

## Water treatment for steam generators

### Reverse osmosis and electrodeionization



Used in many leading industries (micro-electronics, biotechnology, optics, etc.) for producing ultrapure water, reverse osmosis and electrodeionization (E.D.I.) are now increasingly used for treating water to be used in steam generators.



At the origin of this evolution, a technological innovation that is still of interest today, manufacturers consistently continuing to improve membrane performance, the drop in the price of membranes made possible by wider diffusion, the remarkable work done by equipment suppliers to simplify industrial applications and the increasingly restrictive legislation on industrial waste.

But to guarantee constant cleanliness and optimal performance when producing steam, it is reliability and high performance that have made reverse osmosis and E.D.I. systems essential elements in the choice of boiler water treatment systems.



Water treated by these techniques enables the quality of steam to be improved, thermal exchanges to be optimised by the complete absence of deposits on exchange surfaces, heat losses to be reduced by reducing the number of blowdowns and the costs of chemical anti-corrosion and anti-scale treatment to be reduced.

## DEPOSITS



Due to the increasingly high heat transfer coefficients to be found in steam boilers, all deposits are liable to have serious consequences in terms of energy consumption and to weaken equipment.

Any defect in cooling wall surfaces will lead to local increases in temperature and a drop in the mechanical resistance of boiler pipes, which may go as far as to make them burst. The phenomena concerned may be complex.

Even so, the more classic problems can be synthesized as follows:

Everyone knows that the solubility of calcium and magnesium salts that are responsible for the degree of hardness in hard water becomes increasingly limited as the temperature rises.

This phenomenon is particularly critical in steam boilers where temperatures are high.

Similarly, above certain levels of concentrate and in specific alkalinity conditions, silica precipitates to form deposits with a high capacity of insulation.

Lastly, input water may contain traces of iron coming from condensate return pipes or corrosion of the boiler feed water container.

At the pH that exists in boiler systems (over 9.5), iron is practically insoluble and will precipitate to form oxide deposits that contribute to the general fouling to be found in boiler pipes and tanks.

## CORROSION

Although numerous parameters must be taken into account, two main factors are responsible for corrosion.

The oxygen dissolved in the presence of metal plays the role of a cathode. A direct electric current forms between the different areas of metal to which the oxygen has easy access (cathode) and those which the gas can only reach with difficulty (anode). This corrosion may be located throughout the whole feed system especially in the boiler feed water container and in the boiler itself, especially when there are stoppages in production.

Bicarbonates ( $\text{HCO}_3$ ) contained in boiler feed water dissolve under heat to become  $\text{CO}_3$  carbonates and carbon dioxide  $\text{CO}_2$ .  $\text{CO}_2$  will escape with the steam to dissolve in the condensate and produce acid water, whose pH may drop below 6 in extreme cases. At these pH levels, corrosion of steel becomes severe and rapidly leads to the formation of perforations.

Obviously, the more bicarbonates there are in the water, the higher the amount of  $\text{CO}_2$  that is formed.



This concerns water droplets from the boiler being transported in the steam due to an excessive concentration of mineral salts, a high level of caustic alkalinity, the presence of turbulence and foam on the surface of boiler water that is promoted by all the preceding phenomena and abnormal variations in vaporisation.

The results are of course a drop in steam efficiency, risks of erosion and fouling in down-line installations.

Therefore, producing steam under optimal conditions requires following a certain number of constraints, including pre-treatment of make-up water.

The minimum level of pre-treatment usually depends on the pressure of the steam produced.

As a result, we may go from a simple softening process right through to complete demineralisation. (See chart below).

