

**The gentle solution with the water hardness:
How to avoid the incrustations in networks without chemicals -
an electro-physics technique effective and innovating**

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Summary:

Calcium and carbonates are present in most natural waters and can potentially form calcium carbonate (CaCO_3), commonly called calcareous. Conditions of use of water make that CaCO_3 can precipitate, thus generating ,incrustations of scale in networks and equipments.

The most frequent scaling problems comes from **a rupture of the calco-carbonic balance** of water, involving a precipitation of calcium carbonate. The modification of some parameters such as the pH, the concentration out of dissolved CO_2 (due to increase of temperature) can cause this rupture of carbonic balance. The precipitation of calcium carbonate is the result of a modification of the carbonic chain. Ions HCO_3^- contained in water react to be dissociated in $(\text{CO}_3)^{2-}$ which then join Ca^{2+} to form CaCO_3 . Whatever the calcium concentration, without the modification of the carbonic chain, CaCO_3 will not precipitate. **Each water has a precipitation potential** depending on its Total Alkalinity and its conditions of use. In some cases, it is advisable to determine and eliminate it to solve the problems.

In order to bring a total, sure and efficient solution, CTE Eautonic developed an innovating and patented process **erca² (Electro - Reduction of Calcium Carbonate) to extract from water, in solid form, calcium carbonate, before water is distributed.**

The process **erca²** carries out an "electro-decarbonation" (official designation) by the only controlled action of electricity, without addition of any chemical: thanks to an electrolysis of water, the process makes it possible to adjust with precision the Alkalinity to the target value desired by extracting in the same proportions the quantities of calcium and carbonate.

The heart of the **erca²** process is a basket of electrodes supplied with a current low tension specific which causes instantaneous germination then crystallization by dehydration of limestone. The calcium carbonate voluntarily formed on cathodes is solid and insoluble. It can then be extracted very simply. It is crystallized perfectly with a purity of more than **99 %** (according to the purity of the water of origin). It does not constitute a rejection but on the contrary under product which may undergo beneficiation of quality.

Water thus treated is rebalanced and can be distributed without risk: it will not fur the networks since its precipitation potential has been strongly reduced.

This process has the approval of health authorities for use in drinking water installations. It is also appreciated by

Administrations in charge of environment (the such D.R.I.R.E. in France) as an active technique of substitution to any chemical technique. The *erca² process* for this treatment requires little maintenance and presents lower working expenses than the other techniques.

Introduction

The calcium carbonate (CaCO_3), usually called calcareous, is naturally contained into water. In some specific conditions of use (degassing, temperature increase, ...) the precipitation of CaCO_3 induces different types of expensive problems (the scaling of distribution network or equipments, the degradation of their efficiency) for the users and may contribute to sanitary problems such as Legionella growth.

In order to bring a total or partial solution, Eautonic developed a new process *erca²* (Electro-Reduction of Calcium Carbonate) to extract the calcium carbonate in solid form before the use of water.

1. Origin and water composition

The principal waters sources for production of drinking water are drilling or underground waters and surface waters, The water characteristics fluctuate in relation to the original type and the region where it is sampled.

“Pure” water doesn’t exist at natural state because water is a good solvent. So a water contains mineral salts, gases and organic materials in solution.

The mineral salts into water are very different, depending on local geological characteristics and climate. In an electrolyte as water, the dissociation of mineral salts creates ions, anions (negative ions) and cations (positive ions). The more common are in the table 1.

Cations	Anions
Na^+ , sodium	HCO_3^- , bicarbonate or hydrogen carbonate
Mg^{2+} , magnesium	CO_3^{2-} , carbonate
Ca^{2+} , calcium	OH^- , hydroxyl
K^+ , potassium	Cl^- , chloride
Fe^{2+} or Fe^{3+} ferrous or ferric	SO_4^{2-} , sulphate
H_3O^+ , hydronium	NO_3^- , nitrate
	PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , phosphates
	SiO_3^{2-} , silicate

Table 1 : principal ions into water

The dissolved gases are essentially oxygen, carbon dioxide, nitrogen gases like NH₃ and H₂S...

The suspended and colloidal materials have very various nature: quartz coming from clay, organic particles, living organisms (bacterium, zooplankton and phytoplankton), vegetal fragments ...

2. The mechanism of pipes scaling

2.1. The carbonic chain and the calco-carbonic balance

The carbonic chain is described by P. LEROY [Ref. 10] as shown in Figure 1 :

The more common scaling in France comes from a **breaking of the calco -carbonic balance** of water, inducing a precipitation of the calcium carbonate. This balance is defined by the following reaction :



So a theoretical constant of pH is defined, called **pH_s**, **pH of saturation**.

