Forced precipitation experiments for study of the electromagnetic treatment of water

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Abstract

The objective of this research is to know the effect of the electromagnetic equipment TK3K to prevention of incrustations in pipes. A method of forced precipitation of calcium carbonate, mixing solutions of $Ca(NO_3)_2$ and Na_2CO_3 with tap water, shows differences in the temporal evolution of turbidity, absorbance and in the final size of the particles formed, which makes it possible to distinguish between treated and untreated water. The latter present higher values of parameters analyzed than the treated ones. A longer treatment time does not produce different results, while an increase in temperature causes a greater decrease. Since there is no immediate technique on the market to verify the effect of electromagnetic treatment, this method, with temperature control, is simple and fast.
Keywords: Calcium carbonate, Electromagnetic treatment, Forced precipitation, Water treatment

1 Introduction

Calcium carbonate scales in water distribution or heating systems form deposits, which involve technical and economic problems, such as clogging of pipes and reduced heat transfer. It affects both domestic and industrial systems, causing an increase in maintenance and energy costs [1]. There are different classical techniques that reduce water hardness and avoid scale formation. However, these techniques have some disadvantages such as altering the chemical composition of the treated water and generate waste. Alternatively, electromagnetic techniques prevent the calcium carbonate scale formation of water without adding or removing compounds [2]. Different equipments have been designed to apply electromagnetic treatment (EMT) and a great variety of studies have tried to describe their effects on water: some authors refer to the type of crystallization observed in the precipitates (calcite-untreated, aragonite-treated) [3-5], other authors observe variations in physical or chemical properties (surface tension, boiling point, etc…) [6-8], or indicate that the treatment influences in colloidal stability [9]. All these factors depend on variables such as the intensity and gradient of the applied electromagnetic field, the room temperature, application time, among others [10,11].

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To know the tendency of a water to form scales, classically the term "hardness" is handled, and it is mainly associated with Ca^{2+} and Mg^{2+}, but other metal cations such as barium, iron, etc can be considered. Hardness is usually expressed in mg/L of calcium carbonate or in the French hydrometric degrees, °HF, equivalent to 10 mg $CaCO_3$/L, and it is obtained according to:

$$°HF=[Ca\ (mg/L)\cdot 2.5+Mg\ (mgL)\cdot 4.2]/10$$

Waters with °HF values between 32 and 54 are considered hard. On the other hand, the Spanish ROYAL DECREE 140/2003, of February 7, of the sanitary criteria of the quality of water for human consumption [12], consider that the water in any moment may be neither aggressive nor encrusting and therefore the result of calculating the Langelier Saturation Index (LSI) should be between +/- 0.5. This index corresponds to the method described in the Standard Methods for the Examination of Water and Wastewater [13], method 2330 B "Indices indicating tendency of a water to precipitate $CaCO_3$ or dissolve $CaCO_3$". Obviously, the LSI calculation explains precipitation capacity more accurately than hardness and can be obtained with PHREEQC version 2 [14] in a very rigorous way. It is a computer program to perform a wide variety of aqueous geochemical calculations and one of the capabilities of this software is speciation and saturation index calculations.

Despite the fact that there are numerous works in this field [2-11] and that the effects of EMT have been experimentally demonstrated, there is no standardized method that allows distinguishing between treated and untreated water. In this work, a method has been carried out that allows differentiating between treated and untreated water with EMT by forced calcium carbonate precipitation, adding $Ca(NO_3)_2$ and Na_2CO_3 solutions to the studied water. Absorbance and turbidity measurements permits observe differences together with the particle size of the formed precipitates. A new EMT equipment have been used in this research work: the TK3K device developed and patented by ECOTÉCNICA ENERGY SYSTEMS S.L. (Resistance RF: 0.25 - 3 kΩ, Inductance: 2.120 - 1000 Hz, Instantaneous peak voltage: 325 V, current: 0 - 1.48 A, Maximum magnetic field: 120 G).The effectiveness of this equipment has been observed in various domestic and sports facilities, where the use of the equipment has led to a reduction in maintenance and better preservation of pipes and taps. In this sense, the measurement of the variation of certain parameters related to the capacity to form scale, both in untreated water and with EMT, will provide technical evidence that scientifically supports what is observed in real facilities. Since there is no immediate technique on the market to verify the effect of EMT, the methodology proposed could be useful and applied to TK3K and other EMT devices to verify their effectiveness.

