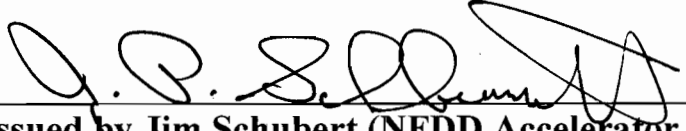
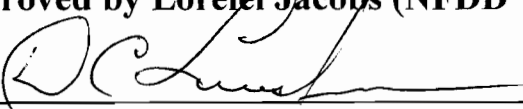


Review of Cooling Water Chemistry At ORNL / SNS

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REVIEW OF COOLING WATER CHEMISTRY AT ORNL / SNS

Final report, 30 June 2010

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Abstract:

The SNS comprises of 24 separate cooling loops to control temperature of the components. Appropriate cooling water chemistry is required in order to avoid corrosion damage of equipment, electric and mechanical malfunctions by deposition, as well as impairment of cooling by plugging of the water passages. Although up to now no severe chemistry related problems have yet occurred at SNS it is nevertheless prudent to consider some upgrades in order to assure reliable long-term performance.

This report gives an assessment of the SNS cooling loops from the power plant generator technology perspective and experience. The most important recommendations are to operate the cooling loops with the highest achievable water purity and the highest reasonable mixed bed flow, to consider efficient main stream filtration, and to make and implement a common concept for water chemistry and for preventative maintenance. Main risk areas are electrochemical corrosion in loops with DC voltage, and materials performance of the RID window.

Keywords: Water chemistry, corrosion, closed cooling system, SNS, accelerator, generator

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1. SUMMARY

The SNS comprises of 24 separate cooling loops to control temperature of the components. Appropriate cooling water chemistry is required in order to avoid corrosion damage of equipment, electric and mechanical malfunctions by deposition, as well as impairment of cooling by plugging of the water passages.

Although up to now no severe chemistry related problems have yet occurred at SNS it is nevertheless prudent to consider some upgrades in order to assure reliable long-term performance.

Except for two loops where chemical additives are used, all other loops are based on high purity water. In some loops, water purification is however throttled to provide less resistive water that is thought to be beneficial for corrosion protection.

This report gives an assessment of the SNS cooling loops from the power plant generator technology perspective and experience. The most important recommendations are to operate the cooling loops with the highest achievable water purity and the highest reasonable mixed bed flow, to consider efficient main stream filtration, and to make and implement a common concept for water chemistry and for preventative maintenance.

Main risk areas are electrochemical corrosion in loops with DC voltage, and materials performance of the RID window.

2. INTRODUCTION

Scope of the investigation is a review of SNS systems water chemistry with regard to long-term functionality of the equipment. Special aspects:

- ❑ corrosion that could challenge component integrity and pollute the cooling water
- ❑ deposition on component surfaces that could hinder heat transfer, block passages, hinder movements (where applicable)
- ❑ electric insulation of high voltage equipment that could deteriorate by conductive deposits

The review is based on experience with water-cooled power plant generators and high voltage transmission equipment. It is evident that not all techniques will be transferable to the SNS facility.

Only aspects related to metallic surfaces in contact with cooling water are considered.

This investigation was performed by Dr. Robert Svoboda, Svoboda Consulting, Switzerland. The review is based on the documentation that was provided by ORNL-SNS. Additionally, an on-site information gathering took place from Aug 12 - 17, 2009.

2.1 Cooling water related chemistry issues at SNS

Up to now, the following issues have come up:

- ❑ Flow meter plugging / binding by deposits
- ❑ Copper plating out on heat exchanger (impact on heat transfer not yet quantified)
- ❑ Copper loading on ion exchange resin
- ❑ Concerns regarding the impact of operating environment on the lifetime of the technical components

At other accelerators, a common reported problem is significantly increased plugging of water flow passages when the cooling loop experiences leaks and the losses were compensated with oxygenated make-up water.

3. COMPARISON SNS AND GENERATOR COOLING WATER FEATURES

3.1 Design aspects

The relevant cooling water features of the SNS facility are summarized in paragraph 4.1, and the features in water cooled generators are presented in some detail in paragraph 7.

Parameter	Generator	SNS
Number of water treatment loops	1	24
Number of cooled components in each loop	3 ... 4	50 - 200 *
Number of parallel cooling sub-paths per loop	500 - 3'000	50 - 500 *
Flexible plastic hoses		
number	80 - 300	100 - 1'000 *
wall thickness	approx. 3 mm	approx. 1mm *
Voltage applied	... 26 kV AC	... 13 kV DC
Main risk factors	overheating	overheating
	corrosion of braze	loss of temperature control
	electric flashing	electric flashing
Copper surface in one loop	200 - 500 m ²	most loops < 10 m ² **
Water volume per loop	2 - 5 m ³	approx. 1 m ³ ***
Operating temperature	40 - 70°C	12 - 50°C
Prime target of temperature control	avoid overheat	- precise temp. adjustment - avoid overheat
Oxygen production within loop	no	radiolysis
Water treatment basics	high purity water, as pure as achievable	high purity water, but highest purity is not target
Water additives used in some loops	if any, then only NaOH	if any, then Snake Oils
Concerns for EHS effects of water additives	disposal	activation disposal
De-oxygenation used	few cases	most cases
Concerns for biological growth	no	yes (?)
Ionizing radiation / contamination	no / no	yes / yes

Table 3-1. Key generic differences between generators and accelerators.

* estimated

** QMCS estimated 14 m², Ring Magnets Cooling System (RN-01) much larger

*** Ring Service Building loops are larger (e.g. RN-01: ca. 20 m³)

3.2 Findings at the visit

The following summary is intended to identify areas of possible improvements. It is therefore mainly focused on findings with negative aspects.

Nr	Finding
1	No main stream filtration
2	Possibly no efficient gas detraining for small bubbles in most loops
3	Sterilization in side-loop is questionable; it is downstream of mixed bed
4	De-ox column not always before mixed bed
5	Make-up supply not before mixed bed, and not before de-ox column
6	No monitoring for the quantity of make-up water
7	No monitoring / criteria for de-ox replacement
8	No monitoring / criteria for mixed bed resin replacement
9	Water resistivity not aimed to be as high as possible
10	No overall water chemistry concept
11	Very difficult to chemically monitor those many loops
12	Mix of chemical monitoring instrument brands
13	No overall calibration plan and procedures for these monitors
14	Water analysis results not trustworthy (problem with sampling)
15	Water probably runs slightly acidic (CO ₂ , decomposed organics)
16	Very difficult to control oxygen ingress
17	No monitoring of individual component temperature, water flow and Δp (in most cases)
18	Inspection of a spent filter cartridge in KL-02 indicated brown 0.1 mm particles on the cartridge and an adherent red deposit film (probably Cu ₂ O) on the steel support rod

Table 3-2. Findings with aspects where improvements can be considered.

Nr	Finding
16	No gross adverse material mix (especially: no Aluminum)
17	Well-tailored water treatment systems
18	Attention is being given to these systems
19	Everything is clean ... this creates an attitude!
20	Background of long experience with accelerators
21 (many more but not much to learn if listed)

Table 3-3. Technical findings with positive aspects.

4. DISCUSSION OF THE SNS COOLING LOOPS

4.1 Overview on the SNS cooling loops

SNS Cooling Loops Cooling Copper Technical Components

LEGEND: blue = activated or potentially active

black = not expected to be activated

Target System	Media	Test	FE	DTL	CCL	SCL	Ring	Loop Volume gal	Design Total Flow gpm	NOTES
Target Water Systems Supported by NFDD Utilities Systems Engineers										
RID Cooling Loop	HQ-DIW						X	600	54	Ring Injection dump
Accelerator Systems	Media	Test	FE	DTL	CCL	SCL	Ring			NOTES
Front End Building										
CHW Pkg Unit 38 kW	Trt Water		X					30	40	RFQ Vane
ChW Pkg Unit 25 kW	Trt Water		X					80	100	RFQ Wall, MEBT Rebunchers
Klystron Gallery - DTL Area										
RCCS-DTL1	HQ-DIW			X				255	120	Drift Tube Linac
RCCS-DTL2	HQ-DIW			X				280	162	Drift Tube Linac
RCCS-DTL3	HQ-DIW			X				280	235	Drift Tube Linac
RCCS-DTL4	HQ-DIW			X				280	215	Drift Tube Linac
RCCS-DTL5	HQ-DIW			X				280	133	Drift Tube Linac
RCCS-DTL6	HQ-DIW			X				280	184	Drift Tube Linac
PS-KL-04	DIW	X	X	X				TBD	885	Rf Equipment, HVCN, MEBT
Klystron Gallery - CCL Area										
RCCS-CCL1	HQ-DIW				X			300	218	Coupled Cavity Linac - RF structures
RCCS-CCL2	HQ-DIW				X			300	257	Coupled Cavity Linac
RCCS-CCL3	HQ-DIW				X			300	257	Coupled Cavity Linac
RCCS-CCL4	HQ-DIW				X			300	257	Coupled Cavity Linac
PS-KL-01	DIW				X			TBD	1143	Rf equipment and power supplies
Klystron Gallery - SCL Area										
QMCS	HQ-DIW				X	X		360	215	CCL & SCL Quadrupole magnets, Rf couplers, Rf windows on CCL, Faraday cups on CCL and the beam stop between CCL and SCL
PS-KL-03	DIW					X		TBD	1680	Rf equipment and power supplies
PS-KL-02	DIW					X		TBD	1680	Rf equipment and power supplies
HEBT Service Building										
PS-HS-01	DIW						X	TBD	885	Power supplies only
Ring Service Building										
PS-RN-03 (PS)	DIW						X	TBD	350	Power supplies
PS-RN-02 (Rf)	DIW						X	981	268	Rf equipment in tunnel
PS-RN-01 (Mag) (Ring Magnet DI)	DIW						X	5102	1250	Magnets in tunnel
RTBT Service Building										
PS-RS-01	DIW						X	TBD	50	Power supplies
Rf Test Facility										
PS-Rf-01 (DIW)	DIW	X						TBD	885	Rf equipment, HVCN

Table 4-1. Summary of SNS cooling loops.

4.2 General remarks

The SNS cooling loops comprise only a small selection of materials, mostly copper, stainless steel, as well as selected plastic materials for tubing connections. Connections are mostly made either by welding or fittings. Together with the use of high-purity water, corrosion will be quite limited.

4.2.1 Corrosion of copper components

Attack of copper. Copper is not attacked in high purity water in absence of oxygen. Together with oxygen, copper will be oxidized and the oxides may dissolve in water. In such systems, the oxidation rate will be very small, and will be of no significance regarding component integrity.

High local water velocities ($> 2\text{m/s}$) however would cause accelerated dissolution of the oxide layer, possibly causing local material loss and increased copper transport.

Corrosion coupons would not add any additional insight.

Re-deposition. The oxides may however re-deposit, causing flow restrictions, hindering of heat transfer, and may cause conductive deposits on insulating hoses. At such low temperatures as in the SNS cooling loops it is expected that this process be less pronounced than in generator cooling loops.

It is however advisable to suppress such re-deposition. The influencing factors are describes in paragraph 7.4, Figure 7-6. The most important parameters for the SNS are summarized in Table 4-2.

Parameter	Oxidation	Release	Migration	Re-deposition
O ₂ ingress rate	1			
O ₂ concentration		1		
pH, ECP		2		2
Conductance				
Temperature		4		3
Hydrodynamics		3		1
Filter and mixed bed flow			1	

Table 4-2. Parameters to control oxide deposition in the cooling loops. The numbers give the appraised priority of effectiveness.

Inhibitors. There is no need to use corrosion inhibitors in pure water systems; their good use is in systems with aggressive waters of high salinity. Concentrations that have to be used for effectiveness are also incompatible with pure water systems. Their use in generator cooling system has been investigated but abandoned for lack of need, but possible detrimental side effects (paragraph 7.4.5).

Bacterial growth or attack on copper surfaces has not been seen in power plant pure water systems; copper acts as biocide.

In case that oxide deposits are observed, alkalization to control oxide migration (and thus also re-deposition) however can be considered.

Conductive deposits may either be formed by plate-out of highly conductive metallic copper, or by some of the copper oxides that may be slightly conductive.

Brazing. In a few cases, copper components are joined by brazing (e.g. internal Klystron copper tubing). Depending on the type of braze, its slow dissolution may be possible even in high purity water.

4.2.2 Corrosion of stainless steel components

Materials attack. Stainless steel is not attacked in high purity water. A certain risk - if the water contains impurities- would be if the steel were sensitized, for example at locations of welded joints. Stabilized or low carbon stainless steel usually avoids this risk.

Corrosion coupons would not add any additional insight.

Inhibitors. There is no need to use corrosion inhibitors.

Microbial induced corrosion (MIC) however has been seen in water systems made of stainless steel. Although this is no surprise with natural waters, it also occurs in ultra-pure water systems. Common is that MIC occurs essentially only in parts with stagnant water (example: emergency cooling water systems in nuclear power plants). Most bacteria also need oxygen, but there are species that thrive also without oxygen (e.g. sulfate reducing bacteria, producing corrosive hydrogen sulfide from drinking water).

4.2.3 Electrochemical effects

Galvanic corrosion (dissolution of a metal that is in contact with a more noble metal) is not to be expected with the present materials. Differences in ECP are small, and the water has a high resistivity.

Attack by impressed currents however may lead to materials attack. This is pronounced in DC applications, while with AC effects are restricted to specific conditions. Effects will be larger with higher DC voltage, and smaller the higher the resistivity of the water is. Attack may however take place already at low DC voltage. The actual risk depends on materials properties, electric configuration, water quality etc and is hard to predict.

Protective anodes can avoid attack by impressed currents. It should however be reminded that the dissolution of sacrificial anodes will pollute the cooling water, and these corrosion products may cause unwanted deposits somewhere in the loop. In case such anodes are ever considered at SNS, careful selection of the anode material, and of water cleaning is therefore recommended. - Another option would be to use corrosion resistant anodes with impressed current. Such impressed current anodes are widely used with components in natural cooling waters; it is however a question how feasible this technology would be with the large number of components in the SNS cooling loops.

The tunnel Ring RF Cavities loop (RN-02 cooling loop) operate at 13 kV DC, all magnets operate with DC. The HVCM do have + and - 1.25 kV DC heat sink plates with hoses interconnecting between them in some places. All magnets are also DC powered, Table 4-3.

Volt	Amp	Number of such magnets located in		
		RSB	HEBT-SB	RTBT-SB
18	770	4	6	4
24	390	4	12	
27	185	4		
51	900	2	3	7
95	1300	6		4
800	1400	8		
390	1405	6	1	
18	4000	5		
440	6000	1		
18	18	1		
50	50	1		1

Table 4-3. List of large DC magnets in the SNS.

Electrolysis of water. DC voltage may also cause electrolysis of the water. This usually requires a certain conductivity of the water. In high purity water, effects are usually not apparent. There is the question on how high voltage DC will act upon high purity water. Investigations with a water-cooled 12 kV DC electrical sub-station indicate that no visible electrolysis took place, but moderate amounts of hydrogen peroxide were formed. Thus, minor quantities of oxidizing species are formed in such system, which would oxidize metallic copper if present.

4.2.4 Radiolysis of water

In some loops, especially in the Ring loops, there is such radiation level that radiolysis of water takes place. This gives at the same time a certain inherent concentration of dissolved hydrogen and oxygen.

Besides the radiolytic gas, there are all the intermediaries and radicals, many of them with a stronger oxidizing potential than O₂ gas.

With all this, copper will be oxidized, with the associated problems.

Efforts should be done to reduce the quantity of oxygen in the water as much as possible.

Note: the oxygen concentration in the water is no unambiguous indicator. If the oxygen is rapidly absorbed by the copper, then the oxygen concentration in the water may be very low. As a result, there is an uncontrolled oxidation of copper taking place.

It is therefore recommended to make regular inspections on the condition of selected components, for example borescope and / or destructive testing. In case of excessive oxide build up, chemical cleaning is indicated at an early stage (paragraph 5.5.4).

4.2.5 Water resistivity and corrosiveness

The specifications on water resistivity are not uniform throughout the systems, evidently mirroring the different origin of design:

DTL, CCL, QMCS loops:	10 - 15 Mohm.cm
KL-01 ... -04 loops:	1 - 3 Mohm.cm

Justification for a lower resistivity is the belief that high purity water is more aggressive (details in paragraph 4.4.4).

This position is however not shared by this review. In order to minimize corrosion, water should have the highest possible purity and resistivity.

There is the question what type of substances decrease resistivity in the SNS loops when the clean-up is running only at small flow. It is probable that decomposing organic matter, or carbon dioxide from air provide a slightly acidic environment. Water analysis data from SNS seem to support this. For a definitive conclusion, more data would however be required.

Water resistivity is an unspecific indication that does not indicate if the impurity is acidic, neutral, or alkaline.

Regarding corrosivity, the following can be said:

- ❑ under the conditions typically found in pure water systems, copper does not react with water in the absence of oxygen (paragraph 7.4)
- ❑ zinc however dissolves in neutral and acidic water, and makes an oxide protective layer in moderately alkaline (pH 8.5 ... 10.5) water (Figure 4-1)

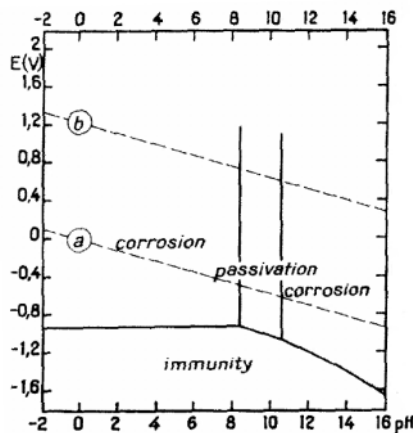


Figure 4-1. Pourbaix diagram of Zn in water at 25°C [26]. It is seen, that Zn dissolves in neutral and acidic, as well as in strongly alkaline water, at an Electrochemical Potential > -0.9 V. Between pH 8.5 and 10.5 it forms a stable hydroxide layer.

- ❑ galvanic couplings between stainless steel, copper, brazing materials will not lead to material dissolution in high purity water. The coupling of dissimilar metals produces an electric potential between the two components, and the corrosion is driven by the electric current that flows through the water, which is lowest when water resistance is highest. - Many braze- and most solder-materials are not very stable in water; they dissolve slowly. Lowering water resistance is not helpful here; depending on pH this can even be detrimental
- ❑ unalloyed iron will however dissolve slowly in pure water, even in absence of oxygen. This dissolution will decrease when the water is alkalized, and increase when acidified. Dissolution will be enhanced by certain impurities (like chlorides) in water, especially in the presence of oxygen. Only when a water additive enhances a protective layer on the surface, corrosion may be reduced or prevented. Such protective layers are for example the calcium-carbonate layer that deposits in potable water pipes, or magnetite layers that may form in alkalized water. Only in such cases, water without the "enhancer" will be more corrosive (-> beware of softened water in potable water systems, or demineralized water in carbon steel pipes).
- ❑ for corrosion protection the water should therefore have the highest possible resistance. Lower resistivity is unspecific and the response of corrosion will depend on pH and other parameters. If lower resistivity results in a lower pH, then corrosion of copper, brass, iron and brazing / solder materials will increase.

4.3 SNS water treatment units

4.3.1 Integration of the water treatment unit into a cooling loop

Each cooling loop has its own water treatment unit ("clean-up"). It is designed to clean 1 - 5%, typically 3% of the recirculating water.

An exception is the Ring Injection Dump system where ca. 34% of the recirculating water flow is treated (13.6 gpm vs. 40 gpm recirculating flow).

In some loops, clean-up water flow is reduced manually in order to provide a lower resistivity of the water which is claimed to be beneficial for corrosion protection.

Comments:

- ❑ for corrosion protection the water should have the highest possible resistance. Lower resistivity is unspecific and the response of corrosion will depend on pH and other parameters. If lower resistivity results in a lower pH, then corrosion of copper and brazing materials will increase. Lower resistivity also increases galvanic effects which could enhance materials dissolution as well as deposition in DC voltage components.
- ❑ for optimum removal of copper oxides and of acidic carbon dioxide, the clean up should be operated at the maximum possible flow

Make-up water is usually added at the recirculation pump suction or into the gas separator tank, that is, directly into the main loop.

Comment:

- ❑ this way, the make-up water is neither polished nor de-oxygenated in the clean-up. It should be added upstream of the de-ox column and mixed bed. It is acknowledged that a booster pump may be necessary. Such way however the requirements for make-up water quality can be kept less stringent; this way it may therefore not be any more indicated to keep make-up water -as being considered- in continuous circulation.

In most systems, an expansion vessel is placed somewhere in a dead end of the main system (e.g. KL loops), or at the outlet of the water treatment system (e.g. RCCS loops).

The expansion vessel in the RCCS systems was designed with a nitrogen cap. Problems with leaking vent valves however have led to the elimination of the gas cap and the sealing of the automatic vent valves.

In most cooling systems, there is a cyclonic air separator with an automatic air separator valve on top downstream of each pump discharge. In some systems (e.g. in the RID cooling loop) the expansion vessel is located in the main loop, permitting venting off the radiolytic gas.

Comment:

- ❑ In systems where there is the possibility of gas buildup a gas detraining feature should be in the main stream of the loop
- ❑ It is to be verified if the cyclonic separator is also efficient for small gas bubbles

The main loops of most systems also contain a 20 mesh (840 micron) or a 30 mesh (600 micron) strainer to remove debris.

Comment:

- ❑ In such cooling loops it is advisable to have a fine filter (1 or 5 micron) for the full flow in the main stream, for the removal of migrating copper oxides. In generator systems, such filters remove a comparable amount of copper to that removed in the mixed beds

4.3.2 Basic design of a water treatment unit

The basic design has the following components, in series in the following order (individual loops may however differ):

- ❑ 5 micrometer pre-filter
- ❑ Oxygen scavenger (usually a 3.6 cuft vessel filled with 3 cuft of sulfite-loaded ion exchange resin; in KL-02 Liqui-Cel membranes are used)
- ❑ Cation exchanger for removal of Be-7 (abandoned)
- ❑ Mixed bed filter (3.6 cuft vessels with 3 cuft resin filling)
- ❑ Charcoal filter for removal of organic matter (only for commissioning)
- ❑ uv-sterilization
- ❑ 1 micrometer post-filter

Comments:

- ❑ except for the resin trap (outlet filter, 5 micron would be sufficient), 1 or 5 micron mechanical filtration should be done full flow in the main system
- ❑ the placement of the uv filtration in such a small side-stream is questionable. It certainly cannot assure sterilization of the whole loop water, nor can it avoid local bacterial growth, especially in areas with stagnant water. Such uv device would be more effective if it would cover the whole cooling water flow.

- ❑ the reason of the placement of the uv unit after the mixed bed should be scrutinized. The uv unit decomposes organic matter (at least partially) to low-chain carboxylic acids, that could be preferentially removed in the mixed bed if this would be downstream of the uv unit. (Note: the numerous non-metallic hoses in the cooling system may slowly release organic matter that will accumulate in the system and its only control is this uv unit.)
- ❑ the placement of the oxygen scavenger upstream of the mixed bed is correct. Such way, any chemicals possibly leaching from the scavenger column are removed in the mixed bed. Physical de-oxygenation devices (Liqui-Cel) that release no chemicals may be placed more liberally.

4.4 Features of the individual cooling loops

It is not intended to give a complete or precise overview of the loop features. Summaries are given from the perspective of relevance to water chemistry. Please note that comments given for one system may also apply to other systems. For brevity, no repetition is made.

