ACCELERATOR MAGNET PLUGGING BY METAL OXIDES

H. Reist, D. George

Primarily in the injection beam line between the Cockcroft-Walton and the Injector 2 cyclotron, magnets and collimators have been overheated due to blockage in the cooling water passages caused by deposition of corrosion products suspended in the water. In order to maintain the reliability and availability of the beam, intensive monitoring and cleaning activities had to be introduced. Investigation of the composition of the deposits and chemical analysis of the cooling water of selected beam line sections of the PSI accelerators supported the thesis that the corrosion is caused by the acidity and by the content of dissolved oxygen and carbon dioxide of the cooling water. It is therefore proposed to take measures to remove the dissolved oxygen and carbon dioxide and to increase the pH-value.

INTRODUCTION

Accelerator components made using hollow copper conductor are routinely cooled with deionised, lowconductivity water. At most accelerators, as well as at electric power facilities, interactions between water and copper are a critical issue. Corrosion of pure copper surfaces by the contact with deionised cooling water is unavoidable. The resulting deposition of corrosion products suspended in the water can lead to overheating of magnet conductors if cooling water passages becoming plugged. Locations with irregular flow patterns or components having a flow rate of <1 m/s preferentially exhibit deposits. The corrosion rate depends on the γ -radiation, the temperature and the flow rate of the coolant. However, the dominant influence is the amount of oxygen and carbon dioxide dissolved in the cooling water.

CORROSION MECHANISM

The corrosion mechanism is illustrated in Fig. 1. Oxygen (O_2) and carbon dioxide (CO_2) are always present in water due to interaction with the atmosphere. No water cooling system is vacuum tight. Atmospheric gases can enter the cooling system even through tiny leaks. An oxide forms at the copper surface, which, in the absence of other influences, is stable. The presence of CO₂ in the water results in the formation of carbonic acid (H₂CO₃), which dissociates into HCO_3^- and H^+ ions. Due to its affinity for the oxygen component of the copper oxide, H^{+} readily recombines to form water. The copper at the surface is now left in ionic form and dissolves. The metal surface, now unprotected by the oxide, is again exposed to water, to dissolved O_2 and to H^+ , and the cycle continues.

A concentration of Cu^{2+} close to saturation results in a reduction of the H⁺ concentration, and thereby to deposition of copper oxide.

Fig. 2 shows the corrosion rate at various operating conditions, marked as regime 1-5, which differ in the concentrations of dissolved O_2 and H⁺ [1]. The highest corrosion rate of >1.0 µg/ (cm².y) occurs in acidic cooling water with a pH below seven. O_2 concentrations between 50 and 750 ppb accelerate corrosion additionally. Fig. 2 suggests three conclusions: (i) The operation regimes 1 and 2 exhibit low corrosion. Either the O_2 concentration should



Fig. 1: Corrosion mechanism at a copper surface due to dissolved O_2 and CO_2 in the cooling water.

be kept <10 ppb and the pH \geq 7.4, or the O₂ concentration >1000 ppb and the pH \geq 7.8; (ii) CO₂ causes acid cooling water with pH below six. Removal of CO₂ raises the pH to seven. (iii) Even small leaks promote obstructive corrosion. A leak of 1.3x10⁻⁵ mole/l raises the oxygen concentration from five to 400 ppb [2].



Fig. 2: Corrosion rates at various operating and conditions. Regimes 1 2: $<0.1 \,\mu g/(cm^2 y),$ regime 3: 0.1-0.4 μ g/(cm²·y), regime **4**· 0.4-1 μ g/(cm² y) and regime 5: >1.0 μ g/(cm² y)

The following table summarises the relative contributions of the basic causes of corrosion, the oxygen content $c(O_2)$, the flow rate v, temperature T and the γ -dose rate dD/dt:

Parameter	Contrib.	Remarks
c(O ₂) [mole/l]	>200	see Fig. 2
v [m/s]	15	0.5 <v< 4m="" s:="" ∼v<sup="">1/2</v<>
T [⁰ C]	3	20ºC <t<50ºc< td=""></t<50ºc<>
dD/dt [Gy/h]	1.6	1 Gy <d<sub>γ<900 Gy</d<sub>

In addition to the dominant influence of the amount of dissolved O_2 and CO_2 , the corrosion due to the flow rate is the next point to consider. The corrosion rate increases proportionally to $v^{\frac{1}{2}}$ for flow rates ~0.8 \leq v< 4m/s. Both very low and very high water flow rates intensify the corrosive ablation of copper.

