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A NEW APPROACH FOR WATER TREATMENT

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Abstract

A quantity of up to 4000 m³/h of water is used at CERN for cooling purposes: experiments, magnets and radio frequency cavities are refrigerated by closed circuits filled with deionized water; other utilities, such as air-conditioning, use chilled/hot water, also in closed circuits. All these methods all employ a cold source, the primary supply of water, coming from the cooling towers. About 500 kCHF are spent every year on water treatment in order to keep the water within these networks in operational conditions. In the line of further rationalization of resources, the next generation of contracts with the water treatment industry will aim for improved performance and better monitoring of quality related parameters in this context. The author will provide a concise report based upon an examination of the state of the installations and of the philosophy followed up until now for water treatment. Furthermore, he/she will propose a new approach from both a technical and contractual point of view, in preparation for a call for tender which is foreseen to be issued during 1999. As the water tower circuits (primary water) are quantitatively dominating, the technical discussion will concentrate mainly on problems linked with these networks.

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1 INTRODUCTION

A quantity of up to 4000 m³/h of water is used at CERN for cooling purposes: experiments, magnets and radio frequency cavities are refrigerated by closed circuits filled with deionized water; other methods, such as air conditioning, employ chilled/hot water, also in closed circuits. These methods all use a cold source, the primary water supply coming from the cooling towers. As the cooling towers operate the refrigeration through the evaporation of a quantity of water and, since the vapour produced is salt free, the water remaining in the basin increases its concentration of salt, mostly calcium carbonate (CaCO₃).

When the salt reaches its solubility limit it starts to precipitate, producing scaling formations. The most critical points are those inside the heat exchangers as the solubility of CaCO₃ decreases with the increase of temperature. Once scaling is present, a sensitive reduction of heat exchange coefficient occurs and hence the heat exchangers must be cleaned. For this reason an anti-scaling treatment is needed.

Two other important features of the water treatment are anti-corrosion and biological treatment: although water with a high scaling power is not corrosive, it is better to perform a light anti-corrosion treatment as a precaution, since different kinds of corrosion can occur. At the same time, biological treatment is essential because the eventual presence of algae and bacteria can obstruct filters as well as heat exchangers.

Another aspect concerns the level of water consumption in the cooling tower circuits, mainly due to evaporation and purges. Even if the CERN towers were operated in an 'open circuit mode', the high level of salt concentration¹ would enforce an anti-scaling treatment. Furthermore, the increased solubility level permits the re-circulation of the water in the towers and hence reduces the number of purges necessary, providing important savings in water consumption.

2 SCALING

Scaling is the precipitation of moderately soluble calcium salts and, possibly, of silica on heat exchange surfaces. It occurs when soluble products become saturated due to high concentrations or high temperatures: in fact for scale-forming salts, an increase in temperature determines a decrease² in solubility

The damage that scaling formations can cause are as follows:

- a) Formation of an insulating film on heat exchange surfaces that reduces the heat exchange coefficient.
- b) Reduction of flow rates due to the diminution of the passage section. This provokes a temperature increase in the secondary circuit.
- c) Possibility of corrosion by differential cell reaction under the scale deposition when the scale is not only CaCO₃. This is localized corrosion.

¹ See the water characteristics in Appendix 4.

² See the stability indexes in Appendix 1.

The most common scale-forming salts are: calcium carbonates¹ [CaCO₃, Ca(HCO₃)₂], calcium sulphates (CaSO₄·2H₂O, CaSO₄·1/2H₂O, CaSO₄·), calcium phosphates [Ca₃(PO₄)₂], and silica (SiO₂). However, calcium carbonates are always the principal cause of scaling formations.