4.4.1 Front End - RFQ chiller loops

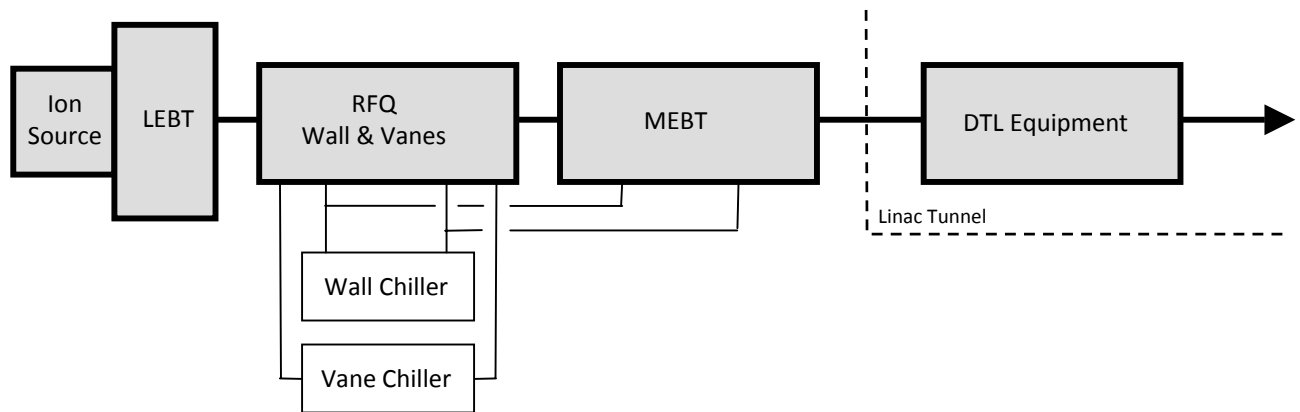


Figure 4-2. Front End / RFQ wall and vane cooling water systems (RFQ: Radio Frequency Quadrupole, LEBT / MEBT: Low- / Medium Energy Beam Transport, DTL: Drift Tube Linac)

The RFQ has its own two cooling loops, with chillers, for cooling the RFQ vanes and the RFQ walls, together with the MEBT rebunchers. As electric conductance is of no relevance here, this cooling water is chemically treated by a mixture of an inhibitor (NalcoTRAC100: borax / molybdate type, tolyltriazole) and a biocide (Nalco 7338). These cooling loops are equipped with 5 micrometer mechanical filter cartridges that are replaced regularly. Make-up is DI water drawn from the KL-04 skid.

Materials in contact with these cooling loops are copper, type 304 stainless steel, brazing material, and plastic hoses. Inner diameter of flow passages is rather small at some components (the RFQ Pi-mode rods are 3.4 mm).

Water related problems in the Front End have been failures in the paddle-wheel type flow meters of the RFQ due to deposits. Note: also occurred in other cooling loops, eg. the DTL-RCCS, CCL- RCCS, and QMCS systems.

In the Front End there is only radio frequency electromagnetic radiation, and no ionizing radiation.

Comments:

The small dimensions of passages of the Ion Source equipment could cause a long-term risk for flow reduction by deposits.

The use of water treatment chemicals in the RFQ equipment is quite useless. Molybdate is an inhibitor applicable for ferrous alloys and aluminum. A borate buffer is added for the necessary

control of pH. However, as the ferrous alloys in the system are stainless steel, there is no need to add an inhibitor to high purity water. - Tolyltriazole is added as an inhibitor for copper corrosion, which is useful if there is a corrosive environment for copper. Copper does however not corrode in high purity water. Only oxygen that enters the system reacts to copper oxide, independent of the presence of an inhibitor. Azoles react with copper ion to form a thin film that reinforces the oxide film on the copper layer, which just adds up to a more complex chemistry that would make troubleshooting (like cleaning) more complicated. Such inhibitors are not used in generator water cooling.

Even though inhibitors in such a system are herewith considered as being useless, they probably do not do much harm. It would be interesting to know the actual background for the use of inhibitors in this loop, if it is only tradition or if there is a specific case behind. If the reason is just "because it is done so in other closed cooling loops", like in power plants, then this would be insufficient reason. Power plant cooling loops contain a varied metallurgy and most of the piping and component shells are made of carbon steel. Here, inhibition is required. In Europe, for environmental reasons, no heavy metals are used; the water is just slightly alkalized with NaOH.

Chemical additives are not used for demineralized water CCW systems. In the event of microbiological activity, a biocide that does not increase system impurities should be used [23].

4.4.2 Front End and DTL Rf deionized cooling water systems (KL-04)

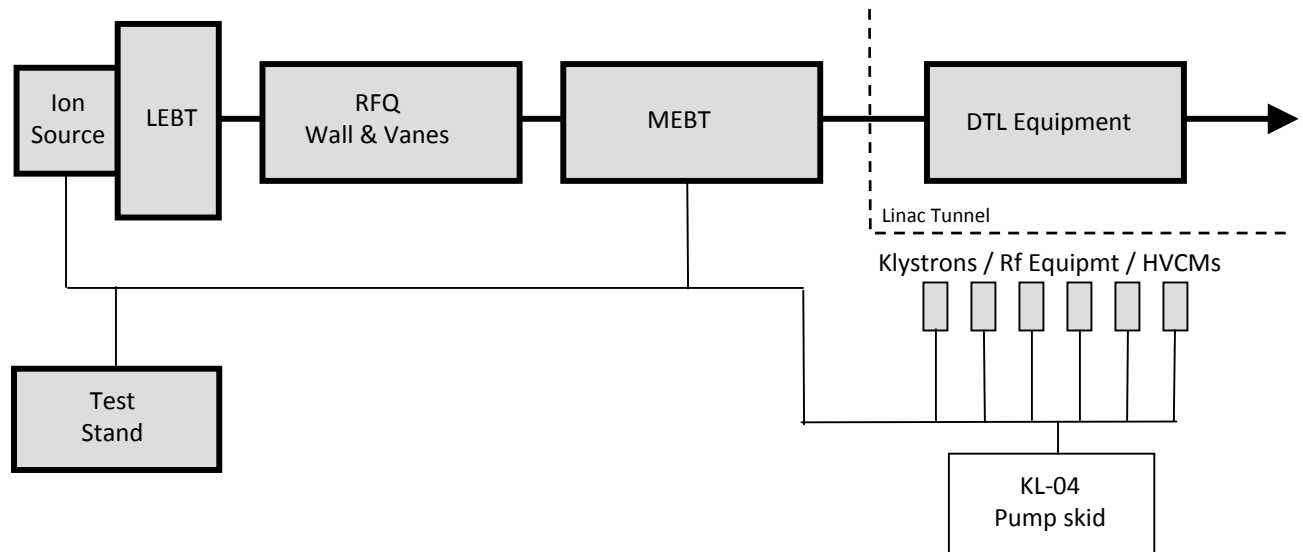


Figure 4-3. Front End and DTL Rf cooling water system (RFQ: Radio Frequency Quadrupole, LEBT / MEBT: Low- / Medium Energy Beam Transport, DTL: Drift Tube Linac, KL Klystron)

The ion source, LEBT and MEBT, test facility equipment, and DTL klystrons and associated Rf equipment are cooled with DI water from the KL-04 water skid.

Materials in contact with these cooling loops are copper, type 304 and 316 stainless steel, brass, brazing material, and plastic hoses. Inner diameter of flow passages is rather small at some components of the ion source and LEBT (e.g. 2.2 mm). These components are subject to frequent maintenance or even replacement.

In the Front End there is only radio frequency electromagnetic radiation. Ionizing radiation in the cooling water has to be considered at beam energies above 7 MeV, that is from the DTL on.

Comments:

The small dimensions of passages of the Ion Source equipment could cause a long-term risk for flow reduction by deposits. As these components are however regularly replaced for other reasons, such problems are not expected.

4.4.3 KL loops (KL)

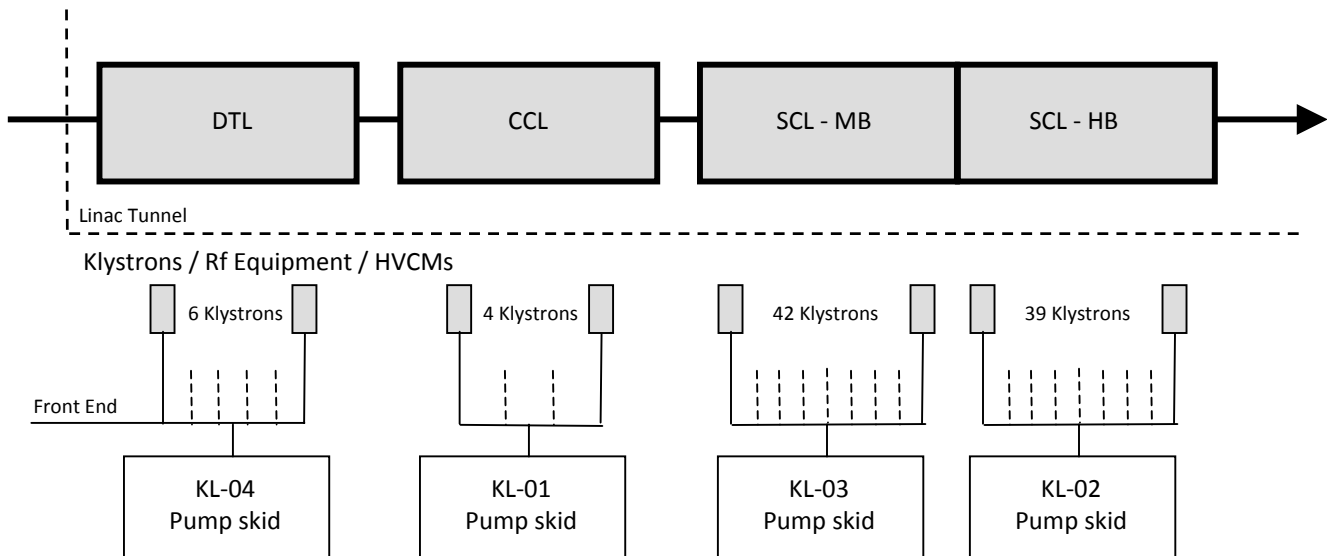


Figure 4-4. Klystron gallery cooling water loops. (KL: Klystron, DTL: Drift Tube Linac, CCL: Coupled Cavity Linac, SCL: Superconducting Linac, HVCMS: High Voltage Converter Modulator). The Linac components are cooled by separate cooling systems, the RCCS (see paragraph 4.4.4).

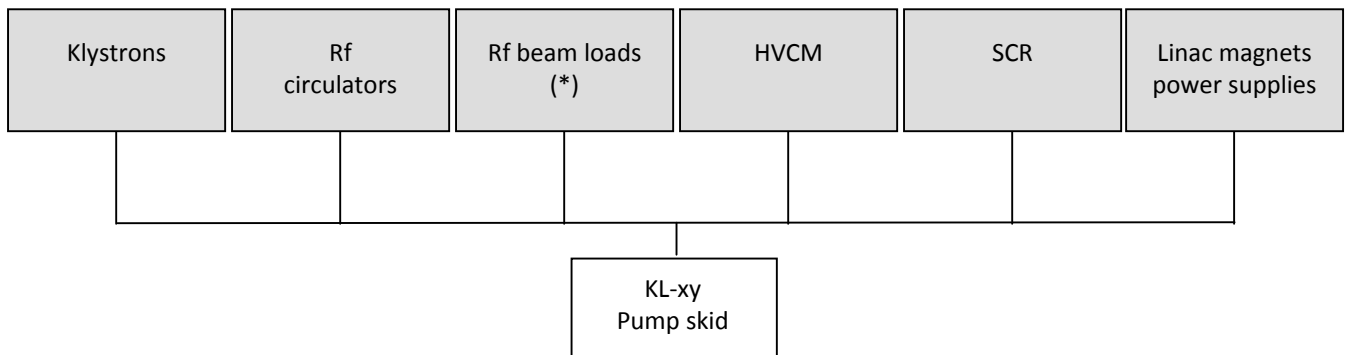


Figure 4-5. The cooled components in the KL loops. Each item is present in multiple numbers. (xy: 01 ... 04, HVCMS: High Voltage Converter Modulator, SCR: Semiconductor Controlled Rectifier, (*): KL-01, -02, -03 only; KL-04 has a separate loop)

The DI water is maintained at a resistivity between 1.0 to 3.0 Mohm.cm on all four loops.

Materials in contact with the cooling loops are copper, type 304 and 316 stainless steel, brass, carbon steel (HVCM heat exchangers), Alumina or Rexolite (Rf wave load windows), braze or solder (on the klystron body plumbing), and plastic hoses.

Each KL loop comprises:

- ❑ Water treatment skid

Each KL loop has its own water treatment skid. According to the P&ID, the water treatment configuration of KL-01, -03, and -04 is basically similar; KL-02 is different.

KL-01, -03: a side stream of the process water is taken at pump outlet. It passes through a de-ox column, followed in series by a mixed bed column, a 5 micrometer resin trap and an uv-sterilization device. The treated water is then fed back to the pump suction, upstream of the air separation tank. This tank is connected to the dead-end expansion vessel, and to the incoming make-up water supply. The P&ID do not indicate any filter in the main loop; there is however a 20 mesh (840 micron) strainer on each pump inlet.

KL-04: as KL-01 and -03, but the de-ox column and the mixed bed are in parallel.

KL-02: two parallel side streams are taken at pump outlet. One stream passes through the mixed bed filter and its 5 micrometer resin trap. The other stream passes through a 5 micrometer pre-filter, followed by a Liqui-Cel membrane-type oxygen removal unit, and then by an uv-sterilization device. Treated water return from both streams, separation tank, expansion vessel, make-up supply and no main stream filtration are like in the other KL loops. The pre-filter was opened, and a filter element could be inspected, Figure 4-6. The filter cartridge was grey-brown, as typical for CuO (but visual appearance may deceive), and there were few brighter colored particles of an estimated 1/10 mm (order of magnitude) size. The inner support shaft (stainless steel) of the cartridge was deep red with a copper tan, typical for Cu₂O deposits. It was very thin and so adherent that it could not be wiped off.

- ❑ Klystron body circuit and magnetic circuit cooling

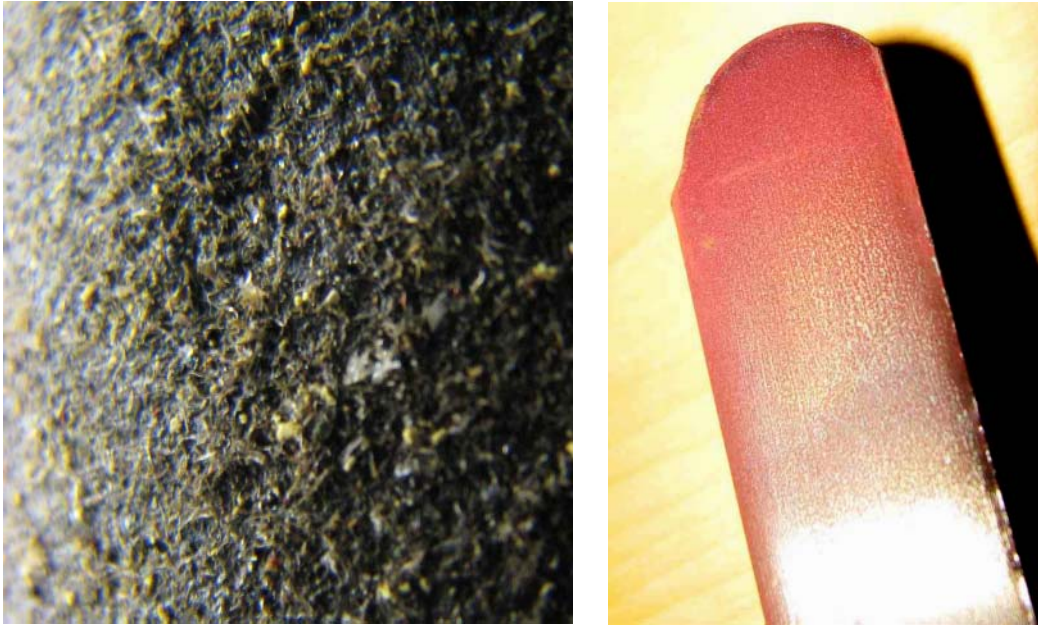
This is relative coarse plumbing of copper tubes (estimated: 3/8"). The connections between the tube segments and klystron components are mostly brazed, some screwed

- ❑ RFQ modulator cooling (HVCM)

The HVCM loop contains a water/oil heat exchanger that is partly made of carbon steel. An open heat exchanger head showed extensive orange deposits, evidently some type of "rust" (Fe-hydroxides)

❑ Klystron load cooling

Each Klystron has a wave-load, that is a stainless steel tank filled with water, separated from the vacuum by an Alumina (SCL) or Rexolite (CCL) window. The wave load is fed and cooled directly by the respective KL loop at the higher frequency Klystrons KL-01, -02 and -03. The 402.5 MHz DTL loop (KL-04) however employs a separate load loop filled with a 50/50 mixture of polypropylene glycol and water.



❑

Figure 4-6. Details from an element from the pre-filter of the Liqui-Cel in KL-02. Left: close-up of the cartridge surface. The basic color is grey with a tint of brown (new cartridges are almost white). On the surface there are brighter loose particles with a size in the order of 1/10 millimeter. Right: stainless steel support shaft inside the cartridge; very fine and strongly adherent red deposit.

The following water related problems were reported by ORNL-SNS:

1. Klystron strainer plugging due to copper and biological fouling. During early startup and first year operation system resistivity and UV sterilization quality varied and failed several times.
2. Iron was discovered in the oil to water heat exchanger and helped explain the iron found in water grab samples. Currently, it is being planned to replace the existing heat exchangers with new stainless steel units.

3. Brass hose barbs on the heat sinks on the HVCM's have collapsed and started leaks due to dezincification of the tips due to difference in electrical potentials. Problems with low water resistivity seemed to cause this problem. Since brass fittings with silver plating on them are used and water chemistry has been improved, the de-zincification collapse of the brazed hose barbs is no longer seen.

Comments:

□ Water treatment systems.

- The comments and concerns given in paragraph 4.3.2 apply.
 - KL-04 has the chemical de-ox column parallel to the mixed bed; it should be in series, upstream
 - the system specifications should be set for the highest possible water purity, although the present plan calls for 1-3 Mohm.cm only (see paragraph 4.2.5)
 - there is no filter in the main KL systems, only a 20 mesh (840 micron) strainer.
- Although most components have wide clearance for water, there may be components with small clearance (e.g. SCR coils) that are susceptible to plugging by deposition of particles.

□ Klystron body

Brazing materials usually dissolve slowly in pure water (although up to 1 mm per year). This is effective on open surfaces. Brazed joints however form a tiny gap filled with braze, from which possibly dissolved material cannot escape easily and thus dissolution will halt. Corrosion may however occur when electrochemical effects make the internal of the gap active [6]. It is estimated that the risk in KL klystrons is low, but it would be worth to check used components on proper occasion (e.g. dissect such joints on occasion of final removal from service). The joint of dissimilar materials Cu / braze however is critical in case of possible chemical cleaning.

□ HVCM

The HVCM do have + and - 1.25 kV DC heat sink plates with hoses interconnecting between them in some places. The attack of the brass hose barbs may be related to DC electrochemical effects, augmented by low water resistivity (paragraph 4.2.3) .

If any, all carbon- or low-alloyed steel object should be removed from any high purity cooling water system (example: the KL-HVCM water/oil heat exchanger; it is already planned to replace it). Such objects will corrode and produce Fe-hydroxides that may transform, with time, into magnetic Fe_3O_4 , or even release Fe particles. These impurities may cause fouling of heat transfer surfaces and electric bridging on insulation hoses.

Magnetized particles in a slowly alternating magnetic field may damage component surfaces; Such "magnetic termites" have caused hollow conductor perforations in generators (electric frequency 50 or 60 Hz).

❑ SCR

If there are any particles circulating in the cooling water system, they may reduce flow in the SCR coils.

❑ Wave loads

- the load windows are made of Alumina (Al_2O_3) in the SCL or Rexolite (cross-linked polystyrene based microwave plastic, possibly reinforced) in the CCL systems, all other wetted surfaces are stainless steel.

In KL-01, -02 and -03 they are cooled by the recirculating water that contains copper oxides and possibly also metallic copper particles (under certain conditions, copper oxides may reduce with time to metallic Cu). KL-04 wave loads are served by a separate, glycol based load cooling loop KL-05. Glycol is known to decompose with time into acid, especially when in contact with air (e.g. in expansion vessel). These substances are not expected to initiate or enhance an attack on stainless steel, Alumina and Rexolite, as long as the water is otherwise pure, like in the SNS loops with DI water.

❑ Klystron strainer plugging and fouling

This was attributed to copper and biological fouling. The presence of biofouling on a site with copper deposits however raises questions. In any case, the inadequate location of uv sterilization (in a side-stream) has been discussed in paragraph 4.3.2.

❑ Corrosion of brass hose barbs

Dezincification is a process affecting brass, where Cu and Zn are dissolved and the Cu re-deposited on the metal surface. It appears typically in high chloride, soft or acidic water. In pure water systems, dezincification is unlikely. - Dezincification is mitigated or prevented in the power industry by the choice of an adequate brass alloy (e.g. Admiralty brass for fresh water cooling, with 1% Sn to inhibit dezincification).

The attack on the brass hose barbs may have been caused by dissolution of Zn from the metal surface layer, enhanced by turbulent water flow that steadily removes the dissolved Zn, and possibly also enhanced by electric or electrochemical effects in water with low resistivity. Lower water resistance is here no help at all, as long as it is not alkalizing. Otherwise, lower resistance will enhance corrosion.

This subject is discussed in more detail in paragraph 4.4.4.

4.4.4 RCCS (RCCS-DTL and -CCL)

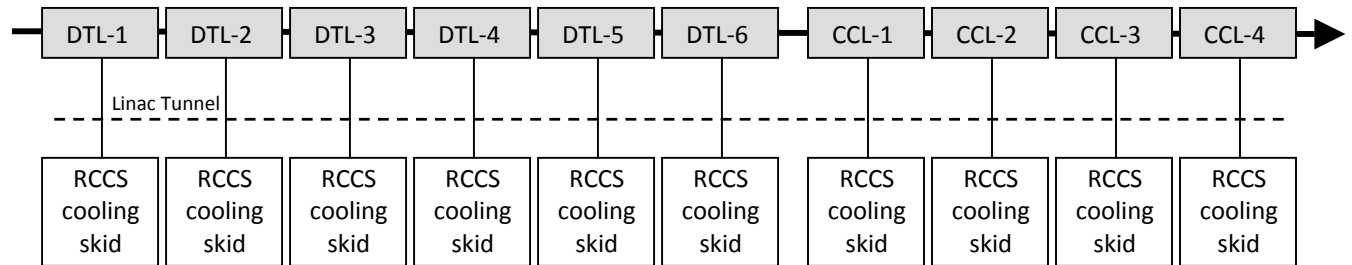


Figure 4-7. Resonance Control Cooling System (RCCS) Skids – One per Accelerator Structure (RCCS: Resonance Control Cooling System, DTL: Drift Tube Linac, CCL: Coupled Cavity Linac).

Each of the ten (10) warm Linac copper structures (DTL's and CCL's) are cooled by an independent cooling system that maintains each structure temperature at ± 0.1 C so that the Rf resonance can be maintained at the desired frequency. Water quality is maintained at 10 to 15 Mohm-cm by varying the flow through the polishing side stream at 1 to 5%.

Materials in contact with the cooling loops are copper, 304 and 316 stainless steel, brazing material, and plastic hosing. The DTL Drift Tubes and the CCL segments on each structure are flow balanced using plate orifices feeding each circuit. The orifices vary from 0.028" up to 0.850". To date no flow blockage at the orifices were experienced.

Water related failures have been flow meter failures and some minor hose leaks.

RCCS-DTL. Each loop comprises:

- ❑ Tank wall cooling
stainless steel cooling channels in grooves (1" wide / 0.5" deep) of the DTL tank
- ❑ End wall cooling
machined cooling channels in Cu endplate
- ❑ Drift tube cooling
cooling channels machined into the copper drift tube body
- ❑ Cooling of: RF windows (ceramic), post couplers, drive risers, slug tuners, faraday cups, dipole electro-magnets

RCCS-CCL. Each loop comprises:

- ❑ CCL cavity element copper wall cooling

- ❑ Cooling of: copper side coupling cells, copper bridge couplers
- ❑ Quadrupole magnets (located between each CCL segment), RF windows, faraday cups: these components are cooled in a separate cooling system, the QMCS (paragraph 4.4.5)

Both loops serve to remove waste heat as well as to provide precise temperature in order to control Linac resonance. System materials are copper, stainless steel, as well as non-metallic flexible hoses. The FlatPlate™ plate-type heat exchanger is made of 316L stainless steel plates brazed together with copper as braze material. The gap between the plates is narrow: the depth of one element (one gap + one plate) is only 2.4 mm. The data sheet specifies the requirement of a 20-40 mesh (0.4-0.8 mm) strainer at the inlet circuit and that water quality should be maintained at pH 6.5 to 8.0.

