

DEGASSING OF DISTILLED WATER-COOLING CIRCUITS AND AFFECTED COPPER-WALLED STRUCTURES

R.P. Kan^{*1}, R. Eichler^{1,2} and A. Weber¹

¹ PSI Center for Accelerator Science and Engineering, Villigen, Switzerland

²University of Bern, Bern, Switzerland

Abstract

Cooling circuits running with distilled water to cool copper structures like magnets or cooling plates are vulnerable to air leaking in. The leaked-in air contains carbon dioxide that lowers the pH from 7 to quite acidic distilled water and makes it possible for the intruded oxygen to react with the surface of the copper tubing, forming copper oxides that can grow and mechanically be displaced to clog in locations where the flowrate is low. The process also reduces the wall thickness of the tubing, eventually followed by water leakage. Regular unclogging causes the circuit to be opened more often and therefore accelerating the destructive process. A good solution to this problem comes with a steep price: Degassing by reverse osmosis in every copper cooling circuit.

PURE WATER TURNING ACIDIC

A Troublesome Copper Cooling Circuit at the Paul Scherrer Institute

Between 2000 and 2005, several water-cooled magnets like in Figure 5 overheated. A muddy residue caused the cooling water not to flow properly. Flushing the lines resulted in even faster interruptions and more residues as can be seen Fig. 1. An investigation, by the responsible beam-line scientist and the leader of the magnet group, resulted in a report[1] on the influence of the dissolution of oxygen and carbon dioxide in distilled water, causing acidic conditions (regime 5 of Fig. 6 due to CO₂) and the steady ablation of the interior of copper coils / tubes (due to O₂).

Ongoing Chemistry at the Surface

The corrosion mechanism is illustrated in Figure 4. Oxygen (O₂) and carbon dioxide (CO₂) are always present in water due to interaction with the atmosphere. No water-cooling system stays vacuum tight. Atmospheric gases can enter the cooling system through tiny leaks and diffusion through non-metallic tubing. The presence of CO₂ in the water results in the formation of carbonic acid (H₂CO₃), which dissociates into HCO₃⁻ and H⁺-ions. This acidity fixes the pH of the coolant between 5 and 6. Oxygen dissolves in water increasing the redox potential. The cuprous oxide Cu₂O (reddish in colour like in Fig. 2) is initially formed at the surface. Upon further oxidation by dissolved oxygen CuO (blackish in colour as in Fig. 3) forms. In the absence of other influences this stable surface, non-soluble in water at these pH-levels, would render this surface stable to further corrosion. However, the mechanical stress from

the coolant flow removes this oxide layer as a solid, leaving the metal surface unprotected again to the oxygen-rich acidic water. This leads to further dissolution of the metal (eventually leaks) and macroscopic slug formation.

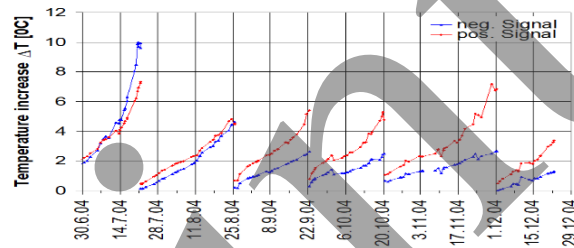


Figure 1: The measured temperatures of a quadrupole magnet in a regular pattern of temperature increases ΔT due to two parallel cooling circuits clogging, then recovering after flushing the deposition products out of the magnet [1].



Figure 2: Accumulations of corrosion sludge ($\phi 6$ mm), consisting of CuO and/or Cu₂O, from behind a flow restrictor. A Swiss 50 centime coin is shown in the background [1].

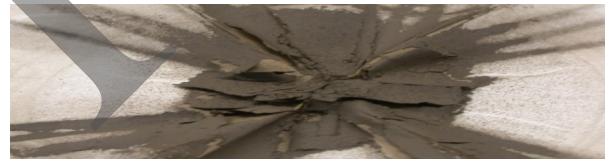


Figure 3: Filtrated deposits of various copper oxides. The pore size of the filter is 12 μm . The dry weight of the residue is 0.72 g [1].

