

ASSESSMENT OF THE CORROSION OF COPPER COMPONENTS IN THE WATER COOLING SYSTEM OF ALBA SYNCHROTRON LIGHT SOURCE; PRESENTATION OF A PROPOSAL TO MITTIGATE THE CORROSION RATE OF COPPER

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Abstract

This paper presents the most recent results on the corrosion of copper components in ALBA water cooling system. The studies have been carried out using a variety of techniques: Scanning Electron Microscopy (SEM), Energy-Dispersive X-Ray Spectroscopy (EDS) and X-Ray Diffraction (XRD).

Representative samples of the Accelerator Facility were examined: Storage Ring Absorbers, Front End Masks, Radio Frequency Cavity Pipes, Experimental Line Mask, Radio Frequency Plant Pipes at Service Area and Booster Quadrupole.

The studies show the presence of intergranular, pitting and generalized corrosion. The presence of Copper Oxide is confirmed, as well as other elements such as Aluminum, Carbon, Sulfur, Silver, Calcium, Silicon, Titanium and Iron in some regions of the samples. Likewise, other elements from circulating water such as Potassium and Chlorine have also been detected. The depth of pitting corrosion is less than 119.4 μm for the samples studied, after 10 years of operation.

To minimize the corrosion problem, an upgrade of the ALBA cooling system is under study. The objective is to reduce the current corrosion rate by a conservative factor of 5. This change is possible by modifying the characteristics of the cooling water, reducing the dissolved oxygen content to values below 10 ppb and increasing the pH above 7.5. Technical aspects of this upgrade are discussed in this paper.

BACKGROUND

The phenomenon of copper corrosion has been studied with special interest in the field of accelerators, due to its impact on the equipment life of the installation, and on the efficient and continuous operation of the deionized water cooling system. Specifically, corrosion can cause an increase in the pressure drop of the components and hydraulic interfaces, loss of thermal dissipation capacity, clogging in water cooling circuit resulting from the deposition of corrosion products, and in a worst scenario crack of the absorbers located inside the vacuum chambers.

At ALBA, after 10 years in operation, there are some indications may be attributed to corrosion, such as: (i) agglomeration of oxide particles in some small cavities of regulation valves that cause a localized decrease in water

flow and (ii) malfunction of flow switches due to accumulation of oxide particles in its orifice plate geometry. In order to understand and mitigate these effects, we are investigating the state of corrosion of copper components and planning preventive actions.

THE ALBA WATER COOLING SYSTEM

By design, the ALBA cooling system is a hydraulic closed loop [1]. It consists of four main rings which feed the local consumption of the Service Area (SA), Booster (BO), Storage Ring (SR) and Experimental Area (EA) (see Fig. 1). The water is heated through all the rings and it is collected in a common return. The total water flow for the accelerator is approximately 525 m^3/h .

By means of a reverse osmosis plant, the conductivity of water is controlled at 0.2 $\mu\text{S}/\text{cm}$. The average values of pH and dissolved oxygen (DO) content are 7 and 6500 ppb, respectively, both properties are not actively controlled.

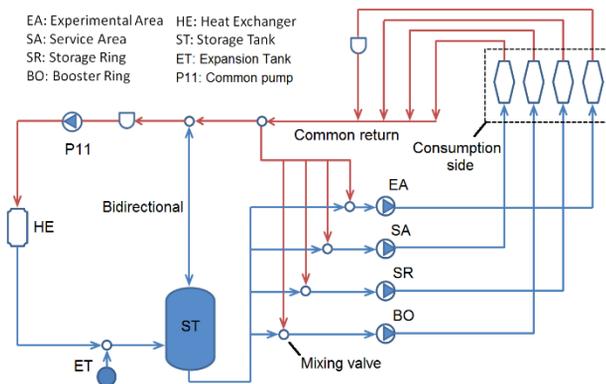


Figure 1: ALBA cooling system scheme.

Antecedent: Irregular pH Evolution

The pH is one of the main parameters involved in copper corrosion. As a practical number, it is recommended to have the water with a pH above 7.5. In Fig. 2 the evolution of the pH in ALBA is represented for the last 9 years. According to this result, most of the time the average pH value has been 7, but irregular values of 5.5 to 6.5 are reported for the years 2013 and 2014. Very high pH values (between 8 and 8.5) have also been found during the year 2012. It is assumed as a hypothesis that the pH data in the first years have been affected by problems in the instrumentation.

