

## Review

# Review of Techniques to Reduce and Prevent Carbonate Scale. Prospecting in Water Treatment by Magnetism and Electromagnetism

Sergio Martínez Moya <sup>1,\*</sup> and Nuria Boluda Botella <sup>1,2</sup> <sup>1</sup> University Institute of Chemical Process Engineering, University of Alicante, E-03080 Alicante, Spain; nuria.boluda@ua.es<sup>2</sup> University Institute of Water and Environmental Sciences, University of Alicante, E-03080 Alicante, Spain

\* Correspondence: s.martinez@ua.es

**Abstract:** Carbonate scale is one of the main problems in hot water systems, and therefore, interest in this subject has grown since 2000s. Water treatments, based on magnetic and electromagnetic (EM) techniques to prevent scale, are being commercialized, but their effectiveness is not clearly demonstrated because it depends on temperature, pressure, dissolved CO<sub>2</sub>, pH, field intensity, water flow, etc. In this paper, a review of these techniques, together with other classical techniques, such as chemical softening, the use of inhibitors, ion exchange, electrochemical and membrane treatments is presented. The latter alter the composition of the water and generate hazardous waste for health and the environment, unlike magnetic and EM treatments, which are considered non-invasive techniques. Different hypotheses are used to explain the effect of these treatments, such as the formation of aragonite instead of calcite or crystal nuclei formation within the fluid. Analysis of salts formed with SEM, X-ray diffraction, or colorimetric tests seem to support the efficiency of these treatments since study in the fluid is not easy. Dissolution of the formed scale or its prevention endorse the commercialization of these techniques, but their effectiveness must be verified in each installation.

**Keywords:** calcium carbonate; magnetic treatment; electromagnetic treatment; scale prevention; water hardness; softening



**Citation:** Martínez Moya, S.; Boluda Botella, N. Review of Techniques to Reduce and Prevent Carbonate Scale. Prospecting in Water Treatment by Magnetism and Electromagnetism. *Water* **2021**, *13*, 2365. <https://doi.org/10.3390/w13172365>

Academic Editor: Carmen Teodosiu

Received: 2 July 2021

Accepted: 24 August 2021

Published: 28 August 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Carbonate precipitation in water systems with exchange heaters is a very common problem. The presence of scale deposits involves technical problems, such as drain obstruction and heat transfer reduction that increase maintenance and energy costs [1].

To avoid these problems, there are different techniques that reduce the water hardness and eliminated scale formation. Some of the most common are chemical softening, precipitation, the use of inhibitors to avoid precipitation or complexation, cation exchange, electrochemical and membrane treatments, among others. In addition to these techniques, considered “classical”, there are also non-intrusive treatments that apparently do not alter the composition, such as magnetic and electromagnetic techniques, that are being commercialized.

Traditionally, water hardness was measured by the water's ability to precipitate soap, mainly as a consequence of insoluble carbonate compounds of calcium and magnesium ions [2]. Other minor ions present in the water, such as silicates, sulphates, and nitrates, can contribute to scale formation [3]. As it is well known, the hardness that disappears with boiling is called temporary hardness, and it is mainly due to the presence of calcium and magnesium bicarbonates. On the other hand, the hardness that remains after boiling is permanent hardness and could include other cations, but it is usually insignificant [3]. There are two methods for determining hardness—by calculation after ions analysis of calcium and magnesium or by EDTA titration [2]. It is expressed as mg/L of CaCO<sub>3</sub>, including

calcium and magnesium, and different ranges could be considered for the classification of water hardness. Kiely provides 4 ranges (Table 1).

