Ball #2 after use	PreDistribution Rotameter #62	
	C sticker	n. a.	-
<b>Quick supply #26</b>	C sticker	Supply (Before Det) #76Ch26	B
	Reference	n.a.	-
<b>Flowcell PT100</b>	#1	Supply (Before Det) #65Ch13	C
	Supply #26	Supply (Before Det) #76Ch26	
	#2	Return (After Det) #65Ch13	E
	Return #26	Return (After Det) #76Ch26	
<b>24 MS</b>	#1	Purifier 1	F
	#2		
<b>R3 11</b>	#1	Purifier 2	G
	#2		
<b>R3 15</b>	#1		
<b>AINi 65</b>	#1		
<b>Needle valve #26</b>	After use	Supply (Before Det) #76Ch26	D

Figure 1 - Samples information and schema of their location



Figure 2 – Some of the samples under study

## 2.2 Equipment

- Field Emission Gun Scanning Electron Microscope (FEG-SEM) Sigma (from ZEISS) with InLens Secondary Electron (SE), Everhart-Thornley Secondary Electron (SE2), and back-scattered electron (AsB) detectors for imaging;



- Focused Ion Beam (FIB)/SEM Zeiss XB540 with Secondary Electron Secondary Ion (SESI), Energy Selective Backscattered (ESB) and Back Scattered Detector (BSD) detector;
- 50 mm<sup>2</sup> X-Max Energy Dispersive X-Ray Spectroscopy (EDS) detector and Extreme detector both equipped with AzTEC software (from Oxford Instruments) for chemical analysis. NOTE: EDS detection: Makes impossible to detect presence of elements below around 0.1 wt. % (the value depends on the weight and the matrix around), or light elements (impossible below Z= 4 and only large amount for Z between 4 and 11).

### 3. Results and discussion

#### 3.1 Ball floats

Both ball's surfaces were inspected by SEM. The observed residue was chemically analysed by EDS at 5 keV and 10 keV with different EDS detectors. In all the studied sites of both samples, the presence of chlorine (Cl), iron (Fe) and oxide (O) and, in lower amount, other elements like chromium (Cr) and silicon (Si) was confirmed. The semi-quantitative results of the residue analysis in ball #1 and ball #2 are included in Table 1.

The residue was thicker in ball #1. Comparative of SEM images on the ball's surface and representative EDS spectrum on Ball #1 are included in Figure 3.

Table 1 – EDS semi-quantitative results (at 5 keV) on the residue present on the float balls surface (values in wt. %)

Element	Float balls	
	Ball #1	Ball #2
<b>C</b>	5.3	6.1
<b>O</b>	4.6	7.9
<b>F</b>	0.0	0.0
<b>Na</b>	0.0	0.1
<b>Al</b>	0.0	0.0
<b>Si</b>	0.7	1.8
<b>Cl</b>	53.0	28.1
<b>Cr</b>	0.0	8.6
<b>Fe</b>	36.5	47.2
<b>Ni</b>	0.0	0.3