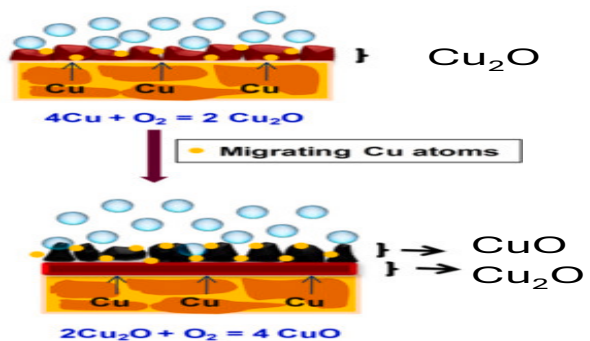


Figure 4: Corrosion mechanism at a copper surface due to dissolved O₂ and CO₂ in distilled water [2]. Even small air leaks promote water leakage and obstructive corrosion.

*Richard.Kan@psi.ch



Figure 5: A quadrupole magnet with copper coil made of small diameter tubes with narrow elbows, filled with distilled water at a low flow rate (to counteract erosion).

Equation 1: Rate of corrosion R [$\mu\text{m}/\text{y}$], see Table 2 for contributing factors

$$R_{\square} = 1.4 \times 10^9 \times c(O_2) \times c(H^+) \times f(T) \times f(V) \times f(\gamma) (1)$$

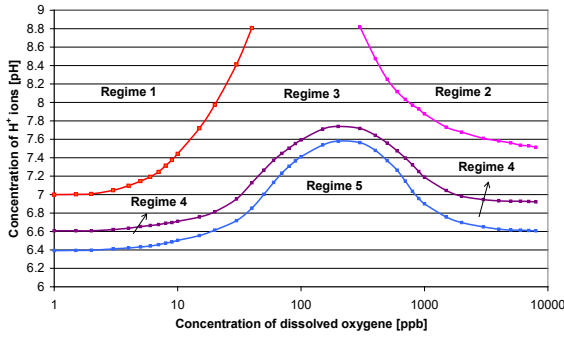


Figure 6: Corrosion rates under different operating conditions, see Table 1 for values in the regimes.

Table 1: Corrosion Rates in Various Regimes as Displayed in the Above Fig. 6 [3]

Regime	Corrosion Rate
1 & 2	<0.1 $\mu\text{g}/(\text{cm}^2.\text{y})$
3	0.1-0.4 $\mu\text{g}/(\text{cm}^2.\text{y})$
4	0.4-1 $\mu\text{g}/(\text{cm}^2.\text{y})$
5	>1.0 $\mu\text{g}/(\text{cm}^2.\text{y})$

Table 2: Contributing Factors to the Rate of Copper Corrosion in the Equation 1 Above [3]

Parameter	C. Factor	Remark
$c(O_2)$ [mol/l]	>200	see Fig. 6
$f(v)$ [m/s]	20.3	$0.5 \text{ m/s} < v < 4 \text{ m/s}$ ($v/1/2$)
$f(T)$ [0C]	3	$20^\circ\text{C} < T < 50^\circ\text{C}$
$f(\gamma)$: dD/dt [Gy/h]	1.6	$1 \text{ Gy/h} < D\dot{\gamma} < 900 \text{ Gy/h}$

The rate of corrosion shown in Equation 1 depends strongly on the concentration O_2 and CO_2 , and the flow rate, but much less on temperature and dose rate [4]. The resulting corrosion rates for specific regimes depending on dissolved oxygen and the pH-level are found in Table 1.

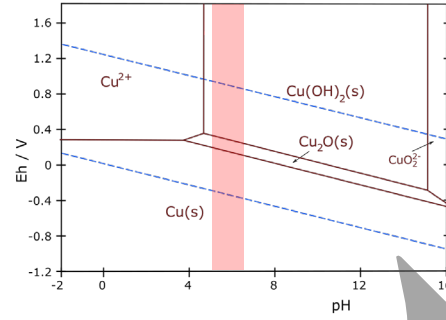


Figure 7: the Pourbaix diagram (redox potential/pH diagram) for copper in water at 25°C adopted from [5], with a red interval shows the pH range for carbonated water.

