

Loss of Alkalization in an Alkaline Treated Stator Cooling Water System

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ABSTRACT

Alkaline treatment of stator cooling water (SCW) systems with copper hollow conductors performs best when pH and dissolved oxygen are kept constant. In the event of loss of alkalization, pH will return to neutral and this will destabilize existing copper oxide layers. Operating experience, however, indicates that infrequent and short-term loss of alkalization does not result in a detrimental buildup of copper oxides in the stator hollow conductors. Thus there is the question as to how long and how often a loss of alkalization can be tolerated.

Although operating experience suggests that loss of alkalization can be tolerated for short periods, it is not recommended to allow this routinely and, to the extent practical, SCW pH should be kept constant. Although there is no hard data to support this, an international expert consensus has been found that loss of alkalization of up to one week, and not more than two occurrences per year, can be tolerated. Upon loss, alkalization should be restored to normal as soon as possible. If the loss of alkalization is longer, it is recommended to monitor the water pressure drop across the coils and, if available, also the stator bar temperatures.

INTRODUCTION AND BACKGROUND

Proper maintenance of a plant's strategic generator stator cooling water (SCW) chemistry regime is essential for minimizing system corrosion and potential operational issues. When the SCW is exposed to air, water-cooled generator stators employing copper hollow conductors are subject to copper corrosion. If not properly controlled, copper oxidation, release and subsequent re-deposition (typically as copper oxides) can lead to reduced flow through the hollow conductors and in some cases result in complete hollow conductor blockage [1]. Mechanical and/or chemical cleanings will then be required to restore generator performance.

Based upon the release rates of copper as a function of dissolved oxygen concentration in high-purity water systems, plants may choose to operate in either a low (typically $< 20 \mu\text{g} \cdot \text{kg}^{-1}$) or a high ($> 2 \text{mg} \cdot \text{kg}^{-1}$) dissolved oxygen (DO) concentration range [1]. While either method is acceptable (depending on plant design), operation with SCW DO in an intermediate concentration band ($100\text{--}500 \mu\text{g} \cdot \text{kg}^{-1}$) can lead to increased copper release rates and potentially hollow conductor plugging [1,2]. In addition to DO, another chemistry factor to consider is SCW pH. The solubility of oxidized copper (formed through reaction of copper metal with DO in the SCW) is highly dependent on system pH [1,3]. Copper oxide solubility is at a minimum in the alkaline pH region of approximately 9–10 pH units and increases significantly

as pH neutrality is approached. Under alkaline treatment, copper release is low due to lower copper oxide solubility at elevated pH. The ultimate goal of alkaline treatment is to minimize copper transport in the bulk water resulting in a stable copper oxide layer in the hollow conductors. The resulting copper oxide layers formed under alkaline treatment are of a different morphology and are potentially thicker than the oxide layers formed under neutral pH conditions [1,3]. As for DO, either a neutral or alkaline pH approach is acceptable, however, the chosen pH target band should be maintained. Deviation from the target pH band should be minimized to prevent unstable copper oxide layers and potentially hollow conductor plugging.

This paper explores the question of how long an alkaline SCW system can be operated with loss of alkalization without risking a detrimental buildup of oxides in the hollow conductors.

SOUTH TEXAS PROJECT EXPERIENCE

SCW Chemistry History

The South Texas Project (STP) power plant comprises two pressurized water reactor units with water-cooled Westinghouse generators of 1 504.8 MVA each, commissioned in 1988 and 1989.

Historically, STP operated both units under a neutral pH, low DO chemistry regime. Although this approach is acceptable, SCW air ingress issues resulting in stator chemical cleanings ultimately led the station to rethink the SCW chemistry operating philosophy [4,5]. Based upon original equipment manufacturer (OEM) recommendation, STP successfully converted both units to an alkaline pH regime, while maintaining low DO target concentrations. STP Unit 1 was converted to alkaline chemistry in May 2013 and STP Unit 2 in December 2013. Alkalization is achieved at STP by dosing 2 % sodium hydroxide with an injection pump into the SCW system, downstream of the mixed-bed demineralizers, to target a pH in the range of 8.5–9.0 (Figure 1).

STP chemistry specifications and typical operating chemistry parameter values before and after implementation of the alkalizer are shown in Table 1. A significant reduction in SCW copper concentrations was apparent in both units after implementation of the alkalizer.

Impact of Alkaline Treatment

Figure 2 (taken from [4]) shows how alkalization successfully maintained STP Unit 1 system temperatures within operational limits during periods of elevated DO concentrations. The figure shows a trend of STP Unit 1 stator coil temperatures following an offline chemical cleaning during the previous outage. Unit 1 started up with DO concentrations averaging $15 \mu\text{g} \cdot \text{kg}^{-1}$ and began experiencing elevated coil temperatures after 4 months of operation. The unit shut down for a planned outage to chemically clean the stator coils and install an alkalizer (represented by point A in Figure 2). Following startup from the planned outage, DO was still present averaging $18 \mu\text{g} \cdot \text{kg}^{-1}$ however, with the alkalizer installed, no increases in coil temperatures or pressures were measured throughout the cycle. The temperature changes and outage at points B and C, respectively, were due to an extraction steam bellows rupture which required repair. Both STP generators have since been rewound and operate in the alkaline pH, low DO chemistry regime.