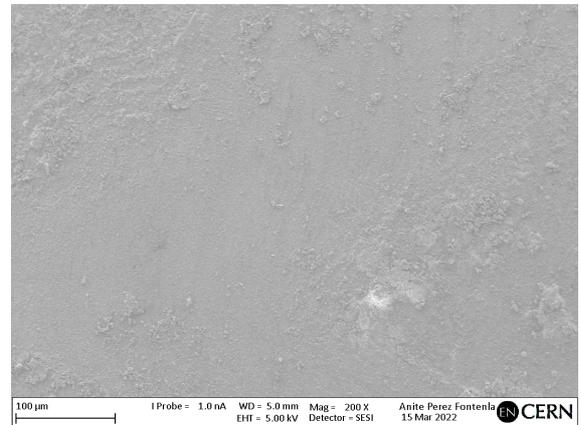
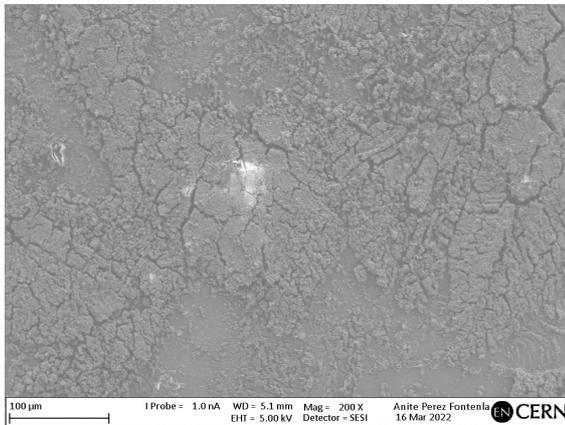
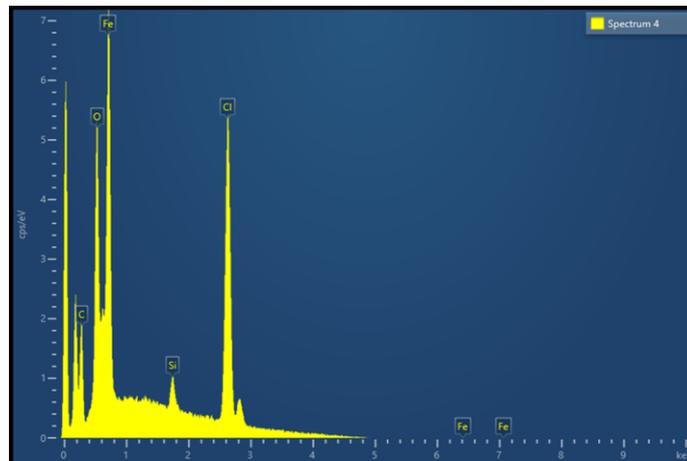
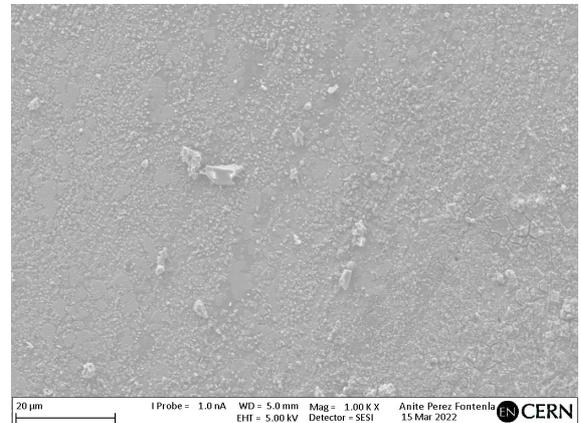
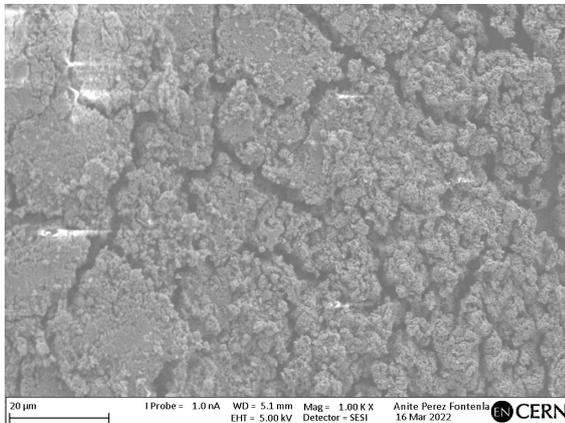
**Ball #1**
**Ball #2**
**200 x**

**1 kx**


Figure 3 – Comparison of ball's surface aspect (200x and 1 kx) and EDS (at 5keV) on the residue present in ball #1

### 3.2 Residue from the inner surface of the quick supply connector #26

The residue was collected on a C sticker from the inner surface of the connector and the averaged results of different analysed particles are summarized in Table 2. The presence of Cl is confirmed in a significant amount (Cl ~38 wt. %).