Elimination of dissolved oxygen by efficient thermal degasification ( $O_2 < 0.02$  mg/l) and/or the use of reducing reactants

Working pressure rate (bar)	≤ 15	15 to 25	25 to 35	35 to 45	≤ 45 to 60	60 to 75	75 to 100
<b>Feeding Water</b>							
pH	≥ 8,5	≥ 8,5	≥ 8,5	≥ 8,5	≥ 8,5	≥ 8,5	≥ 8,5
TH (° f)	< 0,5	< 0,2	< 0,2	< 0,1	< 0,05	< 0,05	< 0,5
Fe total maxi (mg/l)					< 0,05	< 0,05	< 0,03
Cu total maxi (mg/l)					< 0,03	< 0,03	< 0,01
O <sub>2</sub>	Dissolved oxygen Elimination by effective thermal degassing ( $O_2 < 0,02$ mg/l) or/and use of reductive reagent						
Steam generator water	< 120	< 80	≤ 60	≤ 40	≤ 15	≤ 10	≤ 5
TAC (° f)	= 0,7	= 0,7	= 0,7	= 0,7	≥ 0,5	≥ 0,5	≥ 0,5
TA (° f)	TAC	TAC	TAC	TAC	TAC	TAC	TAC
SiO <sub>2</sub> (mg/l)	< 200	≤ 150	≤ 90	≤ 40	≤ 15	≤ 10	≤ 5
SiO <sub>2</sub>							
TAC	≤ 2,5	≤ 2	≤ 1,5	< 1	< 1	≤ 1	≤ 1
Total salinity (mg/l)	< 4000	< 3000	< 2000	< 1500	< 500	< 300	< 100
Free NaOH (mg/l)	≤ 800	≤ 600	≤ 400	≤ 300	< 20	≤ 10	≤ 5
Phosphate (mg/l)	30 to 100	30 to 100	20 to 80	20 to 80	10 to 60	10 to 40	5 to 20
pH	10,5 to 12	10,5 to 12	10,5 to 12	10,5 to 12	10 to 11	10 to 11	9,5 to 10,5



The usual techniques used are ion exchangers. They are used for softening, decarbonising or demineralising water. They call on the capacity of certain synthetic resins to replace unwanted ions by ions that are acceptable for the process.

As a result for water-softening a strong polysterene/sulfonic type cationic resin will be used, which will exchange sodium ions, whose salts are highly soluble, for the calcium ions at the origin of scaling phenomena.

These resins in the form of carefully calibrated balls have limited powers of exchange, beyond which they must be regenerated.

Sodium chloride is used as a regenerating solution for softening, hydrochloric acid for decarbonising and acid and caustic soda for demineralising.

Equipment includes a tank for containing the resin balls, a set of valves for controlling supply and regeneration flows and a storage unit for the chemical reactant used for exchanging the ions during the regenerating process.

It must not be forgotten that no purified water can be produced during this operation, which may last several hours.

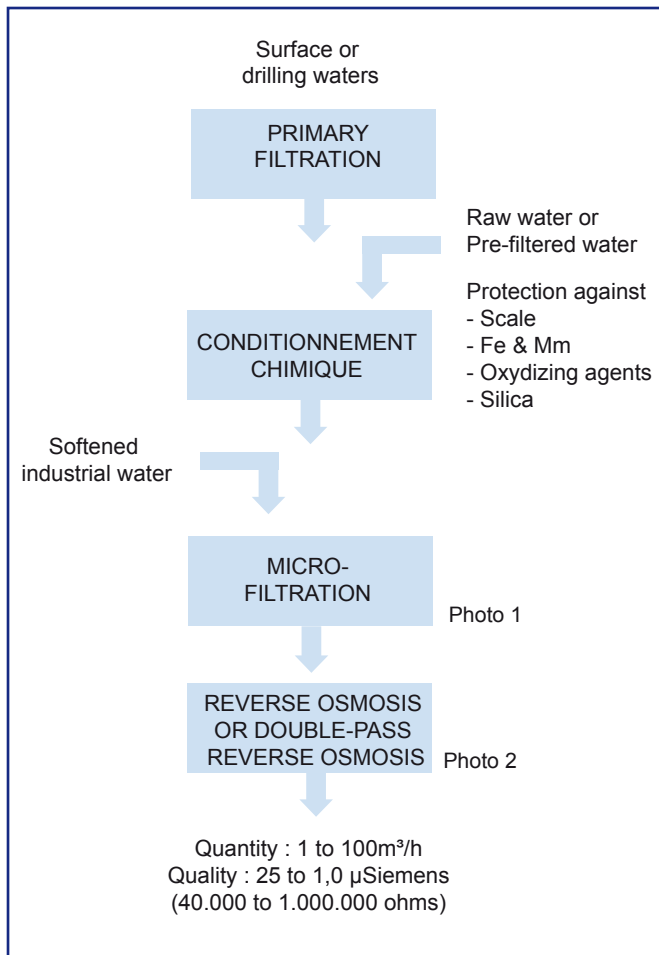
Therefore, two tanks should be made available, one for production, the other for regeneration or to be ready-for-use in continuous production systems.