**Table 1.** Relative hardness of waters [4].

Hardness	mg CaCO <sub>3</sub> /L
Soft	0–75
Moderately hard	75–150
Hard	150–300
Very hard	>300

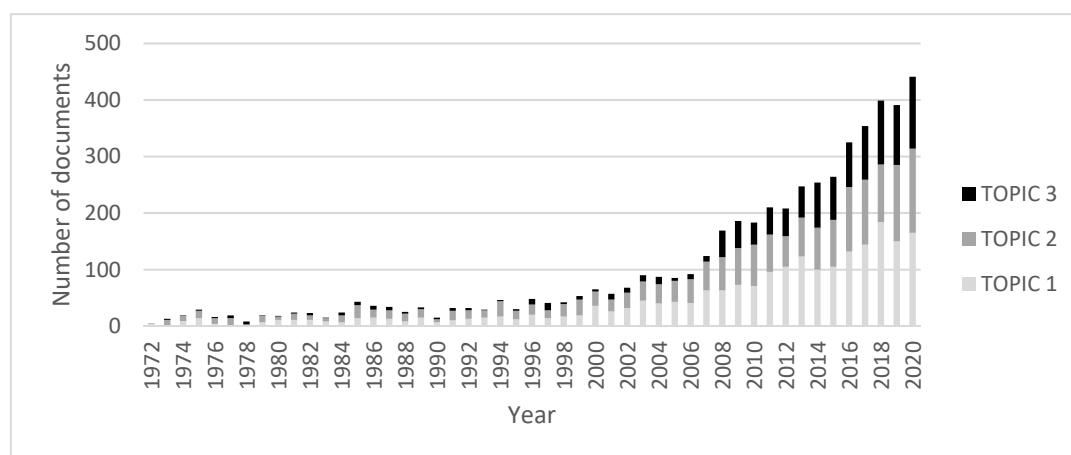
The study of the formation of calcium carbonate polymorphs and their identification is very interesting to understand the transformations and possible variations produced by magnetic and electromagnetic techniques. In this way, this article aims to analyse the calcium carbonate scale formation processes, as well as analyse of the current state of the main techniques for removing calcium carbonate scale, knowing the advantages and disadvantages. Then, an exhaustive review of the magnetic and electromagnetic techniques as an alternative to classical techniques that modify the composition of the water and generate waste, is presented.

## 2. Methodology

The bibliometric analysis of calcium carbonate incrustations and water treatments supports the interest of this work. Therefore, the bibliographic databases of the Elsevier group (Scopus and Science direct) were used to search for papers on different topics [5]. Figure 1 includes a total of 5105 records retrieved. The time span was established for all time, and English and Spanish were selected. Three topics or search terms were selected to distinguish between the basis of calcium carbonate precipitation in hard waters, classic treatments to avoid scale but which modify the composition of the water, and magnetic and electromagnetic treatments. These three blocks are the ones in which the review is mainly distributed. Figure 1 shows the keywords used for the search as well as the articles found each year according to each topic. The papers were analysed individually, and those that were finally part of the review were selected. They were organized using the Mendeley reference manager for better management.

Figure 1 shows that, especially during 2000s and since the 2008, there is increased interest in all the topics to increase knowledge around the basis of scale formation and into the techniques to prevent calcium carbonate precipitation. Indeed, the results and the improvements in classical techniques stand out, trying to reduce their impacts by using more environmentally sustainable materials and reducing waste. Magnetic and electromagnetic treatment, and other related terms, show important growth, and more research on this technique is expected in the coming years due to the need to prevent calcium carbonate incrustations without using invasive techniques that alter water composition and generate waste, which may cause health or environmental problems.

In general, this bibliographic analysis shows the need to continue developing environmentally sustainable techniques that reduce the impacts produced by classical water softening techniques, and the use of the magnetic and electromagnetic techniques with devices effective at avoiding carbonate scale. Section 3 presents the basis of the carbonate precipitation. Section 4 is a review of the classical treatments to avoid scale formation, and Section 5 is dedicated to the application of magnetic and electromagnetic techniques for water treatment, which could have a great number of applications in the future.