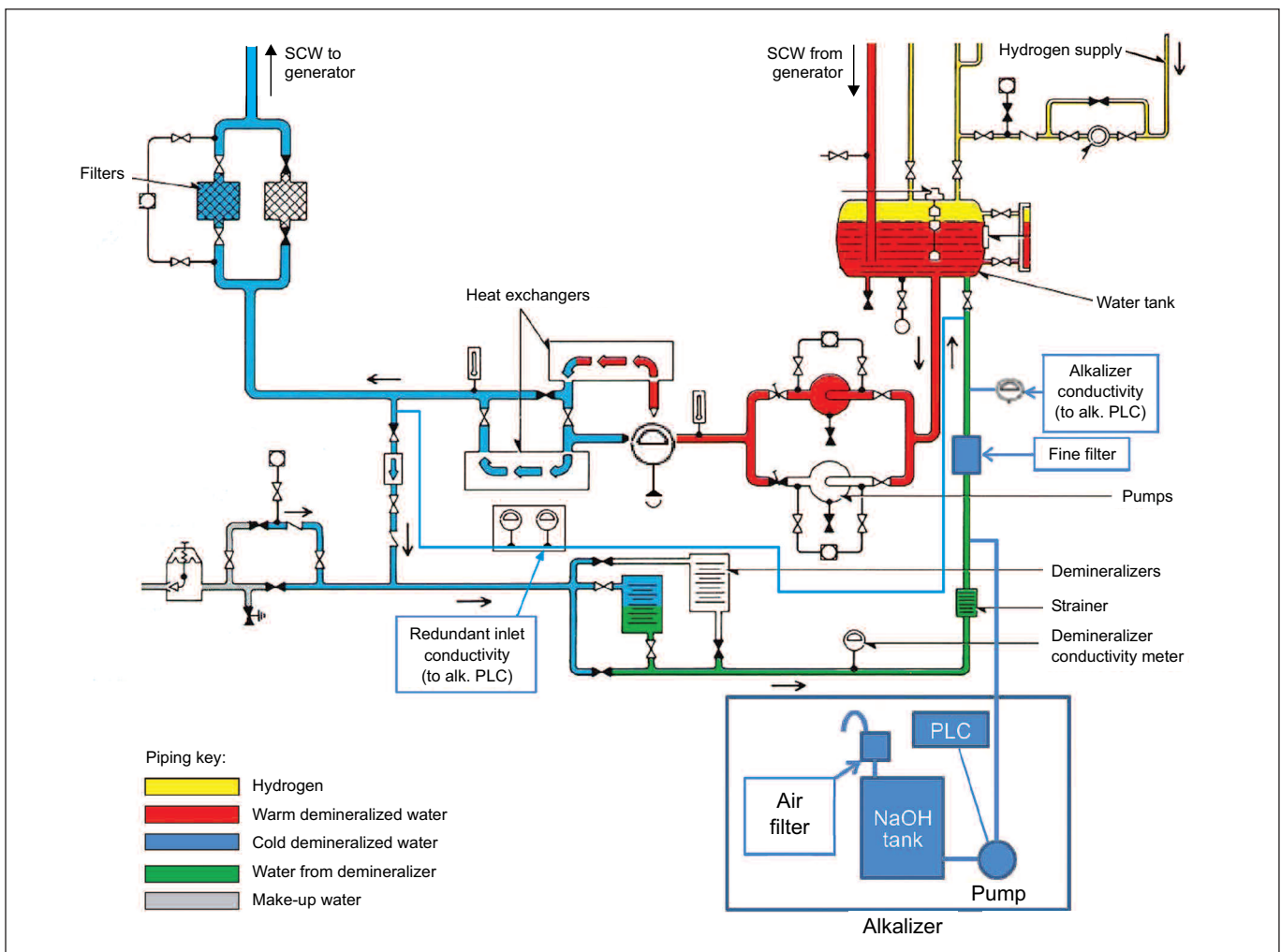


Figure 1: South Texas Project (STP) alkalizer layout. PLC programmable logic controller

STP SCW chemistry parameters	STP Specifications		STP Unit 1		STP Unit 2	
	Neutral pH	Alkaline pH	Before	After	Before	After
pH [25 °C]	5.8–7.0	8.5–9.0	6.0–7.0	8.6	6.0–7.0	8.6
Dissolved oxygen [$\mu\text{g} \cdot \text{kg}^{-1}$]	< 20	< 20	0–20		0–20	
Copper [$\mu\text{g} \cdot \text{kg}^{-1}$]	< 20	< 10	10–20	< 1	5–15	< 1
Iron [$\mu\text{g} \cdot \text{kg}^{-1}$]	< 5	< 5	< 2		< 2	
Sodium [$\mu\text{g} \cdot \text{kg}^{-1}$]	–	< 300	–	149	–	137
Specific conductivity [$\mu\text{S} \cdot \text{cm}^{-1}$, 25 °C]	< 1.5	1.0–2.5	< 0.2	1.5	< 0.2	1.5

Table 1:
South Texas Project (STP) stator cooling water (SCW) specifications and typical chemistry parameter values before and after alkalizer installation.