Even if they have numerous inconveniences - storing and handling large amounts of chemical reactant, highly saline effluent that often requires treatment before it can be discharged, fluctuations in the quality of the water produced, mainly at the end of the cycle and difficult maintenance – ion exchangers owe their success to a technology that has remained unequalled for years and to moderate operating costs.



Photo 1

## Process scheme for reverse osmosis or double-pass reverse osmosis



Reverse osmosis is constituted by polysulfone type synthetic membranes, normally rolled in pressure modules in spiral configurations. A 20-bar high pressure pump feeds the modules, in which the water is filtered tangentially through the membranes.

In this way, the water is separated into two flows, one of demineralised water called "permeate" and the other containing a mineral salt concentrate that needs to be eliminated called "concentrate".

The qualities of the water obtained are approximately 3 to 25 µS/cm for a single stage osmosis unit down to 1 megohm for a two stage system, or for two single stage units set up in tandem.

The conversion rate, close to 75 % for recent installations defines the percentage of demineralised water produced compared with the amount of water fed into the system.

Contrary to ion exchange resins, the interest of reverse osmosis is that it does not require any aggressive reactants such as hydrochloric acid or caustic soda for running it.

Effluent from osmosis units does not give rise to any waste disposal problem for the environment and it is often recycled for use in other applications. However, these types of system are sensitive to calcium salts, chlorine and SM.

Therefore any reverse osmosis treatment needs to be preceded by filtration and by adding small amounts (10 to 30 g/m<sup>3</sup>) of anti-scalant products to the water to be treated, such as polyphosphates or phosphonates, or even chlorine reducers such as sodium bisulphite.

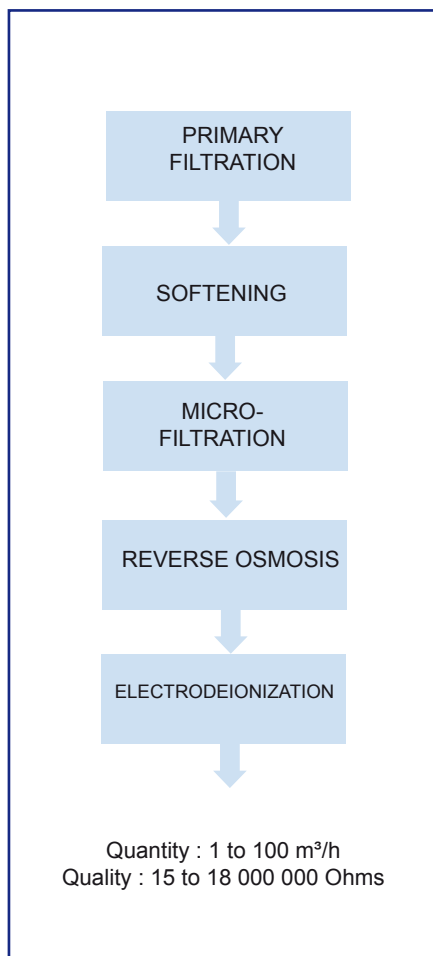
On account of the simplicity of the single stage filtration process, reverse osmosis enables compact installations to be used that can be completely automated and which do not require qualified personnel to run them. Due to these qualities, the reliability of reverse osmosis has remained unequalled up until now.