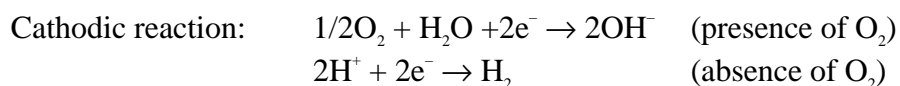
3 BIOLOGICAL GROWTH

Algae and bacteria are the most common microbes that can be found in water. In particular, algae need sunlight and aerobic bacteria need oxygen to grow² making them typical of aerated water systems such as cooling towers. Anaerobic bacteria may also be present in cooling towers, especially in under-oxygenated zones such as, for example, under deposits. The presence of anaerobic bacteria, although not very common, are quite dangerous as they can cause localized corrosive action by secreting corrosive wastes. On the other hand, aerobic bacteria are divided in slime and not-slime-forming. The most critical are the slime-forming type as they facilitate fouling phenomena and other micro-organism growth.

In water cooling circuits, the environment can be considered well treated from a biological point of view when aerobic bacteria are up to 10'000 colonies/ml, with slime-forming aerobic bacteria up to 1'000 colonies/ml.

4 CORROSION

When referring to a water cooling system, it is possible to explain corrosion as an anodic process that leads to oxidation of iron Fe⁰, and to the passage into the water solution of iron at the oxidized state Fe²⁺. Corrosion may occur in the presence or the absence of oxygen, the latter case producing the cathodic reduction of hydrogen ions instead of the formation of hydroxyl ions from O₂. The relevant reactions are given below:



Corrosion in the absence of oxygen is also called chemical or acid corrosion and is limited by high pH values, as is the case with the situation analysed. In water cooling systems, it is likely that a kind of localized corrosion called *differential cell corrosion* occurs. This happens when a concentration gradient of substances such as O₂, Cl⁻ or SO₄⁻, is established between the bulk and a limited area, for example under deposits. This zone soon becomes poor in O₂ as, in the beginning, normal corrosion reactions occur. But then, oxygen diffusion from the bulk is prevented by the presence of the deposit. At this stage, the initial normal corrosion becomes a differential cell corrosion: the lack of oxygen generates a small anodic zone, just under the deposit, so that localized corrosion occurs. As the Fe²⁺ ions leave the anodic surface, other negative ions such as Cl⁻ and SO₄²⁻ migrate, in order to maintain the neutrality, thus aggravating the corrosion rate by increasing their concentration under the deposit. In addition, anaerobic bacteria that reduce sulphates to sulphides contribute in creating an even more aggressive environment³. Localized corrosion is very dangerous as it

¹ See the balance of carbonates in Appendix 1.

² See the aspects linked to the biological treatment in Appendix 2.

³ See the aspects linked to corrosion in Appendix 3.

can lead to severe damage of the equipment in a very short space of time (see Fig. A-2 in Appendix 3).

It is therefore clear why, although water is not corrosive according to the stability index of Ryznar and Langelier¹, it is worthwhile treating it against corrosion in any case.

5 SCOPE OF THE CONTRACT

The previous paragraphs have briefly shown a few of the reasons that justify an investment for the cooling towers water treatment: avoiding scaling, fouling, and corrosion at low costs, and saving water.

It has to be taken into consideration that an unexpected problem in a heat exchanger could provoke serious accelerator stoppages which would be one of the most critical situations in the laboratory.

A lack of internal competence in this field, and the important reduction of CERN personnel, coupled with the possibility of improving the quality of the service, drove us to search for new formulas in order to work with external contractors with an increased level of outsourcing.

Furthermore, the nature of the activity has incited CERN towards a 'results obligation contract'. This solution will be suitable once a number of technical improvements are made on the CV installation.

6 HEAT LOAD AND WATER CONSUMPTION

In order to have real supervision of the cooling tower system, an on-line control of the real value of the cooling power must be installed. This datum is the first important parameter which will permit the calculation of the real water consumption and the concentration ratio.