Table 2 - EDS semi-quantitative results (at 5 keV) on the residue from the inner surface of the quick supply connector #26 on a C sticker (values in wt. %)

Element	Residue
<b>C</b>	9.2
<b>O</b>	12.4
<b>F</b>	1.5
<b>Si</b>	0.3
<b>S</b>	4.0
<b>Cl</b>	<b>38.4</b>
<b>Ni</b>	18.2
<b>Zn</b>	16.0

### 3.3 Resistance type PT100 of the flowcells

Five resistances were analysed by EDS at their blue region. Semi-quantitative results of their surface analysis are included in Table 3.

Table 3 – EDS semi-quantitative results (at 5 keV) on PT100 samples (values in wt. %)

PT100					
Element	Reference	Used #1	Used #2	Supply #26	Return #26
<b>C</b>	7.3	9.7	11.2	2.5	6.9
<b>O</b>	16.4	21.4	16.1	30.8	43.4
<b>F</b>	0	0	0	1.61	0.1
<b>Al</b>	0.4	1.3	1.0	8.5	15.8
<b>Si</b>	1.8	11.0	3.7	18.5	12.8
<b>P</b>	5.7	2.7	5.4	0.0	0.0
<b>Cl</b>	<b>0.0</b>	<b>10.9</b>	<b>0.0</b>	<b>12.0</b>	<b>0.0</b>
<b>Co</b>	0.0	0.0	0.0	9.8	2.4
<b>Zn</b>	2.6	6.7	3.5	6.5	3.2
<b>Pb</b>	65.9	36.4	59.2	9.9	15.6

### 3.4 Additional material

Six specimens from various materials present on the gas system were analysed by EDS at 5 keV (24Ms, R3 11, R3 15 and AlNi 65). Semi-quantitative EDS results of their surface analysis are included in Table 4.

Table 4 - EDS semi-quantitative results (at 5 keV) on additional materials (values in wt. %)

Element	Additional material					
	24 MS		R3 11		R3 15	AINi 65
	#1	#2	#1	#2	#1	#1
<b>C</b>	3.0	3.3	10.6	13.3	8.8	7.9
<b>O</b>	45.7	46.6	33.4	34.3	25.0	26.6
<b>F</b>	0.2	0.2	0.0	0.0	0.0	0.0
<b>Na</b>	12.1	10.6	0.0	0.0	0.0	0.2
<b>Mg</b>	1.7	1.7	8.3	7.7	0.0	0.0
<b>Al</b>	15.0	15.5	0.2	0.3	5.1	26.2
<b>Si</b>	20.6	21.3	13.9	12.7	0.0	0.1
<b>Cl</b>	0.00	0.00	0.04	0.00	0.06	0.00
<b>K</b>	0.1	0.0	0.0	0.0	0.0	0.0
<b>Ca</b>	0.9	0.7	0.0	0.0	0.0	0.0
<b>Mo</b>	0.6	0.0	0.0	0.0	0.0	0.0
<b>P</b>	0.0	0.0	0.1	0.0	0.1	0.4
<b>Ni</b>	0.0	0.0	0.0	0.0	0.0	38.7
<b>Cu</b>	0.0	0.0	33.5	31.8	31.4	0.0
<b>Zn</b>	0.0	0.0	0.0	0.0	29.6	0.0

The presented values are averaged from 3 spectra performed per sample. The presence of Cl was detected only in very low amount in 2 out of 16 studied sites (very close to the technique detection limit<sup>1</sup>). As it is not a generalized presence, it will be considered negligible (only included for information).

### 3.5 Needle valve

The needle valve, presents a region where a whitish residue accumulated and is even visible by eye. Representative SEM images of the residue area are included in Figure 4. FIB-SEM cross section was performed in order to evaluate the residue thickness and it was estimated in  $\sim 35 \mu\text{m}$ .