How This Problem Was Countered at First

In 2004 a cooling circuit (nr.9) with troubled magnets was monitored and temporarily connected to a self-developed setup that pushed out the gases after it had flushed out the residue. However, every time the water circuit had to be opened, (a lot of) oxygen and carbon dioxide were able to enter, also the pH level 5.6-6.65 was measured [1], which puts the system into the orange band where Cu reacts with O_2 into Cu_2O (see Fig. 7). Weekly flushing was necessary until this cooling was coupled to an online degassing system based on the reverse osmosis principle in 2005. A total of >85 g (dry weight) metal oxide was flushed out in 12 months' time. Without this intervention the corrosion rate can be calculated by Equation 1, with the use of the Table 2 for the contribution factors of the parameter [3].

A Costly, But Effective Solution

A degassing system (see Figure 8) continuously removes oxygen and carbon dioxide, working on the principle of reverse osmosis. It is connected in series with ion exchange filters on a bypass of the water circuit (Fig. 9).



Figure 8: The degassing system

With roughly €200k plus yearly maintenance of about €15k, it is costly, and it needs to be installed in many different water-cooled circuits, depending on the possible containment of radioactive particles and on the metal (Cu / Fe) walled structures. The pH-value measurement is not necessary, as this is difficult, costly and it rejects much water. Most distilled water circuits at PSI are equipped with such degassing systems (10 circuits in total with Cu or Fe walled structures – circuits with Al are not degassed). A

one-week failure of the degassing system in cooling circuit nr.9 in 2021 abruptly caused a cooling-water blocking of the deflection magnet AWD. One of the last cooling circuits (PROSCAN P5 for inactive power supplies (pH6.9)), is still without a degassing system, and recently heat exchangers in power supplies needed to be replaced. PROSCAN P6 for components in the vault, has a degassing system and pH7.2 was measured). P5 & P6 are relatively small circuits and measures are taken to ensure they are kept free of both air and water leaks, as they are part of the medical proton facility.

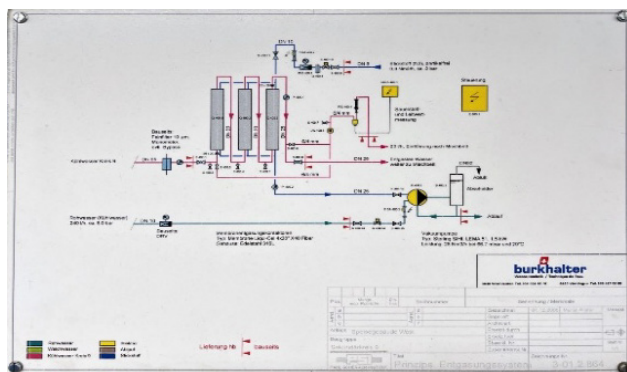


Figure 9: The diagram of the degassing system, as seen in Figure 8 above the yellow box

The Current Application of Degassing Systems at Paul Scherrer Institute

PSI has chosen a system that reduces the oxygen content from <50 ppm to <5 ppb and carbon dioxide to <3%, while the water resistivity is reduced from 1 $\mu\text{S}/\text{cm}$ to 0.1 $\mu\text{S}/\text{cm}$ -0.2 $\mu\text{S}/\text{cm}$. The exchange of the resin of the deionization is done every two years about. The pH level is kept this way between pH 6.8 and pH 7.2. The system generates no water reject stream or liquid exhaust, but it does produce a gas exhaust with oxygen, carbon dioxide, nitrogen and argon including their radioactive isotopes and needs a connection to the controlled and protected exhaust air system monitored by the PSI-radiation protection. The typical flow rates in cooling circuits at PSI are 1.5 m/s – 1.8 m/s with the resistivity of 0.1 $\mu\text{S}/\text{cm}$ -0.2 $\mu\text{S}/\text{cm}$. Cooling circuits for water that can become radioactive have a separate degassing system than cooling circuits where the water is not exposed to radiation (in case of power supplies cooling circuits). Also, cooling circuits for aluminium structures should never be mixed with copper cooling circuits due to galvanic corrosion enhancement facilitating the dissolution of aluminium. Although, aluminium is highly susceptible to acidic attack in water cooling systems, at PSI cooling circuits for aluminium structures are not degassed. Aluminium's corrosion mechanism with air leaks is different but equally detrimental to system longevity. Aluminium relies on a thin, natural passivation layer of Aluminium oxide (Al_2O_3) for protection. Aluminium forms "white rust" (aluminium oxide/hydroxide deposits) at intermediate pH levels, which can clog tubes and reduce thermal performance. Otherwise, the amphoteric aluminium is very sensitive to pH levels; its protective oxide layer is only stable

