CORROSION OF COPPER BY DEIONIZED COOLING WATER[*]

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Summary

Corrosive carry off of pure copper surfaces by the contact with deionized cooling water is unavoidable in any accelerator setup. Confining ourselves in the wide field of corrosion to this fundamental process, we investigated the quantitative influence of the most important variables. It turned out that the corrosion rate can vary by about a factor 15 with the flow velocity of the coolant (0-4m/sec), by a factor 3 with its temperature (20 - 50 °C) and only by a factor 1.6 due to γ-radiation (1 - 900 Gy/h). The by far dominant influence however is the amount of oxygen and carbon dioxide in the cooling water, by this corrosion can be enhanced by a factor of 200 and more. -The absolute carry off of copper is about 0.05mm/year under bad conditions.

Introduction

For a long failure free lifetime of an accelerator setup the design and the operating conditions of the cooling water system play an important role. Especially in modern compact high power designs, where the coolant is often confined by rather thin walls only and the accessibility to many components is very cumbersome after assembly, corrosion may cause catastrophic failures.
Corrosion is a quite manifold phenomenon. We confined our investigation [1] to the interaction of pure copper with deionized water, because this is an unavoidable fundamental process in any setup using e.g. big magnet coils and rf-structures, whereas other mechanisms as electrolytic or stress corrosion can be principally avoided by a proper choice of materials.
The model by which we visualize this process - and which partly guided our investigations, partly resulted from them - is in short the following (Fig. 1): the gases oxygen and carbon dioxide coming e.g. from contact of the coolant with air, are dissoluted in the water up to an equilibrium which is proportional to their partial pressure (Henry's law). Oxygen molecules are adsorbed at the copper surface and decay in two atoms, taking electrons from the metal [2], this electric double layer is quite stable. The CO_2 partly (to ~ 1%) forms carbonic acid with the water. Now three reactions can go on: the hydrogen-ions from dissociated H_2CO_3 react with the O^{--}, forming water and Cu^{++} is going into solution (1). At higher concentrations of dissolved Cu^{++} also the process $Cu^{++} + O^{--} \rightarrow CuO$ comes up (2), black layers of CuO are deposited on the copper, the Cu^{++}-solution is going on. At saturation of Cu^{++} in the water complex blue-green copper carbonates form on the metal surface (3) (e.g. $2\,Cu^{++} + HCO_3^- + 2OH^- \rightarrow CuCO_3 \cdot Cu(OH)_2 + H^+$). The overall corrosion, i.e. the carry off of copper metal is nearly independent of the Cu^{++}-concentration.
The parameters for corrosion are therefore: a) the concentrations of various gases in the water dependent on b) their partial pressure, c) the water temperature influencing the gas solubility and the rate of chemical reactions, d) the water flow velocity, changing the concentrations at the reaction areas and e) for an (electron-) accelerator setup the level of γ-radiation in the cooling water.
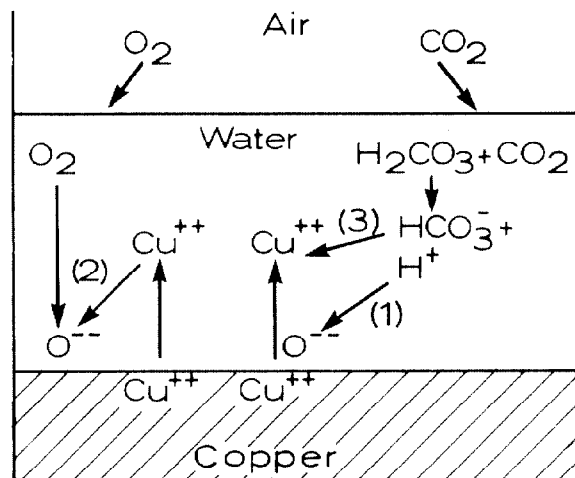
Fig. 1 Schematic model to visualize the corrosion process.