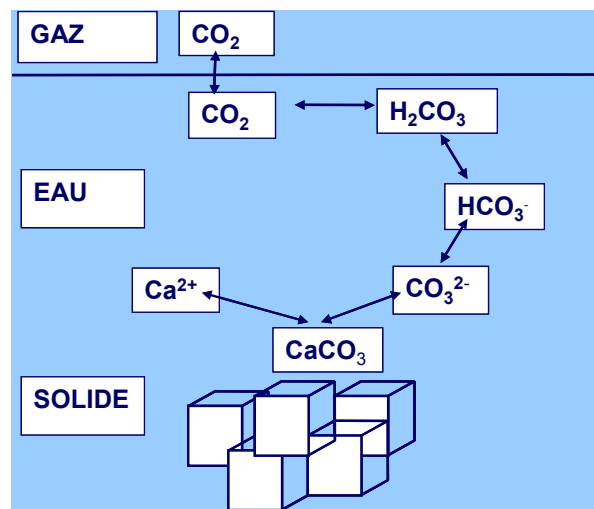


Figure 1 : the carbonic chain

2.2. Phenomena that may induce the dissociation of the carbonic chain

Ventilation, degassing, the rise in temperature of water, the addition of chemicals are the principal phenomena which can generate a modification of carbonic balance and induce precipitation.

These phenomena are noted by a modification of the pH, of the content of CO₂, of the conductivity.

The increase of the temperature is not directly responsible for the precipitation of CaCO₃. As it is specified front, the rise in temperature acts on the solubility of CO₂ and it is the "departure" of CO₂ which makes modify the carbonic chain.

Water is classified according to three definitions:

- 1. balanced:** when the coefficient of saturation is neutral.
- 2. aggressive:** when water is able to dissolve calcium carbonate . In this case, **water dissolves the "marble"**.

Rq : aggressive to CaCO_3 does not inevitably mean corrosive.

3. scaling: when water is able to precipitate calcium carbonate . In this case, **water precipitates on the "marble"**.

Rq : scaling (CaCO_3), does not inevitably mean that precipitation and incrustation will occur.

In common usage of water for human consumption or for "industrial" process, factors usually starting the process of the precipitation of calcium carbonate are:

- The addition of chemicals resulting in an increase of pH, which allows the dissociation of bicarbonates.
- The degassing or ventilation, which reduced the concentration in dissolved CO_2 , thus increasing pH
- The increase in the temperature of the water which makes CO_2 less soluble and enables it to escape by unbalancing the carbonic chain.

2.3. The chemical indicators of hardness measure

2.3.1. Total Hardness

TH (Titre Hydrotimétrique in French, Total Hardness in English), gives the sum of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions concentrations.

We can also determinate the calcareous hardness, which is the concentration in calcium ions and the magnesian hardness, which is the concentration in magnesium ions.

2.3.2. The Total Alkalinity

The **Total Alkalinity** is the alkalis (hydroxides), carbonates and bicarbonates (or hydrogen carbonates), alkaline and earth-alkalis contents into water.

2.3.3. The conductivity

The conductivity gives information about the quantity of dissolved ions into water. When the calcium carbonate precipitates, the conductivity decreases.

2.4. Conclusion

When the CaCO_3 precipitates, the calcareous hardness and the Total Alk decrease simultaneously:

$$\Delta \text{Ca} = \Delta \text{Alk}$$

The precipitation depends on the calco-carbonic balance and not only on the calcium content of a water.

Each water has a very precise potential of precipitation depending on its characteristics and temperature. To solve problems, it has to be evaluated and reduced if needed.

