Investigation of corrosion-erosion phenomena in the primary cooling system of SPIDER

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SPIDER dedicated cooling plant has to remove up to 10 MW thermal power from in-vessel components and auxiliary systems. The circuit is characterized by three main heat transfer systems: primary, secondary and tertiary systems. The primary system is made of four circuits, with only three operating so far, these are called PC01, PC02 and PC03. These three circuits respectively cool SPIDER power supplies and the beam source components using ultrapure water. During 2019 SPIDER experimental campaigns, it was observed that electrical resistivity of water degraded considerably and more quickly (~25 MΩ cm h^{-1} in PC01) than estimated by design. To overcome this issue, water had to be restored very frequently to maintain the desired characteristics and avoid possible detrimental leakage currents throughout the circuit. The reason for this severe water degradation has to be better understood before issues such as abrupt failures may arise. This work presents a preliminary analysis of the two main circuits (PC01 and PC02) where an estimation of water degradation induced by general corrosion of stainless steels and copper components was made. This preliminary estimation showed that PC01 could be more prone to general corrosion than PC02; however, the rate of water conductivity increase was 5.3 times smaller than that observed during experiments in 2019 and 2020.

1. Introduction

SPIDER is the 100 keV full-size Ion Source prototype of the ITER Neutral Beam Injectors and it is operating at PRIMA (Padova Research Injector Megavolt Accelerated) site in Padova (Italy) [1]. It is mainly composed by actively cooled components, located inside a vacuum vessel, that need to be thermally controlled by removing the heat loads generated during beam operations. Corrosion-erosion phenomena are thought to occur in the cooling circuits of primary heat transfer systems. The cooling plant [2] is characterized by three main heat transfer systems:

- Primary Circuits (PCs) are directly connected to the test facilities to remove the experiments' thermal power. Each primary circuit is a closed hydraulic loop with one heat exchanger, a pump, a pressurizer, valves and other instruments;
- Secondary Circuits (SCs) transfer the absorbed heat from PCs to water basins used to store the thermal energy;
- Tertiary Circuits (TCs) are open circuits that transfer the thermal power from the basins to the environment via cooling towers and air coolers [3].

Primary circuits are the most critical ones in terms of water degradation since these circuits use ultrapure water as coolant media and are directly connected to the test facilities components that operate at different electrical potentials (up to -100 kV) and are made of copper and stainless steels.

SPIDER entered into service mid-2018 and fast water quality degradation was observed during the 2019 experimental campaign. In this paper, the analytical estimation of water degradation is presented and compared with the experimental value. Future activities are also discussed to better identify and possibly solve the issue.

2. Water quality in SPIDER cooling plant

Ultrapure water is used as coolant in SPIDER PCs (Table 1) to allow electrical insulation of in-vessel components at different voltage levels by limiting the leakage current. The ultrapure water is produced by a dedicated system named Chemical Control System (CCS) that supplies two types of water at different grades:

- W-I with resistivity of 5.0 - 10 MΩ·cm at 25 °C
- DW with resistivity of 0.05 – 0.1 MΩ·cm at 25 °C

These water quality levels are obtained after pre-chlorination, ultrafiltration, softening, dechlorination, microfiltration, reverse osmosis, oxygen stripping and electro-deionization steps [4].

Two more type of water can be produced by mixing the abovementioned waters:

- W-II with resistivity of 1.0 - 2.0 MΩ·cm at 25 °C, obtained by mixing 96% W-I and 4% DW
- W-III with resistivity of 3.3 - 5 MΩ·cm at 25 °C, obtained by mixing 99% W-I and 1 % DW

Currently, only W-I water type is produced by the CCS and stored in tanks. When water achieves the maximum allowable value of conductivity in PCs, the circuits must be stopped to allow a complete (or partial) replacement of the coolant: the conductivity requirements for W-II and W-III waters are obtained by

partial refilling the degraded water of cooling circuits with W-I water, pH or dissolved oxygen of the water in the circuits are not verified. Since the water re-filling takes place through this offline system, it is essential to minimize the conductivity degradation as much as possible in order to maximize the experimental time.

Water circulating in pipes reacts with inner channel surfaces made of copper and stainless steel, causing thinning of cooling channel walls. Chemical and electrochemical reactions are involved in the material general corrosion process, whereas liquid at high flow velocities leads to a mechanical surface modification, called erosion. The conjoint action of corrosion and erosion, that causes the wastage of a material, is here defined as "corrosion–erosion". Corrosion-erosion phenomena have to be prevented and monitored to improve experimental performances not only of SPIDER cooling plant, but also of future nuclear fusion facilities to support reliable operations. Water chemistry plays an important role in order to minimize the formation of corrosion products and to insulate components subjected to high tension [5].