The cooling power can be easily calculated with the formula:

$$P = F \cdot (T_{in} - T_{out}) / 860 \text{ ,}$$

where F is the flow rate in m³/h and T_{in} and T_{out} are the inlet and outlet temperatures of the primary water circuit² in °C. Once this punctual value is available, a set of average values can be automatically calculated. Starting from the cooling power values, the evaporation rate can be defined as:

$$\begin{aligned} ev &= 1.44 \cdot P \quad (\text{m}^3/\text{h}) \\ Ev &= ev \cdot 24 \quad (\text{m}^3) \text{ ,} \end{aligned}$$

where 'Ev' is the water consumption due to evaporation on a precise day of the year. Then 'P' and 'ev' must be calculated as average values during the day taken as a reference. At this point, since the evaporation ratio is known and the value of concentration ratio 'RC' is fixed, it is possible to calculate the quantity of make up water (Q_{MU} in m³) needed, as well as the water discharged in purges (Q_{BD}, m³):

¹ See the stability indexes in Appendix 1.

² In this paper, the 'primary circuit' always corresponds to the primary circuit of the heat exchangers and the secondary circuit of the cooling towers. The primary circuit of the cooling towers will always be termed as the 'raw water circuit'.

$$Q_{MU} = Ev \cdot RC / (RC-1)$$

$$Q_{BD} = Ev / (RC-1) .$$

6.1 Concentration ratio

This parameter (RC) can be rigorously expressed as:

$$RC = [salt]_{MU} / [salt]_{BD} ,$$

where $[salt]$ is the concentration of any of the salts contained in the discharged (BD = Blow Down) and in the make up (MU) water, respectively. In order to have a reliable value, the calculations have to be made taking as a reference a salt that does not precipitate; for this reason we employed the concentration of Cl^- or SO_4^{2-} . Another way to express the concentration ratio is:

$$RC = Q_{BD} / Q_{MU} ,$$

where Q (m^3) is the quantity of make up (MU) and discharged (BD) water, respectively. RC represents a value that can intuitively be explained as the number of times that the same water is re-circulated. It is then clear that a reduced value of RC provokes a higher quantity of make up and a higher quantity of chemicals injected into the circuits as a direct consequence.

It is also clear now that the value of RC must be fixed by CERN as a minimum threshold (RC_{min}) in order to force the contractor to perform water treatment which aims at reducing water and chemical consumption.

7 THE CONTRACTUAL APPROACH

Once a base level for RC_{min} has been established and P, RC, Q_{BD} , Q_{MU} data are available, the supervision of the cooling treatment becomes an easy matter.

In the call for tender the bidders will be asked to provide the best price per m^3 of treated water ('C' in CHF/ m^3), including scaling, corrosion and biological analyses. Once a reference value of the cooling power (P_{ref}) during the year has been established, the bidders will also be asked to provide a second parameter: the estimation of a maximum value of Q_{MU} in m^3 (Q_{MUmax}).

At the end of the contractual period CERN will apply the following retribution formula:

$$R = K + C \cdot Q_{MU} + f \quad (\text{CHF}) ,$$

where 'K' is a constant representing the costs related to services, personnel, and equipment, and 'f' is a function that assumes negative values in case there are any penalties that have to be imposed on the contractor.

At the end of each contractual period CERN will compare the value of Q_{MU} with the value of Q_{MUmax} declared at the start-up.

If $Q_{MU} > Q_{MUmax}$ then CERN will check the absorbed cooling power 'P' compared with the reference value ' P_{ref} '.

If $P > P_{ref}$, then the reasons of higher water and chemical consumption are not related to the performances of the treatment, and the contractor consequently has the right to receive payment.

If $P < P_{ref}$, then $RC < RC_{min}$ which shows a contractual responsibility. Then CERN can decide to pay up to $Q_{MU_{max}}$, and enforce a penalty on the contractor in order to compensate for their higher water consumption fees in the energy budget.

Furthermore, each new contractual period will start with an initial cleaning treatment in order to eliminate all scaling or biological pollution previous to the start of the contract. Then a set of analyses and tests will be performed periodically in order to guarantee the conditions of the cooling system. All damage or performance reduction of the CERN installation due to scaling, corrosion and/or fouling will also result in a specific penalty for the contractor.