between pH 4.0 and pH 8.5. If the pH drops below this range due to CO_2 content in the water, general acid corrosion can occur. At high pH levels Aluminium will also dissolve forming various hydroxy-complexes $\text{Al}(\text{OH})_x$ - $x+3$ with $x=2-4$, see Fig. 10 and Fig. 11. Since the pH level in Al cooling circuits has been around pH 6.8, these problems did not arise. The cooling circuits for groundwater at PSI are also not degassed.

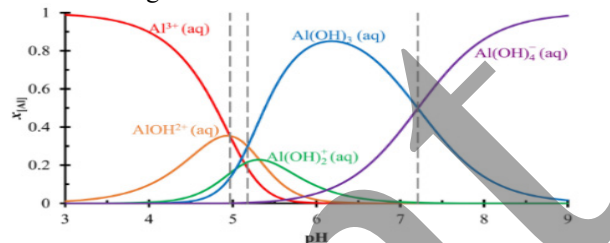


Figure 10: The calculated speciation diagram for monomeric Al aqueous species at 298 K and 1 bar [6]

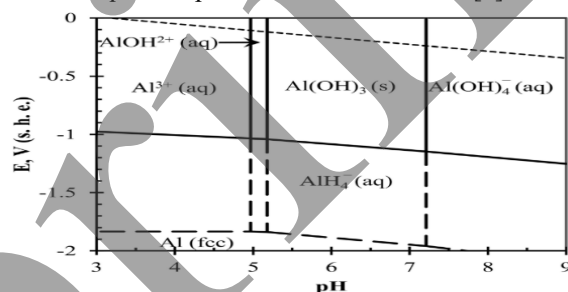


Figure 11: The Pourbaix-diagram of Al in an aqueous environment at 298 K, 1 bar and $a[\text{Al}]=10^{-8} \text{ m}$ [6]

CONCLUSION

Air leakage into a cooling circuit cannot be prohibited and all copper cooling circuits corrode (even OFE copper) and should therefore have a degassing system to prevent water leakages and clogging of the circuit due to oxidation.

REFERENCES

- [1] H.W. Reist, D. George, "Accelerator Magnet Plugging by Metal Oxides", *PSI Scientific and Technical Report 2004*, Vol. VI, pp.142-145
- [2] N. Hossain et al., "Advances and significances of nanoparticles in semiconductor applications – A review", *Results Eng.*, vol. 19, pp. 101347, 2023. doi:10.1016/j.rineng.2023.101347
- [3] H. Schöler, H. Eutener, "Corrosion of Copper by Deionised Cooling Water", EPAC, Rome, It., pp. 1067-1068,1988
- [4] R.Dortwegt, E.V.Maughan, "The chemistry of Copper in water...", in *Proc. PAC-01, Chicago, II, USA, Ed, in PAC01-01, vol.2, IEEE, pp.1456-1458. doi:10.1109/pac.2001.986712*
- [5] B.Beverskog, I.Puigdomenech, "Revised Pourbaix diagrams for copper at 25 to 300°C", *J. Electrochem. Soc.*, vol. 144, no. 10, pp. 3476-3483, Oct 1997. doi:10.1149/1.1838036
- [6] P. A.Nikolaychuk, E.Kozeschnik, "Thermodynamic Evaluation of the aerial and aqueous oxidation of Al-Mg, Al-Si and Al-Mg-Si System alloys at 298K", *npj Materials Degradation* 8, no. 1, Sep. 2024. doi:10.1038/s41529-024-00446-w