Clearances for water flow in the individual components are small. The CCL elements have an inner diameter of approx. 4mm, the dipole magnets 1.5 mm, and the QMSC quadrupoles 1.5 x 4 mm, Figure 4-8.

The systems include a heater for temperature control. All wetted surface are made of stainless steel. The heaters have never been used, and flow through the heaters has been minimal as the bypass valve is always fully open. There is a concern of potential dead leg issues.



Figure 4-8. Left: DTL drift tube (opened), and one coil of a quadrupole magnet. Right: dimensions of the QMCS quadrupole magnet coil hollow conductors; the squares on the paper have 5mm size.

RCCS water skids

The RCCS water skids correspond mainly to the basic configuration described in paragraph 4.3.2. The Final Design Reports (SNS-104020500-DE0001-R01 and SNS-104040500-DE0001-R01, April 2001) give the information summarized in Figure 4-9 and Table 4-4. It must be noted that these features evolved during project progress, reflecting updates of knowledge.

The actual systems differ. The cation exchangers intended for the removal of Be-7 were deemed not to be required and thus omitted. The nitrogen blanket in the expansion vessel has been abandoned because of leaky valves leading to loss of nitrogen. The carbon bed was used only for commissioning.

According to the P&IDs (if they are correct), the 5 micron filter at the purification loop outlet was replaced by a 1 micron filter. As built, there is a Y-strainer with 30 mesh (600 micron) screen on each RCCS system just prior to mating with Rf structures manifolds in the tunnel.

There is a cyclonic air separator with an automatic separator valve downstream of each pump discharge (not shown in Figure 4-9)

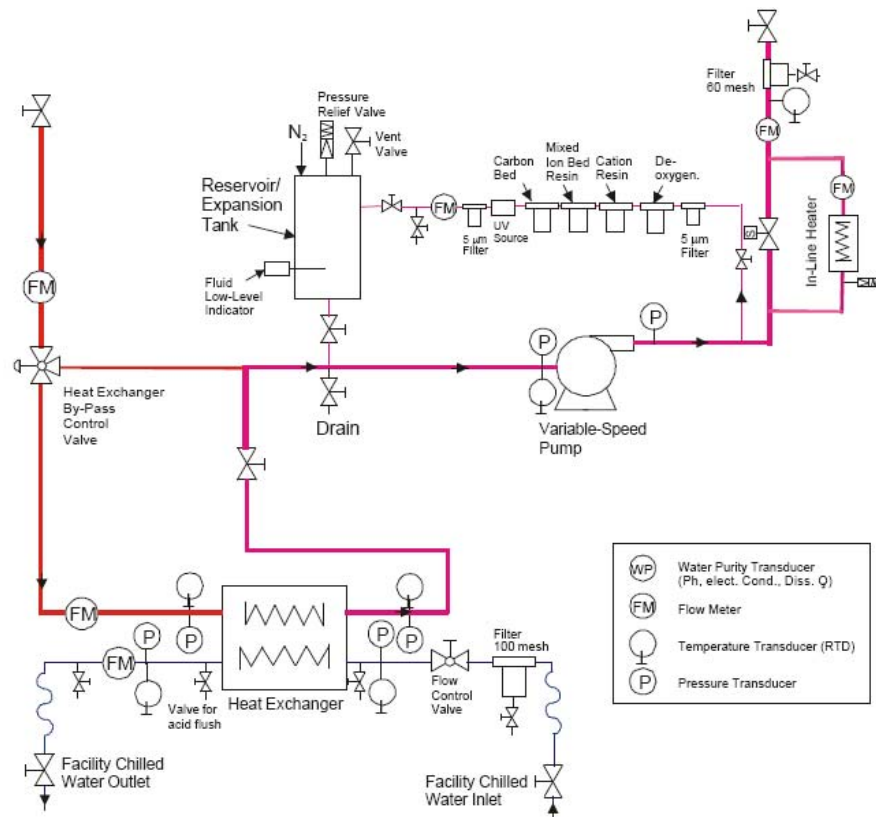


Figure 4-9. RCCS water skid piping and instrumentation diagram (status April 2001).

Parameter	Recommended Value
Flow rate	1 - 5 % of total flow
pH	8 ± 1
Electrical Resistivity	10 - 15 Mohm.cm
Dissolved Oxygen content	< 20 ppb
Particulate size	≤ 1 micron

Table 4-4. Design specification for the RCCS water treatment units (status April 2001).

The DTL and CCL Final Design Reports (SNS-104020500-DE0001-R01 and SNS-104040500-DE0001-R01) include the following wordings (page numbers refer to the DTL report), which are not shared in this review:

page 165: *"The ultrapure deionized water is very aggressive and will attack materials such as copper, brass, and bronze. The water will begin to remove iron oxide particulates and allow them to reattach on other surfaces." "However, brass is significantly more susceptible to the aggressive nature of the ultrapure water. The use of these materials would require a periodic flushing of the entire closed loop system to remove the iron oxide."*

page 166: *"System components such as the heat exchanger and the pump would be constructed from stainless steel whether the piping system was copper or stainless steel. This would require a galvanic insulating material to prevent corrosion at the joint if the plumbing material were copper. Even copper to copper brazed or soldered joints may create potential problems. Many of the standard flux materials used in solder joints are susceptible to the aggressive nature of deionized water. Such joints may potentially cause soldered particulates to break off and cause damage to the pump impeller or inhibit flow through an orifice plate."*

page 214: *"Typically an electrical resistivity value above 6 MO drastically reduces scaling [5.9]. However, it is important to keep the resistivity below 15 MO, particularly in copper structures and piping. Due to the polar nature of ultrapure water, a very high resistivity tends to strip away ions from the metal surface of piping, particularly copper when dissolved oxygen is present [5.10]. Maintaining the resistivity below 15 MO minimizes this effect."*

page 216: *"Due to the corrosive nature of deionized water, brass and carbon steel components are not acceptable."*

Comments:

❑ Water treatment systems

- the comments and concerns given in paragraph 4.3.2 apply.

- there is no filter in the main KL systems, only a 30 mesh (600 micron) strainer.

Although most components have wide clearance for water, there may be components with small clearance that are susceptible to plugging by deposition of particles.

- the system specifications should be set for the highest possible water purity, although the design specification calls for 10-15 Mohm.cm only, and the Design Report text suggests even lower resistance (see also paragraph 4.2.5).

❑ Heat exchanger

The narrow channels between the plates make this heat exchanger sensitive to deposits. Such would manifest by increased pressure drop. The combination of stainless steel joined together with copper as the braze material (?) is certainly not favorable for good corrosion resistance: on one hand, the dissimilar materials combination, on the other hand possible sensitization in the heat affected zone. The manufacturer's requirement for water pH 6.5 to 8.0 indicates awareness of these risks. - For high purity water, such design and materials combination may be oK.

❑ Comments to the statements given in Final Design Report regarding the corrosiveness of ultrapure water

A detailed response is given in paragraph 4.2.5.

4.4.5 QMCS loop (CCL and SCL)

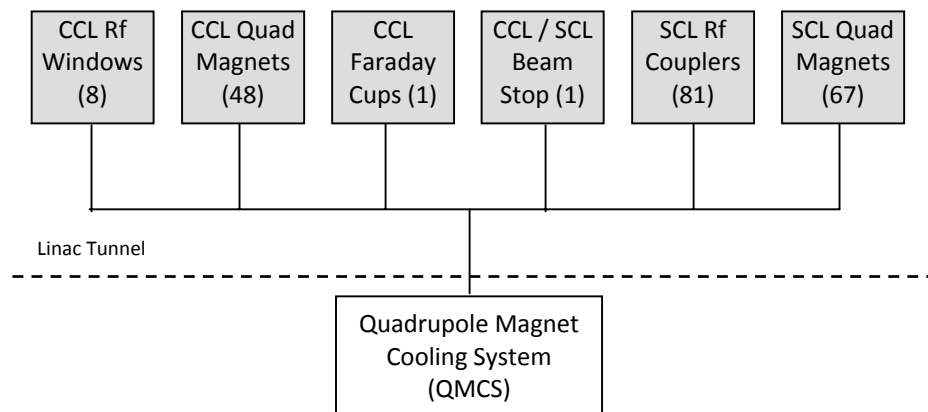


Figure 4-10. The Quadrupole Magnet Cooling System (QMCS: Quadrupole Magnet Cooling System, CCL: Coupled Cavity Linac, SCL: Superconducting Linac).

The Quadrupole Magnet Cooling System (QMCS) cools a total of 115 DC magnets, 89 Rf windows/couplers, a Faraday cup, and a beam stop used for beam testing. All of these components are located in the accelerator tunnel and are in radiation fields above the 7 MeV level.

Materials in contact with this cooling loop are copper, type 304 and 316 stainless steel, and plastic hoses.

Each quadrupole magnet contains 4 electrical coils with internal water cooling passages. The 4 coils are plumbed in parallel and connected to small supply and return sub-manifolds. With a total of 115 quadrupole magnets, there are thus 460 coils in parallel, with a flow cross section of approx. 1.5 x 4 mm each (Figure 4-8). Together with an assumed length of 5 meters copper hollow conductor in each coil, it makes a copper surface area of 14 m². This is already a large copper surface that may lead to a significant release of copper. Having so many coils in parallel brings the risk of plugging up individual coils slowly without indication in the overall system performance. This is a common problem mastered in power plant generators. - In the SNS there is no individual flow control for the coils, but each coil has a thermoswitch, shutting it off in case of overheating.

The QMCS water treatment skid is -according to the P&ID- of the same design as the RCCS discussed in paragraph 4.4.4. Here again, the lack of a main loop filter brings the risk of plugging small bore components, like the magnet coils.

Water related problems have been flow meter failures due to copper plating on the turbine meter bearings or bushings, flow switch failures on the couplers, and some hose leaks.

Comments:

- ❑ In order to minimize copper release from the large copper surface area, oxygen in the water should be tightly controlled.
- ❑ However, if the plate-out was indeed by metallic copper and not by copper oxides (would need to be analyzed by XRD), then a moderate oxygen level (10 - 30 ppb) would be beneficial to transform the metallic deposit into its less conductive oxide. Drawback is that such way larger quantities of oxide are produced.
- ❑ The potential presence and migration of copper oxides indicates the usefulness of main stream fine filtration (1 or 5 microns).
- ❑ This loop contains components (the magnets) fed with DC voltage, which could cause electrochemical plate-out across the voltage drop. Such plate-out can be minimized by a) keeping water resistivity as high as possible, and b) keeping dissolved metal concentration in the water low by operating the mixed bed at high flow.
- ❑ further related comments see paragraph 4.4.6 (Ring magnets)

4.4.6 Ring Magnet Cooling Systems for the HEBT/Ring/RTBT Accelerator Magnets (RN-01)

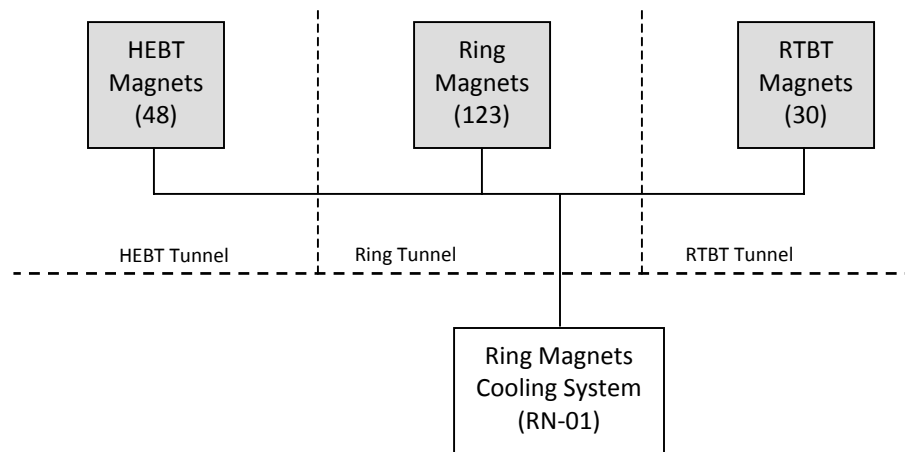


Figure 4-11. Ring Magnets cooling system (HEBT: High Energy Beam Transport from Linac to Storage Ring, RTBT: Ring to Target Beam Transport from Storage Ring to Target)

The Ring Magnet Loop is the largest volume loop in the SNS complex with over 5000 gallons of deionized water circulating 1250 gpm cooling to 201 water cooled Dipole, Quadrupole, and Sextupole magnets along with some electrical bus bars in the HEBT, Ring, and RTBT tunnels. The magnets are DC magnets with water cooled buses in the magnet coils. Due to the larger number and larger size of the magnets, the copper surface area is probably considerably larger than in the QMCS. - Because of the potential of a significant radiation level, radiolysis of the water can take place.

Materials in contact with the DI cooling water are the copper coils, 304 stainless steel distribution piping, and connecting plastic hoses.

The cleanup bypass is quite similar to the RCCS/KL-01, 03 (paragraph 4.4.4). A side stream of the process water is taken at pump outlet. It passes through a de-ox column, followed in series by a mixed bed column, a 5 micrometer resin trap and an uv-sterilization device. The treated water is then fed back to the pump suction, upstream of the air separation tank. This tank is connected to the dead-end expansion vessel, and to the incoming make-up water supply. The P&ID do not indicate any filter in the main loop; there is however a 20 mesh (840 micron) strainer on each pump inlet.

The mixed bed flow in this system set manually to achieve a water resistance in the main loop of 1-3 Mohm cm, with the intent to reduce corrosion.

Overheating of the individual magnets is prevented by multiple thermo-switches (klixons) on each magnet and bus-bar.

Water related problems in the Ring Magnet Cooling system has been:

1. Initially variable pressure balancing valves were installed on each magnet to minimize the amount of flow balancing required on this very large system. The valves that were used were Griswold valves with variable area orifices in them to maintain a set flow over a range of differential pressures. These valves worked very well initially, but within a year the valve orifices started plating copper over the orifice area dropping the set flow to each magnet. The valves were finally removed from the system and periodic flow balancing is required for the system.
2. Early on a makeup mixed resin bottle strainer separated and loaded several cubic feet of resin into the distribution system. It was found that there was no filter downstream of the resin bottle (this was quickly corrected). This also complicated the Griswold valve operation and took almost a year of added filtering and mechanical breakdown of the resin before this problem went away.
3. Hoses are used as electrical isolators between the magnet coils and to the distribution headers. It has been noted at several other accelerators that copper will plate out on the ID of the insulating hose and eventually allows stray currents to leak from the magnet. To date SNS has not experienced this problem.

Comments:

❑ Keeping oxygen in water low

- in order to minimize copper release from the large copper surface area, oxygen in the water has to be tightly controlled.
- radiolysis will however provide an oxidizing environment, independent of any de-oxygenation (paragraph 4.4.10).
- in order to minimize this oxidation, it is nevertheless helpful to use de-oxygenation. A sulfite based de-ox column would not be much useful, as it would be consumed rapidly and an easy indication of exhaustion is not available. A LiquiCel device may be more suitable.
- injecting a chemical reducing agent to the water would be another option. Here, hydrazine would be technically suitable, although inconvenient to handle. Hydrazine would decompose to nitrogen, water, and maybe to a small degree to ammonia. The later would be removed in the mixed bed. It must however be noted that the steady clean-up flow would also require steady injection of hydrazine. This would cause regular

exhaustion of the mixed beds. - Hydrazine is a key additive to the feedwater in power plants. It has also seldom been used in generator cooling systems. Hydrazine, as well as ammonia has alkalizing properties. Ammonia can form chemical complexes with copper oxides (but not with copper metal) that may enhance the dissolution of oxide layers. This will however not be an issue as long as the concentration of oxygen is kept low (<10 ppb), but could be problematic with periods of elevated oxygen levels.

❑ Keeping a moderate oxygen level in the water

- first of all, the nature of the deposits should be clarified (XRD analysis): is it metallic copper or is it copper oxide? It may easily be possible that the Griswold valve orifices suffered plate-out from oxides, while the insulation hoses, where the DC voltage drop takes place, are plated with metallic copper.

- if the plate-out material was indeed metallic copper, and not copper oxides, then a moderate oxygen level (10 - 30 ppb) would be beneficial to transform the metallic deposit into its less conductive oxide. Drawback is that such way larger quantities of oxide are produced.

❑ Main stream filtration

The potential presence and migration of copper oxides indicates the usefulness of main stream fine filtration (1 or 5 microns).

❑ Managing the effect of DC voltage

The magnets are fed with DC voltage, which could cause electrochemical plate-out across the voltage drop. Such plate-out can be minimized by

- a) keeping the electrical current that drives the plate-out as low as possible, that is water resistivity as high as possible, e.g. > 12 Mohm.cm, see also (paragraph 4.4.4), and
- b) keeping dissolved metal concentration in the water low by operating the mixed bed at very high flow. In oxidizing generator cooling systems, power industry uses 10% or more mixed bed flow, relative to main stream.

4.4.7 Ring Rf Cooling Systems for the Ring Accelerator Cavities and Amplifiers (RN-02)

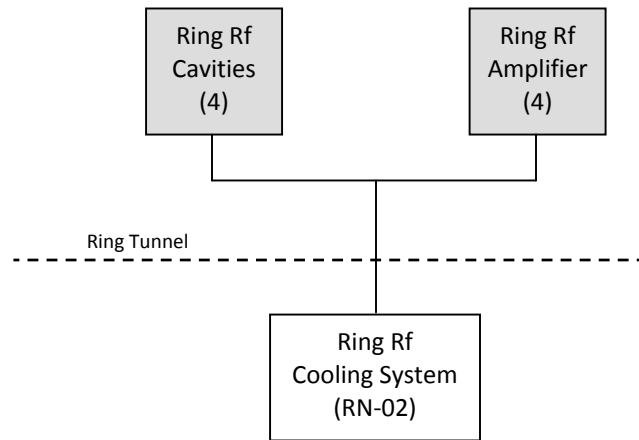


Figure 4-12. Ring Rf cooling system

The Ring Rf loop cools the 4 Rf cavities and 4 power amplifiers located in the ring tunnel. The system is maintained at 70°F by use of chilled water through the skids heat exchanger.

Ring Rf amplifiers include components with 2 KV DC.

The water treatment skid is similar to the RCSS/KL-01, 03. A side stream of the process water is taken at pump outlet. It passes through a de-ox column, followed in series by a mixed bed column, a 5 micrometer resin trap and an uv-sterilization device. The treated water is then fed back to the pump suction, upstream of the air separation tank. This tank is connected to the dead-end expansion vessel, and to the incoming make-up water supply. The P&ID do not indicate any filter in the main loop; there is however a 20 mesh (840 micron) strainer on each pump inlet.

Materials in contact with the DI cooling water are the copper, brass valves, 304 stainless steel distribution piping, and connecting plastic hoses.

Water related problems in the Ring Magnet Cooling system has been:

1. Plugging strainers on both manifolds that feed the Rf cavities and power amplifiers.
2. The small flow switch on the power amplifiers have had to be replaced.

Comments:

- ❑ The potential presence and migration of copper oxides indicates the usefulness of main stream fine filtration (1 or 5 microns).
- ❑ High voltage DC has the potential to dissolve metals galvanically, as well as to cause galvanic deposition. In order to minimize these effects, water should have the very highest achievable resistivity.
- ❑ High Voltage DC produces in high purity water not primarily bulk electrolysis, but oxidizing species and radicals (Brown Boveri research results). This has to be considered with regard to materials performance. - The mentioned investigation has been made at 12 kV DC. It is probable that such effects may be negligible at lower voltages such as 2 kV. - Radiolysis in the radiation field will however provide such species.

4.4.8 HEBT/Ring/RTBT Magnet Power Supply Cooling Systems (RN-03, HS-01, RS-01)

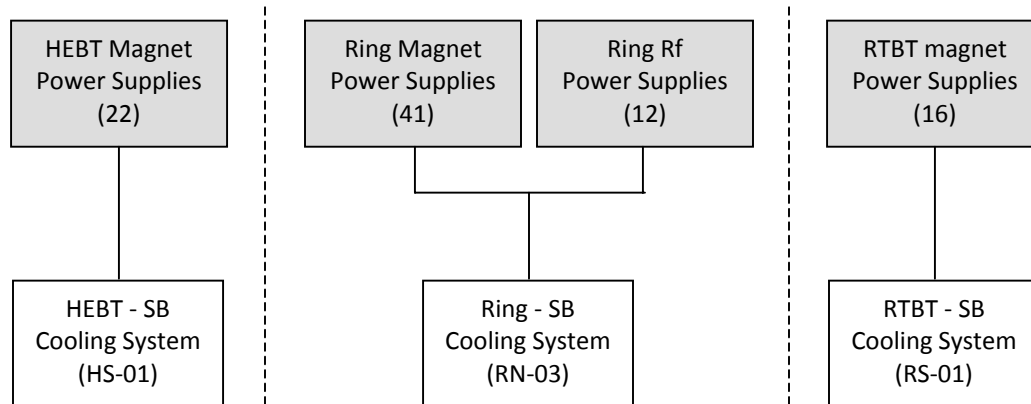


Figure 4-13. . Ring Magnets and Rf power supplies cooling (HEBT: High Energy Beam Transport from Linac to Storage Ring, RTBT: Ring to Target Beam Transport from Storage Ring to Target, SB: Service Building)

There are three (3) separate service buildings that house the magnet and Rf power supplies for the HEBT/Ring/RTBT tunnel magnets and Ring Rf cavities.

The materials in contact with these cooling loops are copper, brass, 304 stainless steel, plastic hoses, and a few iron fittings with the Rf power supplies.

The water treatment skid is similar to RN-02 (paragraph 4.4.7). There is no filter in the main systems, only a 20 mesh (840 micron) strainer. The gas detraining device is in main loop.

Water related problems in the Service Building (SB) cooling systems have been:

1. Initially variable pressure balancing valves were installed on each power supply to minimize the amount of flow balancing required on these systems. The valves that were used were Griswold valves with variable area orifices in them to maintain a set flow over a range of differential pressures. These valves worked very well initially, but within a year the valve orifices started plating copper over the orifice area dropping the set flow to each supply. The valves were finally removed from the system and periodic flow balancing is required for the system.
2. The power supplies have piston type flow switches as interlocks for low flow to the power supplies. These switches fail periodically due to copper coating the shuttle.

Comments:

- ❑ First of all, the nature of the deposits should be clarified (XRD analysis). Is it metallic copper or is it copper oxide. It may easily be possible that the Griswold valve orifices suffered plate-out from oxides, while the insulation hoses, where the DC voltage drop takes place, are plated with metallic copper.
- ❑ If the plate-out material is indeed metallic copper, and not copper oxides then a moderate oxygen level (10 - 30 ppb) would be beneficial to transform the metallic deposit into its less conductive oxide. Drawback is that such way larger quantities of oxide are produced.
- ❑ If the plate-out is copper-oxide, then
 - minimizing oxygen content of the water
 - maximizing mixed bed filter flow, and
 - using 1 or 5 micron (or smaller) main stream mechanical filtration would be beneficial

4.4.9 HEBT/Ring/RTBT Collimator Cooling Systems

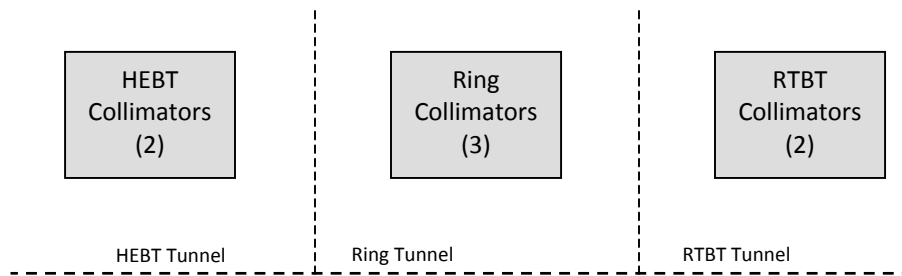


Figure 4-14. Ring Collimator cooling system (HEBT: High Energy Beam Transport from Linac to Storage Ring, RTBT: Ring to Target Beam Transport from Storage Ring to Target)

There are three (3) separate operating collimator cooling systems, one located in each of the HEBT, Ring, and RTBT tunnels. Due to the cooling water being exposed directly to the accelerator beam all the cooling skids and associated piping are located in the tunnels. The HET, Ring and RTBT collimator cooling systems serve 2, 3 and 2 collimators, respectively. The Ring system also cools the upstream scrapers. A fourth collimator system, which served the HEBT Momentum Dump, is no longer in service.

