DEGASSING OF DISTILLED WATER-COOLING CIRCUITS AND ITS EFFECTS COPPER-WALLED STRUCTURES

R.P. Kan*[1], R. Eichler[2,3] and A. Weber[1]
[1] PSI Center for Accelerator Science and Engineering, Villigen, Switzerland
[2]PSI Center for Nuclear Engineering and Sciences, Villigen, Switzerland
[3]University 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 acidic conditions in distilled water and enables dissolved 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 as dissolved oxygen is the main problem.

PURE WATER TURNING ACIDIC

A Troublesome Copper Cooling Circuit at the Paul Scherrer Institute

Between 2000 and 2005, several water-cooled magnets like in Fig. 1 overheated. A muddy residue (Fig. 2), taken from a flow restrictor, caused the cooling water not to flow properly. Flushing the lines at an increasing frequency resulted in even faster interruptions (Fig. 3) and more residue, as can be seen in Fig. 4. An investigation, by the responsible beamline scientist and the leader of the magnet group, resulted in a report [1] on the influence of the dissolution of oxygen (O_2) and carbon dioxide (CO_2) in distilled water.

Ongoing Chemistry at the Surface

O_2 and CO_2 are always present in water due to interaction with the atmosphere. Hardly any water-cooling system stays airtight. Atmospheric gases can enter the cooling system through tiny leaks and diffusion through non-metallic tubing. The presence of CO_2 in the water results in the formation of carbonic acid (H_2CO_3), which dissociates into HCO_3^- and H+ ions. This acidity fixes the pH of the coolant between 5 and 6. O_2 dissolves in water increasing the redox potential. The cuprous oxide Cu_2O (reddish in colour like in Fig. 2) is initially formed at the surface. Upon further oxidation by dissolved oxygen, CuO forms (blackish in colour as in Fig. 4). In the absence of other influences this non-soluble surface would remain stable against further corrosion at these pH levels. 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 (and eventually leaks) and macroscopic slug formation. The corrosion mechanism is illustrated in Fig. 5 which was adapted form [2].

Figure 1: 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).

Figure 2: Accumulations of corrosion sludge (ø6 mm), consisting of CuO and/or Cu2O, from behind a flow restrictor. A Swiss 50 centime coin is in the background [1].

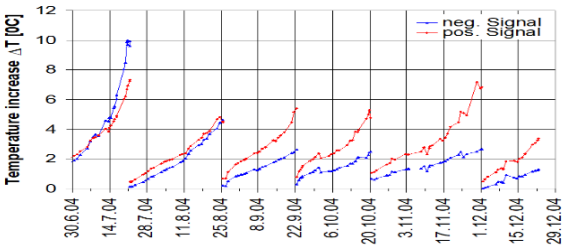

Figure 3: The measured temperatures of a quadrupole magnet in a regular pattern of temperature increases ΔT due two parallel cooling circuits clogging, then recovering after flushing the deposition products out of the magnet [1].

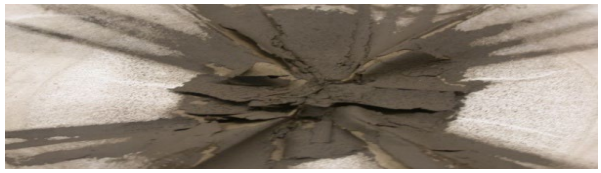

Figure 4: Filtrated deposits of various copper oxides. The pore size of the filter is 12 µm. The dry weight of the residue is 0.72 g [1].

*Richard.Kan@psi.ch

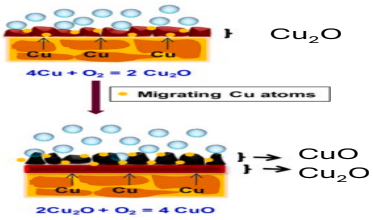

Figure 5: Corrosion mechanism at a copper surface due to dissolved O_2 and CO_2 in distilled water [2]. Even small air leaks promote water leakage and obstructive corrosion.

How This Problem Was Countered at First

In 2004 the cooling circuit, nr.9, (cooling a 20-year-old beamline) with troubled magnets was monitored and temporarily connected to a self-developed setup, based on a remark in [3], that pushed out the gases after it had flushed out the residue. This paper also presented a method for calculating the rate of corrosion shown in Equation 1 with the use of the Table 1 for the contribution factors. The parameters depend strongly on the concentration O_2 and CO_2, and the flow rate, but much less on temperature and dose rate (i.e. within the range between 1 Gy/h and 900 Gy/h) [3]. At dose rates above the range described in this experiment, however, the water undergoes radiolysis – rapid molecular decomposition by ionizing radiation. Normally, this water is contained in a tertiary cooling circuit and is occasionally "refreshed" by secondary cooling circuits.