3. Other types of decarbonation or hardness reduction treatment

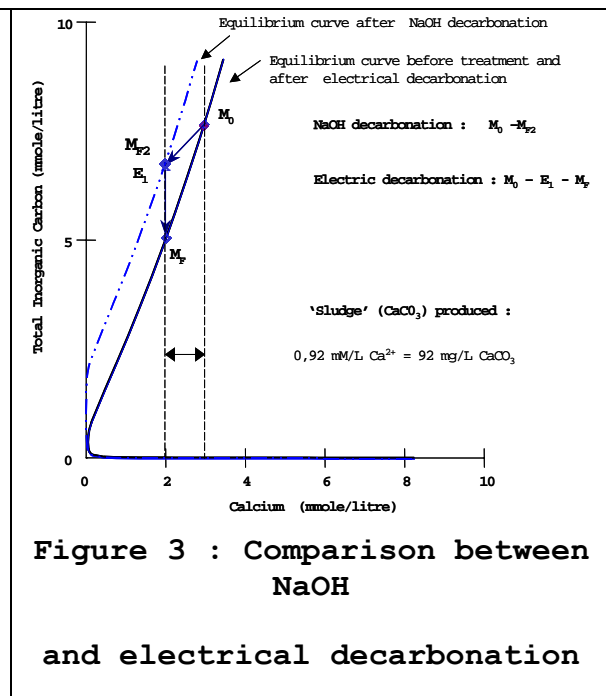
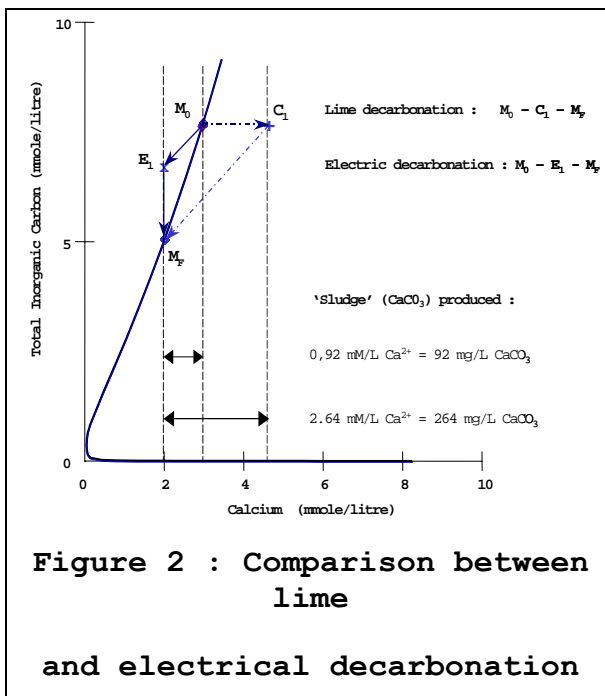
Lime Decarbonation : the principle is that the lime reacts with carbonic species forming calcium carbonate precipitate. It needs use of lime and induces the production of a large volume of sludge (~ 3 X greater than with Erca² process) to eliminate. (Figure 2)

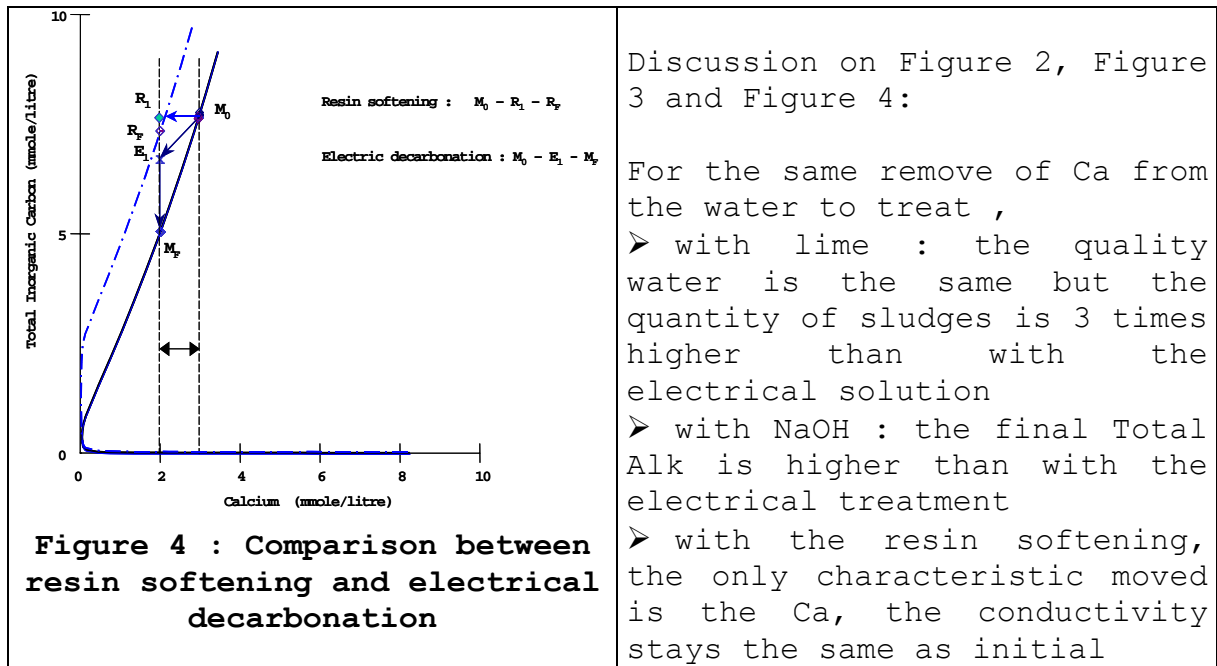
NaOH Decarbonation : the principle is to precipitate calcium carbonate on sand particles. It needs use of NaOH and sulphuric acid (??) and induces the production of sludge (sand + calcium carbonate). For the same hardness in treated water, the alkalinity will be higher than when lime decarbonation or Erca2 are used. (Figure 3)