2 Materials and methods

2.1 Sampling water

Before carrying out the experimental process, water samples of different origins and characteristics were taken. The samples were collected and stored in opaque plastic containers with a capacity of 5 L and remained at a regulated temperature inside the experimental laboratory. The origin of the waters used is shown in Tab. 1 and the geographical locations are shown in Fig. 1. The namely of water from different origins are: Villena (Alicante), San Vicente del Raspeig (Alicante), Bogarra (Albacete) and Altea (Alicante).

Table 1. Towns and cities of sampling points.

Town	City
San Vicente del Raspeig	Alicante
Altea	Alicante
Villena	Alicante
Bogarra	Albacete

Figure 1. Geographical location of the sampling points (blue markers).

The tap waters of different origins have been characterized. The results for the main ions and some important parameters are shown in Tab. 2.

Table 2. Parameters analysed for the different tap waters.

Analysed variable	Villena	San Vicente del Raspeig	Bogarra	Altea
pH	7.87	8.33	7.62	8.27
Conductivity (µS/cm)	991	1026	552	409
Na^+ (mg/L)	55	96	4	10
K^+ (mg/L)	2	3	1	1
Ca^{2+} (mg/L)	87	66	68	71
Mg^{2+} (mg/L)	41	32	26	10
Cl^- (mg/L)	148	185	6	15
NO_3^- (mg/L)	20	8	4	2
SO_4^{2-} (mg/L)	53	79	8	23
HCO_3^- (mg/L)	290	173	340	250
Hardness (°HF)	39	30	28	22
LSI	0.78	0.90	0.54	1.09

Villena is the hardest water, classified as hard, because it has the highest concentration of magnesium and calcium. San Vicente is a medium hard water, since it has a significantly lower calcium and magnesium content than in the previous case. Bogarra, for its part, is also classified as medium hard water, showing average values of calcium and magnesium, very similar to those of San Vicente. Finally, Altea, despite being the one with the highest calcium concentration after Villena, is the one with the lowest hardness, mainly due to its low magnesium content.

Regarding the LSI, Bogarra would be a non-encrusting water with an LSI close to 0.5, while the rest of the waters would be encrusting, the order would be: Villena<San Vicente<Altea, the latter being the water with the greatest tendency to produce scales.

2.2 Reagents

The reagents used were $Ca(NO_3)_2*4H_2O$ (99% Fisher Scientific), Na_2CO_3 (99.5% Fisher Scientific) and distilled water (0.9 µS/cm).

2.3 Electromagnetic treatment assembly

A general scheme of the experimental set-up for electromagnetic treatment are show in Fig. 2. The recirculation pump and the water to be studied are introduced into a 1 L glass beaker. This is filled with the sample, with enough volume to completely cover the pump and prevent air entering the system. The pump drives the water through the pipes in a closed circuit that allows the water to pass through the TK3K electromagnetic device. The deposit of sample (glass beaker) is inside a thermostatic bath to control the temperature at 23°C. In addition, this assembly was placed in a room with a controlled temperature (23°C) to maintain the stablished conditions for the experiment. The samples were subjected to EMT for up to 3 hours, taking small portions for analysis every hour. The characteristics of the different parts of the assembly are shown in Tab. 3.

