

Dechlorination / Oxidation

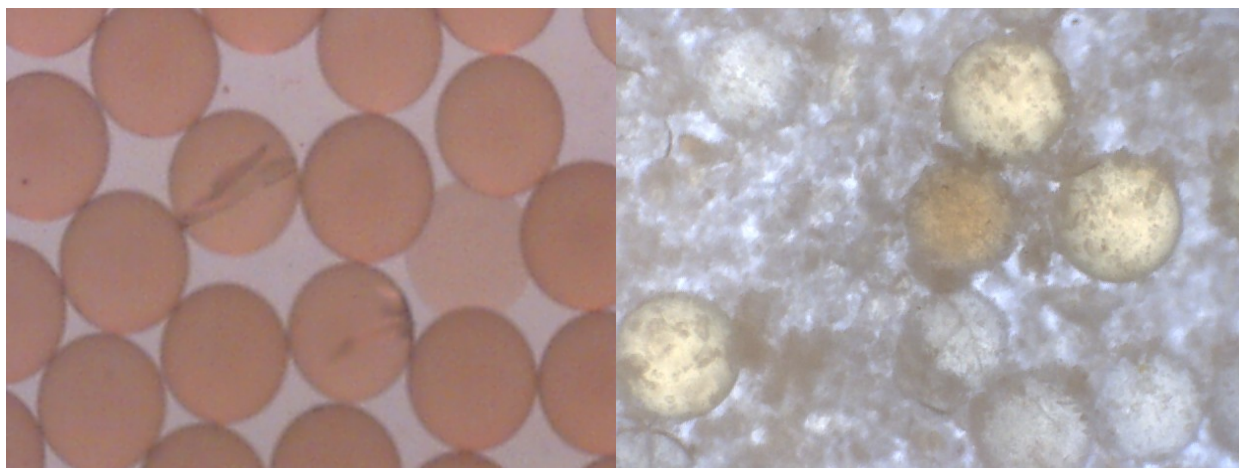
Pretreatment

This bulletin addresses the issue of dechlorination and oxidation damage as it relates to CEDI modules and systems. This information may be applicable to electrodeionization modules overall as well.

General

A main cause of CEDI module failure is oxidation of the ion exchange resin, typically by chlorine. Other strong oxidants such as ozone and hydrogen peroxide will also cause module damage. While oxidation can be caused by improper chemical cleaning, it is more commonly due to incomplete removal of chlorine from the feed water (most occurrences of this type happen in systems using chemical dechlorination by sodium bisulfite or sodium sulfite).

Strong oxidants will cause the resin matrix to decrosslink and become soft. The damaged beads swell and fracture, blocking the interstitial volume through which the water normally flows, which results in an increased pressure drop across the module. The ion exchange membranes used in the CEDI process will also deteriorate in the presence of oxidants. Any oxidation damage to either the ion exchange resin or membranes is irreversible.



New Resin Beads

Oxidized Resin

RO membranes are also sensitive to oxidation. For this reason it is extremely important to put the proper dechlorination measures in place in the pretreatment to both the RO and CEDI system.

The ideal concentration level for oxidants is non-detectable (make sure the chlorine test kit is sensitive to 0.02 mg/l as Cl₂).

When to Suspect CEDI Module Oxidation

The first symptoms of oxidation are a small drop in product water quality accompanied by an increase in module resistance. Unfortunately sometimes the first symptom noticed by the end user is when a CEDI module shows a drop in product flow rate or an increase in pressure drop, at which point irreversible damage has already occurred. Continued exposure to oxidants will cause the drop in flowrate / pressure increase to become severe, and rebuilding or replacement of the module may be necessary. If these symptoms are observed there is a test to confirm resin oxidation that can be carried out in the field. Contact your local Ionpure Technical Manager for assistance.

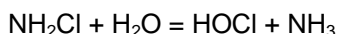
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Common Locations on the System to Measure Chlorine

A) Free Cl₂ in RO Permeate

It is usually assumed that if the feed to an RO system does not contain any free chlorine, then the product from the RO will also be free of chlorine. Therefore it is typical to regularly check the RO feed water with a chlorine test kit, but it is not common to check the RO permeate. This can lead to problems with RO/CEDI systems. We have observed a number of cases where the concentration of free chlorine in the RO feed water is zero (below detection limit) *while there is measurable free chlorine in the RO permeate*. This appears to be more common in systems where the raw feed water contains chloramines, but it may not be limited to these cases. We are not certain of the mechanism involved, but one possibility is the hydrolysis of chloramines according to the following reaction:



In a recent example, the RO feed water was found to contain 0.1 ppm combined chlorine and no detectable free chlorine. The RO permeate contained 0.07 ppm combined chlorine and 0.04 ppm free chlorine. This is consistent with some of the combined chlorine being converted to free chlorine on the permeate side of the RO membrane. In another case there was no detectable free chlorine in the RO feed, but 0.9 ppm in the CEDI feed! This may explain why we have seen cases where the TFC RO membranes do not show signs of chlorine attack, while the downstream CEDI module appears to have been oxidized.