<sup>1</sup> See detection limit in §2.2

### Needle residue area

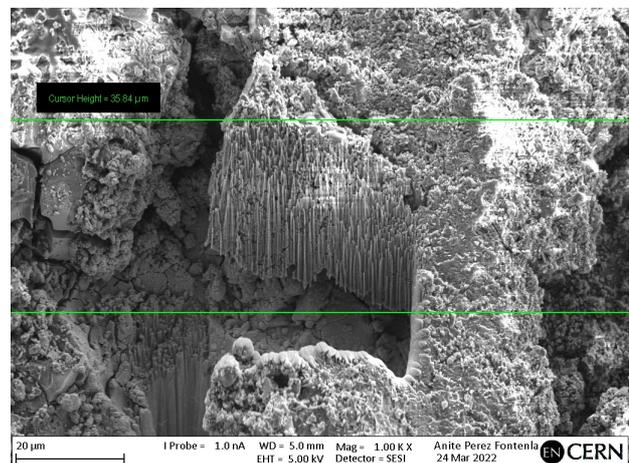
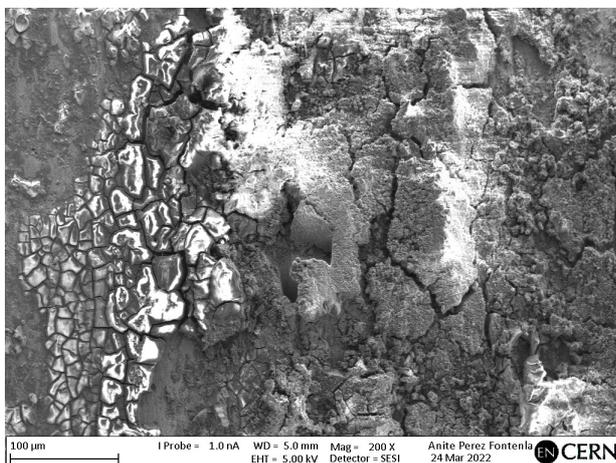
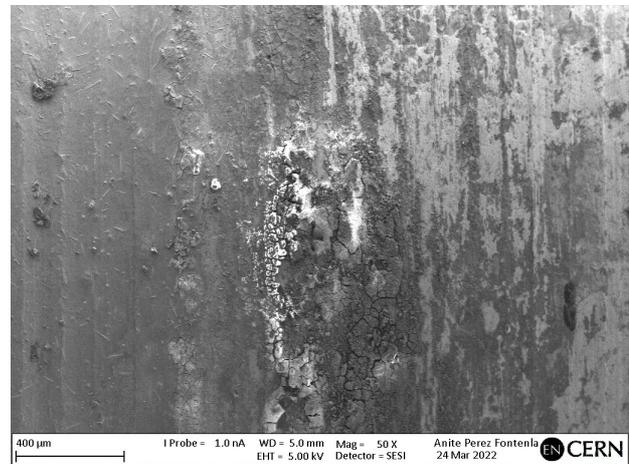
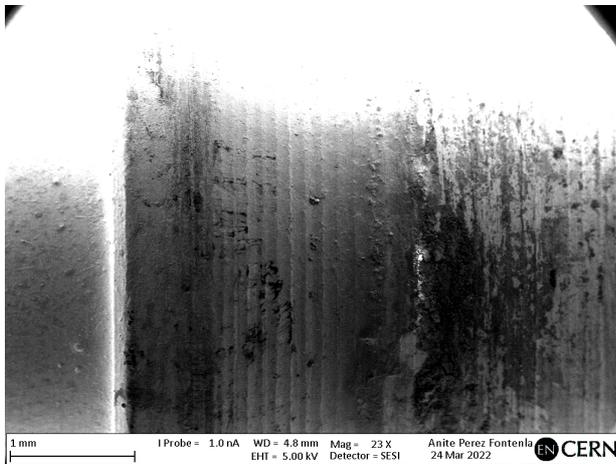


Figure 4 – Needle valve surface at the location where the residue accumulated and FIB cut to estimate the residue thickness (23x, 50x, 200x and 1kx)

Neighbouring areas, in principle non-affected, were also imaged and analysed. Surface A (Figure 5) and surface B (Figure 6) exhibited damaged surface. FIB cutting was performed in Surface B in order to evaluate the affected layer and features were visible even at an estimated depth of  $\sim 5 \mu\text{m}$ .