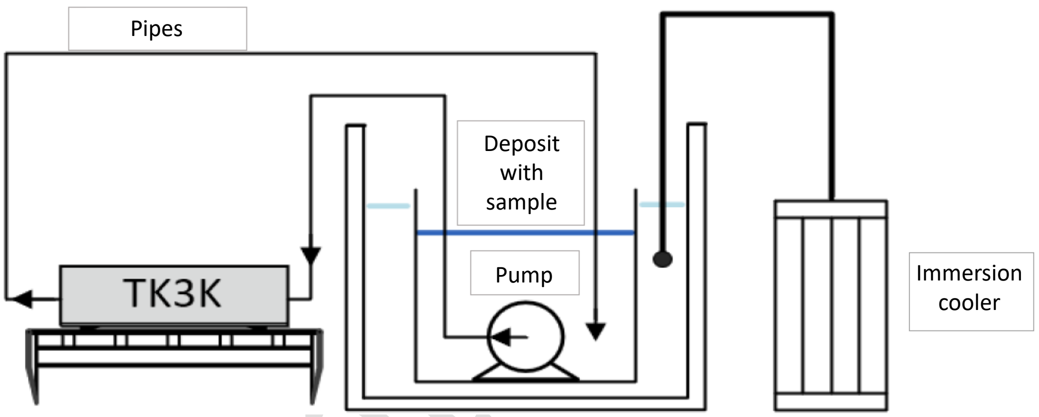

Figure 2. General scheme of the experimental set-up for electromagnetic treatment.

Table 3. Equipments used in the electromagnetic treatment system.

Equipment	Model
Electromagnetic device	TK3K
Recirculation pump	Fuente decor 08 ESPA
Thermostatic bath	Selecta
Heating head	Digitherm S150
Immersion cooler	Selecta
Pipes	Non-toxic PVC (13 mm)

2.4 Experimental methods

Experimental studies of calcium carbonate precipitation from waters of different qualities were carried out without and with EMT; in the latter case, samples were taken at 1, 2 and 3 hours of treatment, in order to test the effects of time in the EMT. The precipitation was forced by adding $Ca(NO_3)_2$ and Na_2CO_3, and two stock solutions of 80 mM for both reactants were prepared previously with distilled water. Two specific volumes of the collected sample were separated, one for turbidity analysis and the other for absorbance analysis. The working concentration of 8 mM was prepared directly in the measurement cell, considering the total volume added of the measurement cell (Tab. 4). The calcium nitrate reagent was added to it first, and then the carbonate sodium. Once both reagents were added, the sample was shaken for 10 seconds and introduced into the different measuring equipments.

Table 4. Volumes of water and reagents used in absorbance and turbidity analyses.

Analysed variable	Water (mL)	$Ca(NO_3)_2$ (mL)	Na_2CO_3 (mL)	Total volume (mL)
Absorbance	2.4	0.3	0.3	3.0
Turbidity	11.2	1.4	1.4	14.0

Absorbance at 350 nm and turbidity measurements were taken for 30 minutes. Data for turbidity were taken every 2 minutes, using a 2100P Turbidimeter (Hach). Absorbance was measured in a UV-1600PC spectrophotometer (VWR) with data acquisition, and data were taken every 1 minute. All measurements were made in triplicate.

For the analysis of the particle size, the sample was collected once the turbidity test had finished. The equipment used was a MICROTRAC SYNC, from the VERDER SCIENTIFIC group, which allows measurements by laser diffraction. The equipment has three measuring lasers, two blue (405 nm) and one red (780 nm), as well as a high-speed camera that makes it possible to perform images simultaneously.

3 Results and discussion

3.1 Analysis of the water used

As mentioned in the introduction, the term hardness is usually used to analyse the precipitation capacity of a water, but the Langelier saturation index (LSI) must be considered in order to carry out a rigorous analysis. This index indicates the tendency of a water to precipitate $CaCO_3$ or dissolved $CaCO_3$. Analysing the LSI, Bogarra is a water in saturation equilibrium ($-0.5<LSI<0.5$), while the rest are supersaturated in calcite, which implies a greater tendency to precipitation. Villena and Bogarra have the lowest LSI values, so they are the least encrusting despite being the ones with the highest hardness. Altea has the highest LSI of all the analysed waters, as a consequence of the higher calcium and carbonate ion activities, so that the solubility product is reached more quickly, which means that it has a greater tendency to precipitate. Altea is the water that presents the least hardness and yet it is the most encrusting, contrary to the usual expectation of greater precipitation from the hardest waters. In practice, it is known that Altea's tap water produces scale at the domestic level, and treatments are used to avoid this problem. For this reason, this water had received a previous EMT at the sampling point.