Equation 1: Rate of corrosion R [µm/y], see Table 1 for contributing factors adapted from [3].

$$R = 1.4 \times 10^9 \times c(O_2) \times c(H^+) \times f(T) \times f(V) \times f(\gamma) \qquad (1)$$

Table 1: Contributing Factors to the Rate of Copper Corrosion in the Equation 1

Parameter	C. Factor	Investigation Limits
$c(O_2)$ & $c(H^+)$ [mol/l]	>200	between 2 cases: a) H_2O saturated with N_2: low on CO_2 & O_2, b) H_2O in contact with air
f (v) [m/s]	20.3	0.5 m/s< v < 4 m/s ($\sim v^{1/2}$)
f (T) [°C]	3	20°C< T < 50°C
$f(\gamma)$: dD/dt [Gy/h]	1.6	1 Gy/h< Dγ < 900 Gy/h

Furthermore, every time in 2004 the water circuit had to be opened, (a lot of) O_2 and CO_2were able to enter, and pH levels from 6.65 down to 5.6-were measured [1], which put the system from back then in Regime 5 of Fig. 6 [4]. And into the orange band where Cu reacts with O_2 into Cu_2O (see Fig. 7) [5], but due to the high concentration of CO_2 any metastable $Cu(OH)_2$ (blue in colour) was skipped and CuO was formed. The amount of >85 g (dry weight) metal oxide that was flushed out in 12 months' time, was exceedingly higher than 1 µg. That copper is missing somewhere and thinning copper tubing. The article [3] concludes that the tubing could thin out 0.5 mm -2 mm in 20 years' time, although there was no leakage in the cooling circuit nr.9 at the time. Weekly flushing to unclog was necessary until this cooling circuit was coupled to an online degassing system in 2005, based on the reverse osmosis principle.

Further measures, besides degassing, taken at PSI to minimize the ingress of oxygen into the cooling circuit included the use of nitrogen gas in expansion vessels to stabilize water pressure instead of air, the use of short and suitable nylon-, polyethylene pipes, or high-pressure water hoses with press fittings, short ceramic insulation (as ceramics also promotes diffusion), and the proper tightening of fittings according to strict instructions of the supplier.

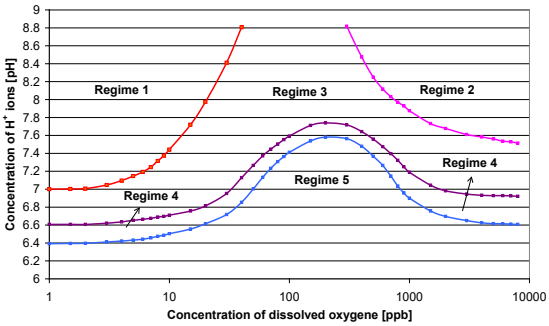

Figure 6: Corrosion rates under different operating conditions, reproduced from Reference [4]. Regimes 1& 2: <0.1 µg/y, regime 3: 0.1-0.4 µg/y, regime 4: 0.4-1 µg/y and the worst regime 5: >1.0 µg/y.

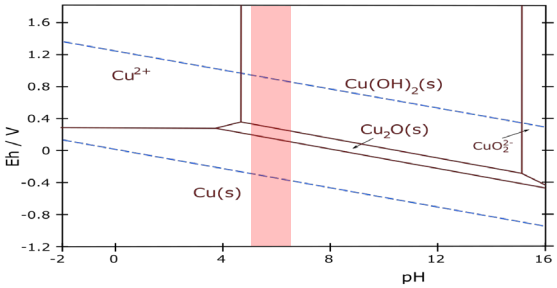

Figure 7: The Pourbaix diagram (redox potential/pH diagram) for copper in water at 25°C adapted from [5], with a red interval shows the pH range for carbonated water.

A Costly, But Effective Solution

A degassing system (see Fig. 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 kind of metal (Cu / Fe) walled structures, to save time, costs and dose. The process in these machines is essentially the reverse of the process by which O_2 and CO_2 entered the cooling circuit, i.e., through plastic tubing. This is because the molecular structure of O_2 forms a linear chain, unlike the branched chain of H_2O molecules (104.45° angle). In the degassing system, the water flows through numerous polyethylene tubes in a container with a nitrogen atmosphere at low pressure. The dissolved O_2 and CO_2 diffuse out of the water through pores in the plastic (the information of the pore size is undisclosed by the manufacturers). The degassing 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, monitored and protected exhaust air system in case of radioactive cooling circuits.