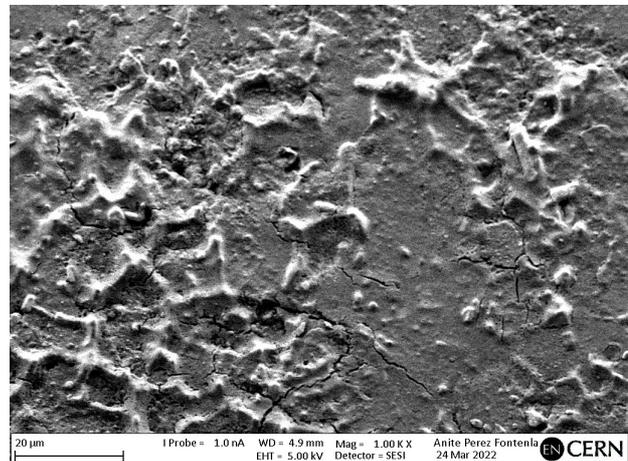
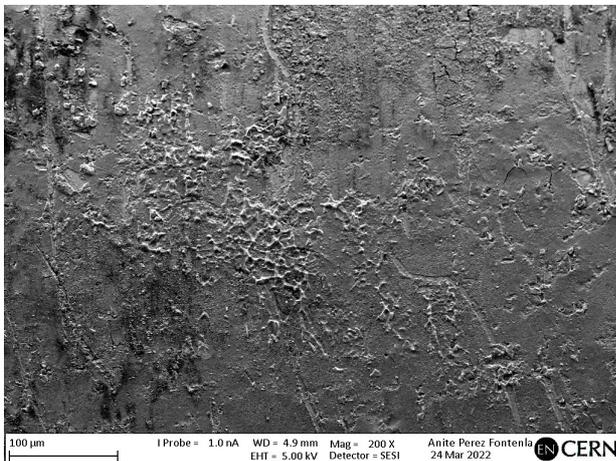
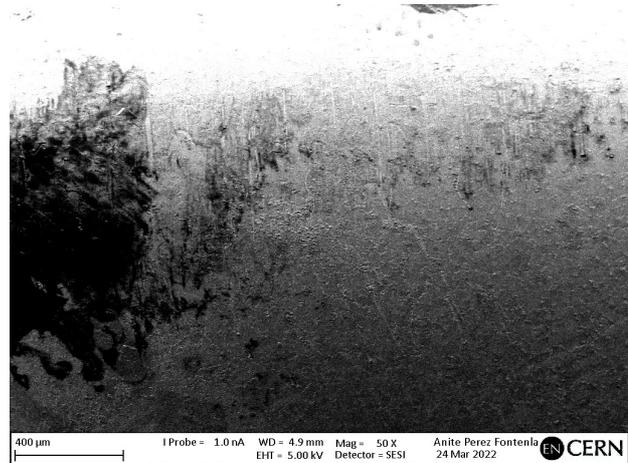
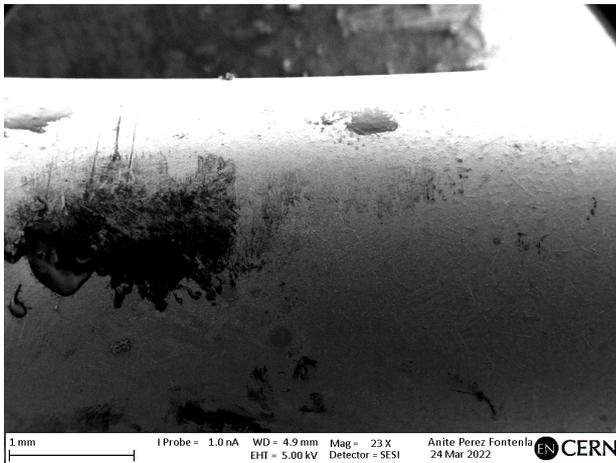
**Surface A**