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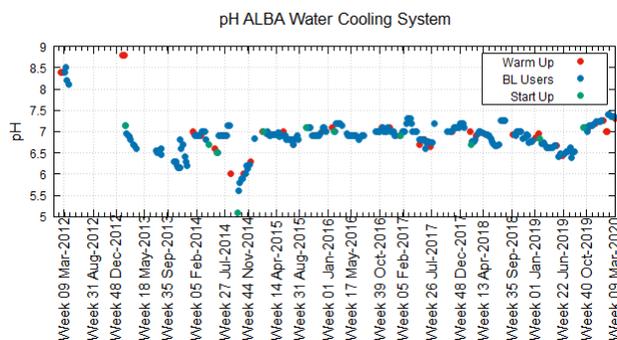


Figure 2: PH values in the ALBA deionized water cooling system, for the period 2012 to 2020. The data are weekly average values.

CORROSION STUDIES OF COPPER COMPONENTS

Nine representative samples of the ALBA deionized water cooling system were analyzed: Glidcop Al-15 Crotch Absorber (S1), OFHC Copper Crotch Absorber (S2), Copper Masks of the Front Ends BL11 (S3) and BL13 (S4), Copper Radio Frequency Cavity (S5), Copper Mask in Beam Line BOREAS (S6), Copper Circulator in Service Area (S7), and Copper straight (S8) and bent (S9) pipes of a Quadrupole of the Booster.

Naked-Eye Detection of Corrosion-Erosion

In the first visual analysis, high roughness was observed on the internal surfaces of the samples, such as the example in Fig. 3a, 3b and 3c, corresponding to samples S4, S3 and S5. In other cases, such as in Fig. 3d, the surfaces were characterized by having a smooth morphology, with a brown dark colour, indicative of the formation of oxide layers. In various parts of the system, deposits of oxide particles have been found, presumably they are copper oxide particles.

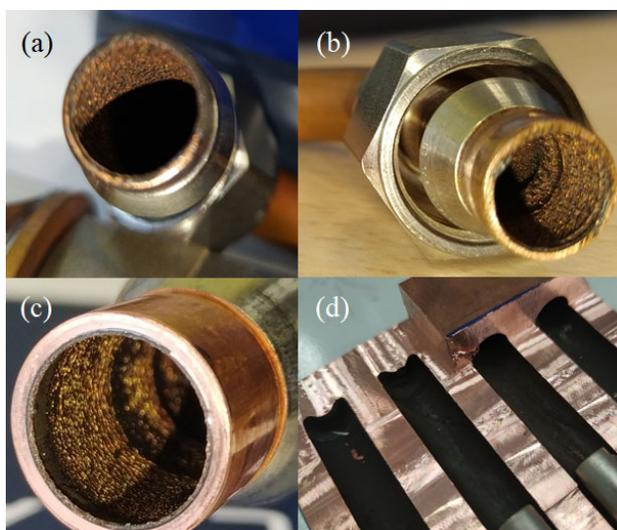


Figure 3: Images of four samples under study: Copper Masks of the Front Ends (a) BL13 and (b) BL11, (c) Copper Radio Frequency Cavity and (d) Glidcop Al-15 Crotch Absorber.

Corrosion Studies Based on SEM, EDS and XRD

We set a cooperation agreement with the Polytechnic University of Catalonia (UPC) [2] for the study of corrosion, by means of superficial observation by Scanning Electron Microscopy (SEM), Energy-Dispersive X-Ray Spectroscopy (EDS) and X-Ray Diffraction (XRD).

The samples S1, S2, S3, S4 and S5 show pitting corrosion on their surfaces (see example of Fig. 4b, sample S1). In addition, the samples S1, S2, S3 and S4 show generalized corrosion. As a particular case, the sample S5 exhibits intergranular corrosion. In some regions of samples S1, S2, S3, S4 and S5 the EDS analysis has confirmed the presence of Copper, Oxygen, as well as other elements such as Sulfur, Silver, Chlorine and Calcium (see example of Fig. 4c, sample S1). The cross-sectional analysis of samples S1, S2, S3, S4 and S5 has determined the pit depth, with values between 3.84 and 101.5 μm . The XRD analysis has confirmed the presence of copper oxide on the inner surface of samples S1, S2, S3, S4 and S5.