Resin softening : the principle is to replace the calcium ions with sodium ions, without effect on the carbonate ions. It needs use of sodium chloride and a most important consumption of water for resins regeneration. (Figure 4)

Softening reduces TH (Calcium and magnesium) but not the alkalinity. Softened water can be more corrosive especially toward ferrous metals.

If we compare the different results obtained with treatment simulations, for a same initial water (Ca initial = 118 mg/l = M_0 and Ca final aimed to be balanced = 80 mg/l = M_F), we obtained the following characteristics :





4. The electrolyse applied to the decarbonation: the [erca²](#) equipment

4.1. Physical description of the device

4.1.1. Disposition of the electrodes into the tank

The common device is composed of one rectangular tank, with conical bottom (various total volumes from 500 litres up to 18 m³). The electrodes (anodes and cathodes) are placed and laid in vertical position inside the tank. The cathodes and the anodes are disposed in alternation.

The quality of materials used for the construction of the equipment is significant, thus the equipment intended to treat drinking water are manufactured out of stainless steel 316 L, the electrodes anodes are in Ti40 or platinized Titanium or Iridic Titanium.

A low intensity current per square meter of electrodes is crossing through the electrodes, the voltage coming of is below 24 volts.

The Figure 5 and Figure 6 schematise one [erca²](#) reactor

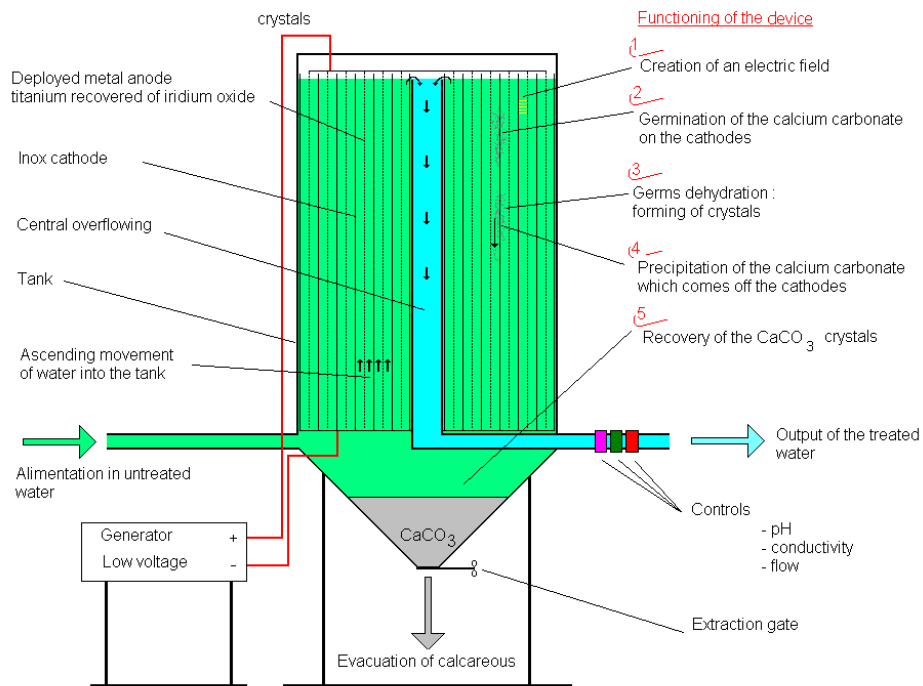


Figure 5: section of the tank, disposition of the electrodes.