The measurement of pH value is not necessary, as this is difficult, costly and it rejects much water.

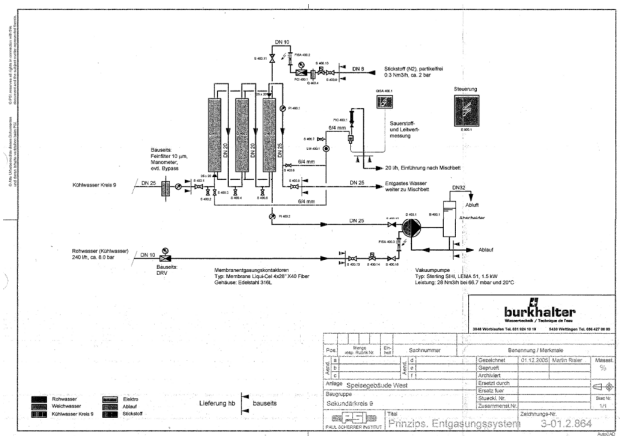

Figure 9: The diagram of the degassing system, as seen in Fig. 8 above the yellow box

The Current Application of Degassing Systems at Paul Scherrer Institute

Most distilled water circuits at PSI are nowadays 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 No. 9 in 2021 abruptly led to a blockage of the AWD deflection magnet by coolant. This proves the importance of continuous degassing. One of the last cooling circuits with 25 years of service, PROSCAN P5 for inactive power supplies (pH 6.9), is still without a degassing system. In 2024, all heat exchangers in power supplies were replaced. PROSCAN P6 (equally old) dedicated to components in the vault, has had a degassing system since 2013 and pH 7.2 was once measured. The P5 and P6 circuits are relatively small, and measures are taken to ensure they remain free of air and water leaks, as they are part of the medical proton facility, which must not be out of service for more than 4 days, because the tumors could continue to grow in patients due to incomplete radiation therapy. PSI has chosen a system that reduces the O_2 content from <50 ppm to <5 ppb and CO_2 should have been reduced to <1 ppm. The latter cannot be measured but is estimated to be well below 1 ppm CO2. This value corresponds to 1.2 µS/cm, and the specific resistance of the water is reduced from 1 µS/cm to <0.1 µS/cm through ion exchange. Since, the installation, the resins in the freestanding ion exchangers are replaced in about every two years, as are the filters. Although the lifespan of the filters and resin has increased somewhat, it depends heavily on other factors, such as the opening of the cooling circuit, through which dirt can then enter. The pH level is kept this way between pH 6.8 and pH 7.2. The typical flow rates in cooling circuits at PSI are 1.5 m/s – 1.8 m/s with the resistivity of 0.1 µS/cm -0.2 µS/cm. At PSI cooling circuits for water that can become radioactive have a separate degassing system (5 in total) than cooling circuits where the water is not exposed to radiation in case of power supplies cooling circuits (2 in total).

Degassing the tertiary cooling circuit is currently not possible because the water usually becomes too hot (above 50 °C) for the plastic material inside the reverse osmosis degassing system. Other systems might be suitable, for example, degassing systems with catalytic oxygen binding using palladium, however, H_2 would have to be added.

Cooling circuits for aluminium structures must never be mixed with copper cooling circuits due to the increased galvanic corrosion that promotes the dissolution of the aluminium. Therefore, aluminium structures such as the cyclotron resonators of Injector II and the flat-top cavity of the ring cyclotron have a separate cooling system without copper tubing. And, for the reason mentioned above, the new copper cavities of the ring cyclotron cannot be connected to the flat-top cavity cooling system. Although aluminium is highly susceptible to acid attack in water-cooling systems, the cooling circuits for aluminium structures at PSI 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.

Also, the cooling circuits for groundwater at PSI are not degassed.

CONCLUSION

The ingress of oxygen into a distilled cooling circuit cannot be prevented, and all copper cooling circuits (including OFE copper) will corrode and should therefore, although expensive, have a degassing system to prevent water leaks and blockages of cooling circuits due to oxidation of the inside copper structured walls and residues.The pH level is not of importance and can be ignored to save costs, as the degassing will automatically balance it towards neutral levels as carbon dioxide is removed along with oxygen in the water. All extracted gases require proper handling.

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 and related studies planned at the advanced photon source", 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