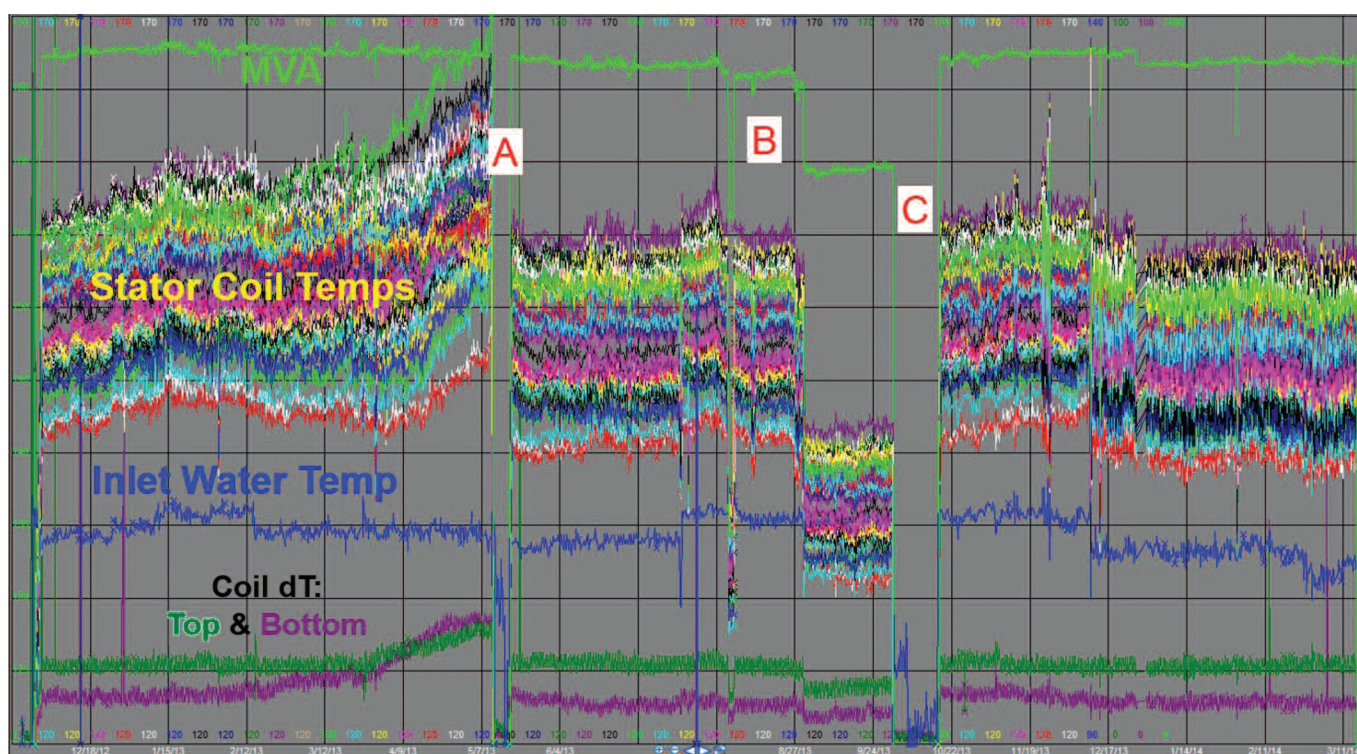


Figure 2:
STP Unit 1 stator performance – neutral and alkaline SCW chemistry regimes [4].

Alkalizer Dosing Issues

On December 26, 2014 (event 1) and February 4, 2015 (event 2), STP Unit 1 SCW alkalizer failed to dose sodium hydroxide into the SCW system. The alkalizer was out of service for approximately 6 days during event 1 and for approximately 12 hours during event 2.

The elevated SCW pH regime operates on the principal of stabilizing the copper oxide layers rather than partially

dissolving them under neutral pH conditions. The morphology of the oxides formed under alkaline pH is different to that formed under neutral pH environments. If the alkalizer pump fails, SCW system pH will return to neutral (due to removal of sodium by the demineralizers), which will lead to the dissolution of some of the copper oxide and ultimately an unstable mixture of cupric and cuprous oxide layers in the system.

Over the long-term (likely many years of operation), switching pH regimes will lead to copper/copper oxide release, transport and re-deposition in the stator bars, ultimately resulting in hollow conductor plugging. It is desirable to minimize the duration the alkalizer is out of service during SCW operation to minimize the potential for copper oxide plugging of the stator hollow conductors.

DATA ANALYSIS AND EVALUATION

STP Response to Loss of Alkalizer

Figure 3 shows the decay profile for SCW specific conductivity (SC) following alkalizer isolation during event 2. It took approximately 8 hours for conductivity to return to $< 0.2 \mu\text{S} \cdot \text{cm}^{-1}$. The cleanup half-life was calculated at approximately 2 hours with a $34.11 \text{ L} \cdot \text{min}^{-1}$ demineralizer flowrate. pH was verified within the neutral range, measuring 7.5 pH units, when conductivity was $< 0.2 \mu\text{S} \cdot \text{cm}^{-1}$.

Figure 4 shows system copper behavior following loss of the alkalizer during event 1. The first sample (taken approximately 30 hours after the loss of the alkalizer) shows a change in system copper concentrations. Typical copper concentrations in the SCW under alkaline condi-

tions before the event were less than the instrument lower limit of detection (LLD) – i.e. $< 1 \mu\text{g} \cdot \text{kg}^{-1}$. A sustained increase in copper above the LLD (between 2 and $2.5 \mu\text{g} \cdot \text{kg}^{-1}$) was observed during the 6-day operational period under neutral pH chemistry conditions. Although the copper remained less than the STP procedural specification of $10 \mu\text{g} \cdot \text{kg}^{-1}$, the increased trend is an indicator of increased copper release in the system, likely from dissolution of existing copper oxides. An immediate reversal in system copper concentrations was observed as soon as alkaline chemistry was restored. System copper concentrations returned below instrument LLD values, indicating that oxidized copper was preferentially staying in the copper oxide form. Under elevated pH, the strategy is to maintain stable, tightly adherent copper oxide layers and minimize copper release rates.

Figure 5 shows similar copper behavior in Unit 1 (event 2) under neutral water chemistry conditions. A sustained increase in copper above the LLD (between 1 and $1.5 \mu\text{g} \cdot \text{kg}^{-1}$) was observed starting approximately 12 hours following the loss of the alkalizer. Although the copper remained less than the STP procedural specification of $10 \mu\text{g} \cdot \text{kg}^{-1}$, the increased trend is an indicator of increased copper release in the system, likely from dissolution of existing copper oxides.