Experiments and results

General formula

The final result of our investigation is a formula, which allows to calculate the corrosive carry off with time $K = dh/dt$ from a copper surface:

$$K = 1.4 * 10^9 * c(O_2) * c(H^+) * f(T) * f(v) * f(\gamma).$$

Here K is measured in μm/year, the gas concentrations $c(X)$ must be inserted in mole/liter at 20°C and all temperature dependence is contained in the dimensionless $f(T)$. The factor $f(v)$ gives the enhancement of K by the water flow velocity compared to standing water and $f(\gamma)$ is a similar factor for the γ-radiation level.

Gas concentrations

To determine the constant factor in the above formula, we made measurements for the influence of different gases on corrosion. We confined ourselves to N_2, O_2 and CO_2, which are contained by 78,21 and 0.03 Vol.% in normal air. Other agressive gases such as NH_3 (which may become important when corrosion inhibitors containing nitrogen are added to the water) or SO_2 were neglected.
The measurement was done on copper sheets contained in hermetically closed glas vessels filled with deionized water (conductivity 0.7 μS/cm; after driving out all other gases by saturation with pure N_2 0.2 μS/cm ($1S = 1\Omega^{-1}$)). The water (20°C) was then saturated with the appropriate gas mixture in such a way, that it remained standing still as far as possible ($v \approx 0$). The corrosion was determined by weighing the copper specimens every 24 h.
Fig. 2 shows the measured corrosive carry off K in water saturated with a mixture of pure O_2 and CO_2 as a function of the respective portions of these gases. In the frame of our model the result is clear: there is very low corrosion a) with lack of O_2, because the double layer O^{--}/Cu^{++} is only very slowly renewed, b) without CO_2, because lack of H^+-ions coming from H_2CO_3

The measured K-values can be described to some extent by the product $c(O_2) * c(CO_2)$ (dashed curve), and $c(H^+) \sim c(CO_2)$. — The two dashed-dotted curves in Fig. 2 show measurable quantities, namely the oxygen content of the water (in ppm, 1ppm = 1mg/liter = $3.1 * 10^{-5}$ mole O_2/liter) and the raise of its conductivity by CO_2 over that of pure water (0.05 µS/cm). By these quantities one can decide, where one is for a certain water specimen on the O_2/CO_2-corrosion curve; from $\Delta\sigma(CO_2)$ also $c(H^+)$ can be calculated by simple physico-chemical relations [3].

In practice there are two limiting pairs of values for $c(O_2)$ and $c(H^+)$: a) the cooling water is permanently saturated with e.g. pure N_2, whereby O_2 and CO_2 are driven out by diffusion. Then, because the O^{--}-monolayer cannot be removed from the copper in this way [2], and slowly reforms via small gas leaks in the cooling system, one can reach $c(O_2) = 1.3 * 10^{-5}$ mole/liter (0.4 ppm) and, since also pure N_2 contains some CO_2, $c(H^+) = 2 * 10^{-7}$ mole/liter; b) the cooling water is in contact with air (p = 0.1MPa), then $c(O_2)$ = $27 * 10^{-5}$ and $c(H^+) = 21 * 10^{-7}$ mole/liter.

Hence there is a factor of 200 in K between these two cases. If the pressure of the air is raised to 0.6 MPa, the corrosion was measured to increase by another factor of 4 (CO_2 obeys Henry's law quite bad). Therefore one should pay attention to air bubbles enclosed in the pressurized part of a cooling system.
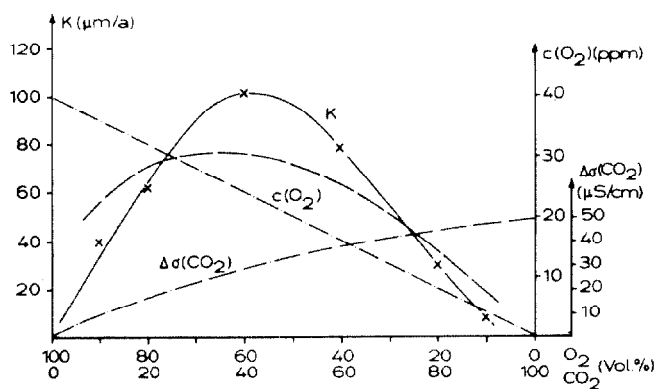

Fig. 2: Dependence of corrosion on the O_2/CO_2-mixing ratio of the gas contact with the cooling water.