Regarding conductivity, a direct relationship with the precipitation capacity (LSI) was not observed, since Altea and San Vicente present the lowest and highest conductivity respectively; however, both have the highest LSI values. Regarding the pH, indicate that this parameter influences the calculation of the LSI. Altea and San Vicente have pH of 8.27 and 8.33 respectively and the equilibrium reaction bicarbonate/carbonate displaces to CO_3^{2-}, consequently giving a higher LSI value.

3.2 Turbidity and absorbance studies

3.2.1 Individual comparison between treated and untreated waters and influence of temperature

All the waters, except Altea, presented a similar behaviour, and the data for the Bogarra water are shown in Fig. 3 as an example. All measurements were made in triplicate, with a standard deviation in turbidity between 7-35 NTU and in absorbance between 0.004-0.1, registering the largest deviations in the first minutes of the experiment. In general, it is observed that the absorbance and turbidity measurements of the untreated waters exceed the measurements of the treated waters in most of the precipitation process during the 30 minutes recorded. A longer treatment time does not imply different results. The waters are altered after the electromagnetic treatment up to a limit, but once this is exceeded they will not suffer notable changes in absorbance and turbidity.

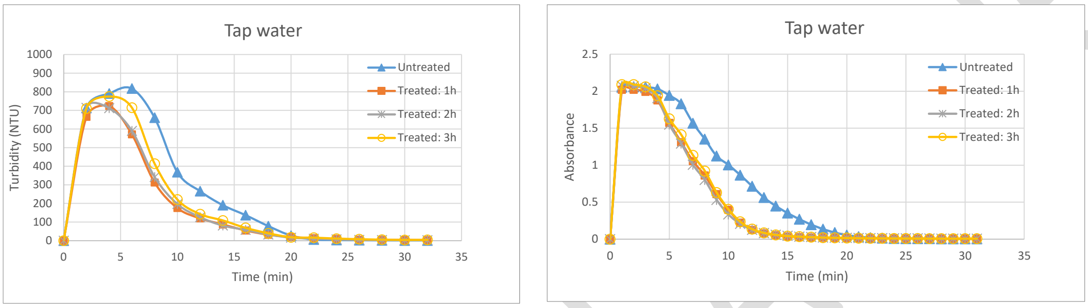

Figure 3. Turbidity and absorbance values for tap water (Bogarra (Albacete) water data).

The effect of the EMT is verified especially in the case of Altea. This water had already received a previous EMT in the neighborhood from where it was taken and as shown in Fig. 4, there is no difference between the water treated and untreated by the TK3K equipment, due to the previous treatment. With this it is verified that the methodology is valid since it identifies the waters that have undergone treatment and the difference from those that have not received it.

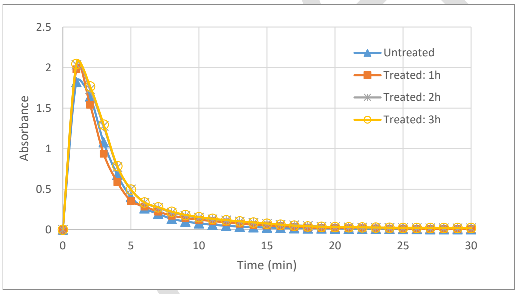

Figure 4. Absorbance values for Altea water untreated an treaded 1-3 hours.

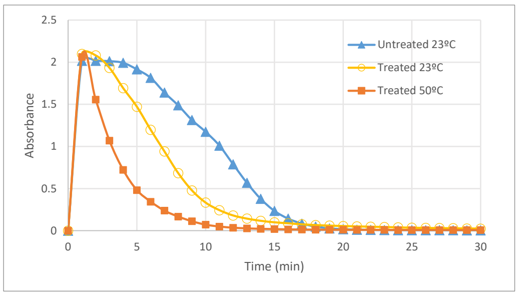

Figure 5. Comparation of absorbance values for San Vicente water untreated at 23°C and treated at 23 and 50°C.