Photo 2



**Process scheme  
for electrodeionization**  
**Process scheme for reverse osmosis  
ou double-pass reverse osmisis**



Electrodeionization is the latest development in technologies used for demineralising water. It can only be used after prior reverse osmosis treatment in order to obtain water of very high quality, close to 18 megohms. E.D.I. is a synthesis of ion-exchange resin applications and techniques that make use of membranes. The resins used are identical to those used in traditional ion exchangers.

But they are regenerated by the H<sup>+</sup> and OH<sup>-</sup> ions contained in the water to be treated with the help of an electric field.

The resins are positioned between two membranes which are impervious to water, but pervious to ions.

Each membrane receives an electric current that gives it the role of either the cathode or the anode.

As the resins act as collectors and conductors of unwanted ions, these ions can then be transported by the electric field to the membranes which handle their elimination or, more often, recycle them to the beginning of the pre-treatment system.

Therefore regeneration is a continuous operation that takes place in the following three stages:

- capture of unwanted ions by the resin,
- regeneration of the resin by the H<sup>+</sup> and OH<sup>-</sup> ions contained in the water being treated, and
- transport of the ions by the electric field up to the membranes which either reject them or recycle them to the beginning of the pre-treatment system.

The quality of the water obtained is close to the absolute value of 18 megohms.

Operating costs are limited solely to electricity consumption of about 0.5 kw/h per m<sup>3</sup> produced and maintenance is virtually inexistent.

They are reserved for high pressure boilers and for when a steam turbine is being used.

## CHEMICAL CONDITIONING



Over and above make-up water treatment, extra treatment of boiler input water must be included by using a prepacked processing solution.

In the absence of a thermal degasification unit for eliminating oxygen mechanically, the amount of oxygen can be reduced chemically by injecting sodium sulphite, tannic acid, tannate or hydrazine.

No matter what the quality of make-up water treatment may be, protection must be given against any possible hardness leakage feeding in a certain amount of phosphates associated with organic dispersing agents to enable any

calcium present to be precipitated in the form of calcium phosphate sludge which is less sticky and has less insulation capacities than carbonate.

The sludge formed is dispersed by the organic products so that it does not settle in the boiler pipes at all or only in very small quantities.

Neutralising or filming amines are used for protecting the condensate network from any corrosion caused by CO<sub>2</sub> and oxygen.

These amines are volatile products injected into the feed water or directly into the boiler, which, together are transported by the steam either to neutralise the CO<sub>2</sub> at the time of condensation, or to form a protective film between the metal and the condensate. It is obvious that the purer the make-up water, the less the amount of prepacked processing solution that will be needed.

## BLOW-DOWN

Blow-downs consist of removing the mineral salts transported by the make-up water and which become concentrated in the boiler due to the losses in pure water produced by the steam.

The quantity of salt produced is inversely proportional to the amount of treatment given to make-up water. As a result, blow-downs may represent 5 to 25% of the steam flow-rate in the case of make-up water that is only treated for softening or decarbonising. Consequently, the efficiency of the boiler concerned is reduced considerably.

For producing demineralised water, reverse osmosis and E.D.I. now stand out as elegant alternatives to resin ion-exchange techniques. In any case, they will be used to replace softeners and decarbonising units wherever steam production efficiency needs to be improved by possessing cleaner exchange surfaces, by reducing the number of blow-downs and by reducing consumption of chemical reactants.

For steam boilers fed with water demineralised by ion exchange resins, reverse osmosis possibly followed, in the case of high pressure systems, by an E.D.I unit, will contribute to easier and safer maintenance on account of its incomparable reliability and flexibility of operation.



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