B) RO and CEDI Feed

It is clear that monitoring for free chlorine at the inlet to the RO is not enough to insure that the CEDI feed water has no free chlorine. It is necessary to regularly check **both** the RO feed water **and** the CEDI feed water with a test kit that is sensitive to 0.02 ppm free Cl₂. The CEDI feed should never exceed 0.02 ppm free chlorine (and more conservatively, should be less than 0.02 ppm total chlorine).

Look for other evidence

If monitoring does not detect chlorine in the feed water, the resin could still have been damaged by exposure to an oxidant at an earlier date. In such cases, the end user should be interviewed to determine if specific evidence of exposure to oxidizing chemicals is available. Such evidence could include:

1. Increase in salt passage through the RO membrane.
2. Decrease in RO operating pressure or increase in RO flow rate.
3. Problems with on-line chlorine or ORP monitors.
4. Interruption in feed of sodium bisulfite.
5. Chlorine breakthrough in the carbon filter requiring carbon replacement. Also look for evidence of increased frequency of sanitization or use of oxidizing sanitants.

METHODS OF REMOVING CHLORINE - There are three principal means of achieving the above requirement:

- Granular activated carbon
- Injection of sodium bisulfite or sodium sulfite
- UV dechlorination

Recommendation: Activated carbon dechlorination is preferred over chemical dechlorination because it is both more reliable and in some cases less likely to cause biological fouling problems. UV dechlorination is a relatively new process, which may have difficulty achieving complete chlorine removal, especially on chlorinated feed water.

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- A) Dechlorination by activated carbon** - It is the responsibility of the system supplier to ensure that the activated carbon filter is sized properly for complete removal of the feed water chlorine, taking into account the concentration of chlorine in the raw feed water. Ionpure would usually design dechlorination carbon filters for a minimum empty bed contact time of 6 minutes.
- B) Dechlorination by chemical injection (reducing agent)** - It is the responsibility of the system supplier to ensure that the chemical injection system is sized properly for complete removal of the feed water chlorine, and includes adequate instrumentation and control safeguard to ensure that the CEDI system is not fed water containing chlorine should there be a change in the feed water conditions or an upset in the operation of the chemical injection system. In systems that contain injection of multiple pretreatment chemicals (for example antiscalant and sodium sulfite or sodium bisulfite and sodium hydroxide) it is recommended that there be a separate injection point and static mixer for each chemical.
- C) Ultraviolet Dechlorination** - It is the responsibility of the system supplier to ensure that the UV dechlorination system is sized properly for complete removal of the feed water chlorine, taking into account the concentration of chlorine and chloramine in the raw feed water.

HOW TO MONITOR FOR CHLORINE - There are three common methods, manual, automated with ORP and automated with a chlorine monitor.

- Manual method** – A water sample is taken from the CEDI system feed and tested using a test kit.
Suggested Test Kit: Use Cl₂ – Hach Model CN-70 (#1454200)
- ORP Monitor** - the most common instruments associated with chemical dechlorination systems have measured either residual chlorine or oxidation-reduction potential (ORP). While residual chlorine can be used for alarming, it cannot be used for control of bisulfite injection to ensure an absence of chlorine (it can only be used for control of hypochlorite injection to ensure the presence of chlorine). Theoretically it should be possible to use ORP to ensure the presence of bisulfite (“reduction potential”) just as it is used to ensure the presence of chlorine (“oxidation potential”), since both can be correlated with a positive value of ORP (millivolts). Unfortunately the operation of ORP meters is often not well understood, and in particular the relationship between pH, ORP and chlorine concentration. The ORP value that will insure the absence of chlorine is site-specific and therefore the desired control point and alarm point must be carefully determined on-site before starting up the RO system. These issues are not insurmountable, and for the most part ORP control of dechlorination can work quite well in start/stop systems (although still not as reliably as activated carbon).
- Recommendation: Residual Sulfite monitor** – This system allows continuous measurement of sulfite residuals over ranges of either 0-2 or 0-20 PPM. **The key advantage is that the sulphite monitors measure an excess of a species, (bisulphite), rather than an absence of something (chlorine).** An analog output from the monitor can be used for control of the chemical feed system to maintain a safe residual sulfite concentration while reducing chemical expense to a minimum.



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REMEMBER THESE MAIN POINTS!

- There should be no detectable chlorine in CEDI feed water!
- Oxidation damage is irreversible
- Chlorine oxidation is one of the most common cause of CEDI failure
- Take free and total Cl₂ readings at RO inlet and CEDI inlet
- RO permeate can contain more free chlorine than RO feed based upon reformation of chlorine when chloramines are in the RO feedwater.

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Modules, call the local Ionpure center:

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