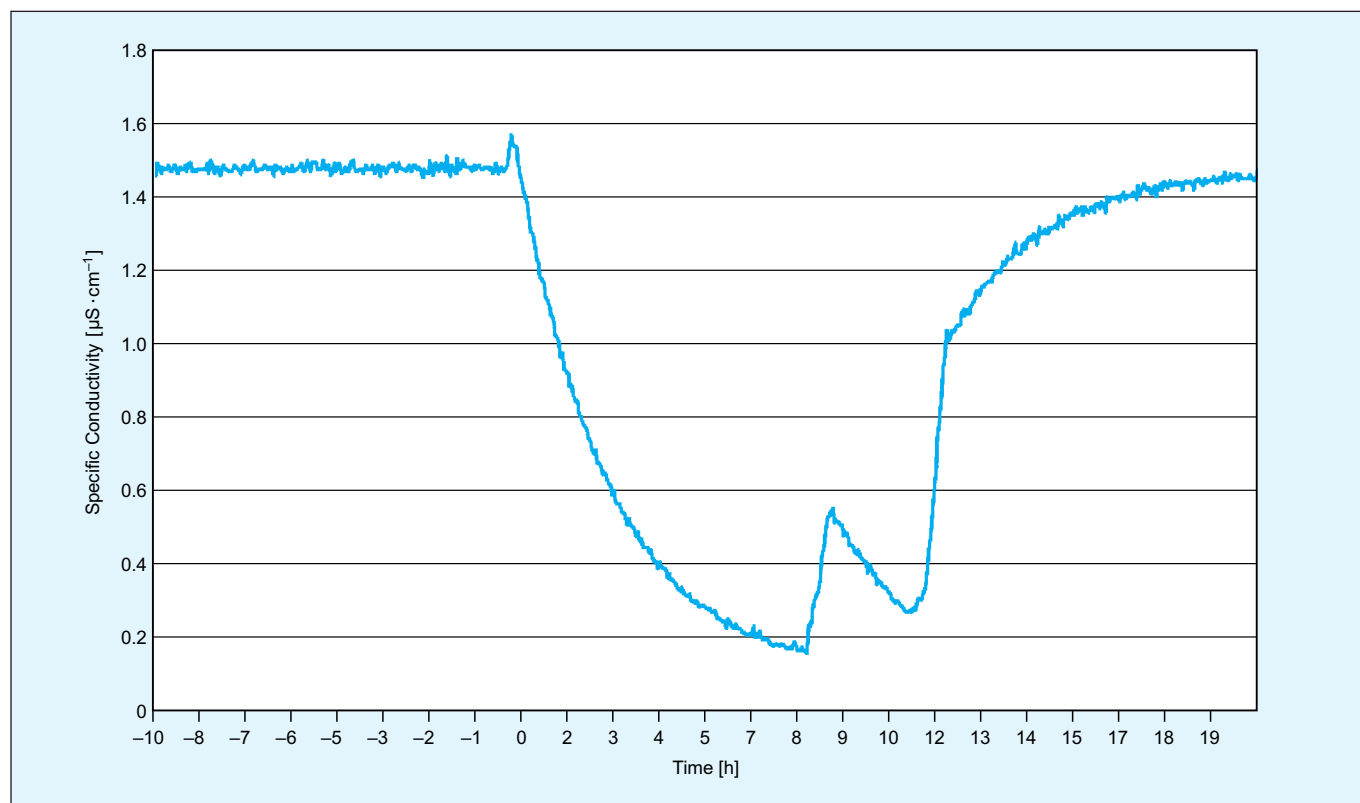


Figure 3:
STP Unit 1 SCW system conductivity following alkalizer isolation (event 2).

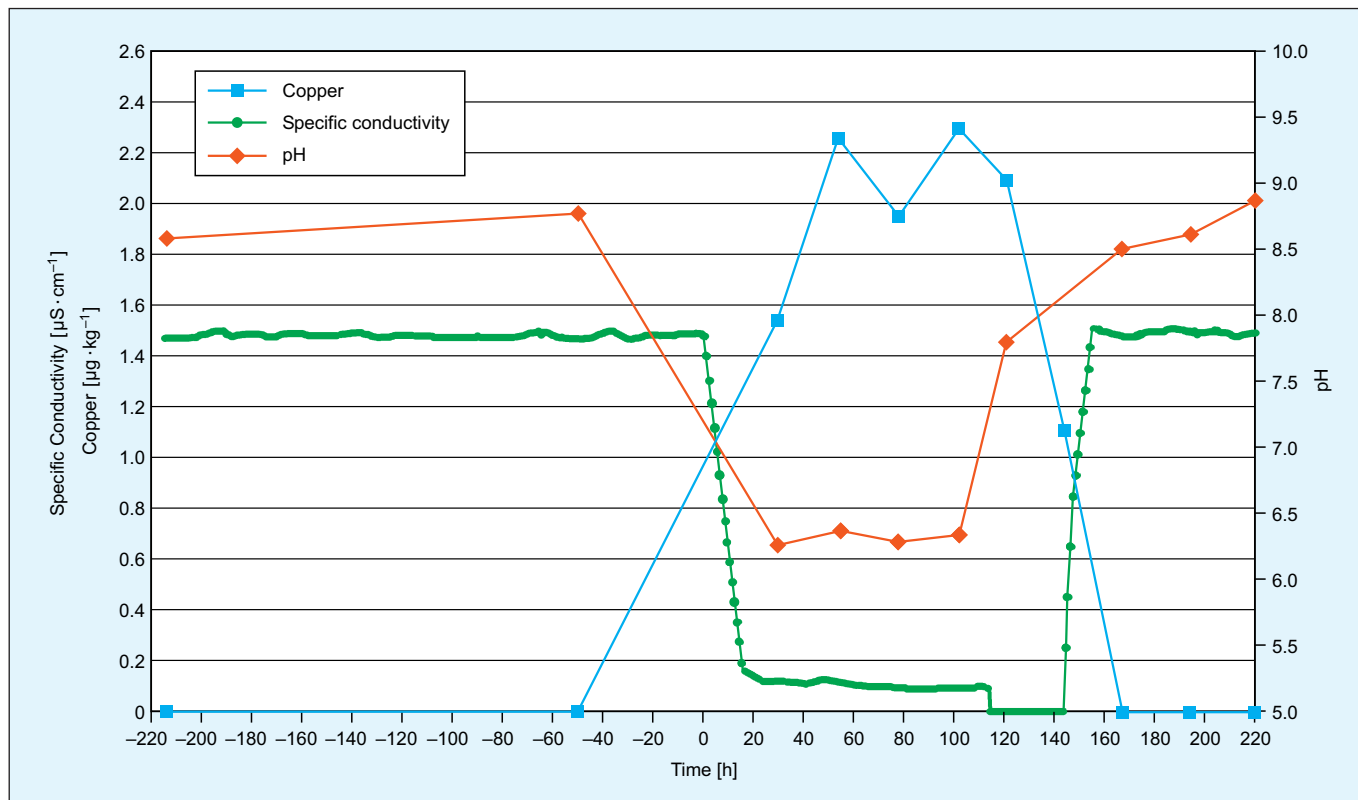


Figure 4: STP Unit 1 SCW alkalizer loss (event 1).