It is very important to remark that, whilst the classical set of analyses states the cooling circuit conditions, the monitoring of the contract is performed by checking uniquely the water consumption (Q_{MU}).

8. CONCLUSION

This contractual approach, as described by the authors, has the principle advantage, of a very simple and clear monitoring of the contract, performed by checking a small number of parameters, mainly Q_{MU} . A set of periodical tests and analyses will complete the supervision of the circuits, and non-professional people will be discharged from the responsibility of following and managing the aspects directly linked to the water treatment. This will also facilitate the procedure of future contract renewals for new companies by recreating a really competitive environment, which is the main factor for a substantial cost reduction.

Furthermore, in a results-oriented contract, once the reference parameters have been clearly fixed, the contractors will have the possibility of working more independently with respect to the general statement and safety rules, easily implementing new products and techniques in order to increase their own benefits.

All the above-mentioned features will bring both CERN and the companies involved more profitable perspectives of collaboration.

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APPENDIX 1

The balance of carbonates

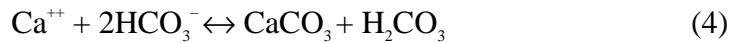
When CO_2 dissolves in water it reacts, forming carbonic acid that immediately dissociates into hydrogen ions and bicarbonate ions according to the following reactions:



Inside the pH range between 4.4 and 8.4, corresponding to the pH of water employed at CERN, bicarbonate alkalinity exists and weak acids (the most common being carbonic acid) may be present, having carbon dioxide in solution (CO_2). It is possible to see that at $\text{pH} > 8.4$, the CO_2 disappears while the bicarbonates start to transform into carbonates:



More or less in the same pH range ($\text{pH} > 9.6$), the hydroxyl alkalinity, due to OH^- ions, starts to become relevant. In this situation the eventual presence of Ca^{++} and Mg^{++} ions cause the following reactions to occur:



They occur when water is supersaturated and hence unstable. In fresh water, calcium carbonate (CaCO_3) is the most common product of instability, whilst in sea water, magnesium hydroxide [$\text{Mg}(\text{OH})_2$] or one of its complex carbonates are the usual precipitate.

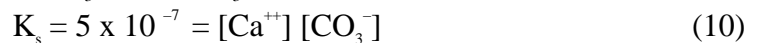
Stability indexes

Before introducing the concept of a stability index it is necessary to define the equilibrium conditions of the water containing carbonates and bicarbonates. The equations concerned are:

- Water dissociation:



- Calcium carbonate solubility product:



- Carbonates equilibrium:



$$[H^+] [CO_3^{2-}] = K_2 [HCO_3^-] \quad (14)$$

Substituting the expression of $[CO_3^{2-}]$ found from Eq. (10) into the Eq. (14) and since:

$$pH_s = -\log[H^+] \quad (15)$$

$$pK_s = -\log K_s \quad (16)$$

$$pK_2 = -\log K_2 \quad (17)$$

it is possible to obtain an expression for pH_s (saturation pH) that is the pH value at which water is neither aggressive nor produces scaling:

$$pH_s = pK_2 - pK_s - \log[Ca^{++}] - \log[HCO_3^-] \quad (18)$$

This value can be calculated and varies according to the contents of salts.

If the water being considered presents a pH value lower than its saturation pH (pH_s), this means that it has a tendency to dissolve carbonate calcium. Therefore, not only does it attack concrete and cement walls, but it also prevents the formation of a thin layer of calcium carbonate that protects metallic surfaces from corrosive action. In this case, the water is under-saturated with calcium carbonate, and it is said that it has a negative saturation index.

On the other hand, if the pH is higher than pH_s , then the water is supersaturated and calcium carbonate precipitates. In this situation, the saturation index is positive.

It is quite intuitive now that the saturation index (SI) is defined as:

$$SI = pH - pH_s \quad (19)$$

This index is also called the *Langelier index* from the name of the scientist who discovered it. The pH_s value can be calculated by the expression:

$$pH_s = C + pCa + pAlk \quad (20)$$

where $C = pK_2 - pK_s$.