IMPAIRMENT OF OPERATIONAL AVAILABILITY

Copper oxides formed in the water system, transported through the system and deposited at predestined locations, lead to impairment of the operational reliability and availability of the beam. Primarily in the injection beam line between the Cockcroft-Walton and the Injector 2 cyclotron, magnets and collimators become overheated due to plugging in the cooling water passages caused by agglomeration of corrosion products suspended in the deionised water. As exemplified in Fig. 3, malfunction of system flow components occur with increasing regularity due to the apparent increase of the copper corrosion rate. Initially, magnet conductors with a small inner diameter of 2.5 mm and low flow rate (≤0.8 m/s) exhibited clogging. At a later stage, we also observed blockages in other magnets and collimators including some with larger cooling holes and higher flow velocities. Intensive monitoring and regular preventive cleaning help to sustain the availability of the magnets in the injection beam line.

The quantities flushed out of the magnets in the injection beam line during a period of operation of 12 months, add up to a dry weight of >85 g.



Fig. 3: The measured temperatures of the magnet QWA16 show a regular pattern of temperature increase ΔT due to clogging of the two parallel cooling circuits and the recovery after flushing the deposition products out of the magnet.

INVESTIGATION OF THE COMPOSITION OF THE DEPOSITS AND CHEMICAL ANALYSIS OF THE COOLING WATER

Investigation of the composition of the deposits and chemical analysis of the cooling water of selected beam line sections of the PSI accelerator facilities supported the thesis that the corrosion is related to the acidity and to the content of dissolved oxygen and carbon dioxide of the cooling water.

Figs. 4 and 5 show examples of flushed out and filtrated deposition products of various copper oxides. Microscopic analysis revealed particle sizes of a few microns, which agglomerate to clusters of ~10 μ m to ~50 μ m.



Fig. 4: Filtrated deposits of various copper oxides flushed out of QWB8, the last quadrupole magnet in the injection beam line. The pore size of the filter is 12 μ m. The dry weight of the residuum amounts to 0.72 g.



Fig. 5: Dried corrosion deposits accumulated on an orifice. The diameter is \sim 6 mm

Physical characteristics of the cooling water

Table 1 lists the flow rates of the investigated cooling systems together with the temperatures, the measured pH values, the concentrations of the dissolved oxygen and the electrical conductivities. The characteristics of the cooling systems of the SLS storage ring cavities differ from the rest. Apart from the water temperature of ~50 $^{\circ}$ C and the high electrical conductivity, the operation conditions lay in regime 2 of Fig. 2 (raised pH from added natron, high oxygen content). The other cooling systems operate in regimes having lower temperatures of ~30 $^{\circ}$ C, pH <7, very low electrical conductivities of a few μ S/cm and oxygen concentrations which develop maximum corrosion (regime 5 of Fig. 2).

Chemical analysis of the deposits

Water samples taken from seven cooling systems of the accelerator and beam line components over a period of eight months, have been analysed. The results are summarised in table 2.

Cooling system	Flow rate	Temperature	рН	Conductivity	c(O ₂)	O ₂ sat.
RF 1 storage ring SLS	13 m ³ /h	46.5 ⁰ C	8.57	155 μS/cm	5050 ppb	97 %
RF 2 storage ring SLS	13 m ³ /h	55.3 ⁰ C	8.66	198 µS/cm	4600 ppb	118 %
RF 3 storage ring SLS	13 m ³ /h	55.5 ⁰ C	8.53	354 μS/cm	4630 ppb	120 %
RF 4 storage ring SLS	13 m ³ /h	45.6 ⁰ C	8.70	187 μS/cm	4650 ppb	87 %
Magnet storage ring, reverse osmosis system; WSLB-IKUSO-0600	203 m ³ /h	28.7 ⁰ C	5.75	1.3 μS/cm	300 ppb	3 %
K5: all power supplies	108 m³/h	27.8 ⁰ C	5.85	52.2 μS/cm	350 ppb	4 %
K6: magnets of ring cycl.+ beam lines+tertiary syst 4-7	360-690 m ³ /h	31.0 ⁰ C	6.80	0.9 μS/cm	1200 ppb	17 %
K9: Injector 2+ beam lines	47 m ³ /h	30.6 ⁰ C	6.65	0.7 μS/cm	400 ppb	5 %
K10: test system magnets + power supplies	36 m ³ /h	30.7 ⁰ C	7.94	1.7 μS/cm	700 ppb	10 %
Copper cavity 2	243 m ³ /h	28-32 ⁰ C	6.85	0.85 μS/cm	4000 ppb	55 %

Table 1: Physical characteristics of the water samples taken from the investigated cooling systems: The shading accentuates cooling systems operating in regimes with raised pH from added natron together with an oxygen concentration at the saturation limit (regime 2 of Fig. 2). The remaining cooling systems all operate in a regime with low pH and deionised water (regime 5 of Fig. 2).