The materials in contact with these cooling systems are either 304 or 316 stainless steel. There are no rubber hoses used in these systems.

Problems encountered in these systems have been:

1. Pump trips and/or failure due to gas generation within water in the collimators
2. Rapid fouling of mixed bed resin during high beam power into the HEBT Momentum Dump collimator system

Comments:

- ☐ What species caused the fouling of the resin?

4.4.10 Ring injection dump loop (RID)

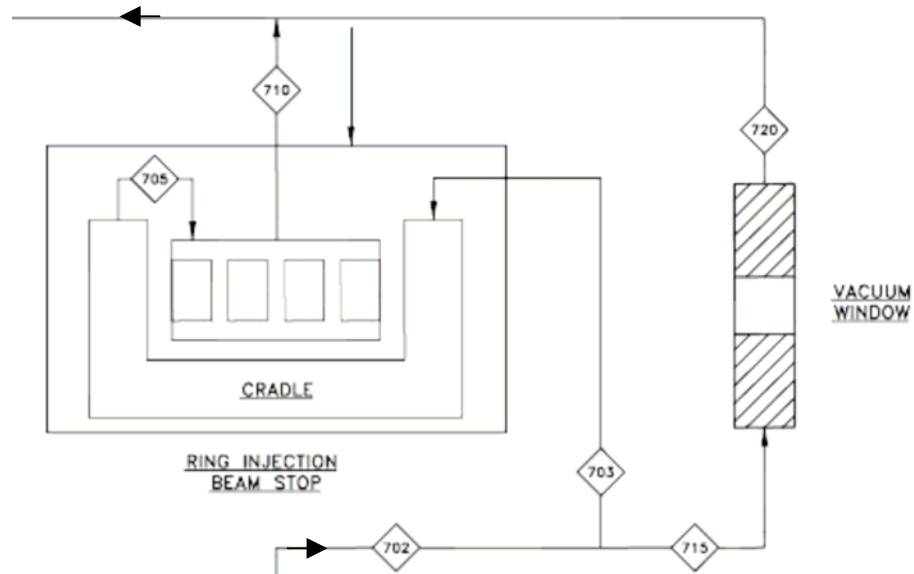


Figure 4-15. The cooled components in the RID cooling water loop.

The RID cooling water loop comprises the following components:

Components to be cooled:

- ❑ Cradle
 - flat water channels (2" x 0.5") in 316L stainless steel
 - water inlet / outlet temperature: 33 / 37°C, maximum local temperatures: water 90°C, surfaces 132°C
 - > the outlet water then feeds in series the beam stop
- ❑ Beam stop
 - 26 copper plates in 316L stainless steel casing; one flat water channel in each of the copper plates, channel height 1.125 mm (widened to 3.375 mm at U-turns), estimated copper surface 3.7 m²
 - water inlet / outlet temperature 37 / 53°C, max local temperatures: stainless steel front plate 226°C, copper 103°C, water 115°C (boiling temperature 138°C); water velocity in channels 1-2 m/s except for side areas where it is lower
- ❑ Vacuum window
 - domed double walled 316L stainless steel structure, wires are welded to the inside of the inner wall as to form a labyrinth of cooling water channels of 1.6 mm height between the walls
 - water inlet / outlet temperature 33 / 34°C, max local temperatures: if beam is

centered: stainless steel 125°C, water 80°C, if beam is offset beam stainless steel 132°C, water 90°C

Auxiliary components:

- ❑ Pumps, coolers, delay tank (for decay of radioactivity), gas separation tank (full flow), vent- and drain system
- ❑ Water treatment loop
pre-filter (to remove suspended articles) -> mixed bed -> after filter (to catch possible resin fines)
- ❑ Sampling system
for withdrawing aqueous samples

Cooling is done with light water. The system is subject to intense proton and neutron radiation, causing activation and radiolysis. The whole cooling water system is in a suitable containment; the removable mixed bed resin tanks in heavily shielded mobile containers.

The system is kept under a nitrogen blanket to control the hydrogen concentration in the separation tank below the lower explosion limit. The radiolytic gas, together with the nitrogen, is then vented off via a special off-gas treatment system. During shutdown, or when the system is (partially) drained, the system is conserved under nitrogen. Earlier efforts with vacuum drying have proven to be impracticable (too large quantities of residual waters in non-drainable pockets and no vacuum pre-condenser).

Comments:

The total metal surface of the cooled components is rather small; copper surface is estimated to be in the order of 1 - 10 m². Besides copper, 316L stainless steel is also used.

While global water temperatures are relatively low, they can have rather high values locally (80-115°C). Metal temperatures can also be locally high (125- on the outside 226°C). Water boiling temperature is on the order of 138°C (beam stop).

The water is subject to radiolysis, that is the production of H₂ and O₂ gas, as well as all the intermediaries and radicals, many of them with a stronger oxidizing potential than O₂ gas.

The gas separation tank is the only feature to control oxygen gas, and there is hardly any device that could control oxidizing radicals. The de-oxygenation in the separation tank is however not very efficient as contact between gas and liquid is limited. The original design intent was to remove bulk gas produced by radiolysis, not removal of oxygen to parts-per-billion levels. Water

entering the tank free falls approximately 12" to the water surface, creating splashing and turbulence that provide some mass transfer with the nitrogen cover gas. Internal baffles then direct and slow the fluid to allow bubbles to rise and separate from the water. For de-oxygenation, a more efficient mass transfer between water and the gas would be needed; in water treatment practice this is either done by spraying or percolating the water in the gas phase, or by bubbling the gas through the water volume. It is acknowledged that such efforts may be inappropriate in such a radioactive system.

One possibility to catch the radicals would be to add hydrazine to the water (at these temperatures it is too slow to control oxygen gas O_2). Besides possibly having a doubtful effect, this would be a practice with no broad reference.

It has to be expected that under such conditions the copper surfaces will oxidize. High local temperatures or temperature gradients may induce oxide migration and re-deposition. The small channel heights as well as the step in channel height in the beam stop could be two of the risk factors. Although never observed on stainless steel stator hollow conductors, re-deposition may also be possible on stainless steel surfaces (window, cradle).

In view of the limited service life of these components, and the relatively small copper surface area, action may therefore not be necessary. Attention should however be given to the possibility of deposits.

Another risk factor is the oxidizing environment for the stainless steel components, especially at those elevated temperatures. While the oxygen concentration may not be a real problem, small quantities of oxidizing radicals may already strongly increase the metal potential, thus the susceptibility to pitting corrosion, crevice corrosion, or stress corrosion cracking. It is seen in Figure 4-16 that, at the same concentration, hydrogen peroxide has a much stronger oxidation potential than dissolved oxygen. Figure 4-16 relates to SS304; behavior of SS316L is similar, except that the limit chloride concentrations are higher and equilibrium potentials are shifted, but the statement on the influence of oxidizing species would be the same. It is recommended to consider literature references [11] and [21] on this matter.

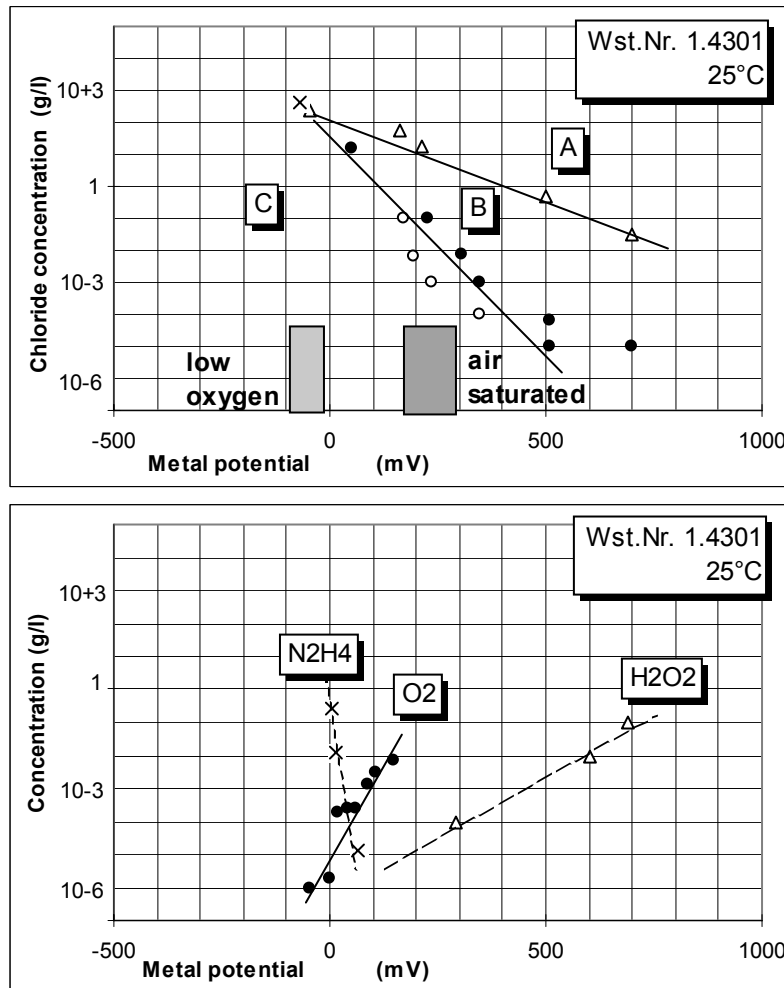


Figure 4-16. Behavior of stainless steel 1.4301 (type 304) in water [21].

The welding of wires to form the labyrinth inside the window structure adds another risk factor. Austenitic steels may become sensitized by the temperature regime of welding, causing risk for stress corrosion cracking around the welding zone. This risk is minimized by use of low-carbon steel (such as SS316L) or by stabilized steel (such as SS316Ti).

If, for one reason or another, the water does boil locally, then the corrosion risk will be even much higher. It is a traditional rule of boiler technology not to use austenitic tubes for evaporators.

To sum it up, it has still to be seen if the stainless steels used, even if it is SS 316L, will cope with the environment on long term. The use of Inconel or other resistant alloys may well be worth considering for the window.

With the present materials, the best solution is to assure very high purity water, that is >10Mohm.cm resistivity as limit, >15 Mohm.cm target.. As alternative for the 15 Mohm.cm target, a chloride limit of < 2 ppb can be applied. In this regard, it is strongly recommended to use only special nuclear grade, low chloride mixed bed resin, such as Amberlite IRN160 or equivalent.

It is acknowledged that the 2 ppb chloride limit may be hard to monitor. Techniques are however available in BWR power plants. Tips are given in paragraph 8.3.

5. RECOMMENDATIONS

Nr	Recommendation
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Water Treatment Regime

- 1 Aim for highest water purity (highest resistivity)
- 2 Have mixed bed bypass always at 3% of main stream flow or more
- 3 Keep oxygen level < 20 ppb
- 4 Evaluate alkalization of this high purity water
- 5 Other types of treatment are not useful in high purity waters with present metallurgy
- 6 When changing loop water chemistry, consider chemical pre-cleaning

System Design Upgrades

- 7 Consider full main-stream filtration, 5 micron or smaller, rinse new elements before use
- 8 Add make-up water upstream of de-ox and mixed bed (may need a booster pump)
- 9 Place de-ox column always before a mixed bed
- 10 Verify the efficiency of the gas detraining features, upgrade if required
- 11 Remove any carbon steel objects and components from the systems (ongoing)
- 12 Move uv treatment upstream of mixed bed

Chemistry Monitoring

- 13 Monitor on-line: Conductivity, possibly ECP (EPRI)
- 14 Monitor with transportable panel: Oxygen
- 15 Monitor with grab samples: pH (par. 8.5), Cu (but improve sampling, par. 8.3)
- 16 Corrosion coupons: not useful in such systems
- 17 Monitor mixed bed performance
- 18 Monitor de-ox column performance
- 19 Calibration and maintenance of chemistry monitors should be done by a chemical technician
- 20 Monitor make-up consumption in each loop (water totalizing meters)
- 21 Monitor flow and Δp at each component as far as possible (...)

Chemistry Related Maintenance

- 22 Make and implement a concept for preventative maintenance
- 23 Make and implement a concept for long-term repeat condition testing

Processes

- 24 When choosing new processes, involve the process owner
- 25 Make and implement water chemistry concept
- 26 Define and implement competences / responsibilities for SNS chemistry management
- 27 Make and implement concept for lay-up (conservation during shutdown)
- 28 Make concept for chemical cleaning

Table 5-1. Recommendations to be considered for implementation in the pure water systems.

5.1 Water treatment regime

It is recommended to use only very high purity, low oxygen water chemistry in all cooling loops.

Target should be the highest achievable resistivity (>15 Mohm.cm). Normal operating values should have a resistivity > 12 Mohm.cm, and the specification limit should be >10 Mohm.cm (at reference temperature 25°C).

Depending on the individual loop requirement, lower resistivity may temporarily be acceptable, as long as the pH does not pass into distinctly acidic ($\text{pH} \leq 6.5$).

Resistivity fluctuations at >12 Mohm.cm are normal and should be considered as being of no concern. Resistivity values should be regarded with 2 significant digits.

The oxygen concentration in the water should normally be <5 ppb, with a specification limit <20 ppb. The value of such oxygen values is however limited, see also paragraph 7.7.2. Efforts should be made to control all possible causes of potential sources of oxygen ingress

Lower resistivity per se does not provide any corrosion protection. The effect will depend on pH, and an uncontrolled low resistivity may increase the corrosion risk.

In order to control resistivity and to minimize the transport of dissolved substances (like Cu^{++}), the mixed bed should be operated at the maximum reasonable flow. The present equipment is designed for 1-5% of main system flow. A normal operation flow of 3% seems a reasonable compromise.

Alkaline treatment may be useful in order to mitigate the migration of copper in the system and in such way reduce the risk of deposits. It can however not prevent the oxidation itself (paragraph 7.4.3), it just induces the oxide to stay in place. Disadvantage of alkaline treatment is the decrease in resistivity that can increase electrochemical, galvanic or electric effects, which may be a problem especially with high-voltage DC components. Alkaline treatment requires significant efforts for operation, monitoring and maintenance, which could easily end up in an undesired situation when done in all 24 cooling loops. Besides, the activation of Na to Na-24 may lead to radiation issues.

Alkaline treatment is usually done by addition of NaOH. It is however also possible to use other products; hydrazine has already been mentioned (4.4.6).

Alkaline treatment is therefore an option to be considered only in case that present performance is severely unsatisfactory and other better options are not suitable. At the moment there seems to be no need for it. It is of course reasonable to test such treatment, with regard to operability, on a non-critical cooling system.

Other types of water treatment are neither necessary nor really useful with the present metallurgy. The use of proprietary products is not advised for pure water systems- they make chemistry unnecessarily complex and obscure.

It is questionable if the small side-stream sterilizing device is effective to control bacteria growth throughout the whole system. If microbiologically induced corrosion is a real issue at SNS, then it is recommended to consider EPRI experiences and recommendations [24][25].

When changing a loop's water chemistry, then consider a chemical pre-cleaning in order to have clear start conditions for a stable oxide layer on the copper.

5.2 System design upgrades

Fine filtration in a small bypass stream is not effective in controlling suspended solids (and their deposition) in the main loop. It is recommended to install a full stream filter with 1 μm or 5 μm selectivity. Recommended choice of filter elements: Cuno Polynet. New filter elements should be rinsed before first use.

The make-up water should be added upstream of the de-oxygen device and mixed bed, so that this water is subject to a fine polishing before entering the main loop. Although it may require a booster pump, it eases requirements on make-up water (which should nevertheless have a resistivity > 2 Mohm.cm before entering the clean-up bypass).

A chemicals based de-ox column as well as uv-sterilization should be placed upstream of the mixed bed so that possible leaching chemicals and organic decomposition products are removed. Physical de-oxygenation units (e.g. Liqui-Cel) do not release chemicals and may therefore be placed more freely.

Efficient gas detraining should be done directly in the main loop. In most cooling systems, a cyclonic air separator is installed downstream of each pump discharge. There is the question, if this separator is also efficient for small air bubbles. If gas bubbles emerge to be a problem in some of the loops, this item needs to be followed up.

If any, all carbon- or low-alloyed steel objects should be removed from the high purity cooling water systems (example: the KL-HVCM water/oil heat exchanger). Such objects will corrode and produce Fe-hydroxides that may transform, with time, into magnetic Fe_3O_4 , or even release Fe particles. These impurities may cause fouling of heat transfer surfaces and electric bridging on insulation hoses. Magnetized particles in alternating magnetic field may damage component surfaces; such "magnetic termites" have caused hollow conductor perforations in generators.

5.3 Chemistry monitoring

Parameter	Importance	Monitoring frequency	SNS
Instruments:			
Conductivity	most important chemical parameter	continuous	(1)
pH	no good in high purity water	-	(2)
Oxygen	useful	continuous	(2)
Electrochemical Potential	most promising novel technology	continuous	(3)
Coil / bar temperatures	critical parameter	continuous	
Coil flow	critical parameter	continuous	(4)
Δp coil inlet / outlet	important indicative information	continuous	(4)
Δp gas / water	important parameter	continuous	n/a
Hydrogen leakage	important parameter	daily	n/a
Make-up consumption	good indicative information	daily	(5)
Laboratory Analysis:			
Copper concentration	limited usefulness	4 weeks or as needed	(6)
Copper in ion exchanger	good indicative information	at each resin change	(7)
Other parameters:	plant specific	-	(8)

Table 5-2. Chemistry related monitoring in generator cooling loops, and recommendation for SNS (last column)

- (1) continuous measurement in every cooling loop, main loop
manual measurement at each mixed bed outlet, if conductivity in main loop is elevated
- (2) manual measurement in main loop, monthly or as needed
- (3) to be evaluated for continuous measurement in each loop (instead of an oxygen monitor)
- (4) due to its large number, it is not possible to monitor each component for flow and pressure drop. Measurement for groups of components may however be efficient. Manual measurements monthly or as needed
- (5) manual reading of an integral water counter or totalizing flow meter (to be installed), weekly or as needed
- (6) manual grab samples, monthly or as needed
- (7) manual, at each change of resin and of the mechanical filters; see special procedures
- (8) corrosion coupons are not useful in a low-temperature, high purity water system. Possible effects will be small and masked by coupon handling effects

5.4 Chemistry related maintenance

5.4.1 Preventative maintenance

It is assumed that SNS already has a philosophy for preventative maintenance. The following view from a power plant perspective may add additional ideas.

In order to assure plant availability and to reduce operating and maintenance costs, it is important that maintenance tasks are focused on the right equipment at the right time. Preventive maintenance (PM) can be an effective tool for improving plant performance. However, improperly applied PM can be an expensive exercise in futility. Effective PM programs adhere to the vendor technical manual and follow up experience from other plants. It is also prudent to focus PM on critical components, that is components whose failures would compromise plant availability or cause other high costs. A thorough review of all system components will identify those whose failure will lead to such serious consequences. It is recommended to set up a plant specific Preventive Maintenance Plan.

Although not key issues, the following should be included in the Preventive Maintenance Plan:

- develop a concept for the expected lifetime of the mixed bed resin; criteria could include increased mixed bed outlet conductivity, insufficient retention of dissolved copper (leakage >20%), a fixed service interval. Use only factory fresh gel type nuclear grade resins
- develop a concept for the expected lifetime of the mechanical filter elements; criteria could be high pressure drop (as limited by the filter vendor, and as tolerable for system operation), and a fixed service interval (e.g. 2 years)
- develop a concept for the expected lifetime of the de-ox column; criteria could be failure of oxygen retention (e.g. oxygen at outlet > 5 ppb), and a fixed service interval (e.g. 1 year, and / or after introduction of a certain quantity of air saturated make up water)
- develop criteria for cleaning of components (paragraph 5.5.4) and a concept for implementation
- develop criteria for replacing insulating water hoses; this can be based on technical criteria (radiation damage, fouling, deterioration), and as well as on a fixed service interval
- Calibration and maintenance of chemistry monitors should be done by a chemist in order to include the sensor in this process

5.4.2 Condition testing

Make a concept for regular inspection and testing of key components, or of components typical for a set of similar ones. Such could include for example:

Remove hoses from a component and inspect inlet and outlet openings of technical components for deposits; make a standardized air (or water) flow pressure drop test across the component and compare with former values, check the condition of windows that separate vacuum parts from cooling water system (RID window, KL wave dump etc). Possibly make destructive testing if a spare is available for easy replacement. Every time, when terminally removing a component from service, use the chance for destructive testing (cut open, measure deposit thickness or wall loss, take and analyze deposit samples by XRD for their nature and structure etc).

It is acknowledged that such testing may require substantial efforts on materials, time and personnel resources and may even introduce risks to the equipment. However, rigorous condition testing has proven to be a valuable tool in power generation to avoid costly failures. It is recommended to have such testing program set up by an unbiased group or person. Have a plan and keep a regular budget on this.

5.5 Processes

When adapting any feature or process of the SNS to a solution from another technology, it is strongly advised to do this only with direct involvement of the technology owner or persons who know the background and experience first hand. (Example: for dual-bed alkalization call on Eskom or on their retired specialist). It is hard to get all the essential fine information just from published media.

5.5.1 Water chemistry concept

After having clarified the issues and recommendations of this report, it is suggested to set up a single water chemistry concept common to all of the SNS cooling loops.

It could comprise for example:

- scope of the water chemistry concept:
 - minimize corrosion
 - minimize deposits
 - maintain high electric insulation (where applicable)
 - minimize activation and transport of activated species (where applicable)

- water treatment regime: see paragraph 5.1
deionized water with highest purity, low oxygen content for all
- design features to maintain water purity:
system materials: stainless steel, copper, selected plastic materials (hoses); airtight system; no water consumption so only little need for make-up; etc.
- water purification methods: see paragraph 4.3, 5.2 and Table 5-1
1-5% cleaning bypass normally operated at 3% or more
- chemistry monitoring: see paragraph 5.3
- chemistry-related preventative maintenance: see paragraph 5.4.1
- condition testing: see paragraph 5.4.2
- lay-up: see paragraph 5.5.3
- cleaning concept: see paragraph 5.5.4

5.5.2 Competences and responsibilities for cycle chemistry management

It is neither the scope of this review and certainly not the intent of the reviewer to look into SNS organization and give recommendations. It is however useful to draw attention to this item. Clearly defined competences and responsibilities, especially who makes rules and who implements them, facilitate efficient chemistry management.

5.5.3 Lay-Up

Corrosion resistant materials in the SNS cooling loops, together with the high purity water do not necessitate special corrosion protection for lay-up. However, certain measures are recommended in order to avoid excessive formation, release and migration of copper oxides.

It is recommended to follow the experiences from power plant generators as given in paragraph 7.6.

It is best to leave the system running.

If this is not possible, it can be left set idle for a limited period of time. The time limit is essentially given by the point when the water quality starts to deteriorate (oxygen, conductivity). This is case specific.

For long-term lay-up "drain and dry" will be the choice.

- Draining the water from the loop
- Isolating off any components that are not to be dried (e.g. mixed bed tanks)
- A series of blow-downs with compressed air
- Pulling a vacuum on the loop
- Monitoring dew point

The loop can be considered to be dry when the dew point is well below the coldest possible point of the component.