The use of this equation is rather simple: once the calcium hardness and the alkalinity expressed as mg/l of $CaCO_3$ are known for the left part of the equation, it is possible to read the corresponding values of pCa and pAlk. According to the total quantity of solids and to the temperature of the water considered, on the right-hand side of the equation, it is possible to determine the value of the constant C.

It is sufficient now to insert the value obtained in expression (20) and to compare the result with the actual pH, measurable, according to expression (19).

Actually, the Langelier index is only qualitative and can only be used to predict the tendency of the calcium carbonate to deposit or dissolve. No information is given about the quantities.

For these reasons Ryznar has empirically developed another expression whose value is called the Stability Index (RI). It is defined as:

$$RI = 2pH_s - pH \quad (21)$$

The stability index is always positive: in general, values lower than 7.0 indicate a tendency to scaling formations, whilst values higher than 7.0 indicate a tendency of corrosive action. More details are given in the following Table 1:

Table 1

Ryznar Index	Tendency
Lower than 5	Relevant scaling
5 to 6	Weak scaling
6 to 7	Equilibrium
7 to 7.5	Light corrosion
Higher than 7.5	Strong corrosion

The stability index also gives information about the quantity of calcium carbonate that may precipitate, and about the entity of corrosive danger. The relationship between the stability index and the encrustation level has been experimentally determined both in the absence and in the presence of treatment, and the results can easily be found in the specialized literature.

APPENDIX 2

Aspects linked to the biological treatment

The action and the effectiveness of biocide products are linked to two parameters: the killing level and the time of permanence inside the basin. A concentration of biocide product lower than the killing level, as well as a rapid evacuation from the basin, would not permit the desired sterilization to be obtained.

For these reasons, the quantity and strength of the biocide product that must be added changes for each different circuit and depends upon the parameters that influence the velocity of the circuits themselves: the dimension (volume) and the value of the concentration ratio.

In order to choose the appropriate biocide, the most important parameter to be evaluated is the Holding Time Index (HTI). It represents the time after which the concentration of a chemical species is reduced to half of its original value.

By writing the differential equation representing the concentration variation inside the basin, it is possible to find a simple expression for HTI. This is demonstrated below.

The variation of biocide concentration inside the basin is expressed by:

$$M \text{ } C = S \text{ } C_b + V \text{ } (dC_b/dt) , \quad (1)$$

which can be written as (biocide concentration in the make up water being zero)

$$0 = S \text{ } C_b + V \text{ } (dC_b/dt) . \quad (2)$$

This is a simple differential equation that can be solved by variable separation:

$$dC_b/C_b = - (S/V)dt . \quad (3)$$

Integrating and employing the initial condition $C_b = C_{b0}$ for $t = 0$:

$$\ln C_b = - (S/V)t + \text{const} \quad (4)$$

$$C_b = C_{b0} \text{ } e^{-S \text{ } t/V} . \quad (5)$$

Equation (5) shows the concentration variation of a substance in the water. An example (initial biocide concentration in the basin $C_{b0} = 50$ ppm, $S/V = 0.15$) is represented in Fig. 1.

The HTI is, as already defined, the time needed by chemical species to reach half of their initial concentration. Introducing the condition $C_b = C_{b0}/2$ into Eq. (5) results in the following expression:

$$\ln 0.5 = -(S/V) \text{ } HTI , \quad (6)$$

so that:

$$HTI = 0.69 \text{ } (V/S) . \quad (7)$$

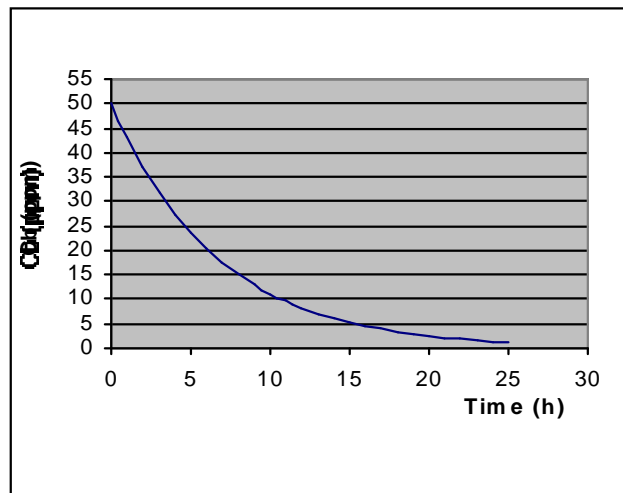


Figure A-1: Concentration variation of a chemical substance inside the basin.

By calculating this parameter, the firm in charge of the water treatment has the possibility of proposing the most appropriate biocide and the dosage needed.

It is now easier to understand that increasing the incoming water conductivity leads to a faster turnover of water in the basin, and thus to a lower HTI value, as well as to a lower permanence time of the biocide. Reasonable values for HTI are around 24 h.

APPENDIX 3

Aspects linked to corrosion

Usually, this control should be made every 30 to 90 days, according to how critical the examined circuits are, and for an acceptable corrosion rate in cooling systems of less than 20 $\mu\text{m}/\text{year}$ for steel and less than 3 $\mu\text{m}/\text{year}$ for copper and aluminium. (The corrosion rate can also be measured in mils per year (mpy): 1 mpy = 0.025 mm/year being 1 mil = 0.001 in, 1 in = 2.54 cm).