In order to study the influence of EMT with temperature, the waters were treated by raising the temperature of the thermostatic bath to 50°C. Fig. 5 shows the behavior of the San Vicente water as an example (the rest of the waters presented the same behavior). As can be seen in this figure, at temperature of 50°C the formation of the precipitate is accelerated, producing a very pronounced drop in absorbance in the first 5 min of the experiment. This trend agrees with the decreases of solubility of calcium carbonate with temperature.

As a conclusion, the treated waters present lower turbidity and absorbance values than the untreated waters, an effect that is accentuated by increasing the temperature. The EMT accelerates the precipitation process, under the conditions used in the test. Therefore, the applied methodology makes it possible to distinguish waters that have been treated with EMT from the untreated water.

3.2.2 Tap water comparison: influence of the composition in EMT

In Fig. 6 the absorbance and turbidity values of all the untreated waters are compared and in Fig. 7 the same comparison is made for the treated waters, using in the latter case the average of the values obtained during 3 hours of treatment. From the comparison made by the type of water, it can be seen that in the case of Villena (Fig. 6), the untreated water does not reach the same minimum levels as the rest of the water, both in turbidity and absorbance, highlighting these last values, which remained high during the 30 minutes. In terms of turbidity, Villena is the water that presents its peak in the shortest time, and is lower than the rest, which all present values above 800 NTU. This means that Villena, being the hardest water of all those studied (39°HF), forms a smaller amount of precipitate, contrary to the general idea that hard water generates more scale. As for the LSI, it is one of the waters with the lowest value and therefore would have the least tendency to form precipitates.

The water from San Vicente shows a delay in the turbidity peak of the untreated water with respect to the rest of the water analyzed. In the case of Bogarra water, the behavior of both parameters in untreated water is very similar to that observed in San Vicente water, with a great coincidence of absorbance values. Altea water presents a more pronounced decrease with a steeper slope and a minimum value is recorded after the first 10 minutes of the experiment, because this water had already been treated with EMT, and its behavior it is like that of treated water at all times.

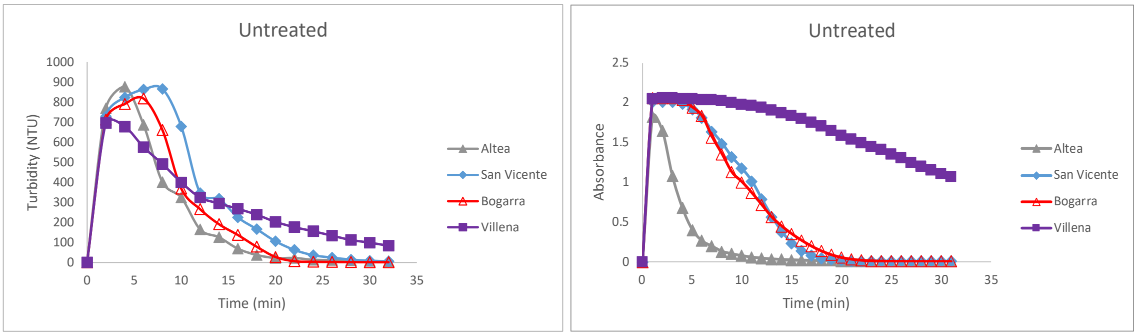

Figure 6. Turbidity and absorbance measurements versus time of all waters without treatment.

When these waters are treated (Fig. 7), they all present almost identical values of turbidity and with few differences in absorbance. Altea water, having a higher LSI, produces a greater amount of precipitate, as observed in the high turbidity values. This precipitate quickly separates from solution, as shown by the large drop in absorbance values.