Temperature

For the influence of temperature on K there are two opposite effects: first, any chemical reaction speed goes up with temperature ($\sim\exp(-A/RT)$, A-activation energy, R-gas constant [4]), but second, the solubility of gases in water decreases with T [5]; the first effect dominates. To determine the value of A, we measured K under similar conditions at 20 and 50°C and interpolated [4,5]. The result is given in Fig. 3, clearly the water temperature is not very important in this respect. However, if the copper ion concentration is near saturation, a raise in temperature favours (e.g. by lowering $c(H^+)$) the formation of CuO deposits and therefore obstruction of narrow cooling channels, especially at low water flow velocity.

Flow velocity

The factor $f(v)$ was measured with standard coolant water ($c(O_2)$ = 7 ppm, σ = 0.7 µS/cm), the result is also given in Fig. 3. The increase in K from standing water to a high flow velocity results from the steady renewal of the O_2^- and H^+- concentrations at the copper surfaces. One should note that f(0) = 1 is uncertain by about a factor 1.4, because the condition v = 0 is difficult to define and the absolute value of K is very low for the water
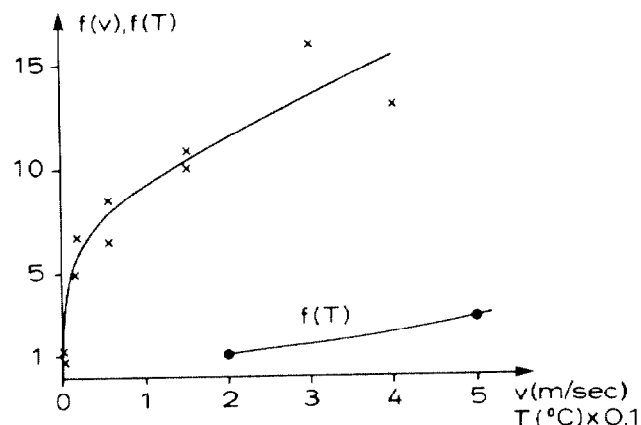

Fig. 3: Influence of water flow velocity and temperature on corrosive carry off.

conditions given above (0.5 µm/a). However, our experience showed, that flow velocities v < 1 m/sec should be avoided anyhow because the danger of obstructions by deposites distinctly increases.

γ-Radiation

To measure the enhancement of K by γ-radiation, the glass vessels containing the copper specimen in deionized water were put for 12 h to the Bremsstrahlung of an 100 MeV electron beam. The water was successively saturated with N_2, O_2, CO_2 and air and in every case a normalization experiment with identical conditions but with zero γ-radiation level was run simultaneously.

The results for the enhancement factor f(γ) were that a) it is independent of the gas type and b) a little surprisingly it can be assumed to be a constant f(γ) = 1.6 within an error of ± 25 % for radiation levels between 1 and 900 Gy/h. It was however well known from reactor engineering [6], that there is not much radiolysis in water by β- and γ-radiation. — The deposition of CuO was clearly enhanced by γ-radiation.

Example

For e.g. a compact magnet coil, where one has at some parts a water temperature of 50°C, a flow velocity of 3 m/sec and γ-radiation present one gets from the formula above a) if the water is permanently saturated with N_2: K = 0.2 µm/a and b) for free contact of the cooling system with air of 0.1 MPa: K = 50 µm/a. We estimate the overall error of this investigation to be a factor of 2. Therefore, within 20 years, which may be a reasonable stand time for an accelerator setup, one must take into account for the latter conditions a corrosive carry off of 0.5 - 2 mm .

References

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