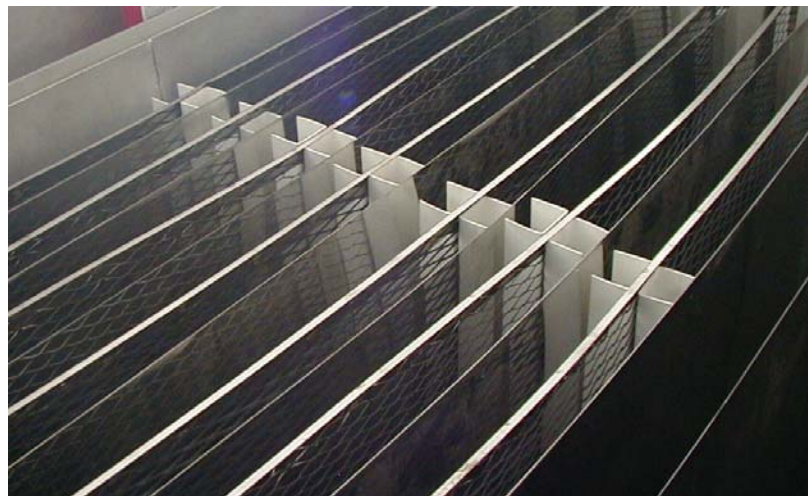
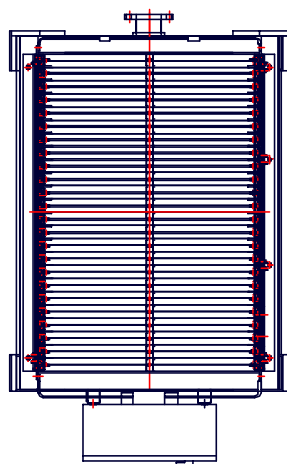


Figure 6: views of the top of a tank (schema) and the electrodes (photo)

4.1.2. The electrolyse into the tank

4.1.2.1. Description of the process (cf. Figure 5)

The **erca²** water processing is achieved at **atmospheric pressure**. The water to treat comes from the bottom of the tank. It runs across series of detectors which allow :

- to **adjust** and survey **the water flow**. The latter depends on the treatment to do.

- to survey the evolution of the water quality (conductivity and pH in option). In comparison with predetermined thresholds, any variation is signalled by an alarm.

Water has an ascending movement and runs across the electric fields created by the electrodes. The current intensity, which crosses the electrodes, is variable and the electrical signal (its intensity, its frequency, its form) is optimised to induce the creation of the calcium carbonate on the cathodes. The contact duration of water with the electrodes is in relation to the required extractions in Calcium and in Total Alkalinity (carbonates).

The treated water goes out of the reactor through the overflowing. The treated water runs across detectors to control the applied treatment. That is to say:

➤ a conductivity detector. As the calcium carbonate has been precipitated and extracted in solid form, the conductivity has decreased.

➤ a pH detector (option). The pH decreases during the treatment. So in some cases, we should survey it to avoid any problem.

Any variation, in comparison with predetermined thresholds, is signalled with an alarm.

For example, evolution of CaCO_3 thickness on cathodes although without effect on the evolution of the treatment or operation, is followed by a simple evolution of an electrical potential difference.

The period of extraction of CaCO_3 of cathodes and the unit is controlled and followed (usually 3 to 4 times per year)

As an indication, a unit of drinking water feeding 3000 subscribers and having a TH of and an Alkalinity of about 300 mg/l CaCO_3 will generate 40 tons of pure CaCO_3 for a reduction of about 100 mg/L as CaCO_3 .

The whole installation can be regulated by an automaton, which fixes the control and eventually the regulation. The different parameters (flow, conductivity, voltage, ...) are memorized. They can be used easily and modified remotely by an ordinary phone connection, as well as the different alarms activated.

4.1.2.2. Cathodic reduction

At the cathode, there is reduction of dissolved oxygen and water. Because of the production of hydroxyl ions OH^- , the environment of the cathode is basic. Moving the calco-carbonic balance, a precipitate of calcium carbonate is due to the forming of this basic environment.

4.1.2.3. Anodic oxidation

At the anode, the water oxidation induces hydronium ions H^+ .

The hydronium ions neutralize the hydrogen carbonate ions forming carbon dioxide, following the reaction above.



This phenomena induces a necessary degassing or a pH correction to solve an eventual problem of corrosivity.

4.1.3. The precipitation of calcium carbonate

After a basic environment forming, the calcium carbonate is produced **on the cathode** and falls at the tank bottom by gravity. The forming of calcium carbonate CaCO_3 is described with the following reaction.



These produced germs are dehydrated to be transformed into crystals. So they fall at the tank bottom, which must be cleaned depending on a periodicity to determine in relation to the volume of solid CaCO_3 formed.