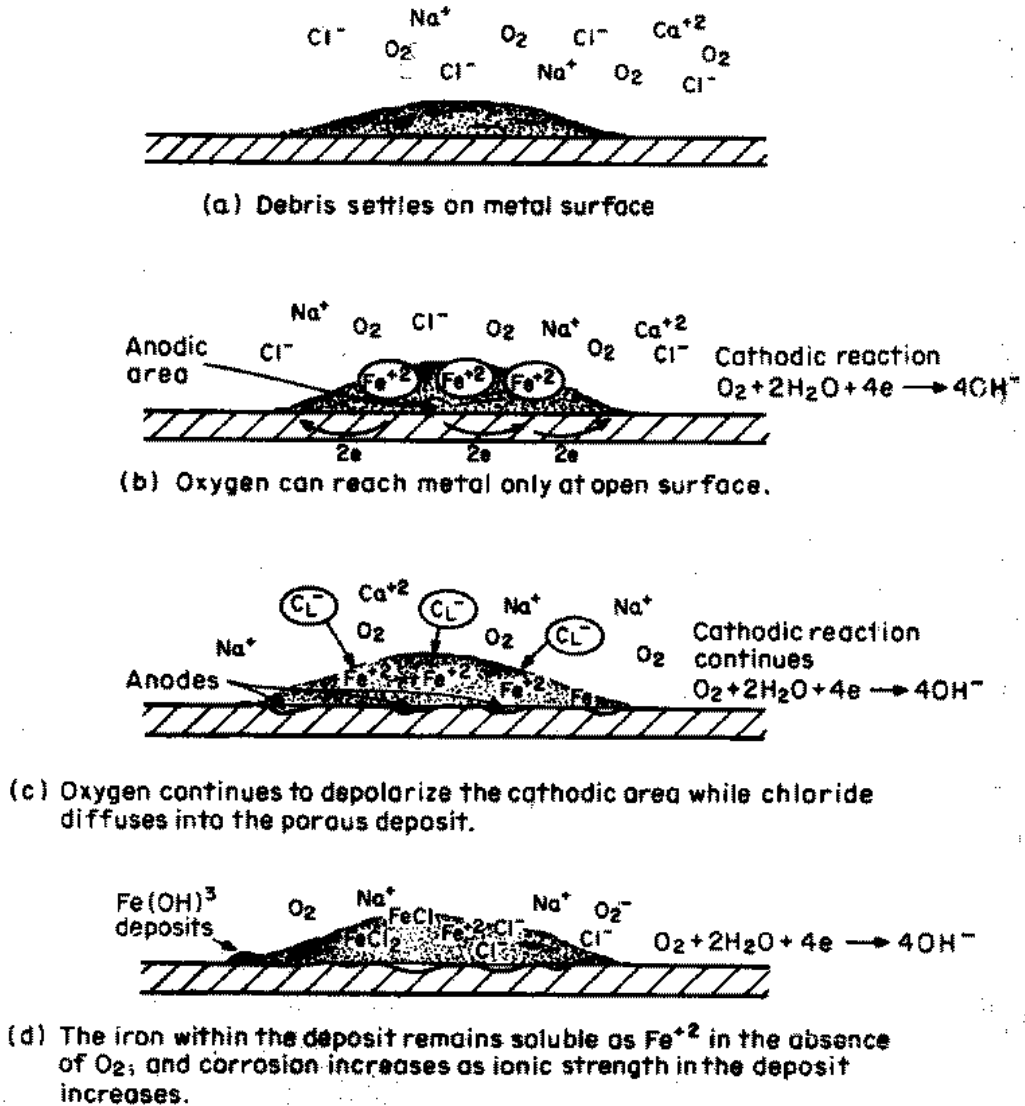


Figure A-2: Steps of localized differential cell corrosion.

In order to have a reliable control of the effectiveness of anti-corrosion treatment, it is necessary to define a precise control programme: during the first month the corrosion rate is quite high as the new coupons still have to reach the same passivate status of the circuit. With the passing of time, the corrosion rate drops. This means that a measurement performed during the first month does not give an idea of the real corrosion rate inside the circuit, but it can be taken as an indication of its criticality. In fact if, for example, during the first month a corrosion rate of 20 $\mu\text{m}/\text{year}$ is found, the anti-corrosion treatment can be reasonably

considered efficient as the corrosion rate decreases over time. On the other hand, if a corrosion rate of 50 $\mu\text{m}/\text{year}$ were found, it means that more frequent controls should be performed in order to keep under control the phenomenon, and to optimize the treatment. In conclusion, depending on the behaviour of the circuit considered, a schedule of controls can be established analysing, for example, some coupons each month, and others at intervals of three months, six months and each year.

APPENDIX 4

Water characteristics at CERN

Currently CERN receives water from two different sources: the 'Lac Lemman' and the 'Puits de Peney'. LEP cooling towers receive as a make up a part of the water employed to refrigerate SPS secondary circuits. The water comes from the lake at a constant temperature of 7–8°C all year round, as it is taken at a depth of 40 m; its characteristics are very favourable as the quantity of salt contained is rather low and the conductivity is very stable (300 $\mu\text{S}/\text{cm}$).

On the other hand, the water coming from the 'Puits de Peney' mostly feeds the PS cooling towers. Its characteristics have been changing considerably over the last few years: the salt concentration has increased and since the Seventies the presence of manganese has obliged CERN to carry out a step of sedimentation. The conductivity varies between 500–750 $\mu\text{S}/\text{cm}$ and its average temperature is around 10–13°C.

Often there is an uncontrolled mixture of these two different kinds of water, causing its characteristics to change and hence generating some troubles with the water treatment.

APPENDIX 5

Technical improvements and fundamental data

In order to have better control of the functions of the cooling tower system, water consumption, and the performance of the firm in charge of the water treatment, a set of control devices must be installed so as to provide information regarding the data listed hereunder:

1. flow rate (m^3/h) and consumption (m^3) of make up water (MU) and purges (BD);
2. conductivity of make up water and purges;
3. flow rate of primary water (in the primary circuit);
4. inlet and outlet temperature of primary water.

An appropriate connection to the network will permit a continuous control of the data. A databank will provide a punctual information source and the 'history' of the system with regard to the thermal load during the year, the consumption of water (purges and evaporation), and the real value of the concentration ratio maintained during the year.

Consequently these technical improvement, will ease the calculation of the parameters which permit a correct evaluation of the performances of the cooling towers and the contract itself.