If such process of "drain and dry" cannot be successfully implemented, then as an alternative it is recommended that when draining the water is replaced by nitrogen, and the loop then be left filled with nitrogen together with the residual water. It is important to prevent air entering such a loop.

5.5.4 Cleaning

It is recommended to have a philosophy regarding cleaning of the system and / or its components, and to have processes available already before troubles have appeared. Recommended literature: references [3] and [9].

When is cleaning required?

The latest point, when cleaning is brought into consideration is when deposition has occurred and deteriorated the operating environment (e.g. local cooling, water flow, pressure drop etc.).

It is also possible to take a pro-active approach and perform cleaning at an earlier stage, before problems have become visible. Criteria might be:

- awareness of an occurrence of badly insufficient lay-up
- visual observation of significant deposits in the loop components
- regular cleaning as part of long-term preventative maintenance

Note:

- ☞ Hollow conductors that are completely blocked and do not have any water flow cannot be cleaned by any type of chemical cleaning. They require a preceding mechanical cleaning.
- ☞ cleaning does not eliminate the cause of plugging; re-occurrence cannot be excluded. Cleaning thus is not the final solution to the problem.

- ☞ Never wait for cleaning until flow and temperature conditions have strongly deteriorated; perform cleaning beforehand. A late decision for cleaning may rush the use of non-optimized methods, may cause loss of plant availability, may result in equipment damage and produces more compact deposit layers that become more and more difficult to be removed. A pro-active approach is recommended to take early action before symptoms are already evident is recommended.

Mechanical cleaning

Backflushing with air, water and or -more efficient- with an air/water mixture is capable of removing gross debris, but it is ineffective for removing oxide deposits.

If possible, nitrogen should be used instead of air in order to minimize oxidation of the copper surfaces. It is however acknowledged that in practice this possibility may be limited.

Another possibility is to back flush with slightly alkalized water in order to get a more favorable oxide layer (see the literature references). Use pH 8-9 with NaOH; consider that the CO₂ from air will lower the pH of this solution.

Chemical cleaning

- ☞ Warning: do not use any non-oxidizing acids (e.g. hydrochloric-, hydrofluoric-, sulfuric- or phosphoric acid). Such may disproportionate possible Cu₂O into metallic Cu and CuO. Deposits of metallic Cu are certainly not compatible with cooling of electrical systems.

In the following it is assumed that any deposits to be removed are copper or copper oxides. Other types of deposits will merit specific consideration.

Acid cleaning is recommended only for targeted cleaning of individual components. It is not recommended to clean a whole loop by a global acid flush, because corrosion attack or even re-deposition of dissolved species may occur.

If an acid is used, it is recommended to use citric acid. This has proven to be effective with plugged generator stator bars. [20]. Although citric acid is not oxidizing, it provides the desired effect as it is at the same time a complexant.

More efficient, but even more aggressive is the use of ammonium-peroxo-disulfate [9].

It must be indicated that any acid cleaning removes base metal substantially [9][20], and presents a risk for other metals (e.g. braze) and possible dissimilar metal joints.

Complexant cleaning is understood as cleaning by use of complexing agents (chelants). This is a soft cleaning process that can be applied as a global flush throughout the whole loop. The chemicals, together with the dissolved copper, are removed with the mixed bed, thus offering a zero-liquid waste process.

Not all complexants are suitable. Most commonly, Disodium-EDTA is used. EDTA reacts only with CuO, and not with Cu(met) and Cu₂O. In order to dissolve also Cu₂O, hydrogen peroxide is added. It is essential that a coordinated balance between these chemicals is applied. Otherwise there is risk of incomplete cleaning, production of excessive amounts of oxides, or increase of plugging, or increased risk of plugging within a short period of restarting the system.

It is recommended to consider the Alstom Cuproplex® process [10]. It has been applied on power plant generators up to date 182 times since 1980. The process has been reviewed, besides others, by Ontario Power who also investigated materials attack, which was found to be negligible [20].

6. REFERENCES

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7. APPENDIX A: WATER COOLING SYSTEMS FOR POWER PLANT GENERATORS

7.1 Cooling configuration of the generator

The generator casing houses the stator, the rotor and other components. The heat losses of the generator require cooling. In small turbo-generators, and in all hydro-generators, primary cooling is achieved by forced recirculation of clean air within the housing. Due to its larger heat removal capacity, hydrogen gas at some 3-4 bar pressure is used in larger turbo-generators. In this case, the generator housing has to be sealed against atmosphere. Generators larger than approximately 300 MW usually have additional cooling of the stator bars, some also of the rotor bars, with water.

It is therefore worth to note that in water cooled turbo generators the water is usually saturated with hydrogen, by leaks or by diffusion, while in hydro generators, there is some very small diffusion of oxygen and of carbon dioxide into the water.

7.1.1 Stator cooling

The stator consists basically of the conductors embedded into an iron core. These conductors are in the form of stator bars, of typically 3 x 8 cm -or larger- cross section and up to 12 m length (Figure 7-1). Each stator bar consists of a certain number of sub-conductors, insulated against each other in order to reduce eddy currents. In water-cooled stators, some (or all) of these sub-conductors are rectangular hollow tubes, commonly called "hollow conductors" (Figure 7-2). Depending on design and manufacture, their inside dimensions are typically 3 to 10 mm wide, 1 to 3 mm high, 3500 to 12000 mm long, and they are packed into the stator bar with numerous bends (Roebel transpositions). These small cross sections and the bends make the hollow conductors susceptible to plugging by copper oxides that are generated in the cooling water system.

The solid sub-conductors are always made of pure copper. The hollow conductors can also be of pure copper, but stainless steel is as well used successfully and with good reference. - The sub-conductors are often referred to as "strands".

At their endings, the hollow conductors are brazed (in case of copper) or welded (with stainless steel) onto a tube plate, which is part of the water chamber (sometimes referred to as "clip") that collects the water from all hollow conductors of a bar. This attachment is often referred to as "clip-to-strand" connection. Some brazing materials have caused corrosion and leakage of the clip-to-strand connection.

The water chambers are then connected via Teflon hoses to stainless steel collector pipes (typically 5 to 10 cm diameter) that provide the connection into the stator cooling water

system. Teflon hoses (typically 18 mm inner, 26 mm outer diameter, 30 to 100 cm length) are used in order to provide electrical separation between the stator bar end (up to 26 kV AC voltage) and the cooling system that is at ground voltage. For this electrical separation it is also necessary that the Teflon hoses stay clean and will not become covered by conductive deposits, and that the water has a high resistivity.

Depending on design, there are typically between 6 and some 50 hollow conductors in a single bar. All hollow conductors of a single bar are hydraulically in parallel. The stator bars themselves may be all in parallel by themselves, or in groups of 2 (in hydroelectric generators often 4 or 6) in series. Taken as example 72 bars all in parallel, and with 32 hollow conductors each, this means that there are $72 \times 32 = 2304$ hollow conductors also all in parallel. Plugging of a single will therefore not be noticed by monitoring temperature or flow, but may already lead to local overheating.

Typical copper surface area of such a water cooled stator is 200 - 500 m².

7.1.2 Rotor cooling

The principle is the same as with stator cooling; there are however major differences. Most notably is that the sub-conductors are much larger, and usually contain only one circular cooling channel inside, with an opening of typically 8 - 10 mm. The voltage against ground is considerably smaller, only a few hundreds of Volt and -also different to the stator- DC.

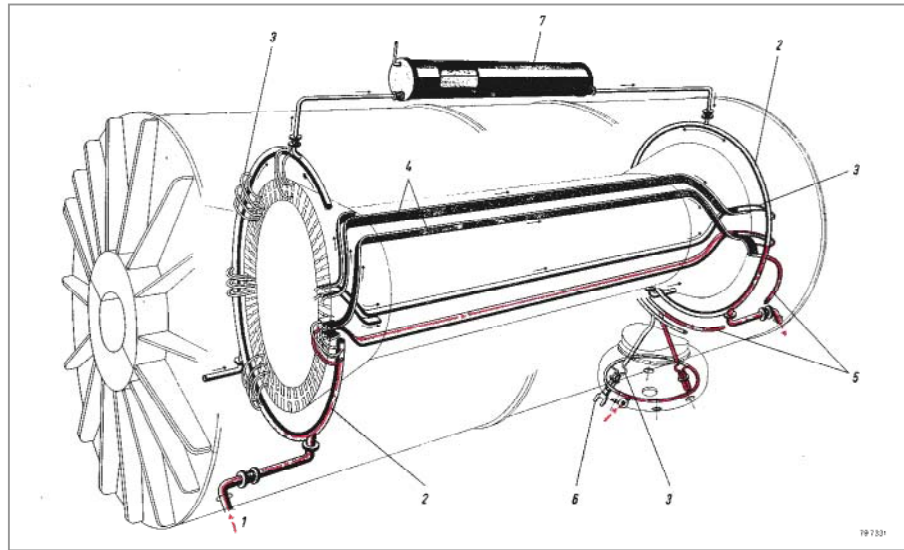


Figure 7-1. Schematic view of a water cooled stator. For clarity, only four stator bars are shown. (1) cooling water inlet, (2) distributor ring for cooling water, (3) electrically insulating water connecting hoses, (4) water-cooled stator bars, (5) water-cooled phase connectors and (6) water cooled terminal bushings, (7) head tank / expansion vessel (Alstom / BBC design).

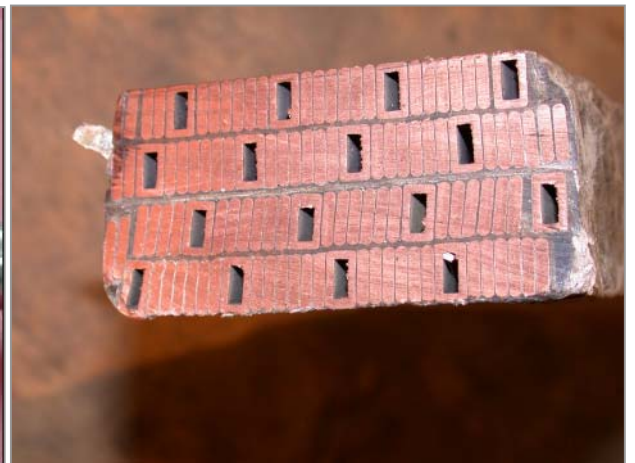
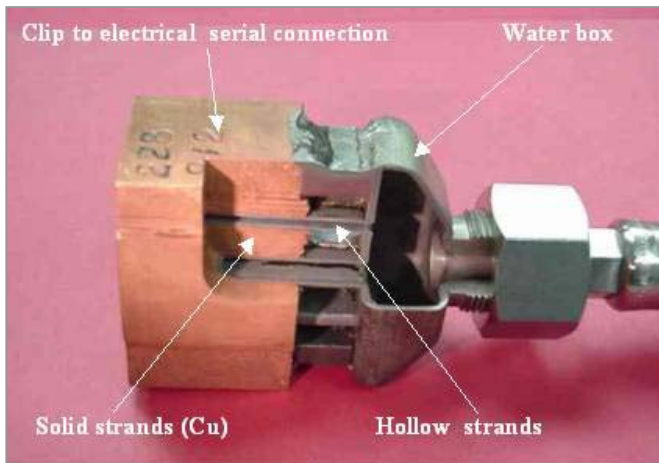


Figure 7-2. Left: cross section through a water chamber, with connection of the hollow conductors, in this case made of stainless steel. Right: cross section through a stator bar; all sub-conductors are here made of copper. (Alstom / BBC design).

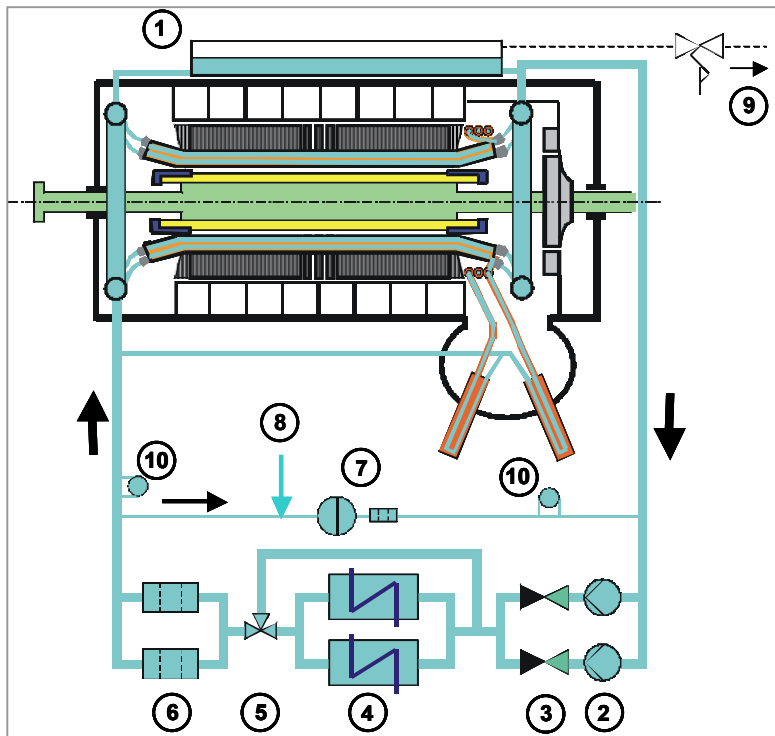


Figure 7-3. Stator water cooling system for low-oxygen chemistry (Siemens, ABB).

(1) Head tank with hydrogen cap (stator water tank), (2) pumps, (3) check valve, (4) coolers, (5) temperature control valve, (6) filters, (7) mixed bed and resin trap (strainer), (8) make-up feed, (9) vent, (10) conductivity cells.

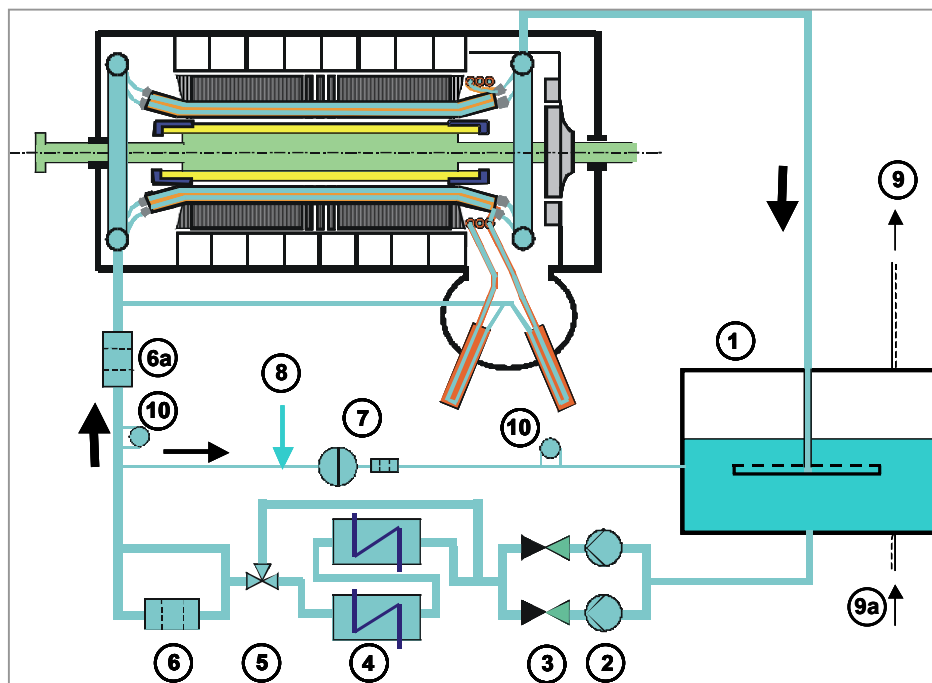


Figure 7-4. Stator water cooling system for high-oxygen chemistry (GE, approx. Alsthom).

(1) Stator water tank open to air, (2) pumps, (3) check valve, (4) coolers, (5) temperature control valve, (6) filter, (6a) strainer, (7) mixed bed and resin trap (strainer), (8) make-up feed, (9) vent, (9a) air injection, (10) conductivity cells

7.2 Generator cooling water system

The details of a generator cooling water system also vary with design. All have however in common:

- recirculation pumps
- full stream coolers with a thermostatically regulated bypass
- 100% mechanical filtration
- bypass ion exchange filters
- some sort of expansion vessel, "stator water tank"
- vent
- make-up water connection
- in-line conductivity cells

The cooling water systems typically have a water volume of 1-7 m³, most commonly 2-5 m³. Recirculating cooling water flow is typically between 40 - 150 m³/h.

Some of these features merit a closer look in regard to the SNS cooling systems.

7.2.1 Recirculation pumps

These are usually large pumps, with sliding seals (usually graphite against hard metal). Deterioration of these seals with time is common, leading to water leaks or even air-inleakage.

7.2.2 Coolers

All common types of coolers and materials are used. Besides service-water side corrosion, there are no special chemistry related issues with these coolers.

7.2.3 Mechanical filters

A large spectrum of mechanical filters is used in turbine generator cooling water systems. Some systems operate only with a 200 micrometers stainless steel strainer, on the other extreme are polypropylene cartridges with a selectivity of 1 micrometer. Common however is that all systems apply 100% filtration, to the whole cooling water flow.

Depending on the OEM, 1 or 2 x 100% filters as well as a bypass are provided. One OEM has an additional 100% fine mesh strainer near the generator inlet. There are many types of filters, the

- Stainless steel mesh, 15 to 100 micrometer
- Organic bound cotton or polypropylene fibers
- Sintered metal filters

- Thermally bonded polypropylene fiber filters
- Woven polypropylene yarn cartridges
- Pleated polypropylene fabric
- Multilayered polypropylene cloth filters

Some filters also contain coated magnetic plates in order to catch possible magnetic particles, which can cause severe damage in the generator.

Filter selectivity

Normally filter elements with selectivity between 1 and 20 micrometer are chosen. There is no unambiguous answer to what type of filter and what selectivity is best. Plants operating with 75 micrometer have their good reference and their share of problems, as do the plants operating with 1 micrometer cartridges.

Best filtration performance with regard to filtration effect and capacity (quantity of particles before running high on pressure drop) is achieved by depth filtration, as is done with thick or multilayered filter elements where the particles penetrate deeper below the surface. Strainers and meshes are surface filters and evidently have some disadvantage here. On the other hand, such elements can be cleaned and re-used which is not possible with depth-filters.

Filter materials and water chemistry

Purely metallic filters are straightforward to what they release into the water. If they are sufficiently clean before use, and if they don't break up, they will not release any impurities. Filter elements made of organic matter however carry a wealth of substances that may cause problems when released into the cooling water system.

Most evident are leaching impurities that increase conductivity when the filter is being put into service. These are usually manufacturing aids such as antistatic products for weaving yarns, lubricants for extrusion of threads, or decomposition products from temperature treatment. The filter elements should therefore be thoroughly rinsed, both at the factory as well as before use, especially after long storage. Some products wash out easily, while other are persistent and release substance even after prolonged use. - Indications of such products are increased conductivity and foaming.

It is also possible that the material degrades slowly under operating conditions, especially by temperature and possibly also by oxidation (high oxygen generators). The melamine matrix in older types of filters shows some degradation while in use and polyester seems to degrade so much that it should not be used in generator cooling systems. Cotton and Polypropylene have proven to be the most useful organic materials for the filters.

Attention is also required for the small parts in the filters. Problems have already arisen from inadequate rubber gaskets and O-rings, and especially glues that are used on some designs.

Some impurities that are released by the filters do not only cause high conductivity. There are cases where the impurity caused an increase of copper concentration in the stator cooling system. The cause of this effect was found to be the formation of a soluble organic Cu complex, and not an effect of pH that did not change during the event.

It is therefore recommended to use filters where all these aspects have been researched by the power industry, and where references in generator cooling systems are available. Filter manufacturers often miss the specific requirements of a generator cooling system.

Some system designs feature a continuous small water flow through the standby filter, in order to avoid the risk of a conductivity burst when the filter is put into operation.

In any case, all filter elements should be thoroughly rinsed prior to inserting into the cooling system.

Replacement of filter elements

Organic matter filter elements have to be replaced regularly. Criteria for generators are

- filter pressure drop
- administrative maintenance intervals
- the filter material should not be longer in service than 2 years

Examples

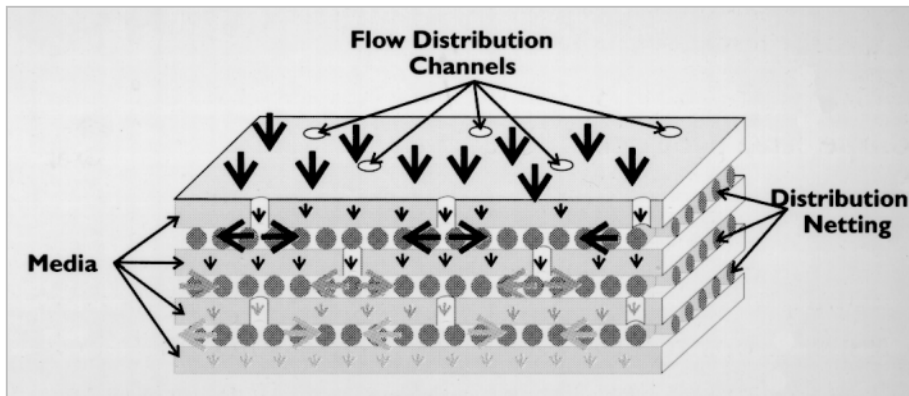
The two following photos (Figure 7-5) give examples of modern filter elements. The first one shows Pall sintered stainless steel cartridges that are especially useful where organic materials cannot be used (temperature, radiation etc). The second one shows a Cuno Polynet cartridge that combines high efficiency, high capacity, and a minimal release of leachable substances.



Figure 7-5. Elements for the mechanical filters.

Left: Pall sintered metal filters

Below: Cuno Polynet filters



7.2.4 Ion exchange filters

The ion exchanger usually consists of a mixed bed, followed by a resin trap. Even though mixed bed return usually is upstream of the filters that would also remove leaked resin and resin fines, the risk of depositing such chemically resistant material in the stator winding warrants the additional use of the resin trap.

The mixed bed has to remove soluble, particulate and colloidal species. Best are highly acidic / highly basic gel-type resin, in fully regenerated and flushed condition. It is recommended to use only factory fresh, gel type resin such as Amberlite IRN150.

The flow rate of the mixed bed varies with OEM. Low-oxygen systems. Some designs are content with 0.5-1% flow relative to stator water flow, other go up to 1-4%. High oxygen systems. As this water chemistry regime releases higher quantities of oxides, a higher mixed bed flow is required. The mixed bed flow is typically 10...20% of the stator water flow.

It is seen immediately that conversion of a low-oxygen system into a high-oxygen system would require major cooling system changes.

Usually there is only one mixed bed. Replacement during operation is easily possible, because the generator cooling system can be safely operated for a few hours without the mixed bed. The key parameter is conductivity. In case that the conductivity unexpectedly rises faster, then unexpected impurity ingress takes place (e.g. cooler leak, dirt etc), and good practice would be to eliminate the source and not to rely on extended operation with the mixed bed.

The mixed bed resin has to be replaced regularly. Criteria for generators are:

- system conductivity and mixed bed outlet conductivity
- calculated or measured loading with copper
- administrative maintenance intervals
- the resin should not be longer in service than 2 years

Only fresh, completely rinsed resin should be used, e.g. nuclear grade, gel-type resin. Used resin should not be recycled back to the stator water cooling system.

7.2.5 Water Tank, make-up water, gas detraining features

Every closed cooling system requires an expansion vessel with a gas cap. In addition, it also buffers the water volume in case of loss or addition of water, and gives the possibility to detraining gases that could cause problems in the stator.

One solution is to use a large main-stream stator water tank. Such tanks typically have a total volume of 3...6 m³, about 2/3 of this filled with water, and 1/3 with gas (hydrogen cap or air). There is sufficient retention time of the water to permit detraining of possible gas bubbles.