Table 1: Characteristics of water used in SPIDER cooling plant

	W-I	W-II	W-III	DW
Resistivity [MOhm·cm] at 25°	5.0 – 10	1.0 – 2.0	3.3 – 5.0	0.05 – 0.1
Conductivity [µS·cm⁻¹]	0.2 – 0.1	1 – 0.5	0.3 – 0.2	20-10
pH	6.5 – 7.5	6.5 – 7.5	6.5 – 7.5	6.5 – 7.5
Dissolved Oxygen [ppb]	≤ 50	≤ 50	≤ 50	≤ 50

3. Analytical estimation of water grade degradation

PC01 and PC02 are analyzed in this paper as representative of the whole plant: PC01 cools down the power suppliers (W-III water type), whereas PC02 (W-II water type) cools the SPIDER components as the other SPIDER PCs. More detailed information regarding each PCs and which SPIDER component they cool down can be found in Fellin et al.[3]. The materials involved are stainless steel (AISI-304 and AISI-316L), copper, alumina and polypropylene (PP). Only metals are considered in the following as the main contributors to water degradation.

The main hydraulic characteristics were calculated for the two mentioned PCs, as shown in Table 2 from which the following considerations can be made: with respect to PC01, PC02 has a bigger volume [m³] and a higher total volumetric flowrate [m³ h⁻¹] estimated at T=20°C. PC01 and PC02 copper wetted surfaces are instead comparable, whereas the wetted stainless steel (SS) area is 5 times higher for PC02.

Table 2: Summary of PC01 and PC02 characteristics

	PC01			**PC02**		
Tot Volumetric Flowrate [m³ h⁻¹]	64.80			181.6		
	Cu	*SS*	*Tot*	*Cu*	*SS*	*Tot*
Length of the pipeline [m]	78.23	128.80	235.98	378.21	449.75	827.95
Wetted Area [m²]	6.20	18.24	24.44	6.94	97.03	103.98
Inner volume [m3]	0.04	0.58	0.81	0.01	2.74	2.75

The conductivity of an ionic solution, k, is usually calculated with:

$$k \left(\frac{\mu S}{cm}\right) = 1000 \cdot \sum \Lambda_i \cdot Ci$$

Where:

Λi = The molar conductance of species i [mho cm² mol⁻¹] or [S cm² mol⁻¹]

Ci = The molar concentration of species i [mol L⁻¹] [6]

The variation in water conductivity was estimated for both PCs considering copper and stainless steel wetted area and the volume of the two circuits. A corrosion rate equal to 3600 µg m⁻² day⁻¹ was considered for copper. This value was taken from T.E. Eriksen [7] where 99.7 wt% copper was exposed for 61 days to deionized and double-distilled water. With regards of stainless steel, Molander [8] reports a corrosion rate trends in the temperature range 134 – 200 °C as a function of specimen time exposure to ultrapure water. No literature was found regarding corrosion of SS in ultrapure water at ambient temperature but, considering that SPIDER has been operating for more than 2 years, we choose a corrosion rate of 480 µg m⁻² day⁻¹ obtained by taking the corrosion rate value in Molander graph [8] for stainless steel at 134°C after 10000 h exposure. Despite this chosen corrosion rate value was obtained at higher temperature than the one used in SPIDER circuits (20-25 °C), this overestimated corrosion rate will provide a conservative water degradation mechanism. In the absence of oxygen, lower temperatures are in many respects considered beneficial from a general stainless steel corrosion point of view [9].

Table 3: Total concentration of metallic ions in solution for PC01 and PC02

	PC01			**PC02**		
	Cu	*SS*	*Tot*	*Cu*	*SS*	*Tot*
ppm in a day	2.6 ·10⁻²	1.1 ·10⁻²	3.7 ·10⁻²	8.6 ·10⁻³	1.7 ·10⁻²	2.6 ·10⁻²
ppm in 1 hour	1.1 ·10⁻³	4.5 ·10⁻⁴	1.5 ·10⁻³	3.6 ·10⁻⁴	7.1 ·10⁻⁴	1.1 ·10⁻³

The total concentration of metallic ions in solution, shown in Table 3, was estimated by multiplying the corrosion rates [mg dm^{-2} month^{-1}] with the wetted surface area of components [m^2] and dividing by the overall PC volume [m^3]:

$$ppm = \frac{Cor.rate\ [\mu g\ m^{-2}\ day^{-1}] \cdot Wet.Area\ [m^2] \cdot 1[day]}{PC\ Volume\ [m^3] \cdot 1000}$$

Table 3 shows that, despite copper wetted area is similar for both circuits, PC02 have a smaller concentration [ppm] of Cu ions in the water after one day of operation due to the larger volume of the circuit.