4.1.4. Other possible effects of electro-decarbonation

For waters with high Chloride (Cl^-) contents, chlorine may be formed ("electro-chlorination"). This phenomena needs to be controlled but it can also be used to disinfect the water intended for human consumption.

5. Tests realized for each installation (Ref. 1)

In order to calculate the ideal sizes of the equipment and to determine the adjusting parameters, we make different analysis of water sampled on the factory site.

5.1. Chemical analysis

Different dosages are realised to determine the TH, Ca, Mg and Total Alk of water in the network. Some pH and conductivity measurements are also done.

5.2. LPL calculation (Legrand-Poirier-Leroy - Ref. 9)

From a physical-chemical analysis of water, this software solves the equations of the calco-carbonic balance.

It allows:

- to determine the water type (aggressive, calcifying, balanced).
- to foresee the evolution of this water subject to fixed strains (increase of temperature or addition of products).
- to determine the theoretical level of the precipitation potential.

As a real example, we have realized this calculation on a water W which had a total alkalinity of 336 mg/l CaCO₃. The LPL showed a potential of precipitation of 100 mg/l CaCO₃.

5.3. PCR (Précipitation Contrôlée Rapide - Fast Controlled Precipitation (Ref. 7 and Ref. 8))

This test allows to characterise the scaling power of water. It consists in simulating the thermal and mechanical strains applied to water into the network, by agitation and temperature elevation.

It could be successively observed :

- an increase of pH until the precipitation point (unbalance).
- a decrease of pH and appearance of a CaCO₃ cloud (return to the balance).

The « precipitable » potential = Ca before test - Ca after test

As a real example, we have realized this test on the W water presented in **Error! Reference source not found.** :

The reactivity of this water to test PCR gives a precipitation of:

- Total Alk 120 mg/l CaCO₃ after 40 minutes for the aerodynamic protocol
- Total Alk 95 mg/l CaCO₃ after 65 minutes for the thermal protocol.

These results (cf. Figure 7) are in accordance with the LPL software results, because both methods give a scaling power of about 100 mg/l CaCO₃ for this W water.

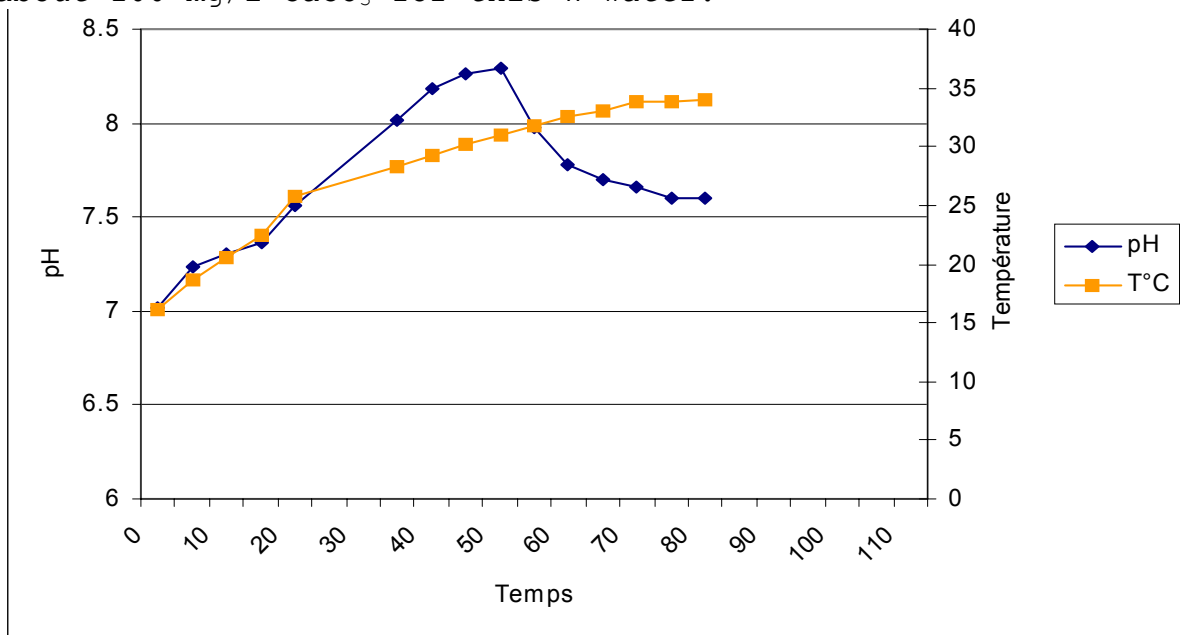


Figure 7 : Result of the PCR test on the initial water W

5.4. Study on site

The principal work remains the study « E3C » which characterizes the Calco-Carbonic Behavior of a water according to the protocol making it possible to realize on site in real size, by homothetic way, the true water treatment.