Another solution is a head tank on top of the generator. Such tanks have volumes from sparse 50 liters to some 400 liters. The tank is connected, via flow-control orifices, to the highest points of inlet and outlet water distribution manifolds of the stator. Possible gas bubbles are here transported into the head tank that provides sufficient retention time for gas detraining.

It is also possible to have the make up water tank in a dead end connected to the suction side of the pump. Water volume typically is 150 ... 300 liter, with automatic refill. Gas detraining is achieved in a separate gas detraining tank at pump suction. Retention time is sufficient to have the gas bubbles rise into the upper chamber, where a water level control vents off the gas automatically once it has accumulated a pre-defined quantity.

The make-up is usually introduced into the system either into the stator water tank, or upstream of the mixed bed, or into the head tank, Figure 7-3 and Figure 7-4.

7.2.6 Make-up water supply

Ideally, de-aerated make-up is used for low-oxygen systems, and aerated make-up for high-oxygen systems. However, de-aerated make-up is not available in all power plants, and it is possible to minimize oxygen ingress by minimizing the quantity of make-up water. It is also possible to de-aerate the make-up at the entrance point to the generator cooling system:

- ion exchanger loaded with oxygen scavenger
- thermal de-aerator
- stripping column with nitrogen
- stripping column with membrane separator
- catalytic recombination in a Pd loaded ion exchanger with hydrogen (present in the stator cooling water of most turbo-generators)

Generally those efforts are not necessary when the quantities of make up can be kept small.

7.2.7 Chemicals injection equipment (if any)

With alkaline water treatment, NaOH is added to the stator cooling water. It can be injected by:

- conventional conductivity controlled injection pumps
- controlled leaching from dual bed filters .

The first application of dual bed filters used a special weakly acidic cation resin downstream of the mixed bed. This cationic resin was loaded with a controlled quantity of NaOH. Design was such that with incoming high purity water the equilibrium of Na^+ at the filter outlet yielded the desired concentration for alkalizing. Such system is sensitive to anionic impurities that may pass the mixed bed and lower pH, in consequence upset the Na^+ equilibrium. This system has been proven in a series of power plants.

A relatively new development is the use of two parallel ion exchangers, one containing the mixed bed, the other one a strongly acidic cation exchanger fully loaded with NaOH. The Na concentration in the cooling water system is controlled by the adjustment of the flow through those mixed beds. The problem is that strong cation resins do not readily release the Na^+ from the resin; the equilibrium concentration is too small. This system has also been proven in a series of power plants, and one major utility has converted a good part of their fleet to this system.

As mentioned, both systems of dual beds have their sensitive points that have lead to oxide deposits in stators. It is therefore strongly recommended to seek advice from the respective developer when establishing such an alkalizing system.

7.3 Chemistry related problems in generator cooling systems

Corrosion-related performance has generally been good, but nevertheless a few issues have emerged on an industry-wide scale:

- Plugging of copper hollow conductors. If the stator cooling water contains oxygen, the hollow conductors release dissolved copper and / or copper oxide particles that, when re-depositing preferentially, may cause flow restrictions in the strands and thus impair cooling. This is the key chemistry related problem in stator water cooling , and will be discussed in more depth in this guide document.
- Clip-to-strand leak. Copper hollow conductors are usually brazed into the coil end water box ("clip"). It is known and considered in design that the usual brazing materials will dissolve slowly. A certain type of braze however produces acid as well as a corrosion potential between braze and copper such that the copper is corroded at a considerably higher rate. The corrosion rate is influenced by stator water chemistry, but the comprehensive solution is to select a more suitable braze material. Although this problem is limited to specific materials, a substantial number of generators have been affected .
- Conductivity of water. The electric conductance of water causes the generation of heat across the stator bar insulating hoses. It is required to keep the water below boiling because a steam blanket may cause electric discharge that can destroy the connecting elements. This is especially critical under out-of-normal low flow conditions. The acceptable conductivity limit depends on design and operating conditions. Usual limit values for safe generator operation are 5...20 $\mu\text{S}/\text{cm}$.
- Deposits on insulating hoses. These are no general concerns for AC applications, as on stator bars, but have been observed on water cooled DC applications like rotor bars or rectifiers in case of very low oxygen 1.

7.4 Basics of generator cooling water system chemistry

This topic has been presented in detail by the author in previous publications that shall not be repeated here. The CIGRE document represents the most recent and internationally reviewed update. It is public and can be obtained at a moderate price.

R.Svoboda, O.Jonas. Corrosion in Electric Generators. Chapter 16 of "Low Temperature Corrosion Problems in Fossil Power Plants--State of Knowledge Report". EPRI Report Nr. 1004924, Dec 2003.

R.Svoboda, H.G.Seipp. Flow restrictions in water cooled generator stator coils - prevention, diagnosis and removal. Part 1: Behaviour of copper in water cooled generator coils. Power Plant Chemistry, 6 (2004) 1, pg 7-14

CIGRE Guide on stator water chemistry management. Study Committee A1, WG A1.01-13. In preparation (www.cigre.org).

Under the conditions typically found in pure water systems, copper does not react with water in the absence of oxygen. Therefore an actual corrosion attack of copper in pure water systems is not to be expected.

Although copper is fairly passive in air and completely in deaerated pure water, it is rapidly oxidized in water under certain conditions of dissolved oxygen, pH and temperature. These oxide may migrate and re-deposit in the system, causing a deterioration of cooling.

A model for the mechanisms leading to copper oxide deposits that may reduce cooling is given in Figure 7-6

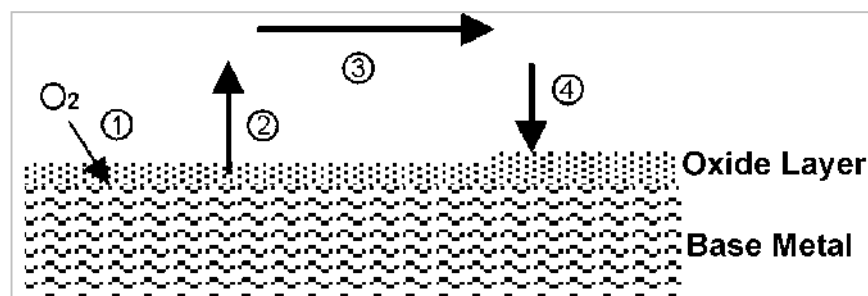


Figure 7-6. Schematics of the Mechanism for Hollow Conductor Plugging :
(1) Oxidation of the Copper, (2) Release of the Oxidized Copper (Particle or Ion), (3) Transport of the Released Copper, (4) Re-deposition of the Migrating Copper

A good water chemistry regime is essential in eliminating the root cause of plugging. Today there are five different water chemistries being applied (Table 7-1). Figure 7-7 shows the

chemical parameters for the different water treatment regimes, in combination with the copper release rates. Table 7-2 gives an overview of the frequency of the water treatment regimes. However, it should be mentioned that all these water treatment regimes have their success if operated properly, but none is without failures.

Type of Water Treatment	Keeps Oxidation Low	Keeps Release Rate Low	Direct Transport into Ion-Exchanger	Keeps Re-deposition Low
Low-oxygen / neutral	x			
Low-oxygen / alkaline	x	x		
High-oxygen / neutral		x		
High-oxygen / alkaline		x		
Cationic purification			x	x

x - target parameter for the respective water treatment

Table 7-1. Strategies for Water Chemistry to Prevent Plugging of the Stator Hollow Conductors.

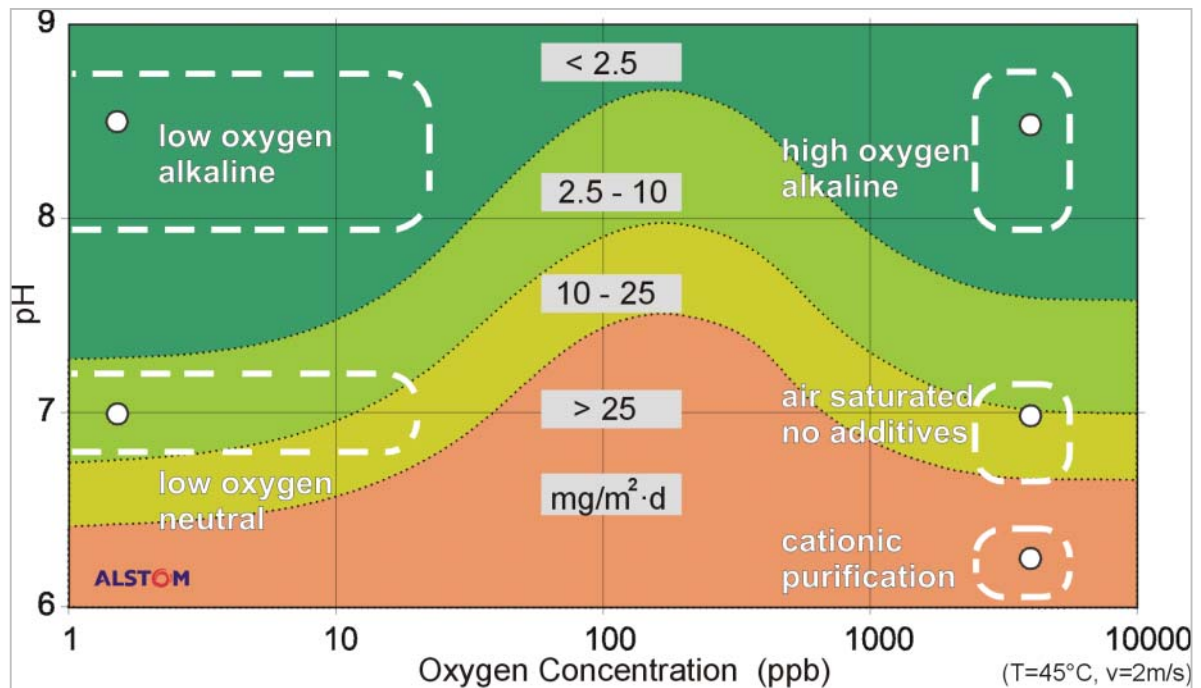


Figure 7-7. Copper release rate in dependence of pH and oxygen concentration. Region of application for various water treatment regimes.

Part of the world	Stators	Rotors	Stator water chemistry		
			high oxygen	low oxygen	hereof alkaline
World ex Russia & China	2000	80	1100	900	200
Russia	700	60	0	700	0
China	1000	many	0	1000	0

Table 7-2. Number of water-cooled generators worldwide, and type of stator water chemistry. These figures are approximate.

7.4.1 Low oxygen treatment

A low-oxygen system is defined as a system normally operating with 20 µg/l (ppb) of dissolved oxygen or less. Target is a stable oxygen level as low as possible, ideally zero. According to the EPRI guideline the generator should be scheduled for shutdown and repair if the oxygen level is > 50 ppb.

A low oxygen regime may be obtained with a well maintained system that has no leaks and hence no make-up. If periods between outages are limited the initial increase in oxygen level will have little effect on the winding condition.

Low-oxygen treatment can also be obtained by having the system sealed against air (for example, by a hydrogen or nitrogen gas blanket at a pressure slightly above atmospheric).

Problems arise when deaeration is violated by air in-leakage. Common causes for air in-leakage in low-oxygen systems are leaky flanges, valves or pump sliding seals, use of significant quantities of aerated make-up water, opening parts of the system for maintenance, or inadequate lay-up. It must also be recognized that air may even be sucked into a high-pressure system by a water-jet effect.

7.4.2 High oxygen treatment

A high-oxygen system is defined as a system normally operating with 2 mg/l (ppm) of dissolved oxygen or more. Target is a stable oxygen level corresponding to saturation of water in the water tank with air. According to the EPRI guideline the generator should be scheduled for shutdown and repair if the oxygen level is <1 ppm.

High-oxygen treatment is obtained by leaving the system (for example the water tank) open to air.

Problems arise when aeration is insufficient. Common causes for insufficient aeration in high-oxygen systems are hydrogen leaks into the water that replace the air cap in the water storage tank. In addition, oxygen is consumed slowly by the copper surfaces in the system. Regular or continuous feed of air may be necessary to maintain high oxygen levels.

High oxygen treatment can be regarded as the simplest form of stator water treatment, and is put into practice where oxygen cannot be excluded from the system. In this treatment regime, the objective is to form evenly distributed stable oxide layers (CuO).

There is always some dissolution of the oxide layer, but the dissolved copper is trapped by the ion exchanger. However, the risk of forming thick oxide layers cannot be excluded. In order to achieve a stable oxide layer, oxygen levels must be maintained high (e.g. forced air flow into the water tank) at all times. By introducing air, carbon dioxide is also added to the system. It is thus imperative to have a large mixed-bed flow (>10% of stator water flow).

With high-oxygen treatment, carbon dioxide is brought to negligible levels by the large mixed-bed water flow.

7.4.3 Alkaline treatment

Alkaline is normally understood to operate with a pH between 8.5 and 9.

Alkaline treatment is obtained by adding a small amount of dilute sodium hydroxide solution (NaOH) to the stator cooling water.

Problems may arise when the pH is not kept stable, for example either by irregular addition of NaOH, ingress of contamination, or by in-leakage of carbon dioxide from air.

Alkaline pH originated in low-oxygen water treatment regimes. Some high-oxygen systems have also been converted to alkaline with promising results.

In low oxygen systems, alkaline treatment does not reduce the amount of copper that is oxidized. As with neutral treatment, all oxygen reacts with the copper to form copper oxide, no matter what the pH is. With alkaline treatment, this process just takes more time.

7.4.4 Cationic purification

This is another variation of high oxygen treatment. The system is kept fully aerated which will result in a slightly acidic pH, ~ 6.0 - 6.5 due to the carbon dioxide from air. For a period of several months a single-bed cation exchanger replaces the mixed-bed ion-exchanger. Copper oxides will dissolve and the copper ions are removed in the cation exchanger and the generator is kept free of oxide deposits. After this "cleaning period", the mixed-bed filter is put back into

normal function again. This operating cycle is repeated at regular intervals. It should be noted that this treatment requires profound knowledge of copper solubility and deposition criteria, as well as expert supervision.

7.4.5 Reducing agents and inhibitors

Consideration has been given to their use for low-oxygen cooling water. Potential problems are the incompatibility of the agent with the low-conductivity limits required for generator operation, and the need for its replenishment when consumed or removed by the system's mixed-bed filter. Moreover, unexpected side effects may occur. Some may cause a compacting of oxide deposits, thus rendering them more difficult to remove. Consequently, there is good reason to recommend maintaining the simple chemistry of the copper / water system, without the use of such products.

7.4.6 Oxygen scavengers

Some generator cooling water systems have oxygen scavengers upstream of the side-stream mixed bed filter. This is achieved either by using scavenger-loaded ion exchangers (sulfite, ascorbic acid, hydrazine), or by using a Pd-catalyzed resin to recombine oxygen with the dissolved hydrogen gas. Those side-stream devices have the disadvantage of having a slow "clean-up" time constant, and oxygen may be more rapidly consumed rather by the copper surfaces than by the scavenger. In generators with slow oxygen consumption (for example with alkaline treatment) or large side-stream water flows, this technique may nonetheless be interesting. However, it requires extra supervision and maintenance.

7.5 Generator water chemistry specifications

The updated EPRI generator water chemistry guidelines for stators with hollow copper strands will be summarized in short. Detailed specifications and actions guidance is found in these guidelines. Values on Electrochemical Potential (ECP) have been updated with newer findings.

EPRI Report 1004004, Dec 2001. Generator Cooling System Operating Guidelines. (Cooling System Maintenance and Performance Guidelines During Startup, Operation, and Shutdown.

The specifications for stators with stainless steel hollow strands are similar; there are however neither specific requirements for oxygen, nor for ECP.

7.5.1 Low-oxygen water chemistry

A low-oxygen system is defined as a system normally operating with 20 µg/l (ppb) of dissolved oxygen or less. Target is a stable oxygen level as low as possible, ideally zero.

Parameter	Normal operating value	Short term action level	
Conductivity (25°C), µS/cm	≤ 0.5	> 10	neutral water treatment
	≤ 2	> 10	alkaline water treatment *
Oxygen, µg/l (ppb)	≤ 20	> 50	
		> 10 above normal	"start troubleshooting"
ECP **, mV SHE	< 223	> 266	

Table 7-3. EPRI specifications for low oxygen stator water chemistry (abridged)

* 8 < pH < 9

** Electrochemical Potential (ECP): tentative specifications

7.5.2 High-oxygen water chemistry

A high-oxygen system is defined as a system normally operating with 2 mg/l (ppm) of dissolved oxygen or more. Target is a stable oxygen level corresponding to saturation of water with air.

Parameter	Normal operating value	Short term action level	
Conductivity (25°C), µS/cm	≤ 0.5	> 10	neutral water treatment
	≤ 2	> 10	alkaline water treatment *
Oxygen, mg/l (ppm)	≥ 2	< 1	
ECP **, mV SHE	> 315	< 305	

Table 7-4. EPRI specifications for high oxygen stator water chemistry (abridged)

* 8 < pH < 9

** Electrochemical Potential (ECP): tentative specifications

7.6 Lay-up when the system is shut down

Corrosion resistant materials in the Stator Water Cooling System, together with the high purity water do not necessitate special corrosion protection for lay-up. However, many water-cooled generators worldwide have experienced plugging of hollow strands or clogging of strainers because of the presence of oxide migration, often having closely coincided with outages.

Lay up guidance will therefore concentrate on maintaining the Stator Cooling Water System integrity so that, with copper hollow conductors, oxides will not produce clogging or plugging. Stators with stainless steel hollow conductors do not require special lay-up except that the remaining water in the system shall have a low conductivity.

	Leave system running	Shut pumps and leave system filled with water	Drain and dry
Short tem lay-up	X	X	
Long-term lay-up			X

Table 7-5. Options for lay-up. Short term lay-up is generally understood to be for 3 days or less.

"Drain and dry" should pursue the following procedures:

- Draining the water from the system
- Isolating the components with copper surfaces from extraneous piping
- A series of blow-downs with compressed air
- Pulling a vacuum on the stator coil
- Monitoring dew point or insulation resistance

The stator can be considered to be dry when the dew point is well below the coldest possible point of the coil.

7.7 Generator water chemistry monitoring

Parameter	Importance	Monitoring frequency
Instruments:		
Conductivity	most important chemical parameter	continuous
pH	no good in high purity water	-
Oxygen	useful	continuous
Electrochemical Potential	most promising novel technology	continuous
Coil / bar temperatures	critical parameter	continuous
Coil flow	critical parameter	continuous
Δp coil inlet / outlet	important indicative information	continuous
Δp gas / water	important parameter	continuous
Hydrogen leakage	important parameter	daily
Make-up consumption	good indicative information	daily
Laboratory Analysis:		
Copper concentration	limited usefulness	4 weeks or as needed
Copper in ion exchanger	good indicative information	at each resin change
Other parameters:	plant specific	-

Table 7-6. Recommended specific instrumentation for a stator water system.

With each of the water treatment regimes, continuous conductivity monitoring assures that high purity water is used. It is also used to indirectly monitor the pH: the known relationship between pH and conductivity for acid and caustic solutions automatically gives the extremes between which the pH must lie. Oxygen monitoring helps to determine if the system operates within the correct operating range. A continuous on-line instrument is a good investment for avoiding problems, but it is not yet common practice. Results from EPRI investigations indicate that monitoring the electrochemical potential (ECP) is a new indicator for adverse conditions and this method may be more robust and require less maintenance than a dissolved oxygen monitoring system.

Other parameters are in general not suitable or meaningful, but may be useful for specific investigations.

7.7.1 Conductivity

Conductivity is the key parameter of the water specifications, paragraph 7.5.

The conductivity of water is dependent on temperature. Conductivity data are usually referred to a temperature of 25°C.

It has to be taken into account that the conductivity cells are usually directly inserted into the generator water cooling system. The sample may have a temperature of 40...60°C. While the conductivity of pure water at 25°C is 0.054 $\mu\text{S}/\text{cm}$, it is 0.25 $\mu\text{S}/\text{cm}$ at 60°C. Pure water has a larger temperature coefficient than its impurities, which complicates temperature compensation. - Instruments with appropriate temperature compensation have to be used.

Built-in conductivity cells are subject to the flow conditions in the pipe they are inserted in. If the location is inappropriate (e.g. strong turbulence in a bend), then the results may be unstable or incorrect. This is a generic problem in some designs.

7.7.2 Oxygen

Oxygen is also an important control parameter for the chosen water chemistry regime (low-oxygen or high-oxygen). Specification values are given in paragraph 7.5, tips on instruments and procedures in paragraphs 8.2 and 8.7.

High oxygen water chemistry

Oxygen measurements are unquestionably of direct use in keeping oxygen sufficiently high.

Low-oxygen water chemistry

Here the information may however be inconclusive.

An ingress of oxygen into a low-oxygen system will cause a rise of oxygen concentration, which is counteracted by removal of oxygen by consumption on the copper surfaces, or by de-aeration. If there would be no such oxygen removal, the system would go into oxygen saturation (5...8 ppm, depending on temperature). An oxygen concentration below saturation always represents the equilibrium between ingress and removal. Let us consider the following two cases:

- The copper may have a surface that consumes oxygen only slowly (tight oxide layer). Then any small quantity of oxygen entering the system will contribute to a visibly increased oxygen level, even though the situation may not be detrimental.

- Or the copper may be very reactive, consuming oxygen rapidly. In such a case, an oxygen ingress is not seen at all, even though it may produce enough oxides, oxide migration and localized copper oxide deposits.

Oxygen level should therefore always be seen in correlation with the speed of oxygen consumption within the system. High oxygen values may then not necessarily be bad if at the same time the consumption rate is low; on the other hand, a rapid consumption rate at long term may be detrimental.

The oxygen consumption rate can be measured, when for example some air-saturated water is brought into the system (e.g. addition of make-up water). The following "decay rate" gives a measure of the speed of oxygen consumption.

7.7.3 Copper concentration

Copper concentration is a useful indicator of copper release in the generator.

Here again, the copper concentration is governed on one hand by the release of copper, on the other hand counteracted by removal in the filters and ion exchangers, as well as by deposition in the coil. As a result, values of copper concentrations are also not conclusive of the actual copper release.

However, copper has proven to be a useful relative indicator, when compared within a user group of similar generators. Typical values are ca. 5 µg/kg (ppb) with neutral chemistry in low-oxygen systems, and 5-10 µg/kg (ppb) in high-oxygen systems. With alkaline water treatment, copper concentrations are lower.

There is a problem with representative sampling for copper, especially when a significant fraction of particulate copper is present. It is good practice for such sampling that there is a sufficient continuous sampling flow. This is however not possible in closed generator cooling systems. In addition, the low levels make analysis difficult and possibly even unreliable. Tips on sampling are given in paragraph 8.3.

Analyses of grab samples may also give only a short term picture. The copper release of the system is best measured by taking a representative resin sample at the same occasion each year. The total amount of copper in the resin bed has to be determined. It should be presented as grams copper per square meter of system "hot" copper surface per year. A comparative empirical value may indicate if oxide deposits are less likely to become a problem. It is therefore recommended to perform such an analysis on a regular basis and to observe the trend. It would also be useful if the OEM, or a user group, were to keep a comparative database for the specific type of generator.

The resin analysis requires a representative resin sample. If the resin is removed, all or a controlled part may be mixed homogeneously and a resin sample can then be taken. For large resin beds it is simpler to withdraw a representative section of the resin bed by established resin sampling techniques (sampling probe). It should be put to protocol if the resin bed also includes insoluble particles; their quantity should be measured and reported separately.

The surface to which the release rate relates should comprise only the "hot" surfaces, that means those that need to be cooled. Surfaces at lower temperatures have a markedly lower release rate and do not contribute significantly to total copper release. In practice, it is mainly the stator (and with rotor water cooling also the rotor) that surface has to be considered; cooler and piping surfaces should be excluded.

In addition to the integrated copper analysis in the ion exchange resin, also the quantity of oxides removed in the filter should be measured or at least be estimated (including the material settled on the vessel bottom).

The result of such measurements will be the release rate as grams ionic copper and grams particulate copper per square meter of system "hot" copper surface per year. Comparative trending is an important tool to diagnose out-of the flock behavior.