From these simplified calculations, the ppm in the circuits could be related to an increase of water conductivity in the system by using conductivity - ppm conversion factors found in Frankel [10] and shown in Table 4 for copper and stainless steel.

Table 4: Resistivity and conductivity conversion taken from Frankel [10] book

Water type	Ppm	Conductivity	Resistivity	Ppm or mg/L				
	as CaCO₃	_[µS/cm]_	_[MΩ·cm]_	_only Cu_	_only Fe_	_only Cr_	_only Ni_	_only AISI 304L_
II	0.850	2.210	0.450	0.541	0.316	0.294	0.495	0.320
	0.420	1.130	0.880	0.268	0.156	0.145	0.245	0.158
	0.170	0.490	2.050	0.108	0.063	0.059	0.099	0.064
	0.130	0.380	2.650	0.083	0.048	0.045	0.076	0.049
III	0.085	0.270	3.700	0.054	0.032	0.029	0.049	0.032
I	0.057	0.200	5.000	0.036	0.021	0.020	0.033	0.022
	0.042	0.160	6.150	0.027	0.016	0.015	0.024	0.016
	0.017	0.098	10.200	0.011	0.006	0.006	0.010	0.006

Therefore, the increase in conductivity observed during SPIDER operation could be directly related to an increase in ionic species dissolved in the ultra-high resistivity water (Table 5) [6].

Table 5: Conductivity increase calculation results for PC01 and PC02

	PC01			PC02		
	_Cu_	_SS_	_Tot_	_Cu_	_SS_	_Tot_
_Δk_ [µS/(cm day)]	1.0 ·10^{-1}	7.3 ·10^{-2}	1.8 ·10^{-1}	3.4 ·10^{-2}	1.1 ·10^{-1}	1.5 ·10^{-1}
_Δk_ [µS/(cm h)]	4.3 ·10^{-3}	3.0 ·10^{-3}	7.3 ·10^{-3}	1.4 ·10^{-3}	4.8 ·10^{-3}	6.2 ·10^{-3}
Water treatments [1/week]		2.06			0.26	

Water degradation in PC01 is more severe than the one in PC02 from estimated calculations: the conductivity variation for each hour is about 0.0073 [µS cm^{-1} h^{-1}] in PC01 whereas in PC02 is about 0.0062 [µS cm^{-1} h^{-1}]. The overall higher ions concentration estimated in PC01 is due to the smaller volume [m^3] of the circuit. Furthermore, the number of water treatments for week was estimated considering 8 hours of operation for 4 days, and it turned that PC01 water needs to be changed about 8 times more than PC02 (Table 5). The results can be explained considering that PC01 degrades faster than PC02 from calculations, and its required water characteristics are stricter in terms of conductivity. In water treatment calculation, it was considered that every morning water circulating in PCs

was purged in part and the other part mixed with fresh ultrapure water to restore the required conductivity value.

4. Experimental Results

Water degradation was experimentally observed during the 2019-2020 campaign.

Figure 1 and Figure 2 show the trends for water degradation and the relative conductivity rate increase [µS cm^{-1} h^{-1}] for PC01 and PC02 during the 20th June 2019, which was taken as a representative experimental day. The other experimental days have similar trends. Figure 1(a) shows the conductivity variation for PC01 and Figure 1(b) the relative total flowrate aiming to show when the circuit is running. Figure 2 shows the same plots but regarding PC02 (since no flowmeter is located on a common branch where the total PC02 flowrate flows, the flowrate shown for PC02 is the one that cools the RF Coils). The conductivity variation was estimated considering 5 hours of operations, starting from 10:40:00 until 15:40:00. This interval of time was chosen since both the flowrates have a constant value and the conductivity a linear trend. The plots make evidence that, when the flowrates are turned off, the conductivity stops almost immediately to increase and reaches a quite constant value.

The conductivity increase rate during experiments is approximately 0.039 [µS cm^{-1} h^{-1}] in PC01 and approximately 0.0032 [µS cm^{-1} h^{-1}] in PC02. The real conductivity increase trend can be compared with the one previously estimated ($Δk_{real}$ / $Δk_{estimated}$):

- PC01: $\frac{Δk_{real}}{Δk_{estimated}} = 5.3$
- PC02: $\frac{Δk_{real}}{Δk_{estimated}} = 0.5$

Water conductivity degrades 5.3 times faster for PC01 than the calculations here presented. By contrast, PC02 reveals a degradation of 0.5 times slower than the estimations reported.