**Figure 1.** Total documents retrieved per year [5] from topics 1, 2, and 3: TOPIC 1 “Calcite” or “Aragonite” or “Calcium carbonate” or “scale” and “Water” and “Hardness”; TOPIC 2: “Water treatment” or “Scale prevention” or “Chemical softening” or “Chemical precipitation inhibitors” or “Membrane treatment” or “Cation exchange resins” or “Electrochemical treatments” and “Water” and “Hardness”; TOPIC 3: “Magnetic field” or “Electromagnetic field” and “Water treatment” (own elaboration).

### 3. Calcium Carbonate and the $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$ System

Calcium carbonate is one of the most abundant minerals in nature and usually the salt with the greatest contribution to water hardness. Some of the most representative carbonates which can appear in nature are shown in Figure 2.

Trigonal	Formula	$-\log K$	Cation radius (Å)	Orthorhombic	Formula	$-\log K$	Cation radius (Å)
Calcite	$\text{CaCO}_3$	8.48	1.12	Aragonite	$\text{CaCO}_3$	8.34	1.12
Magnesite	$\text{MgCO}_3$	8.24	0.72	Strontianite	$\text{SrCO}_3$	9.27	1.18
Rhodochrosite	$\text{MnCO}_3$	11.13	0.84	Witherite	$\text{BaCO}_3$	8.56	1.42
Siderite	$\text{FeCO}_3$	10.89	0.74	Cerussite	$\text{PbCO}_3$	13.1	1.18
Smithsonite	$\text{ZnCO}_3$	10.01	0.83				
Otavite	$\text{CdCO}_3$	13.74	0.99				
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	17.09					

**Figure 2.** Mineralogy and solubility product (K) of some carbonates at 25 °C [6].

In natural waters, calcium and magnesium are the most common elements and the main reactions involved in the scale precipitation are (1) and (2):



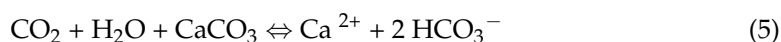
When the concentrations are limited by their solubility product ((3) and (4)), at a determined temperature:

$$K_{\text{CaCO}_3} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \quad (3)$$

$$K_{\text{MgCO}_3} = [\text{Mg}^{2+}] [\text{CO}_3^{2-}] \quad (4)$$

Precipitation of calcium carbonate salts has a different tendency to other minerals since the solubility product decreases as the temperature increases, giving rise to the precipitation of carbonate. This occurs in heat exchange systems when high temperatures cause the apparition of carbonate scale [3]. Furthermore, atmospheric  $\text{CO}_2$  is very important in the carbonate/bicarbonate system. This relationship between  $\text{CO}_2$  and  $\text{CaCO}_3$  shows that an

increase in  $\text{CO}_2$  results in the dissolution of  $\text{CaCO}_3$ , and the elimination of  $\text{CO}_2$  causes the precipitation of  $\text{CaCO}_3$ , through the reaction (5) [6]:



The sum of all carbon species is the TIC (Total Inorganic Carbon), which is given by the Equation (6) [6].

$$\text{TIC} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (6)$$

where  $[\text{H}_2\text{CO}_3^*] = [\text{CO}_2] + [\text{H}_2\text{CO}_3]$

The presence of different species is related to the pH of the water (Figure 3) which is another factor to consider in the formation of scale [7]. Moreover, the pH has a great influence on the solubility of heavy metals, in addition to being able to form carbonate salts, as a consequence of the low solubility product, shown in Figure 2.

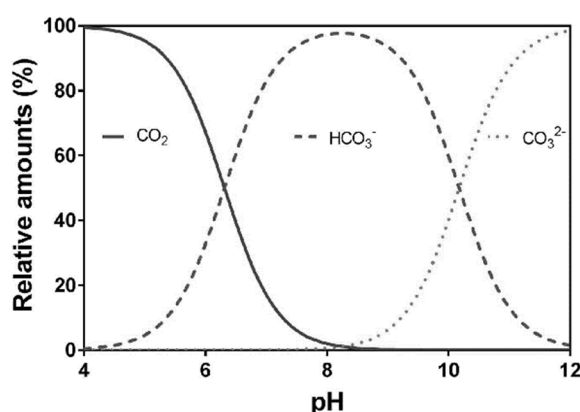


Figure 3. Relative speciation of  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  in water as a function of pH [8].