Figure 5 – Needle valve surface A (23x, 50x, 200x and 1kx)

Chemical composition results from top view in the various locations of the needle valve (residue, surface A and surface B) as well as the analyses performed in the FIB cross section comparing the base material (spectrum #28) and the visible features (spectrum #29) are included in Table 5. EDS analysis confirmed a significant Cl wt. % in all the analysed surfaces and that the features observed in cross section are also areas affected by interaction with the Cl.

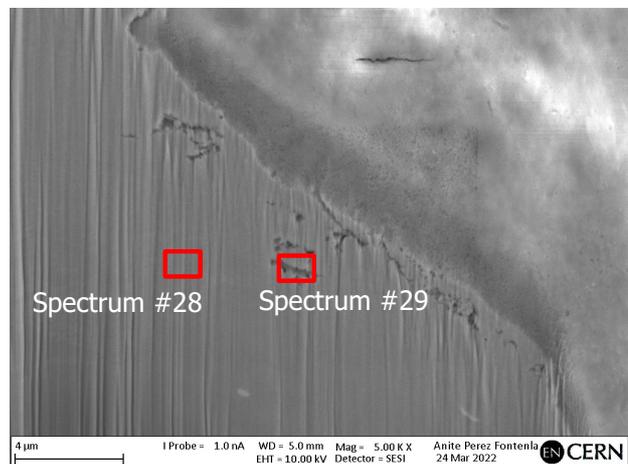
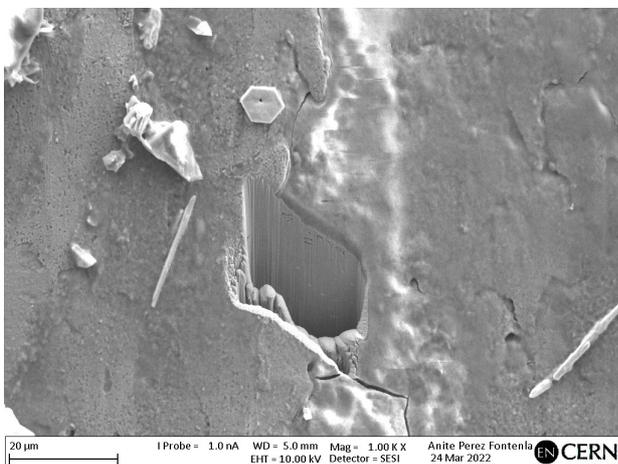
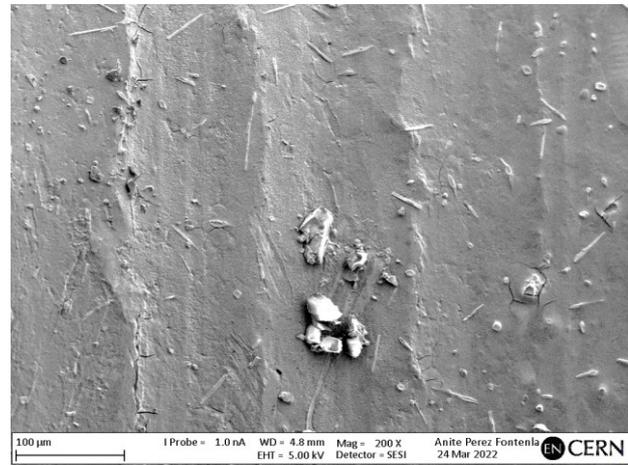
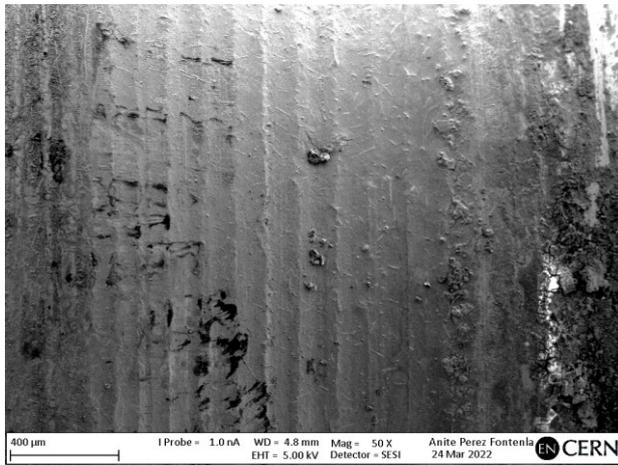
**Surface B**