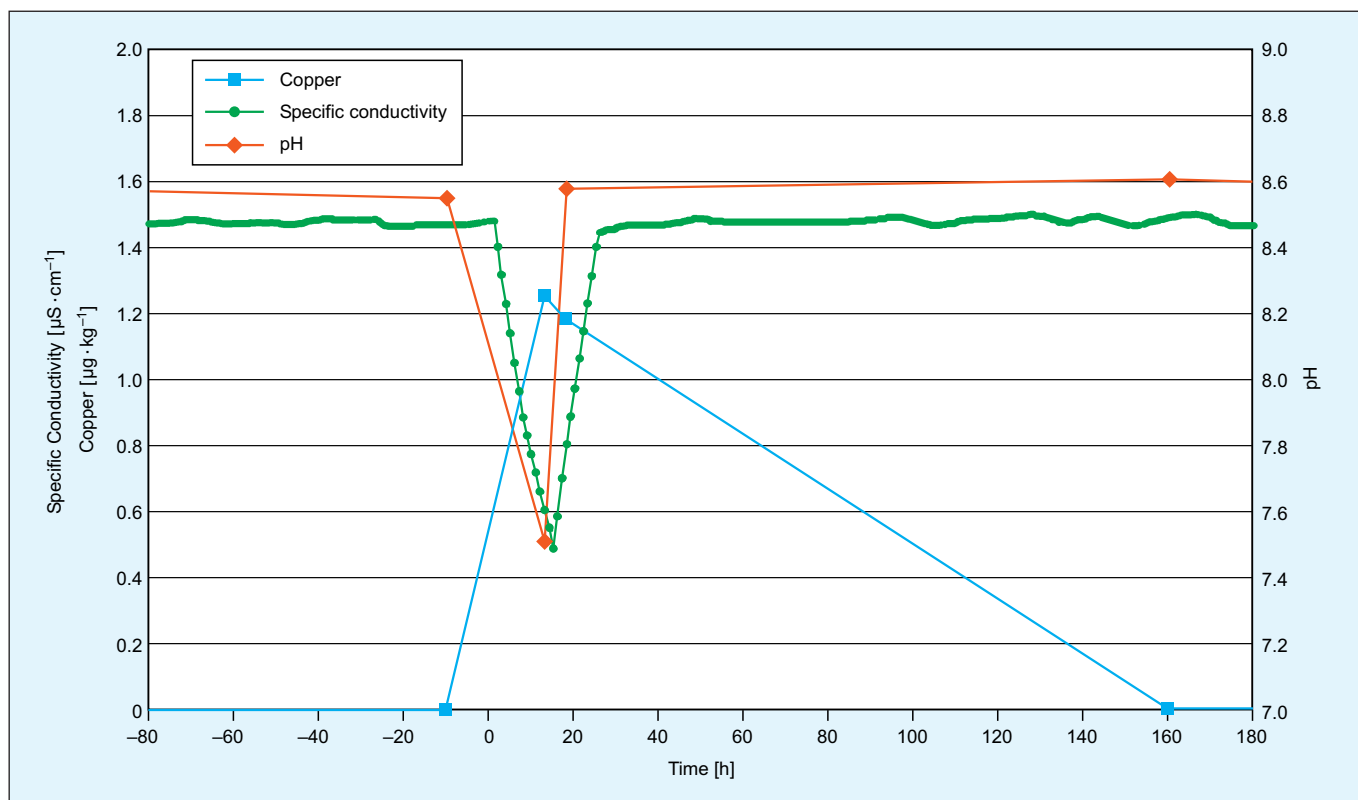


Figure 5: STP Unit 1 SCW alkalizer loss (event 2).

SCW Chemistry

Ingress of DO into SCW systems will lead to copper oxidation. Depending on DO concentrations and pH, the two mechanisms below (Eqs. (1) and (2)) describe typical copper oxides formed in the SCW system. Phase changes between Cu_2O and CuO can lead to particulate release and copper re-deposition, possibly in the hollow conductors [1,2].

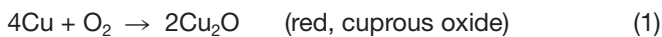


Figure 6 (taken from [6]) shows the different stable forms of copper or copper oxide under various chemistry conditions and can be used to explain the difference between operating under neutral and alkaline pH regimes.

A small increase in DO in neutral water chemistry will increase the potential and will allow formation of cuprous oxide (indicated by diamonds in Figure 6). Due to the kinetics of the real system, pH fluctuations due to air ingress and the relatively high solubility of copper oxides at neutral pH, soluble copper ions will be predominant in neutral chemistry and copper dissolution will occur. Higher soluble copper concentrations will be measured

in the SCW. Copper ions will be removed by the demineralizers.

Figure 6 also shows results of two tests at another plant with alkaline treatment. Test 1: A change in pH to alkaline for 16 days without a system chemical clean (green line with squares in Figure 6) shows stabilization of oxides formed in the system. Oxides tended towards the cupric oxide stability region but did not reach there due to the short time (16 days) the system was exposed to alkaline treatment. Test 2: A change in pH for 8 months following a stator clean (red line with circles in Figure 6) shows that metallic copper is initially favored (as expected after a system clean). A slight ingress of DO over time led to the initial formation of cuprous oxide followed by the transition to cupric oxide. The return to neutral pH (by isolation of the alkalizer) in both cases showed oxide dissolution was favored again. It appears in both cases that alkalization first brings the system into the cuprous oxide domain, followed by a transition ultimately to the cupric oxide domain.

The morphology of oxides formed under alkaline pH is different from that of oxides formed under neutral pH [1]. According to references 1 and 2, particulate copper release seems to be connected to phase changes between cuprous and cupric oxide, possibly by stresses