### 3.1. $\text{CaCO}_3$ Polymorphs

Calcium carbonate can constitute different minerals depending on the conditions of the medium and the presence of other elements. The most abundant minerals are calcite, aragonite, and vaterite (Figure 4), the latter being the less common.

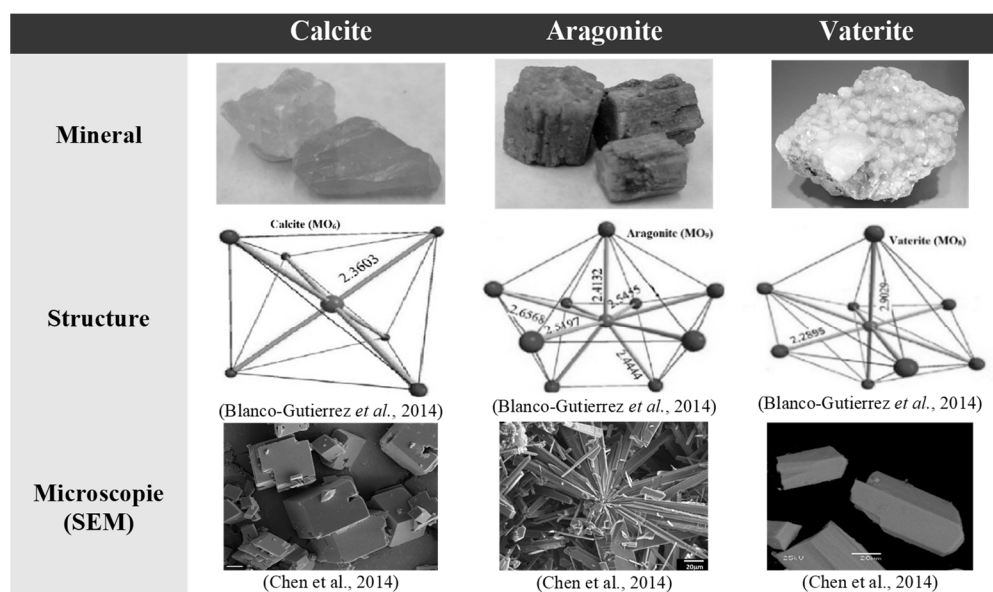
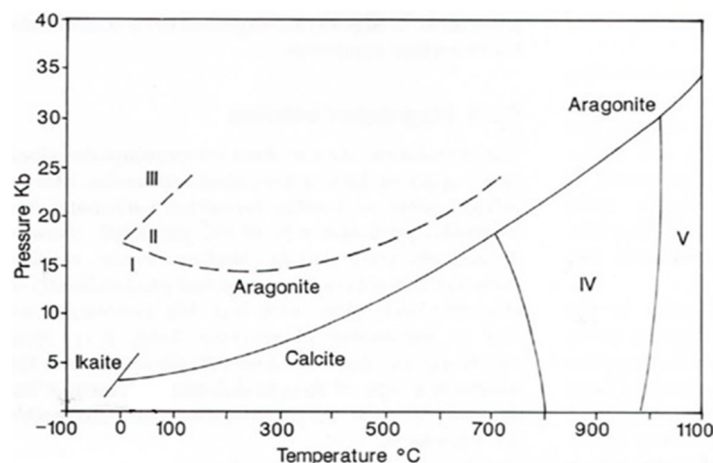


Figure 4. Main mineral shapes of calcium carbonate [9–11].

One of the main differences between calcite and aragonite is their crystalline shapes. Calcite has a rhombohedral structure and aragonite has an orthorhombic structure. In the stability diagram of calcite-aragonite, their great dependence on temperature and pressure is observed. At elevated temperatures and/or pressures, five other  $\text{CaCO}_3$  polymorphs are known from experimental work (Figure 5).