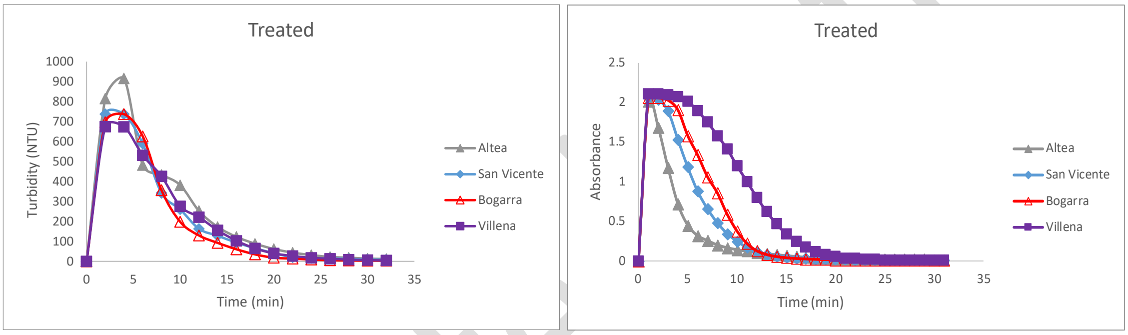

Figure 7. Turbidity and absorbance measurements versus time of all waters with 3 hours of treatment.

In conclusion, the turbidity values present smaller differences than the absorbance values for both untreated and treated waters, with few differences for the latter. With respect to the absorbance, the sequence is the same for untreated and treated waters. The latter have a more pronounced decrease, attributed to EMT.

3.3 Particle size

The particle size data of the waters of Altea and Villena, untreated and treated for 1 hour, were obtained. The results are shown in Fig. 8 and 9 and Tab. 5.

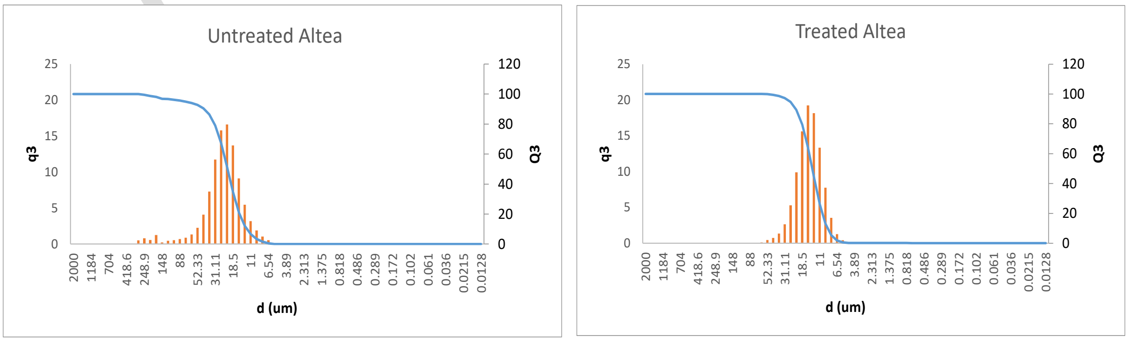

Figure 8. Particle size of Altea water, untreated and treated for 1 hour.

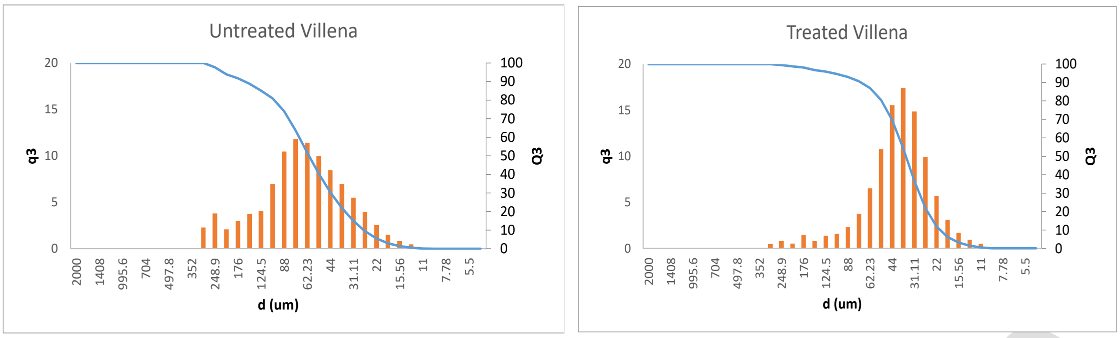

Figure 9. Particle size of Villena water, untreated and treated for 1 hour.