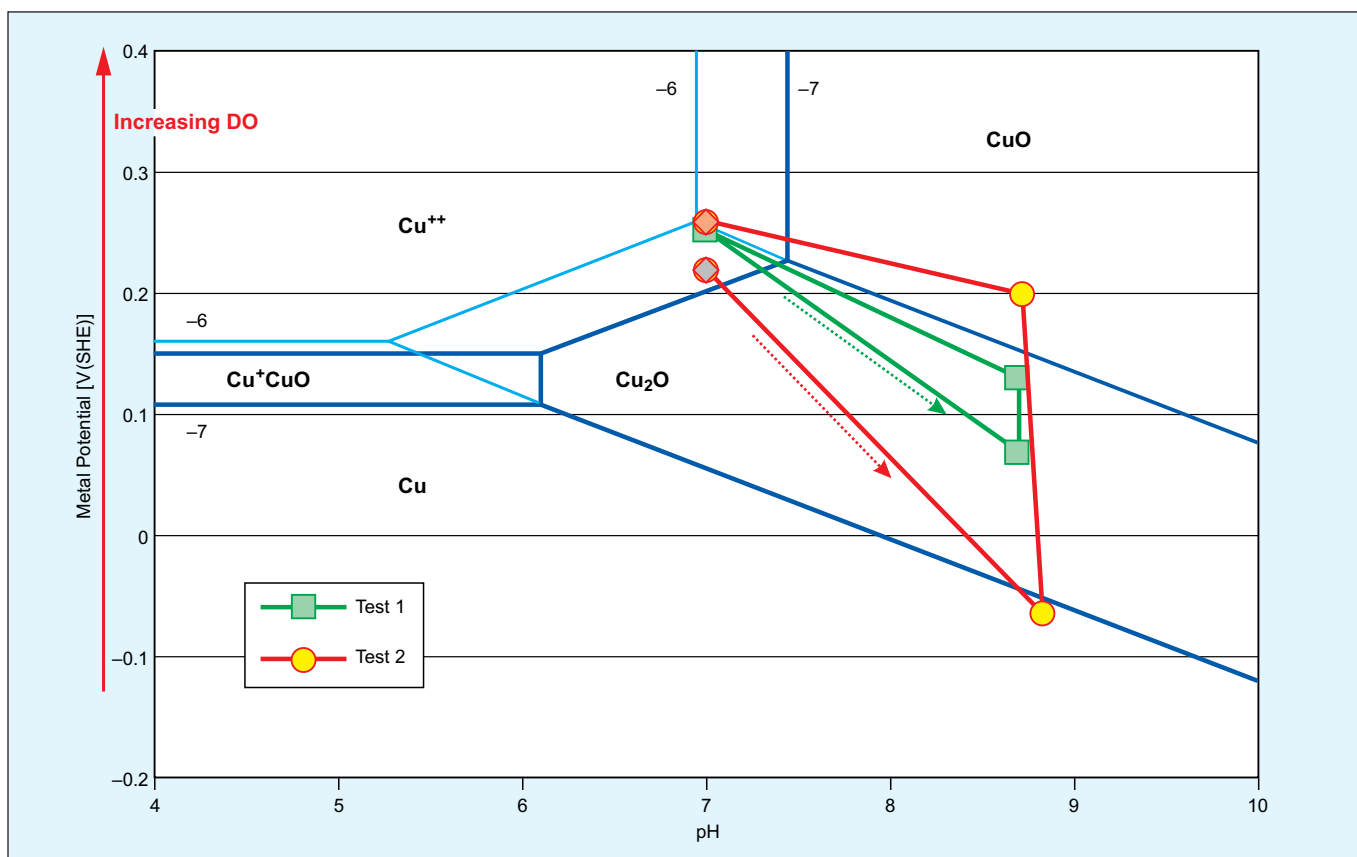


Figure 6:
Copper corrosion – Pourbaix diagram of Cu [6].

from the change in oxide structure. Minimizing changes in pH (by maintaining stable alkalinization for example) would be expected to minimize the cycling between different oxide types and a potentially unstable mixture of oxides in the SCW system.

Figure 7 (taken from [6]) shows that electrochemical potential (ECP) and conductivity react simultaneously following the termination of sodium hydroxide injection, suggesting that copper oxide dissolution likely starts quickly after loss of the alkaler. This is consistent with the immediate and sustained increases in system copper concentrations observed following the loss of alkalinization during STP events 1 and 2.

In summary, by converting to alkaline pH treatment, copper oxides formed in the SCW system will be stabilized instead of going through dissolution (which is observed under neutral water chemistry). Cycling SCW system pH (by starting and stopping the alkaler) will lead to copper/copper oxide release, transport and re-deposition in the stator bars, ultimately resulting in hollow conductor plugging in the longer term. It is desirable to maintain a stable injection of sodium hydroxide into the SCW system and to minimize the dura-

tion the alkaler is out of service during SCW operation to minimize the potential for long-term stator hollow conductor plugging with copper oxides.

STP Data Evaluation and Industry Survey

During STP events 1 and 2, the alkaler was returned to service in both cases within 1 week. DO remained within specification during both events. No increase in system temperatures or differential pressure across the stator bars was observed. System copper concentrations increased and remained elevated during neutral pH operation, however copper concentrations never approached or exceeded the STP upper procedural alert limit of $10 \mu\text{g} \cdot \text{kg}^{-1}$, even after approximately 6 days of operation under neutral pH conditions. Following a recommendation taken from reference 7 and as discussed above, it is recognized that the impact of the change from alkaline to neutral pH on the copper oxide mix in the SCW system and the likelihood of stator hollow conductor plugging will likely be more evident over long-term operation of the stator. However, short-term actions to maintain alkaline chemistry will help preserve the long-term health of the stator by minimizing short-term copper dissolution and longer term change in oxide morphologies.