**Figure 5.** Stability diagram of calcite-aragonite. I–V, calcite intermediate polymorphs [12].

On the other hand, calcite crystallisation is favoured in high concentration gradients [13]. Within the Mohs hardness scale, calcite would be at 3 while aragonite would be at between 3.5 and 4. It is important to note that aragonite has a higher density than calcite and is less prone to produce scale [14]. One of the factors that can determine that aragonite forms a less compact scale may be the acicular morphology of its crystals [15]. Calcite is thermodynamically much more stable than aragonite, and calcite formed by the reversion of aragonite appears to be much harder than natural calcite. It has been observed that the presence of  $\text{Fe}^{2+}$  can inhibit this reversal and aragonite remains longer [16]. On the other hand, some studies determine that the presence of impurity ions, such as copper or silicon, help in the effective preferential formation of aragonite or vaterite [17].

In recent studies carried out at the University of Alicante, the mineral phases present in scale samples from domestic water systems have been determined. The majority presence of calcite was observed in samples from taps, at the outlet of pipes or in the scale, however, the majority presence of aragonite was determined in the samples inside heaters. As a consequence, at higher temperatures the formation of aragonite is favoured [18].

On the other hand, organisms contain forms of biogenic calcium carbonate similar to geological calcite and aragonite, commonly having similar crystalline structure and thermodynamic stability similar to their geological forms [19]. The fixation of this calcium carbonate is called biomineralisation, with the shell of molluscs being one of the best examples. During the shell formation process of many marine organisms, the first mineral to form is a highly disordered form called amorphous calcium carbonate (ACC) [20]. Later, this ACC will be transformed into the crystalline aragonite or calcite phase [21]. For example, the shell is composed of three layers: the outer periostracum, middle prismatic, and inner nacreous layers. The nacre layer is made up of 95% aragonite, having a hardness 3000 times higher than that of the mineral aragonite, thanks to the remaining 5% of the organic matrix [22].

### 3.2. Identification of Mineral Phases of Calcium Carbonate

The main techniques for mineral phase differentiation of calcium carbonate are scanning electron microscopy, X-ray diffraction, and colorimetric test. Starting with these tests, the differentiation between calcite and aragonite is carried out in geological researches with the Meigen test and the Feigl test [23]. These colorimetric techniques have been developed

for minerals, but their applicability to samples from pipe scale or water samples, and the obtention of scales after evaporation, has been very poorly studied [18].

The Meigen Test was described by W. Meigen in 1901 [24] and used the different behaviour of the two crystalline structures of calcium carbonate, when boiled with a cobalt nitrate solution of 5–10% weight for twenty minutes [25]. Togari and Togari [26] performed this test by boiling 0.2 g of the sample in 2 cm<sup>3</sup> of cobalt nitrate solution 0.1 N, where the inconvenience of this determination is that it must be done in the laboratory. The aragonite soon takes on a purple colour while the calcite always remains unaltered. The cause of the difference in the reactivity of calcite and aragonite is found in the slightly higher solubility of aragonite [27].

There are some cases where the Meigen test can give incorrect results. When the test was applied to samples of foraminifera, they determined the samples were aragonite, but when the samples were analysed by X-rays, it was shown that the sample was calcite [28]. Difficulties also arise when working with fine-grained samples. Cobalt solution spreads over both minerals to a similar degree and discrimination becomes difficult. To try to solve this, the method can be made more sensitive by applying ammonium sulphide. In this case aragonite turns black and calcite does not change colour [24].

It should be noted that some possible interferers can complicate the identification of minerals, such as the presence of elements that react with cobalt and modify the coloration. Another factor is the oxidation that occurs in the sample with the presence of oxygen, going from violet to brown. In a study carried out at the University of Alicante [29], some of these interferences were observed and they were analysed where a wide range of colours was observed, that can go from blue-green, due to chloride ion or excessive alkalinity, to dark brown due to the presence of an oxidant [18].