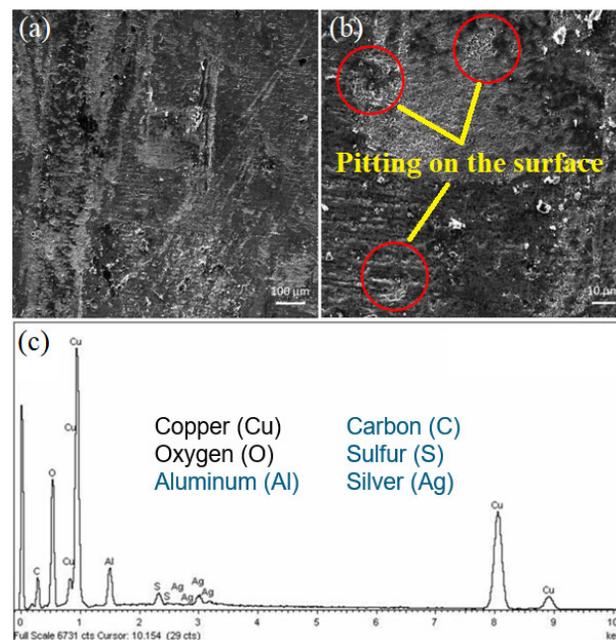


Figure 4: Study of sample Glidcop Al-15 Crotch Absorber. SEM images, (a) and (b): internal surface with detail of pitting. (c) EDS results reveals Copper, Oxygen and Aluminium as original components; also, Sulfur in the corroded areas is observed, as well as Carbon and Silver in some regions.

The samples S6, S7, S8 and S9 show pitting corrosion on their interior surfaces, with the presence of Cl⁻ ions in some of their semi-quantitative EDS composition spectra. The samples S6 and S7 show generalized corrosion on their inner surface, in the form of a dark-colored oxide layer. The samples S8 and S9 did not show the presence of a homogeneous oxide layer, but rather signs of pitting and crevice corrosion, respectively (see example of Fig. 5a and 5b, sample S9). In some regions of samples S6, S7, S8 and S9 the EDS analysis has confirmed the presence of Copper

and Oxygen, as well as other minor elements of the different base metal compositions such as Sulfur, Silver, Carbon, Silicon and Iron (see example of Fig. 5c, sample S9). Likewise, other elements from circulating water such as Potassium and Chlorine have also been detected. The recurrent presence of Chlorine in the EDS spectra carried out on the corrosion oxides present in the samples S6, S7, S8 and S9, would establish a cause-effect relationship between the presence of chlorides in the circulating water and the action of pitting and crevice corrosion. The pit depth present in samples S6, S7, S8 and S9 is in the range between 1.82 and 119.4 μm and the XRD analysis of the oxidized surfaces has confirmed the presence of two crystalline copper oxide phases on the inner surfaces, a first phase corresponding to metallic copper (JCPDS 85-1326) and the second corresponding to standard copper oxide (JCPDS 48-1548).