Pilots, various capacities, led by specialized engineers are in measurement, over only one week, to define the various significant parameters of a water.

During these studies, test PCR and software LPL come to corroborate the intrinsic results obtained.

5.5. Real cases

A pilot **erca²** installed on the site of the W water to treat, was parameterized to eliminate 10°F from CaCO₃ of water.

The erca² treatment reduced Total alkalinity of 114 mg/l CaCO₃.

This treated water was subjected to same test PCR to check the effectiveness of the treatment .

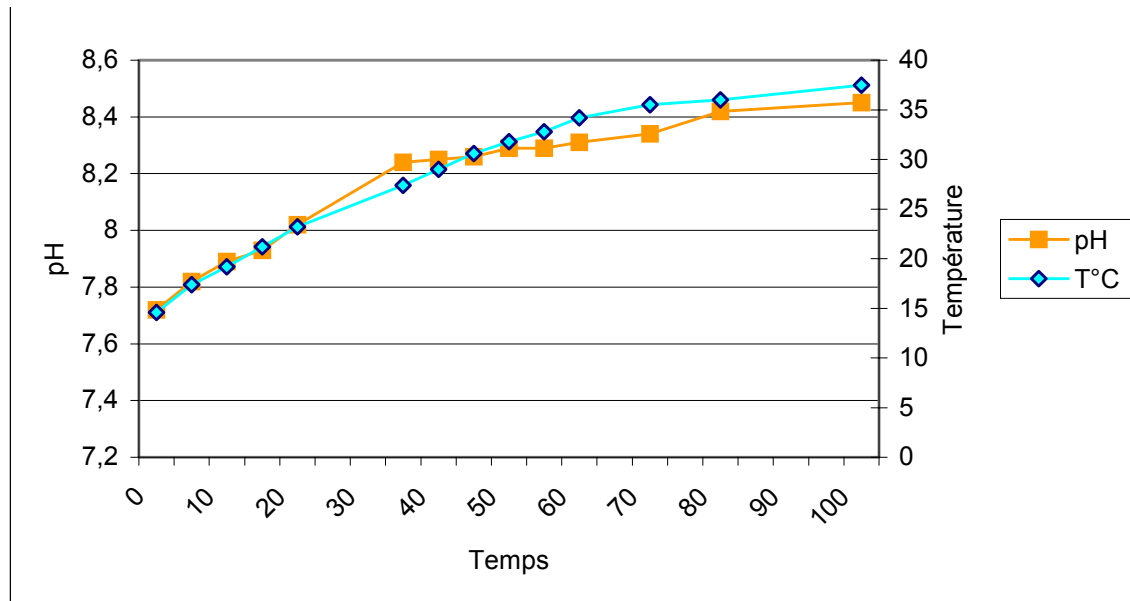


Figure 8 : PCR test on treated water (after balanced : 36 hours)

No precipitation is observed after 2 hours of test.

The elimination of precipitable calcium carbonate of only 100 mg/l CaCO₃ as indicated it calculation LPL and test PCR and like made the process **erca²** makes it possible to obtain a stable water which does not fur any more.

The total alkalinity of the treated water W is of ± 190 mg/l CaCO_3 what corresponds at the general level of obtaining a stable water to scaling.

It is not necessary no to eliminate totality or from calcium or Total alkalinity to obtain a water which does not precipitate any more under the usual conditions of use.

6. Impact of decarbonation on water corrosivity

The solubility of lead and copper corrosion products, which controls their concentration in water, is strongly influenced by pH and total alkalinity (Ref. 2, Ref. 3, Ref. 4, Ref. 5) (hardness itself does not have a major influence).

pH and alkalinity are also very important parameters in the corrosion and formation of protective corrosion products for ferrous materials although other parameters (e.g. chloride, sulfate calcium...) have to be considered (Ref. 6)

For lead and copper, the solubility of corrosion products decreases when the pH increases. Very low alkalinity (typically $< 0,5$ mmole/L) does not permit the formation of a stable and protective corrosion layer. At the opposite, at higher concentrations (> 3.5 to 4 mmole/L), the solubility increases when alkalinity increases.