	Cooling systems						
Weight %	SLS RF 1	SLS RF 2	SLS RF 3	SLS RF 4	System K6	System K9	SLS mag.
Cu	2.240	2.950	8.560	3.010	64.700	78.100	89.300
Fe	51.200	30.100	42.200	41.100	2.410	0.789	0.033
AI	0.558	0.836	0.877	0.489	0.045	0.047	0.006
Са	4.110	3.520	3.060	4.920	0.060	3.590	0.008
Ni	0.606	0.303	0.535	0.282	0.036	0.015	0.032
Zn	0.348	1.030	0.544	0.745	0.128	2.210	0.487
Mg	0.143	0.216	0.203	0.250	0.038	0.103	0.009
Mn	0.297	0.711	0.448	0.382	0.003	0.008	0.088

Table 2: Analysis data of the residua of the filtrated cooling water samples: Shading accentuates cooling systems operating in regimes with raised pH by added natron and high oxygen content (regime 2 of Fig. 2). No shading identifies cooling systems operating in a regime with low pH (regime 5 of Fig. 2). In the last column, "SLS mag." refers to magnets in the SLS storage ring.

The analysis of the residua of the filtrated cooling water samples taken from the cooling systems K6, K9 and from the magnet cooling system of the SLS storage ring, reveal high copper concentrations of \sim 77% by weight. This means that copper oxides account for >97% of the flushed out deposits.

The findings of the analysis of the residua of the cooling system of the SLS storage ring cavities differ from the other cooling systems with respect to the smaller abundance of copper and the large amount of iron due to the cast iron body of a circulating pump installed in the cooling circuit.

Chemical analysis of the cooling water

The chemical analysis of the water samples revealed large differences between the cooling system of the SLS RF-cavities and the other systems. The amount of metals and non-metals found in the water of the RF-cavity cooling system exceed the quantities measured in the water of the K6 and K9 cooling systems by up to three orders of magnitude (see table 3). This is partially due to the use of groundwater with added natron, which contrasts strongly with the deionised water used in the other systems.

DISCUSSION OF THE ANALYSIS DATA

Cooling system of SLS storage ring RF-cavities

The measured oxygen concentration of >4600 ppb, and the pH, which has been raised to a value of >8.5, yield corrosion rates of <0.1 μ g/ (cm² year); (see regime 2 of Fig. 2). In this respect, the cooling system operates in a passive regime. The high iron concentration found its explanation in the cast iron body of the installed circulation pump, which had to be replaced because of serious overheating due to cooling blockage. In order to minimise the inevitable corrosion, the pump must be made of inert metal or with suitably passivated internal surfaces. Besides the indications of a silting-up of the cooling systems with organic material, the relatively high abundance of other metals, like AI, Ni, Zn, Mg and Mn indicate corrosion at the corresponding surfaces.

Cooling system	Cu [mg/l]	Fe [mg/l]	Zn [mg/l]	Ca [mg/l]	Mg [mg/l]
RF-cavity 1 storage ring SLS	0.34	0.76	<0.05	23.30	3.50
RF-cavity 2 storage ring SLS	10.70	9.74	0.60	26.85	4.10
RF-cavity 3 storage ring SLS	1.93	2.79	0.10	47.35	6.10
RF-cavity 4 storage ring SLS	1.56	2.94	0.06	18.20	5.20
K6: magnets of ring cycl.+ beam lines +tertiary syst. 4-7	16.5 μg/l	3 μg/l	0.4 μg/l	5.4 μg/l	0.3 μg/l
K9: Injector 2 + beam lines	9.0 μg/l	0.1 μg/l	0.2 μg/l	0.32 μg/l	0.3 μg/l
Cooling system	SO ₄ ²⁻ [mg/l]	NH₄ ⁻ [mg/l]	PO₄ ³⁻ [mg/l]	C [mg/l]	Hardness
Cooling system RF-cavity 1 storage ring SLS	SO₄²⁻ [mg/l] 10.10	NH₄[mg/l] <2.00	PO₄³⁻ [mg/l] <0.01	C [mg/l] 13.00	Hardness 6.8 ⁰ f
Cooling system RF-cavity 1 storage ring SLS RF-cavity 2 storage ring SLS	SO₄²⁻ [mg/l] 10.10 16.50	NH₄[mg/l] <2.00 <2.00	PO₄³⁻ [mg/l] <0.01 <0.01	C [mg/l] 13.00 50.00	Hardness 6.8 ⁰ f 7.5
Cooling system RF-cavity 1 storage ring SLS RF-cavity 2 storage ring SLS RF-cavity 3 storage ring SLS	SO₄²⁻ [mg/l] 10.10 16.50 19.50	NH₄ [mg/l] <2.00 <2.00 <2.00	PO ₄ ³⁻ [mg/l] <0.01 <0.01 0.04	C [mg/l] 13.00 50.00 199.00	Hardness 6.8 ⁰ f 7.5 16.6
Cooling system RF-cavity 1 storage ring SLS RF-cavity 2 storage ring SLS RF-cavity 3 storage ring SLS RF-cavity 4 storage ring SLS	SO₄²⁻ [mg/l] 10.10 16.50 19.50 12.80	NH₄⁻[mg/l] <2.00 <2.00 <2.00 <2.00	PO4 ³⁻ [mg/l] <0.01 <0.01 0.04 <0.01	C [mg/l] 13.00 50.00 199.00 19.00	Hardness 6.8 ⁰ f 7.5 16.6 6.5
Cooling system RF-cavity 1 storage ring SLS RF-cavity 2 storage ring SLS RF-cavity 3 storage ring SLS RF-cavity 4 storage ring SLS K6: magnets of ring cycl.+ beam lines +tertiary syst. 4-7	SO₄²⁻ [mg/l] 10.10 16.50 19.50 12.80 -	NH₄ ⁻ [mg/l] <2.00 <2.00 <2.00 <2.00 -	PO4 ³⁻ [mg/l] <0.01 <0.01 0.04 <0.01	C [mg/l] 13.00 50.00 199.00 19.00 -	Hardness 6.8 ⁰ f 7.5 16.6 6.5 -