Paragraph 8.6 outlines procedures for such measurements.

Such analysis has been successfully implemented for a number of Brown-Boveri type of generators (low-oxygen, neutral, <1% mixed bed flow). A release rate of < 5 mg/m².day (< 1.8 g/m².year, or < 0.2 mm/year) was found to indicate that oxide deposits are less likely to become a problem. This value corresponds well to the related range indicated in Figure 7-7. For other types of generators, it may be useful to compare within the respective users group.

7.7.4 Electrochemical Potential (ECP)

Phenomena like corrosion and deposition are governed by the ECP. The ECP is a complex parameter, being determined by oxidizing and reducing agents in the water, pH, temperature, impurities, materials, etc. The ECP is therefore a summary parameter that describes the chemical reactivity better than any single parameter even like oxygen.

Laboratory investigations by EPRI have indicated a correlation between copper release, oxide deposition and ECP. Suitable ECP sensors have been developed and their use in a generators with high oxygen as well as with low oxygen been demonstrated.

ECP specification values have been tentatively developed (see paragraph 7.5). Future application will lead to a refinement of the technology.

7.7.5 pH

Direct pH measurement in high purity water is delicate and prone to errors. Special instruments would be required with such low conductivity as in generator cooling water. The electrode membranes of such commercial instruments would let either pass sample backflow into the electrolyte, or contaminating electrolyte flow into the stator water, depending on pressure conditions.

The efforts for a suitable instrument are however not necessary as pH can easily be indirectly controlled by measurement of conductivity, Figure 8-1. Thus, with a conductivity of $0.15 \mu\text{S}/\text{cm}$, pH will automatically be within $6.5 < \text{pH} < 7.8$, which is considerably better than the precision of a pH meter.

With alkaline treatment, conductivity can also be used as a substitute for pH measurement. In this case, the information has to be supplemented by regular analysis of the alkalizer (sodium). Here the conductivity is compared to the theoretical conductivity of NaOH. Smaller conductivity indicates the presence of an anion, thus lower pH.

It is better to have no pH meter than an unreliable one that opens up more questions than it answers. Conductivity is a good substitute parameter.

Paragraph 8.4 gives tips for manual pH measurement.

7.8 Mechanical and chemical cleaning of copper hollow conductors

When the hollow conductors are plugged, cooling may be restored by mechanical and / or chemical cleaning.

A significant number of utilities have taken pro-active measures against hollow conductor fouling and performed preventative chemical cleaning. Among the motives were:

- awareness of an occurrence of insufficient lay-up
- visual observation of deposits in the stator bar water boxes, filters, strainers, other system components
- opening of the stator coil (water side) during outage or repair works, some times a case related to warranties, liabilities and insurance matters
- partial rewind: starting up all stator bars in equal condition (there have been cases where the new bars were fouled by the oxides from the old bars)
- full rewind: to provide the new stator bars a clean cooling water system

- some utilities choose regular cleaning as part of long-term preventative maintenance

Note:

- ☞ Hollow conductors that are completely blocked and do not have any water flow cannot be cleaned by any type of chemical cleaning. They require a preceding mechanical cleaning.
- ☞ With all the cleaning methods available, one important point should, however, be kept in mind: the cleaning does not eliminate the cause of plugging; re occurrence of clogging cannot be excluded. Cleaning thus is not the final solution to the problem.
- ☞ Never wait for cleaning until flow and temperature conditions have strongly deteriorated; perform cleaning beforehand. A late decision for cleaning may rush the use of non-optimized methods, may cause loss of generator availability, may result in equipment damage and produces more compact deposit layers that become more and more difficult to be removed. A pro-active approach is recommended to take early action before symptoms are already evident is recommended.

7.8.1 Mechanical cleaning

Mechanical cleaning is understood here to be the removal of substance by means of a tool. Flushing is discussed separately. Traditionally, wires or scrapers are used to loosen the deposits. A novel method is dry - ice blasting.

Mechanical cleaning is capable to locally remove severe and even complete plugging, but it does not provide a complete overall removal of deposits. Even if it helps reinstating a basic flow, the remaining deposits may still cause unsatisfactory flow and may be the nucleus for renewed deposition. Also, mechanical cleaning may require considerable efforts for disassembling the stator bar connections.

If the generator is heavily fouled, mechanical cleaning should be considered. This applies especially if hollow conductors are plugged. Mechanical cleaning should be followed up by acid cleaning or by complexant cleaning, depending on the efforts to be involved.

7.8.2 Water-flushing, air / water flushing

A useful technique to remove substance from the conductors is reversing the water flow. This especially liberates the conductor inlets from larger debris, but is also capable for flaking off copper oxide deposits.

Water flushing may be an easy first try for removal of clogging. It is relatively simple, but likely with only limited effectiveness. It will neither remove severe plugging nor provide a complete

removal of deposit layers. There may even be the risk that particles may get more stuck than before in the conductors with reverse flow flushing. When there is no visible success, flushing should be terminated in order not to solidify deposits more than they already are.

7.8.3 Acid cleaning

The matter to be removed, or part of it, is chemically dissolved by an acid and thus permits flushing out the matter. Common acids used are: citric acid, ammonium-peroxo-disulfate, sulfuric acid in combination with hydrogen peroxide, and phosphoric acid. Nitric acid would be very effective, but it requires complicated handling if applied on site. It is important that the acid solution is either oxidizing, or complexing; otherwise it will not be suitable to remove cuprous oxide (Cu_2O).

Acids need a certain minimum strength in order to be active for a dissolution process; if it is used in too dilute form it is not effective for cleaning. It is important to consider its effect on all other involved materials and components. Especially the effect on the brazing material for the hollow conductors and the water boxes need close attention.

Acid cleaning can be effective for severe and persistent plugging, but is not effective on completely plugged strands.

It, however, attacks base material substantially. In order to minimize adverse effects on system materials and to permit a better control it should be performed either by targeted cleaning of single bars that have been identified by low-flow or high-temperature measurements, or of a small group of bars in parallel. This requires part disassembly of the generator. The risk of acid leaking out of the system has to be taken into account. Acid cleaning is possible only when the generator is off-line.

7.8.4 Complexant cleaning

Complexant cleaning is the recommended option for removing copper oxides.

The matter to be removed or part of it is chemically dissolved by a complexing agent and thus permits flushing out the matter. A common agent is Disodium EDTA (Disodium salt of Ethylene-Diamine-Tetraacetic-Acid). It is important that the oxidizing agents are added; otherwise it will not be very effective to remove cuprous oxide (Cu_2O).

Different to acids, complexants do not need a minimum strength for reacting with copper-oxides. The process can be done with a sufficient dilute solution so it does not interfere with any conductivity limits. Complexant cleaning therefore can be done off-line, as well as on-line, that is, with the generator in operation.

Complexant cleaning employs relatively benign reagents so that attack on base materials is very small. On the other hand, it is also softer on the oxides to be removed, so it may not always be as efficient as acid cleaning.

The art of complexant cleaning consists of choosing the appropriate complexing agent together with the right balance of oxidant. Too much oxidizer may produce more oxides than the complexant can dissolve, too little oxidizer makes the dissolution incomplete or may even leave conductive deposits on the isolating hoses. It has to be considered that some oxidizer is lost for cleaning by reactions other than with deposits of copper and copper oxides, e.g. by formation of oxygen gas that may vent off.

Cuproplex™ is an advanced development of complexant cleaning. It has a long successful reference for both off-line and on-line cleaning.

7.8.5 Cationic purification

The stator cooling water system is kept at a slightly acidic pH ~ 6.0 - 6.5 by means of carbon dioxide from air. Under these conditions, copper oxides are slowly dissolved and Cu-ions are removed in the ion exchanger. This is intended as a temporary treatment and not suitable for permanent operation. - Cationic purification has so far only been applied by one single utility, and only with high-oxygen chemistry systems.

7.8.6 Combination of methods

The combination of some of the above-mentioned cleaning methods takes the most efforts and time to perform, but also give the best results. If a stator is badly plugged, the efforts of such cleaning outweigh the risks of operating with the plugged machine.

7.9 Precautions

This paragraph has pointed out various options on stator water chemistry, design, materials and operation. It should however not be left without a disclaimer and a warning,

Any change from an existing condition to another option should not be undertaken without an in-depth analysis of the implications to the rest of the cooling water system. The risks associated with such changes may be higher than just simply missing the actual targets; they may affect the integrity and reliability of other components in the cooling water system.

The guide is not intended to provide instructions for the implementation of such modifications. The advice of an institution that has practical experience or expertise on this implementation is strongly recommended.

8. APPENDIX B: ADDITIONAL INFORMATION

The following information is intended as additional information to existing laboratory practice, and there is no claim that this is the only way to achieve good results.

8.1 Conductivity and pH in aqueous solutions of Na^+ and CO_2

The Figure 8-1 identifies the possible and impossible regions for pH data. This should be used for a first check of plausibility.

The Figure 8-2 details the situation for CO_2 and Na^+ dissolved in water. It should be noted that the outer border curve is the same also for other acids and alkali, but the inner curves vary with species. CO_2 is a gas that partly dissociates into HCO_3^- and CO_3^{2-} . The Figure takes account of this dissociation. - This Figure is in a format where it can be copied, pasted (Paste Special / Picture, Enhanced Metafile) and re-sized as useful.

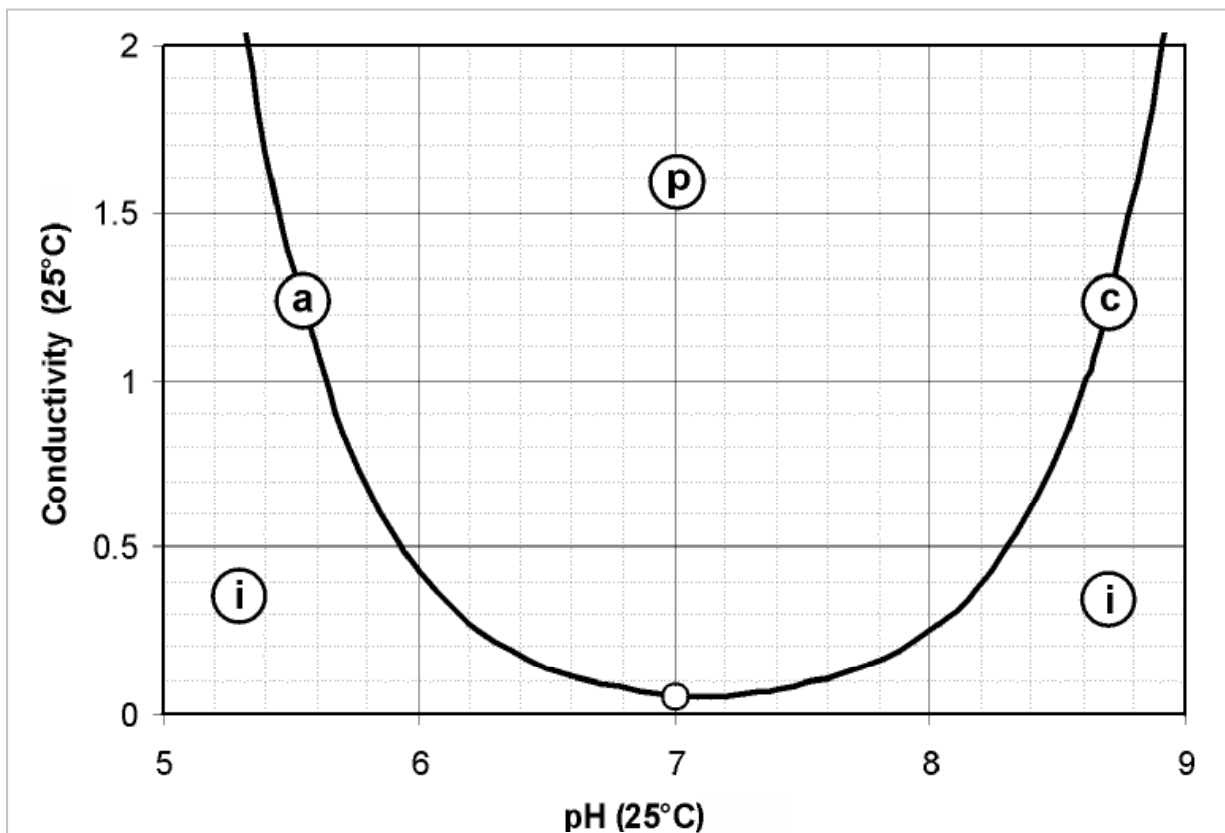


Figure 8-1. Conductivity ($\mu\text{S}/\text{cm}$) Versus pH: (a) Relation for Strong Acids, (c) Relations for Strong Caustic, (i) Impossible Region, (p) Region for All Possible Electrolytes

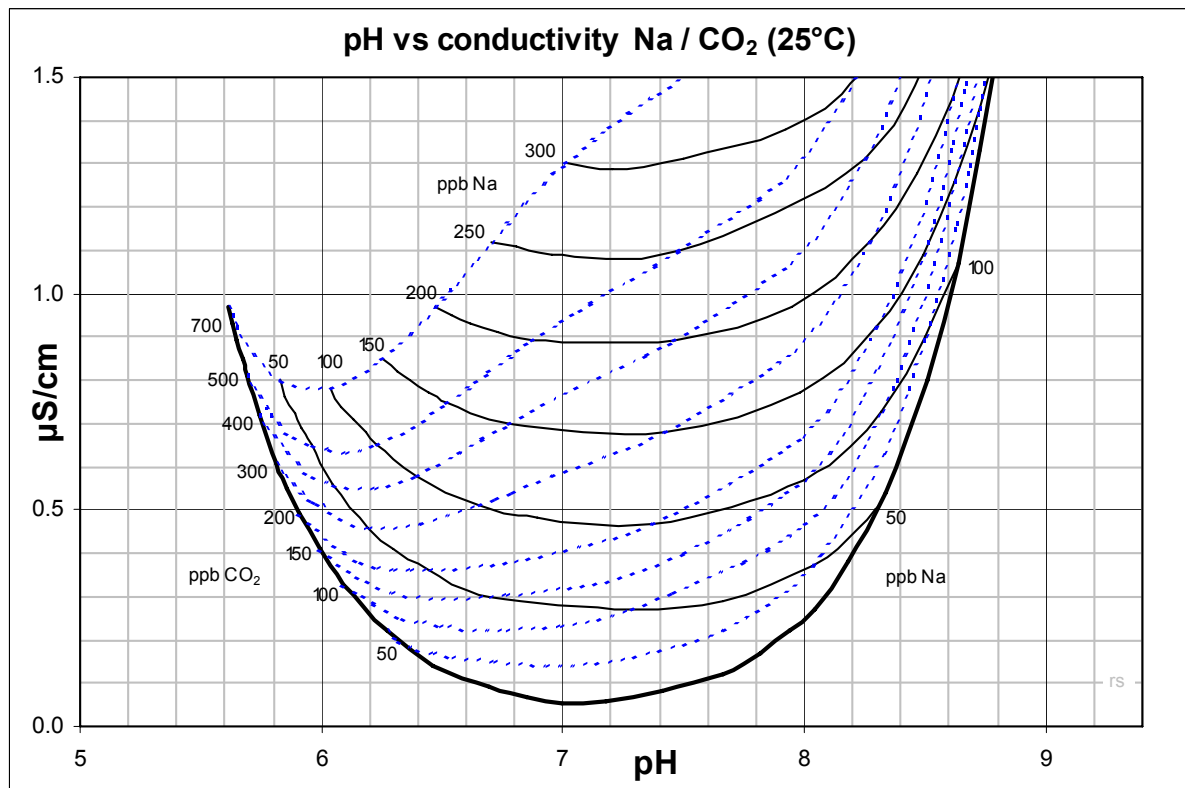


Figure 8-2. Conductivity ($\mu\text{S/cm}$) Versus pH: (a) Relation for various concentration of Na^+ and CO_2 in water.

8.2 Experience with Orbisphere G1100 Luminescence oxygen sensor

A new Orbisphere 410-G1100 luminescence oxygen meter was cross-tested with a traditional Orbisphere 3655-31130 / membrane 2956A electrochemical oxygen meter.

This type of electrochemical instrument was qualified in numerous investigations and tests in the steam / water cycle of thermal power plants . It must absolutely be considered as being reliable. Therefore we took this instrument, after proper calibration, as reference for the performance of the luminescence meter.

The luminescence instrument is specified to measure in a range of 0-20'000 ppb of oxygen, with a detection limit of 0 ± 2 ppb.

Figure 8-3 summarizes the results. Ideally, the two instruments should give the same values. Above 50 ppb, the correlation between the instrument readings is good. The linear deviation is probably an issue that could be resolved with new adjustment of the calibration of the instrument. However, at low concentrations the luminescence sensor refused service by dropping off to zero at all concentrations below ca. 15 ppb. Lower concentrations could therefore not be monitored. This is not sufficient for monitoring low-oxygen cooling systems.

In the meantime Orbisphere has developed more sensitive sensors (PPChem 12(2010)5, pg 296-303, May 2010); sensor K1100 (K1200): range 0-2'000 ppb, detection limit 0.6 ppb. - The G1100 instrument however is certainly not plug-and play for low ppb concentrations.

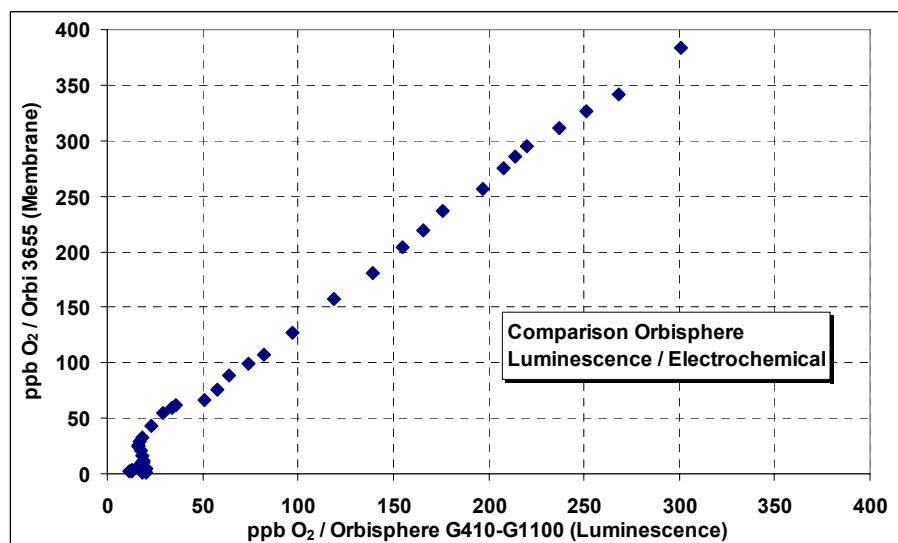


Figure 8-3. Comparison of oxygen measurement data in the same sample made by two different instruments.

8.3 Tips for water sampling

8.3.1 Taking the sample

Sampling of water that contains only truly dissolved substances is easy. The only needs are to withdraw the water from a representative point of the bulk liquid, that is just to avoid taking samples from dead legs, to flush the sample line and sample vessel thoroughly, and to avoid contamination while handling.

However, if the water also contains particles and / or colloids (such as copper- and iron-hydroxides and their oxides), the situation becomes more complicated. The sampling nozzle may influence collection efficiency, and the particles may deposit in the sampling lines, valves etc either yielding too low sample concentrations, or samples contaminated by a cloud-burst of deposited particles. Therefore an adequate sampling device and adequate sampling procedures are essential. Otherwise, any analysis results must be treated with reservation.

From the wealth of existing publications, the following two are recommended to illustrate this matter (provided by R.Svoboda on demand):

R.Svoboda, G.Ziffermayer, S.Romanelli, W.Kaufmann, L.Sozzi, M.E.Schäfer; *Trace analysis of corrosion products by integrating sampling techniques*; Conf. BNES "Water chemistry of nuclear reactor systems", Bournemouth / GB, Oct 1983, pg 331-338

P. Srisukvatananan, D.H. Lister, R. Svoboda, K. Daucik; *Assessment of the state of the art of sampling of corrosion products from water / steam cycles*; Power Plant Chemistry 10 (2007) 10, pg 613-626

As is seen in these papers, there are no special requirements for sampling nozzles, especially in high purity cooling water system with relatively small piping. On the other hand, particles may accumulate in the connecting piece of the sampling tube to the system pipe. As there is no continuous sample flow, this piece may collect particles that will be partially washed out upon opening the sample flow, thus contaminating the sample. It is therefore necessary to flush the sample line beforehand and let the system equilibrate again before taking the sample.

Based on experience from sampling in power cycles, the following procedure is recommended for corrosion products

- ❑ flushing: open shortly to high flow and close the sample valve two to three times, then adjust a sample flow of 100 -200 ml /min
- ❑ equilibration: run the sample at constant flow (at a value between 100 - 200 ml/min) for ca. 5 minutes; use this water to flush the sample bottle and its cap

- ❑ take the sample: without changing sample flow, fill the desired quantity of sample into the bottle. Do not contaminate by handling.

Additional procedures for sampling anions (chloride, sulfate etc)

- ❑ Assure that the space around sampling is clean, including the ambient air
- ❑ wash your hands thoroughly and wipe dry with clean paper
- ❑ flush the sample outlet:
 - dip sample outlet for at least 10 seconds in running sample water (you may use a sample bottle for this)
- ❑ flush the sample bottle:
 - open bottle, flush cap as well as the outside of the bottle's neck with sample water
 - fill cap with sample water and put it (inside up) on the tray besides the sampling point
 - fill bottle with sample water, put it upside down and shake it until empty
 - repeat above step (fill and empty) 4 more times
- ❑ now take sample within 2 minutes

8.3.2 Storing the sample

Once the sample is in the bottle, it can be altered in two ways: it can be contaminated by release of residues that have been adsorbed to the bottle wall or from the bottle material itself, or in reverse, the species to be sampled could be lost by adsorption onto the bottle walls.

Glass bottles, for example, are known to have a rather active surface. Also plastic bottles, especially after prologues exposure to air and light, also may develop active surfaces.

The following paper describes systematic investigations on the stability of samples during storage. Although the focus of this investigation were fully dissolved ionic species, major conclusions can also be drawn for corrosion product samples.

M.Koebel, R.Svoboda; *Investigations on the Temporal Stability of Ultrapure Water Samples by means of Ion Chromatography*; Power Plant Chemistry 5 (2003) 11, pg 653-659

The present procedures have produced samples consistent with results from independent methods (corrosion product transport balances in the steam water circuit of power plants).

Choice of the sample bottles

We have qualified Nalgene™ PP and FEP bottles. For corrosion products, HDPE and LDPE bottles should also be appropriate. We suggest to stay with Nalgene™ products because they are precision products and their wide use implies consistency in product quality.

Use 60 ml or 120 ml narrow-mouth bottles, as they are easier to handle under clean conditions than larger bottles. Caps are made of a different (harder) material. Narrow-mouth bottles have a minimal cap surface.

Conditioning of the sample bottle

New sample bottles should be completely filled with water (also to cover the inside of the cap) for at least 48 hours, then rinsed and filled again for storage. Only high purity water should be used.

The bottles should then be stored in a dark place, and left filled with water.

Prior to use, the bottles should be emptied and rinsed again. These empty bottles may then be used for sampling on the same day.

After its first use, the bottles should be saved for later re-use. It is strongly recommended to use a set of bottles only for samples that have similar quality, e.g. set "dirty water bottles" aside and never use them for pure water.

After the sample has been analyzed, the bottle should be either filled with new high purity water, or the sample left in the bottle and only top it up with water. Correct labeling and handling is important, especially if the sample has been acidified for analysis.

Preparing for sampling

For metal analysis it is common to acidify the sample in order to bring particulate species into solution. For copper and its oxides, hydroxides, nitric acid is the most appropriate. (Non-oxidizing acids may not dissolve Cu_2O and Cu_{met}). Commonly 1-2ml of 15% nitric acid are added to a 100 ml sample; quantities vary with laboratory procedures.

It is recommended that this acidifying is done already when the sample is taken. This may be by already having the acid in the empty bottle, or probably a bit safer, adding it to the sample after it has been taken. It is essential to observe safety precautions and good laboratory practice. - Acidifying at a later time may already have some of the copper lost on the bottle walls.