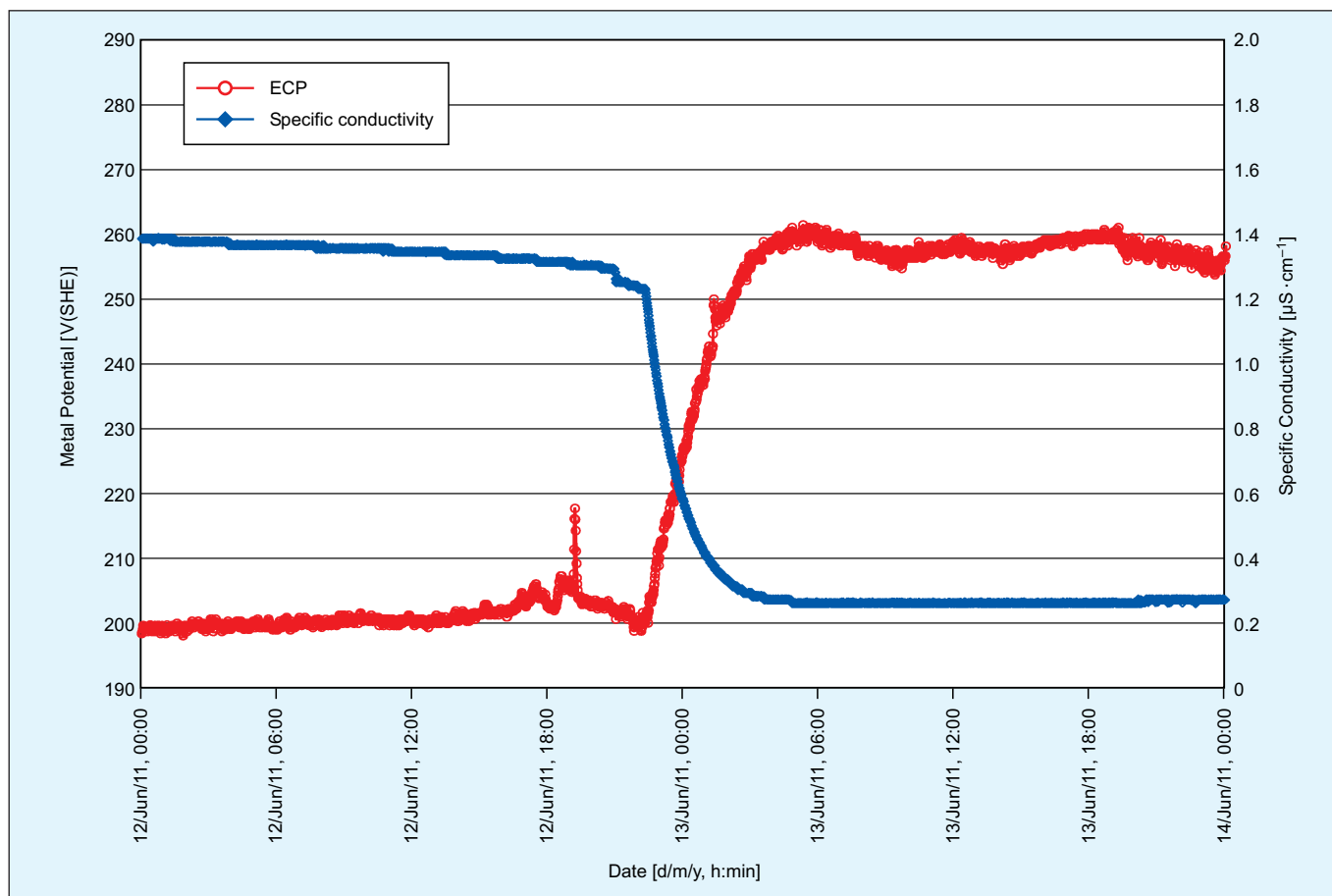


Figure 7: SCW ECP and conductivity following loss of alkalinization [6].

Guidance was sought from industry experts on how long the alkalizer can be realistically kept out of service before action to restore alkaline pH becomes necessary. According to reference 7, industry experts are comfortable with a loss of the alkalizer for one week, after which action should be taken to restore alkaline chemistry (it should be noted that this recommendation was not from the OEM). The OEM (Siemens) was contacted for their recommendation [8]. According to Siemens, there is no significant impact of short-term alkalizer downtime (i.e. a couple of days). The impact will be minimized by keeping the oxygen concentration within the recommended range ($< 30 \mu\text{g} \cdot \text{kg}^{-1}$). Siemens operational experience shows that the alkalizer can remain out of service for a couple of days before action is required to restore alkaline pH. The alkalizer downtime should be kept as short as possible and should not exceed one week in length [8].

Industry chemistry peers were contacted to survey utilities using an alkalizer for SCW chemistry control. The following question was asked: *If your utility controls stator cooling water (SCW) pH in the alkaline regime, how long do you allow operation of your SCW in the neutral pH*

environment if maintenance (planned or unplanned) is required on your sodium hydroxide dosing system (alkalizer or sodium-form mixed bed)? The survey responses are tabulated in [Table 2](#) and summarized below.

Of the 17 utilities that responded to the survey, the majority (approximately three-quarters) did not operate their SCW systems in the alkaline pH regime. This is not surprising since the approximate number of plants worldwide that operate in the alkaline pH region is only $\sim 7\%$ [3]. Approximately one-quarter of the utilities responding to the survey (four utilities) operated their SCW systems in the alkaline pH regime. Two of the utilities implement an alkalizer for pH control whilst the remaining two utilities use a sodium-form mixed bed.

None of the responding utilities that operate with alkaline chemistry had formalized any written instruction which addressed this concern, and all operate under the assumption that the system should be returned to service as soon as possible (it should be noted that the concern is primarily with plants using an injection-type alkalizer skid since the sodium-form mixed beds should generally

Plant/Utility/Company	Response
SvoBaTech, Inc. (Previously with Alstom)	I would say the shorter you deviate from alkaline the better, as you probably are moving copper oxides at an increased rate. You could measure changing copper content in the water and even check for changes in solids. This would be valuable information for the industry.
Svoboda Consulting (Previously with Alstom)	(Taken from [7] and [9] and not from this survey effort.) We always have a mix between CuO and Cu ₂ O, more CuO with high-oxygen regime than with a low-oxygen regime, and more CuO with alkaline treatment, than with neutral treatment. Because the oxide mix is gradual, I do not expect immediate changes when changing water chemistry. This would rather be mid-term or long-term effects. What I would recommend, for periods of up to 1 week, to just "break an egg over it" (as we say in German for "forget it"), and if it is going longer to install a temporary device. As for operation without a mixed bed in service: running without a mixed bed is absolutely a no-go and a nice business case for chemically cleaning the stator. Operational experience has shown that operation with no mixed bed in service can lead to hollow conductor plugging within weeks.
McGuire	McGuire started using alkalizer injection on Unit 2 in the fall of 2012 and Unit 1 in the fall of 2014 after stator replacements. McGuire does not currently have any guidance to drive a quick restoration if injection is lost. The assumption is as soon as possible but nothing is formalized.
ChemStaff Inc. (Consulting)	Based upon some personal experience with this approach, it is felt that 1 week is reasonable. I would propose the following programmatic controls: <ul style="list-style-type: none"> • If oxygen is $< 30 \mu\text{g} \cdot \text{kg}^{-1}$, the goal should be to restore alkalizer to service within < 96 hours, and the limit should be within < 7 days. • If oxygen is $> 30 \mu\text{g} \cdot \text{kg}^{-1}$ at any time when the alkalizer is not in service, the alkaline pH control should be restored within < 12 hours.