Table 3: Analysis data of the cooling water: The shading accentuates cooling systems operating in regimes with raised pH by added natron and high oxygen content (regime 2 of Fig. 2). No shading identifies cooling systems operating in a regime with low pH (regime 5 of Fig. 2).

Cooling of cyclotron and beam line magnets

These cooling systems depend on deionised water in order to keep the electrical conductivity <5 µS/cm. This is accomplished by strongly basic anion and strongly acidic cation exchange resins blending bed filters, and by the reverse osmosis module, which is a part of the preparation process of the cooling water. Whereas the high oxygen content is caused by air exposure, the low pH is due to the reverse osmosis. Reverse osmosis lowers the pH from 7.32 to 5.72. The measured oxygen concentrations develop corrosion to the maximum, and corrosion is even further enhanced by the acidic cooling water with pH values distinctly below seven. This causes corrosion rates of >1 μ g/ (cm² year), and results in the plugging of magnet conductors. The total dry weight of the deposits flushed out of the magnet conductors in the injection beam line between the Cockcroft-Walton and the Injector 2 cyclotron, amounts, averaged over 12 months of operation, to >6.5 g/month. Monitoring and cleaning activities help to maintain reliability and availability of the beam, but do not solve the problem.

MEASURES TO BE TAKEN AGAINST CORROSION

Cooling system of SLS storage ring RF-cavities

For cooling the rf-cavities, deionised water is not necessary. This allows the implementation of the proposal from Acquaflex, a company specialised in water chemistry. All exposed surfaces are cleaned and passivated using the agents CLEAN 332, POLYFLEX 181 and 177. After cleaning, metered addition of POLYFLEX 181 and 177 prevents deposits of metal oxides, of phosphates, silicates and organic silt, protects the surfaces by a passivating anioniccationic film, and inhibits corrosion, respectively. Combined, they give a cooling fluid with pH ~8.5 and good protection of iron and copper surfaces, as long as the concentrations of the agents and the pH are monitored and maintained.

Cooling cyclotron and beam line magnets

These cooling systems depend on deionised water. Since dissolved CO₂ is the cause of the low pH of the cooling water, removal of dissolved oxygen and carbon dioxide from the water should reduce the corrosion. SIWAtec provides degasification by a novel technique, which uses modules of hydrophobic semipermeable hollow fibres attached to a vacuum pump on one side and optionally scavenged with pure nitrogen gas fed from the other side. The water flows around the fibres, and the dissolved O_2 and CO_2 diffuses into the fibres. The hydrophobic properties of the fibres prevent penetration of water. This process is enhanced by the strong gradient of the partial pressures between the outside and inside of the hollow fibres. Thousands of thin fibres ensure a large ratio of the total surface to the volume. This results in provide units. which space saving efficient degasification. As a first step, the cooling water supply section will equip the cooling system K9 with a suitable degassing unit.

REFERENCES

- R. Dortwegt, E.V. Maughan, *The Chemistry of Copper in Water*, Proceedings of the 2001 Particle Accelerator Conference, Chicago, USA, June 18-22, 2001, pp. 1456-1458.
- [2] H. Schöler, H. Eutener, Corrosion of Copper by Deionised Cooling Water, EPAC, Rome, It., 1988, pp. 1067-1068.