8.4 Tips for calibration and function control of chemistry monitors

8.4.1 Conductivity meter

The reading is dependent on the combination of cell constant and data processing in the transmitter.

The cell constant is given by design and manufacturing, the data processing by the adjustment of the transmitter.

Function control. It is recommended to perform a two-point check of the complete chain of measurement: the sensor together with the transmitter. The first point is the "zero", the dry cell on air. The second one is the measurement of a standard solution (e.g. 0.01 m KCl). Solutions < 50 $\mu\text{S}/\text{cm}$ have to be mixed up and measured avoiding contact with air (flow-cell). - The measurements should be done as close as possible to 25°C in order to avoid uncertainties with temperature compensation.

The instrument passes function control if both values are within tolerance

Calibration. Calibration is done by adjusting the instrument, so that it will provide correct readings at function control. This comprises the sensor and the transmitter separately.

As the sensor has no means of adjusting the cell constant, it can only be tried to restore the factory value by cleaning the electrodes and the insulator between them. If this does not restore the correct value, then the sensor should be discarded and replaced by a new one. It is not recommended to continue using a defect sensor by using a new cell constant. The deviation from the factory value then has a reason that should not be downplayed by adjusting data processing.

The transmitter may have means for calibration. Here the calibration values are simulated by precision resistors (here again: two point calibration, preferably zero and maximum value of interest). It is however questionable if in-house instrumentation specialists should perform such adjustment of the transmitters on a regular basis. This may lead to an obscure situation, where the causes and the time of occurrence of the deviation may get out of attention. - If such adjustments can be easily done in the programming mode of the instrument, it should be given thought if the instrument is not over-sophisticated for such a simple measurement, making it potentially unreliable ("too many buttons").

8.4.2 Oxygen meter

Function control is performed by a two-point check, one at zero, the other one either with atmospheric air, respectively air saturated water. Temperature and atmospheric pressure have to be measured separately.

If the instrument range does not go up to full atmospheric conditions, then a precisely metered (rotameters) mix of air and nitrogen can be used, or a certified calibration gas.

Calibration is done by the procedures given in the instrument manual.

8.5 Tips for manual pH analysis

pH analysis in ultrapure water is very difficult. pH meters measure the potential between the electrode and the reference electrode, which gives a measure for pH. Due to the varying potentials that develop across the reference junction, when attempting to measure deionized water it is common to attain incorrect pH values even with new, sealed electrodes that calibrate perfectly in pH buffers. More information on this can for example be found in:

<http://www.coleparmer.com/techinfo/techinfo.asp?ID=556&htmlfile=pHPureWater.htm>

There are instruments on the market that meet these challenges (e.g. "AMI Inspector pH", www.swan.ch), but they are mostly for fixed installation and continuous flow use. Portable instruments usually have a single combination electrode. These may work fine, if there is always enough conductance in the liquid diaphragm. This is best be done by soaking the electrode in a neutral salt solution; the electrode will then function properly for a limited length of time until the salt has been washed out from the diaphragm.

Useful results have been obtained with the following method:

Preparations

- ❑ use a portable instrument with a combination electrode (which combines the glass electrode and reference electrode into one body).
- ❑ calibrate the instrument with buffers according to the manual; at the end, immerse the electrode again into the pH=7 buffer, so that possible residues in the diaphragm are at this pH
- ❑ immerse the electrode into a ca. 1 molar solution of very pure KCl or NaCl ("soak solution"). It is important that the product is really neutral and does not contain any excess of acid or alkali. Soak the electrode for at least 1 hour in this solution in order to

wash out buffer residues, and to fill the liquid junction in the diaphragm with highly conductive neutral water.

- ❑ measurements should then be made within 3 hours; between measurements, the electrode should be stored in a clean soak solution (change if it gets contaminated from samples).

Measurement

- ❑ use a small, narrow unbreakable (plastic) beaker, with the sample coming from a Tygon tube
- ❑ put the Tygon sample tube outlet to the bottom of the beaker, let the sample flow slowly so there is no turbulence carrying water from the surface (pick-up of CO₂ from air) back into the beaker
- ❑ insert the electrode into the lower part of the beaker
- ❑ now let sample flow for 3-5 beaker volumes, withdraw Tygon tube slowly from the beaker in such way that there is no flow-back from the surface
- ❑ wait for a few seconds until the reading has stabilized (10 - 30 seconds) and make the reading
- ❑ after the measurement, return the electrode to the soak solution

Of course, other devices than the beaker can be used. It is just important that the sample near the electrode is not contaminated by water that had contact with air, that the reading is done with no water flow, and that the diaphragm (liquid junction) of the electrode is always filled with a highly conductive, neutral solution. If the diaphragm gets depleted with conductive water, the measurement becomes unstable and unreliable.

It is recommended always to cross-check pH with conductivity; it should be within the "permitted range" (paragraph 8.1).

8.6 Procedures for integration copper analysis in SNS cooling waters

The integrated copper release within a cooling loop is determined by the quantity of copper that has been removed by the mixed bed resin and in the mechanical filter.

8.6.1 Basic data to be collected

- ❑ operating time of the mixed bed resin since last resin change
- ❑ quantity of mixed bed resin used
- ❑ operating time of the filter elements since last replacement
- ❑ quantity of filter elements used
- ❑ total inner copper surface area of all hollow conductors

8.6.2 Sampling and analysis of copper in the deionizer resin

It is essential that samples representative for the total quantities of the mixed bed resin are taken.

Core sample

Resin core samples are withdrawn by using technology common for resin sampling in make-up water plants.

A plastic (or metal) tube of 1-2 cm (3/8" to 3/4") inner diameter is pushed through the resin bed, which is still filled with water. When arriving at the bottom, the top opening of the tube is closed, and the tube pulled out. Opening the tube top again will then result in the discharge of the resin that has been trapped.

The success of the method will depend on the choice of the right tube diameter, and the quantity of air that has been trapped when closing the top of the tube. Too large diameters will result in resin pouring out already when the tube is withdrawn from the resin. Air entrapped in the top of the tube will expand when the tube is lifted out of the water, thus expelling some of the trapped resin, and the water flow resulting from this expansion may well mobilize the rest of the trapped resin.

It takes some skill and practice to take core samples. This is however an established technique in industrial water treatment.

It is recommended to take 3...5 core samples to mix up the resin sample.

Not all designs of mixed bed vessels however provide sufficient access for core sampling.

Grab sample

The total quantity of removed resin should be completely mixed. Then a grab sample of resin may be taken.

Mixing resin however may be very laborious, especially when quantities > 1-2 cuft have to be treated.

As mixed bed resin would separate when mixed in water, the resin must be drained before mixing.

Small quantities can be spread in a flat trough, and then mixed manually with a flat paddle. Larger quantities may be a good challenge for the ingenuity. Core samples may be the easier option.

Particulate copper in the deionizer

The drain water or flushing water of the deionizer is usually quite turbid, indicating undissolved particles. Even though the turbidity is visually quite impressive, the quantities involved are rather small. For example, a concentration of 10 mg/l (ppm) already blocks visibility within 2-3 cm (1") of water, but the total quantity in -for example- 30 liters (1 cuft) of water will then be only 0.3 grams, negligible compared to the quantities found on the resin. It is of course possible to take a sample and verify this consideration for the given case.

Analysis of the resin samples

Beforehand, the mixed bed should be separated into cationic and anionic resin. This is done by the standard technique to float up the resin in water and let the less dense cationic resin settle as the bottom layer. The copper in cationic resin is then eluted by conventional laboratory regeneration techniques (for example slow flushing with 3% HCl in a molar quantity of 300% of the cationic resin capacity). Copper analysis of the eluent liquid is done by conventional laboratory methods. Result is the total quantity of copper, that is the measured copper concentration multiplied by the quantity of eluent.

The report should contain the quantity of copper found, and the quantity of resin that was analyzed.

8.6.3 Sampling and analysis of copper in the mechanical filters

1. take one or more representative filter cartridges as samples
2. collect all possible deposits on the filter vessel floor (if any)

3. put samples in a vessel and dissolve deposits with a measured quantity of an oxidizing acid (e.g. 5-10% nitric acid, or 5-10% sulfuric acid plus 5-10% hydrogen peroxide)
4. determine the copper concentration in the acid by means of an appropriate chemical analysis method
5. analyze floor deposits in the same manner

Note: if metallic filter elements are used, this sampling can be combined with the total cleaning of all filter elements.

The report should contain the quantity of copper found on the filter cartridge, and on other places in the vessel.

8.6.4 Calculation of the copper release

Mixed bed

Q_{Cu}	quantity of copper in the resin sample	(grams)
Q_{sample}	quantity of resin sample	(liters)
Q_{resin}	total quantity of mixed bed resin	(liters)
t_d	time the mixed bed resin has been in service	(days)
R_m	Release rate for Cu in the mixed bed	(g / m ² .d)
S	Total inner copper surface	(m ²)

$$(1) R_m = Q_{Cu} * (Q_{resin} / Q_{sample}) / (S * t_d)$$

Mechanical Filter

The release rate for Cu in the filters R_f is calculated in the analogous manner by extrapolating the quantity of copper on the sample to the total of filter elements, and adding the quantity of deposits on the filter vessel floor.

Total release rate

The total release rate is

$$(2) R = R_m + R_f.$$

In most cases the quantities found on the filters will be smaller than the quantities found in the deionizer: $R_m \gg R_f$.

8.6.5 Evaluation

Comparison of data within a group of similar cooling loops at the same temperature level.

8.7 Procedures for oxygen analysis with Orbisphere 36xx series

8.7.1 Range of application

Valid for water with a temperature between 0 – 70 °C.

This method is valid only for the use of the specified instruments.

Application range	:	0 – 20'000 µg/kg
Tolerance	:	± 5% of the reading, but at least ± 0.5 µg/kg
Detection limit	:	0.5 µg/kg

8.7.2 Instruments and reagents

For the measurement is needed

- ☐ Orbisphere Oxygen Meter Series 36xx with Sensor Series 311xx, Membrane 2956A
- ☐ operating manual
- ☐ Orbisphere Recharge Kit for this sensor
- ☐ magnifying glass

and for low oxygen levels additionally

- ☐ Orbisphere Flow Chamber (specific for sensor type; sensor 31130 → flow chamber 32001), with connections
- ☐ connecting piping or tubing to the water source
- ☐ the cell is operated without guard ring

For the calibration is additionally needed

- ☐ Na₂SO₃ (Sodium Sulfite) p.a., powder
- ☐ 100 ml beaker
- ☐ tripod with clamp to hold the sensor
- ☐ 50 ml airtight glass bottle to store Na₂SO₃ solution
- ☐ if calibration better than ±5 % is desired: a calibrated pocket barometer (only for models that do not have a barometer built in, see instrument manual, e.g. Model 3603. Model 3655 has it built-in)
- ☐ paper pads

8.7.3 Measurement

- (1) Adjust correct flow (→ operating manual; for membrane 2956A: ca.150 ml/min).
- (2) Wait for stabilization of the reading.
- (3) Reading of the oxygen level on the instrument display.

With low oxygen concentrations stabilization may take several hours, especially if the sensor is used directly after having been exposed to higher oxygen concentrations for longer times. Stabilization requires that the sensor be connected to the switched-on instrument.

8.7.4 Evaluation

The instrument reading gives directly the oxygen concentration.

8.7.5 Function control

Visual check of the sensor

sensor with membrane upside and horizontal, close-up inspection under good light conditions, preferentially with a magnifying glass:

- ☐ the membrane must be clean, clear, transparent and sitting smoothly and tight
- ☐ the membrane must be undamaged
- ☐ the electrode must be undamaged
- ☐ no gas bubbles are permitted in the electrolyte chamber below the membrane; special attention to bubbles caught in the holes of the membrane support
- ☐ reading in air within $\pm 20\%$ of the theoretical value

Tolerance

None.

☞ The electrodes of the sensor are adjusted to within few micrometers tolerance. If this arrangement has deteriorated, the instrument may not function properly. Broken or scratched membranes will lead to early failure of calibration.

Frequency

- ☐ before and after each calibration
- ☐ before each insertion of the sensor into the flow chamber.
- ☐ after each change of membrane

Deviations

In case of deviation replace membrane (Enclosure 8.7.9) or overhaul sensor (→ operating manual). If the deviation persists, consult the manual or the manufacturer.

8.7.6 Calibration

Two-point check at the high and at the low end

Detailed procedures in the Enclosure

- (1) Temperature equilibration of sensor
- (2) Function control.
- (3) Check in air.
- (4) Adjustment of the instrument.
- (5) Check in air.
- (6) Check in sulfite solution.

Tolerance

Steps (1) to (6) have to comply with the following tolerances:

- (1) sensor to ambient air within 2°C
- (2) no tolerance
- (3) within $\pm 20\%$ of theoretical value
- (4) -
- (5) within $\pm 5\%$ of theoretical value
- (6) trend to $<1 \mu\text{g/kg}$

Frequency

A calibration has to be made

- ☐ after each change of membrane
- ☐ after each instrument storage / transport >7d *
- ☐ before each measurement series *
- ☐ if irregular function is suspected
- ☐ or as defined in the particular project's Calibration Plan

* not applicable for permanently installed in-plant instruments

Deviations

In case of deviation replace membrane (see Enclosure) or overhaul sensor. If the deviation persists, consult the manual or the manufacturer.

8.7.7 Remarks

Low oxygen sampling is sensitive on any ingress of air. Thus sampling connection must be done by specially qualified personnel.

The Orbisphere meter is a complex instrument and the sensor is very sensitive to mechanical damage. Thus the operation and maintenance of the instrument requires trained personnel.

Observe technical and safety instructions given in the instrument manual.

Instructions for extended storage when the instrument is not in use for > 2 weeks are given in the Enclosure.

8.7.8 Enclosure: Details on calibration

Set-up



Figure 8-4. Setup for calibration:

- small tripod and clamps to hold sensor
- narrow plastic beaker for sulfite solution, optimized to immerse the sensor tip, but to require only a minimum of solution.
- glass bottle with thick (gas-tight) cover, for short-term storage of sulfite solution; do not prepare more solution than the capacity of the bottle
- paper pads, to be used to lift beaker in such a way that the membrane is close to the sulfite bottom layer

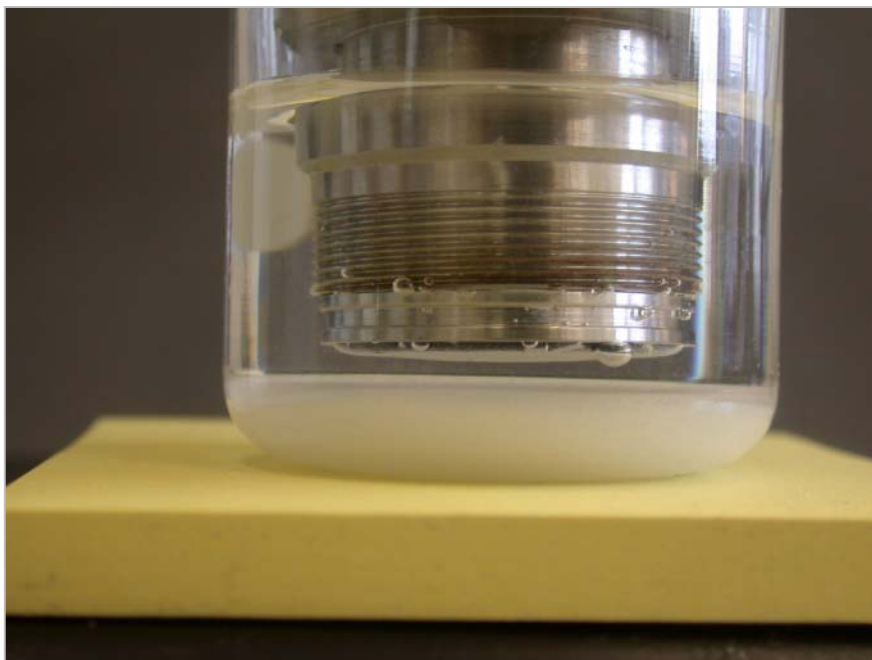


Figure 8-5. Example: The sensor in the sulfite solution.

For making a photo, a glass beaker was used. This is technically fine, there is a risk for braking.

The beaker was lifted with the paper pad, so the membrane is 3-5 mm from the sulfite crystal bottom layer, but still covered with >2 cm solution. Adjusting the distance with the tripod clamps risks jamming the membrane into the crystals.

⊗ Some air bubbles stick to the membrane; they must be removed before calibration.

Procedures for calibration and adjustment

(1) Temperature equilibration

Wait until the sensor temperature indication is within about $\pm 2^{\circ}\text{C}$ of ambient air temperature.

(2) Function control

Check visually that the membrane and electrode are clean and undamaged, and that there are no gas bubbles below the membrane. If this is not right, readings may not be reliable, and therefore calibration is not useful. The membrane must be replaced or the sensor overhauled.

(3) Check in air

The reading should give the theoretical value (see below), within $\pm 20\%$ tolerance. If it is outside, replace membrane.

(4) Adjustment of the instrument

Follow the instrument manual for adjusting the instrument. In the manual, this is referred to as "calibration in air".

(5) Check in air

Re-do the check in air. It has to be now within $\pm 5\%$ of the theoretical value. If not, consult the manual. A replacement of the membrane or an overhaul of the sensor are the prime options for improvement.

(6) Check in sulfite solution

Immerse the sensor in a sulfite solution and check that the indication trends to $< 1 \mu\text{g/kg}$. If not, consult the manual. A replacement of the membrane or an overhaul of the sensor are the prime options for improvement.

Theoretical value for check in air ("oxygen saturation")

Altitude	20 °C	25 °C	30 °C	35 °C
0 m	9.31	8.52	7.88	7.35
500 m	8.77	8.03	7.43	6.93
1000 m	8.27	7.57	7.00	6.53

Table 8-1. Oxygen content in water at saturation with air in dependence of altitude and water temperature at normal meteorological condition (1013 hPa at sea level). Local weather conditions may cause $\pm 2\%$ variation.

For an extended table, see the operating manual.

With the aid of a calibrated barometer it is possible to account for local weather conditions more precisely: multiply the tabulated saturation values by $a/1013$, where a is the local barometric pressure in hPa, reduced to 0 m sea level.

Procedures for the check in the sulfite solution

- (1) All work to be done in due consideration of the Materials Safety Data Sheet
- (2) remove the guard ring, if there was any
- (3) connect the sensor to the instrument, switch the instrument on
- (4) mount the sensor onto the tripod as seen in the photo, fix at about 10 cm above the base plate
- (5) fill 40 ml of clean water into the beaker (tap water is sufficient)
- (6) add 1-2 teaspoon-quantity of Na_2SO_3 (Sodium-sulfite) crystals
- (7) stir well; it will however not dissolve completely
- (8) let rest for 5 minutes; stir a last time. From here on do not any more stir the liquid, in order to allow the formation of a low-oxygen layer below the surface
- (9) put the beaker below the sensor
- (10) lower the clamp with the attached sensor so the membrane is about 1-2 cm above the crystals. Lowering the sensor deeper should not be made with the tripod clamp; there is a big risk that the sensor crashes into the sulfite crystals
- (11) insert sufficient paper pads so the membrane is about 3-5 mm above the crystals

- (12) the membrane must now be > 2 cm below the liquid level
- (13) check visually that there are no air bubbles sticking to the membrane. If there are bubbles, lift membrane out of the liquid and insert it again slowly, repeat until successful
- (14) now let the sensor measure oxygen level until equilibrium. It is important that the sensor has full electrical power all the time; the instrument must stay switched on
- (15) equilibrium may take a few minutes (when the sensor has been in low-oxygen sample not longer than 5 minutes ago), to ½ -1 hour (new membrane), or to several hours (when the sensor has been idle on air for extended periods; in this case: check membrane).
- (16) the equilibrium has to be <1 ppb. If there is a clear trend for positive achievement it is not necessary to wait until <1 ppb is actually reached
- (17) put the value to protocol
- (18) if the value does not trend to <1 ppb, it may have one or more of the following reasons:
 - the sulfite solution may have not been sufficiently prepared
 - the sulfite solution may have been stirred up and oxygen may have entered the lower parts of the liquid
 - there may be some air bubbles clinging to the membrane
 - there is the need for a membrane change or a sensor overhaulAs a first step, an upgrade on the sulfite solution is recommended. If not successful, the second step will be membrane replacement, and the next step sensor overhaul.
- (19) pull out sensor, rinse with water, dry with Kleenex tissue
- (20) make a final check of reading on air
- (21) stow the sensor away safely so that it is protected
- (22) fill the sulfite solution into the glass bottle. It may be necessary to break the crystals which have solidified into bits. Close bottle tightly. Save for next use
- (23) wash all equipment; dispose of chemicals solution in a proper way

8.7.9 Enclosure: Details on changing the membrane

The operating manual governs all actions for changing the membrane. In addition to this, it is strongly recommended to respect the following practical advice:

Nothing goes without the Recharge Kit. A stable table, a chair and a bright light is required, also a magnifying glass. The table shall have a cover that can take up some milliliters of liquid chemicals (paper, tray). Soft paper is needed for cleaning (e.g. Kleenex). A water supply for flushing and cleaning should be nearby (tap water is sufficient). There should be no air draft, as it will blow the membrane away.

Change the membrane only, when there is no time pressure, and you have a firm hand and a patient mood.

☞ The electrodes of the sensor are adjusted to within few micrometers tolerance. If this arrangement has deteriorated, the instrument may not function properly. Therefore great care has to be taken to avoid any mechanical damage to the electrodes.

☞ The electrolyte is a moderately concentrated caustic. Respect the material Safety Data Sheet. Special care should be taken to avoid contact with eyes; in case of an event flush with plenty of water.

Remove the cable from the sensor. Screw the electric plug of the sensor to the base support plate. Take care not to forget the O-Ring at the base plate. It gets easily lost. Without O-ring, electrolyte may run into the plug socket, which may cause electrical failure.

Put the sensor on the table, so the sensor stands firmly with the membrane on top. Remove the membrane holding ring with the special tool. Remove the old membrane with tweezers. Pour the remaining electrolyte to waste. Dry the sensor with the paper.

By means of the syringe with needle, introduce the electrolyte into the sensor head until it emerges from all four holes. Take care that there are absolutely no air bubbles in the liquid. The meniscus of the electrolyte should cover the sensor head completely. Now check for air bubbles with the magnifying glass.

By means of the tweezers, position new membrane on the ledge that is inside the cylinder of the mounting tool. Now mount this cylinder on top of the sensor.

Put membrane holding ring onto the piston of the mounting tool, and put piston carefully on top of the cylinder. Mount ring and membrane by pressing piston firmly down.

Now the membrane should sit tightly and without any air bubbles in the electrolyte. Perform Function control (visual check) with the magnifying glass. Special scrutiny deserve the four holes of the membrane support, which should not show any air bubbles.

If a proper membrane change has not been achieved latest at the third attempt, it is best to wait for another biorhythm or to have someone else to try it.

Now flush sensor with water and dry off water with paper, but do not touch membrane.

Whatever is intended with the sensor in the near future, the membrane should always stay moist.

Put your gloves away, and wash your hands. Avoid getting electrolyte into your eyes or your mouth. In case of an event, flush with plenty of water.

8.7.10 Enclosure: Storage when not in use

It is understood that the equipment is stored in an environment suitable for sensitive electronic equipment (clean, dry, limited temperature range etc.). The manufacturer manual gives details.

Sensor

When not in use for > 4 weeks, remove the membrane, flush and dry the sensor. When it is assured that the sensor is dry, mount the protecting cap.

Longer storage with electrolyte may lead to degradation of the electrode surface, indicated by discoloration and loss of ability for calibration. In such case, the electrodes need to be chemically cleaned (see the instrument manual). If leaked electrode enters the thread between the electrode and the protecting cap, the thread may be blocked and this may necessitate brute force to remove the cap, with the danger of damaging the sensor.

Instrument and cables

Remove batteries (if any). Dry completely; check especially cable connectors for being dry.