Table 5. Particle sizes at the 10/50/90 percentiles, at the maximum peak of the distribution and width of the distribution peak to untreated (UT) at 23 °C and treated (T) waters at 23 and 50°C

Water	d10(µm)	d50(µm)	d90(µm)	d max(µm)	peak width
Altea UT(23ºC)	12.4	21.7	42.9	21.3	18.4
Altea T(23ºC)	8.70	13.7	22.4	13.7	10.1
Villena UT(23ºC)	26.7	60.6	158	57.0	63.2
Villena T(23ºC)	21.0	35.5	71.0	34.8	28.9
Villena T(50ºC)	13.6	20.1	32.1	20.1	13.6

At the maximum peak of the distribution the particle size is 57.0 µm in the Villena sample and 21.3 µm in the case of Altea. However, the treated water reflects significantly lower particle size values than in the previous case, reaching the maximum peak of the distribution at sizes of 34.8 µm (23 °C) and 20.1 µm (50 °C) in Villena and 13.7 µm (23°C) in the Altea sample. Likewise, the peak width is reduced (peak width in Tab. 5), which demonstrates the tendency of the particles not only to reduce their size but also to have more similar dimensions, forming a more delimited range. This reduction in particle size, as well as the greater similarity of dimensions, is due to EMT, which accentuates its effect with temperature. In the case of Altea, which is already treated at source, the smaller size of the particles is observed in the water not treated with TK3K, even so, a second treatment with this equipment continues to reduce the size of the particles.

4 Conclusions

The analysis of the quality of the tap waters showed that soft waters, as in the case of Altea, can become more encrusting (LSI>0.5) than those with higher hardness values (Villena). The differences in the conductivity of the waters is not a determining factor in the precipitation capacity (LSI), pH directly influences the LSI calculation: higher pH causes a higher LSI value.

Electromagnetic treatment alters the characteristics of the water to which it is applied, as observed from absorbance and turbidity measurements. The turbidity values show smaller differences than the absorbance values, and therefore this parameter is better when it comes to evaluating the effect of EMT.

A longer treatment time does not imply different results. The waters are altered after the electromagnetic treatment up to a limit, but once this limit is exceeded, they will not suffer notable changes in absorbance and turbidity.

The absorbance and turbidity measurements of the untreated water exceed the measurements of the treated water, during the 30 minutes recorded in the precipitation process.

A water that has received a previous EMT does not present differences when treated with TK3K. When the EMT is carried out at a higher temperature, the formation of the precipitate is accelerated, producing a very pronounced drop in absorbance, in accordance with the decrease in the solubility of calcium carbonate with temperature.

The particle size of treated water is smaller than that of untreated water. This could favor its permanence within the water that circulates through the pipes, not adhering to the walls of the same, which would avoid incrustation problems.

Therefore, the forced precipitation method applied to mains water makes it possible to distinguish water that has been treated with EMT from untreated water, with absorbance and particle size measurements.

Acknowledgment

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Symbols used

EMT electromagnetic treatment

LSI Langelier saturation index

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Table and Figure captions

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Figure 4. Absorbance values for Altea water.

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Figure 6. Turbidity and absorbance measurements versus time of all waters with 3 hours of treatment.

Figure 7. Particle size of Altea water, untreated and treated for 1 hour.

Figure 8. Particle size of Villena water, untreated and treated for 1 hour.

Graphical abstract

A method of forced precipitation of calcium carbonate, is used to distinguish between electromagnetic treated and untreated tap water, by measures of temporal evolution of turbidity, absorbance and the final size of the particles formed. There is an immediate technique to verify the effect of electromagnetic treatment, with temperature control.