From these plots, it's clear that PC01 quickly reaches the upper limit of operation of 1 [µS cm^{-1}] within few hours and water has to be restored every morning before starting a new experimental day. PC01 water treatments were estimated to be about 2 times in a week whereas, in reality, water is restored every morning, before a new experimental session.
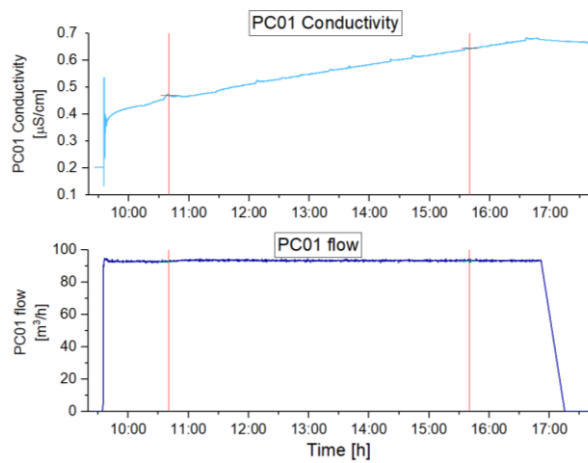
Figure 1: 20th June 2019. PC01. Conductivity range [10:40:00; 15:40:00]. (a) PC01 conductivity variation; (b) PC01 flowrate trend
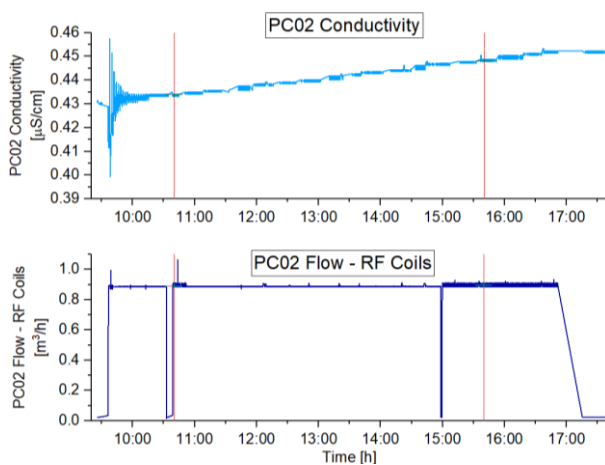

Figure 2: 20th June 2019. PC02. Conductivity range [10:40:00; 15:40:00]. (a) PC02 conductivity variation; (b) PC02 flowrate trend

5. Future activities

The only water parameter taken into consideration so far to evaluate the water resistivity degradation is the water conductivity value. Corrosion phenomena are not only affected by water conductivity but also by dissolved O_2, pH, temperature, flow velocity (turbulence), imposed voltage, galvanic potential difference [5]. Currently, no definitive data have been collected to understand whether the degradation is related to a particular component in PC01.

A new experimental campaign is foreseen to monitor whether the oxygen content and the pH are affected after water is circulated for a fixed amount of time in the cooling channels of PC01 and PC02, consecutively. In order to focus only on hydraulic related problems, the electric equipment (i.e. Ion Source and Extraction Power Supply - ISEPS and the Acceleration Grid Power Supply – AGPS) shall be kept switched off during this campaign, implementing different hydraulic configurations to help and identify the most polluting systems. Every single loop in PC01 will be isolated and analyzed in terms of pH, O_2 content, conductivity, ions dissolved in solution and precipitates. At the end of each

session, water samples will be collected, stabilized and stored. After that, the samples will be analyzed by using ICP-MS technique to quantify the metal ions concentration. The same analyses will be carried out for PC02 but considering the overall circuit, without isolating each cooling branch. This choice relies on the fact that we would like to investigate specifically on the causes that bring to the fast degradation of PC01 water resistivity.

6. Conclusions

SPIDER primary circuits have shown a considerable water degradation issue during operation. In particular, the water conductivity rate increase of PC01 was approximately 0.039 μS cm^{-1} h^{-1}, which is about one order of magnitude larger than that observed in PC02. A preliminary assessment was made to understand the source for this degradation: the wetted areas made of copper and stainless steel and the PCs volumes in PC01 and PC02 circuits were calculated. The corroded mass in the circuits induced by general corrosion was then estimated from corrosion rates data from literature. The increase in conductivity induced by the calculated corroded mass was estimated and compared to the real data obtained during SPIDER operation. PC01 was shown to be more prone to general corrosion than PC02 however, the calculations here presented underestimated the degree of water degradation in PC01 by about 5 times.

Further analyses are therefore needed to understand the causes that give rise to the stronger water resistivity degradation with respect to the other primary circuits. The third SPIDER Primary Circuit PC03 will be analyzed soon. An experimental campaign is foreseen to monitor not only the conductivity in SPIDER Primary Circuits but also the oxygen content and the pH. Chemical analyses will be performed on water samples taken from each test carried out to quantify the presence of metallic ions in solution and compare them to the estimated values here presented.

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