Eskom and Independent Consultant to Eskom (South Africa)	The simple answer is that we operate differently and cannot offer any useful input. Our alkalisation comes from a sodium-form mixed bed and there is not any issue which could cause it to break-down. The STP system uses a sodium hydroxide continuous dosing system with a hydrogen form mixed bed to continuously purify the circuit but which as stated can break down. I would prefer some redundancy or standby. Seems a small price compared with the cost of cleaning stator bars. So, there is no guidance we can provide other than base it on personal experience – a week out of operation does not seem to be a heavy penalty provided this is not a frequent occurrence, say no more than two incidents per year.
Diablo Canyon	We operate Unit 1 with an alkalizer skid and a sodium-form mixed bed. The way we operate our system we could probably tolerate the alkalizer being out for a while since it rarely kicks in during steady state operation. That being said if we were unable to maintain the required chemistry I do not believe we would tolerate such a condition for 6 days. Any work of this type would be classified as requiring extended hours and would fit in our work control process as emergent/ urgent due to chemistry control issues. It is not ideal to remove all sodium from the system. Possible recommendation: an immediate response to the loss of the alkalizer system may be for Operations to isolate the SCW demineralizer from service. For short periods of time, ingress of contaminants that affect conductivity should be negligible. Diablo Canyon Unit 1 operated in this fashion prior to stator replacement and implementation of the current alkaline chemistry regime. With the mixed bed removed, sodium removal from the SCW by the demineralizer will not occur. The possibility of a lower pH than the normal target may be likely if there is a significant time delay between loss of alkalizer and removal of the demineralizer. However, efforts to maintain sodium concentrations in the system would help minimize the pH fluctuations.
Comanche Peak	We have no formal guidance for how long the alkalizer can remain turned off. Typically, for routine maintenance, it is off for ~12 hours and pH is neutral for only a few hours. Six days sounds long to me.
Beaver Valley	Not applicable: Beaver Valley does not have stator cooling water system.
Callaway	Not applicable: Callaway does not use an alkalizer injection system. Neutral pH, high-oxygen system.
Hope Creek/Salem	Not applicable: Hope Creek and Salem do not use an alkalizer injection system.
Cook	Not applicable: Cook does not use an alkalizer injection system.
Exelon	Not applicable: Exelon do not use an alkalizer injection system at their plants.
Farley	Not applicable: We do not have a stator cooling system at Farley.
Fermi 2	Not applicable: Fermi 2 is neutral pH.
Monticello	Not applicable: Monticello does not use an alkalizer injection system.
OPG	Not applicable: We are still running on neutral pH, not yet converted to alkaline pH. I don't think that in 6 days of maintenance, any major issue will happen. I am sure that makeup water is deoxygenated.
Prairie Island	Not applicable: Prairie Island electrical generators are cooled by hydrogen.
Surry	Not applicable: Surry does not have the SCW system like STP. The generators are cooled by hydrogen.
Columbia	Not applicable: Columbia operates with a pure water low oxygen regime for our stator.
Vogtle 1&2	Not applicable: Neutral pH, high-oxygen system.

Table 2:

Industry survey results.

Question: *If your utility controls stator cooling water (SCW) pH in the alkaline regime, how long do you allow operation of your SCW in the neutral pH environment if maintenance (planned or unplanned) is required on your sodium hydroxide dosing system (alkalizer or sodium-form mixed bed)?*

always elute sodium). Two of the utilities operating in the alkaline pH regime expressed concerns with having no alkaline treatment for time periods up to one week and would recommend restoring alkaline treatment as soon as possible. On the other hand, one responding utility commented that operation with the loss of alkaline treatment for up to one week would likely not have a significant impact based upon personal experience (as long as the total number of these occurrences were minimized to say no more than two incidents per year). One utility suggested removing the demineralizer if the alkalizer was lost (to retain sodium concentrations in the SCW system), however this recommendation was not in line with operating experience and subsequent recommendation from other industry experts [9].

Based on the survey (Table 2), the consensus from industry experts and consultants was that alkaline chemistry should be restored as soon as possible (consistent with STP and current industry practices), however periods of operation up to one week would likely not cause significant issues. This advice was consistent with that of the OEM [8]. Efforts should be made to minimize the total number of such occurrences (targeting no more than two incidents per year) to reduce the possibility of future hollow conductor plugging.

As discussed above, the loss of pH has an immediate effect on system copper concentrations. However, when considering return to service of the alkalizer, a realistic balance between the immediate chemistry effects and station maintenance priorities should be recognized. Based upon the system copper response during loss of alkaline treatment, industry expert advice, OEM recommendations and industry survey results, the following is recommended:

If the alkalizer is secured when the SCW pumps are running, the alkalizer skid should be returned to service as soon as possible and should be back in service no later than one week after being secured (to minimize copper/copper oxide release, transport and re-deposition in the stator bars).

STP operations procedures were revised to add guidance which will heighten awareness as to the importance of returning the alkalizer to service following short-term maintenance issues. Additionally, actions were taken to identify critical parts of the alkalizer system and minimum stocking levels for these parts to ensure prompt alkalizer return to service should a failure occur in the future.

CONCLUSIONS

Alkaline treatment of SCW systems with copper hollow conductors performs best when pH and DO are kept constant. In the event of loss of alkalization, pH will return to neutral and this will destabilize existing copper oxide layers. Operating experience, however, indicates that infrequent and short-term loss of alkalization does not result in a detrimental buildup of copper oxides in the stator hollow conductors.

Although operating experience suggests that loss of alkalization can be tolerated for short periods, it is not recommended to allow this routinely and, to the extent practical, SCW pH should be kept constant. Although there is no hard data to support this, an international expert consensus has been found that loss of alkalization of up to one week, and not more than two occurrences per year, can be tolerated. Upon loss, alkalization should be restored to normal as soon as possible. If the loss of alkalization is longer, it is recommended to monitor the water pressure drop across the coils and, if available, also the stator bar temperatures.

Monitoring stator water chemistry with the ECP can give an immediate picture of the consequences of the pH change for the oxide structure.

ACKNOWLEDGMENTS

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