Ideally, a water with an alkalinity around 2 mmole/L and a pH around 8 will generally give the lower concentrations for both copper or lead (from copper or lead pipes) in drinking water (although other parameters, like TOC, may have an impact).

Water decarbonation, allows to lower water alkalinity and to increase equilibrium pH and consequently will decrease lead and copper solubility (decarbonation using soda ash has a lower impact on alkalinity and equilibrium pH for equivalent hardness reduction).

An experimental example of this positive influence of decarbonation is shown in Figure 9. The experiments (Ref. 3) have been carried out with copper pipes in a dynamic pipe rig installation with different waters in parallel :

1. A medium-hard water (Alk ~ 4 mmole/L, pH ~ 7.7);
2. Water in 1, after decarbonation, using a small ERCA2 system (Alk ~ 2 mmole/L);
3. Water in 1, with phosphate dosing (~ 1 mg P/L, reduced to 0.3 at the end).

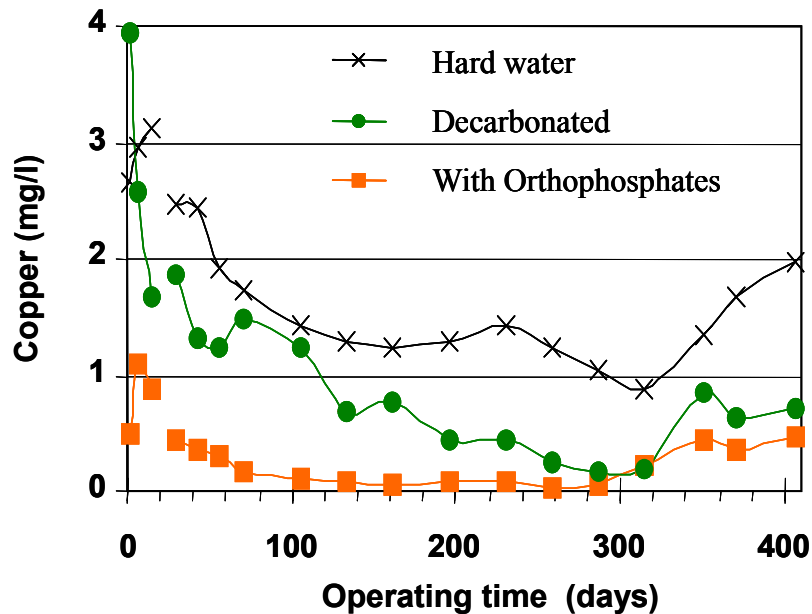


Figure 9 : Copper concentrations after 16 hours stagnation in dynamic test rig experiments with 3 test waters.

The results of the experiments (example in Figure 9) show that, for this water, decarbonation strongly reduces copper concentrations (- 50 % to - 70 %) and may be almost as efficient as phosphate dosing after sufficient operation time.

7. Range of products [erca²](#)

7.1. Standard equipment

Each equipment of the [erca²](#) range of products is composed of:

- a tank,
- an electrodes basket,
- a low voltage alimentation,
- a board putting together the electric alimentation, the conductivity meter and its detector, the flow indicator, the input and output gates, etc,
- the hydraulics pipes,
- a level indicator.

The range of flows treated is very large : from 0,5 to 36 m³/h with basic models and other flows to 500 m³/h (and plus) by coupling the latters.

Conclusion

The [erca²](#) reactors allow to obtain a balanced water and reduce scaling problems. They treat as well industrial water as drinking water. This process has in fact [the approval of the health authorities](#).

As the process allows to reduce lead and/or copper solubility, the treated water can be used like domestical and drinkable

waters, waters for process, into cooling network, for air conditioning systems, ...

The *erca*² reactors require little maintenance and have exploitation costs lower than other techniques.

The *erca*² process realizes an « electro-decarbonation » (official designation) by the only controlled action of electricity, without addition of any product.

Moreover, the extracted CaCO₃ is perfectly crystallised with purity over 99% (according to purity of the original water).

It does not represent a rejection but, on the contrary, an enhancing by-product of quality.

The *erca*² process is appreciated by the Administrations in charge of environment (like DRIRE in France) as active technique of substitution of any chemical techniques.

Innovating devices such *erca*² make it possible to eliminate, without addition of chemicals, precipitations of calcium carbonate in water installations, strongly reducing maintenance costs and increasing the lifetime of installations for industry and for consumer. Decarbonation is also an efficient mean of reducing solubility of metals like lead or copper and consequently exposure of consumer's and also release in the environment of these metals.

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