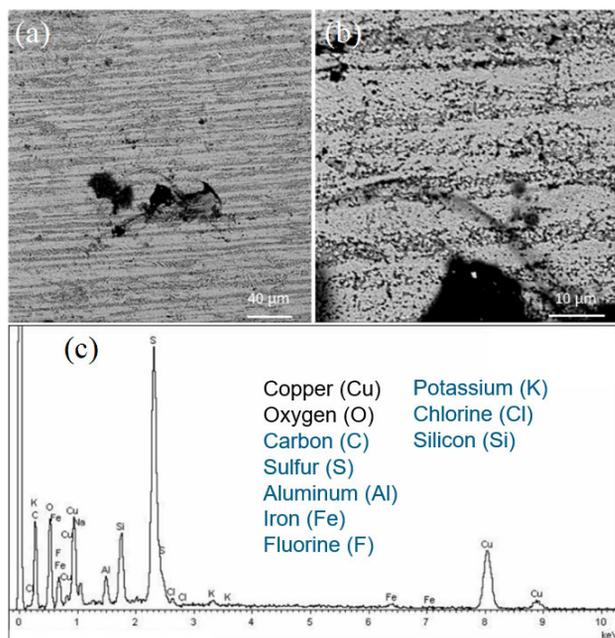


Figure 5: Quadrupole sample (bent pipe). SEM results, (a) and (b): not generalized corrosion with presence of pits. (c) EDS spectra: presence of Copper, Oxygen, Potassium, Aluminium, Silicon, Iron, Carbon, Fluorine, Sulfur and Chlorine.

CONCLUSIONS

This work shows that generalized, pitting and intergranular corrosion are present in the studied samples.

The depth values in the pits are less than 119.4 μm . From the point of view of mass loss, this value is not critical for masks and crotch absorbers, but pits are the sources for crack initiation.

Corrosion products, in the form of copper oxide, tend to accumulate in cavities with complex geometries such as regulating valves. This fact explains the flow reduction that appears occasionally in local components, especially after periods of shutdown.

The agglomeration of corrosion products in the flow switches, around their orifice plate, is an explanation of the

malfunction of this equipment, problem that occurs sometimes in ALBA.

To minimise the effects of corrosion, there is a consensus solution applied by complex facilities: improve the quality of deionized water [3–9]. This alternative is represented in the experimental curve in Fig. 6. Depending on the combination of pH versus (DO) content, the copper components have different corrosion rates (regimes 1, 2, 3, 4 and 5). Regime 1 is the preferred option, where the water is characterized by having (DO) content values < 10 ppb and $\text{pH} > 7.5$. In the case of ALBA, due to the fact that the pH has varied irregularly during the last 10 years, is assumed the hydraulic system has operated in regimes 3, 4 and 5.

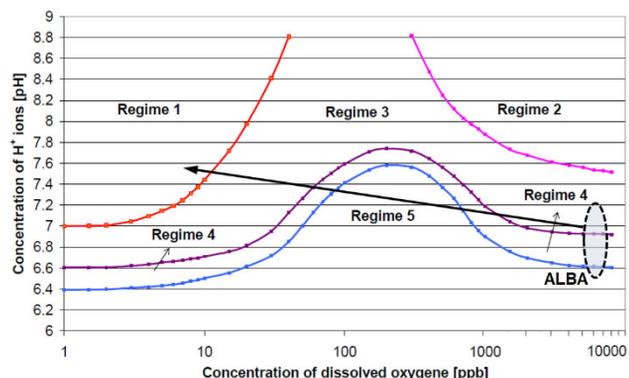


Figure 6: Copper corrosion rates. Regimes 1 and 2: < 0.1 $\mu\text{g}/(\text{cm}^2\text{y})$, regime 3: $0.1-0.4$ $\mu\text{g}/(\text{cm}^2\text{y})$, regime 4: $0.4-1$ $\mu\text{g}/(\text{cm}^2\text{y})$ and regime 5: > 1.0 $\mu\text{g}/(\text{cm}^2\text{y})$. According to historical data, ALBA has operated in regimes 3, 4 and 5. The optimization objective is to operate in regime 1.

For the future, the ALBA's objective is to operate in regime 1. It is planning to have an Oxygen Degassing Plant to reduce the current (DO) content from 6500 ppb to values below 10 ppb. This means an average reduction of corrosion rate by a factor of 5. But prior to this step we are investigating the causes of the very high values in (DO) content that we have, considering that by design our circuit is a hydraulic closed loop. For a closed system (assuming negligible oxygen ingress), the concentration of DO will approach zero because all DO will be consumed by the corrosion process. This does not occur at ALBA.

It is known that a high velocity between a corrosive fluid and a metallic surface tends to accelerate the corrosion. The modification of the criteria of the maximum velocity for the design of components in ALBA, from 3 to 2.5 m/s, is under discussion.

As part of the optimization task, the instrumentation for the control and monitoring of pH, Conductivity and (DO) content will be expanded. The monitoring of rings EA, SR, BO and SA is of special interest.

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