Figure 6 – Needle valve surface B (50x, 200x, 1kx and 5kx)

Table 5 - EDS semi-quantitative results (at 5 keV) on the needle valve surface and FIB cross section (values in wt. %)

Element	Residue	Top view		FIB cross section	
		Surface A	Surface B	Spectrum #28 Base material	Spectrum #29 Feature
C	2.6	11.8	3.5	5.9	5.1
O	28.1	14.0	6.8	0.0	1.7
F	8.2	0.8	2.2	0.0	0.0
Al	28.9	0.3	1.0	0.0	0.0
Si	0.5	0.4	0.0	0.0	1.5
Cl	22.5	25.1	32.3	0.0	6.4
Cu	1.8	3.8	1.8	66.2	63.6
Zn	7.3	43.8	52.3	27.9	11.8
<b>Total:</b>	100	100	100	100	100



## 4. Summary of observations

SEM inspection and EDS analysis were performed on various provided samples from different locations of the CMS RPC gas system.

Presence of chlorine was confirmed in a significant amount (up to 60 wt. % in some cases) until the chambers (locations from A to D both included) as shown in Table 6. Chlorine was not detected on the sector E and it was not detected or considered punctual contamination (not generalized) on the samples from the purifiers (location G and F).

In the case of the needle valve (brass component with Cu~ 66 wt. %), the residue visible by eye presented an important amount of chlorine (Cl~ 23 wt. %), aluminum (Al~ 29 wt. %) and fluorine (F~ 8 wt. %). The thickness of the residue was estimated by FIB-SEM in 35  $\mu\text{m}$ . FIB-SEM was performed also on an area (in principle) non-affected and the presence of Cl was confirmed at the surface and features rich in Cl were identified at a depth of ~5  $\mu\text{m}$ . The obtained results indicate a general damage of the needle valve due to the interaction with the Cl (and most probably an electrolyte presence).

Table 6 - Summary of Cl detected presence on the samples

Sample	ID	Information	Location	Cl?
<b>Rotameter float ball</b>	Ball #1 after use	PreDistribution Rotameter #64	A	Yes
	Ball #2 after use	PreDistribution Rotameter #62		
	C sticker	n. a.		
<b>Quick supply #26</b>	C sticker	Supply (Before Det) #76Ch26	B	Yes
	Reference	n.a.	-	No
<b>Flowcell PT100</b>	#1	Supply (Before Det) #65Ch13	C	Yes
	Supply #26	Supply (Before Det) #76Ch26		
	#2	Return (After Det) #65Ch13	E	No
	Return #26	Return (After Det) #76Ch26		
<b>24 MS</b>	#1	Purifier 1	F	No
	#2			
<b>R3 11</b>	#1	Purifier 2	G	No
	#2			
<b>R3 15</b>	#1			
<b>Al Ni 65</b>	#1			
<b>Needle valve #26</b>	After use	Supply (Before Det) #76Ch26	D	Yes