Another test that differentiates these minerals is the Feigl Test [30], which is based on the slightly different dissolution rates of calcite and aragonite in water. When treating a sample with a solution containing Ag<sup>+</sup> and Mn<sup>2+</sup> ions for 10 min, aragonite becomes black, while no change of colour is observed in calcite, dolomite, and witherite.

Colorimetric tests are a quick and easy source of information to distinguish mineral phases, but for a more precise identification of calcite and aragonite techniques such as X-ray diffraction (XRD) and scanning electron microscopy, (SEM) should be used.

Scanning electron microscopy (SEM) is a technique that allows the study of samples between the nanometre and the micrometre scale, producing a three-dimensional image. An electron beam irradiates the sample and generates an image. The signals produced from the interaction of the electron beam with the sample mainly include [31]:

- Secondary electrons. Produced from the emission of valence electrons. They are of very low energy so only the most superficial come out of the sample and provide information about the topography of the surface.
- Backscattered electrons. They have higher energy than secondary electrons, therefore they provide information on deeper parts of the sample and are sensitive to the composition of the sample.
- Characteristic X-rays. The energy of transition from one layer to another is characteristic of the element from which they come. Provides chemical information for the sample.

On the other hand, X-ray diffraction is a technique to determine crystalline materials by providing information on structures, phases, and other parameters. This technique has a considerable number of applications in various fields due to its ability to determine and differentiate crystalline phases. X-ray diffractometers consist of a sample holder, an X-ray tube, and an X-ray detector [32]. The diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles of each set of reticular planes in a sample [33].

In summary, these techniques allow the mineral phase of the sample to be accurately determined, but it is important to emphasize that colorimetric techniques can help provide initial information on the composition of the sample that must then be confirmed by



SEM with three-dimensional image about the topography of the crystal surface, or with X-ray diffraction by determination of crystalline phases with specific angles of each set of reticular planes.

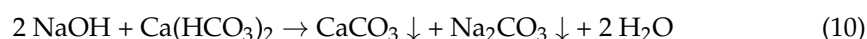
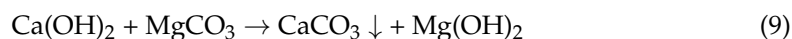
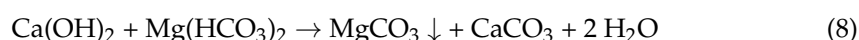
#### 4. Treatments to Avoid Scale Formation

Among the classical techniques for reducing hardness are chemical softening by adding reagents to provoke precipitation, complexing agent or chemical inhibitors of the precipitation, electrochemical treatments, cationic exchange with resins, membrane treatments, and other treatments.

##### 4.1. Chemical Precipitation

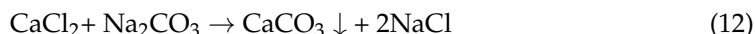
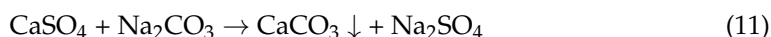
This water treatment consists in the addition of chemical compounds that cause reactions with the calcium and magnesium ions in solution. This addition transforms them into very poorly soluble compounds, precipitation occurs and solid can be eliminated by physical procedures. Calcium and magnesium ions are eliminated by formation of  $\text{CaCO}_3$  and  $\text{Mg(OH)}_2$ , adding hydroxide ions and raising the pH [3]. Calcium precipitation occurs when the pH is raised, causing the transformation of bicarbonate ions to carbonate. The increase in carbonate ions causes the ionic activity product to exceed the solubility product and precipitate calcium carbonate. For the precipitation of magnesium, hydroxide ions should be added until the ionic activity product of magnesium hydroxide exceeds the solubility product, causing precipitation.

- Using calcium and sodium hydroxide ((7)–(10))



To remove the remaining calcium, an external source of carbonates, usually sodium carbonate, must be added [34].

- Using sodium carbonate ((11) and (12))

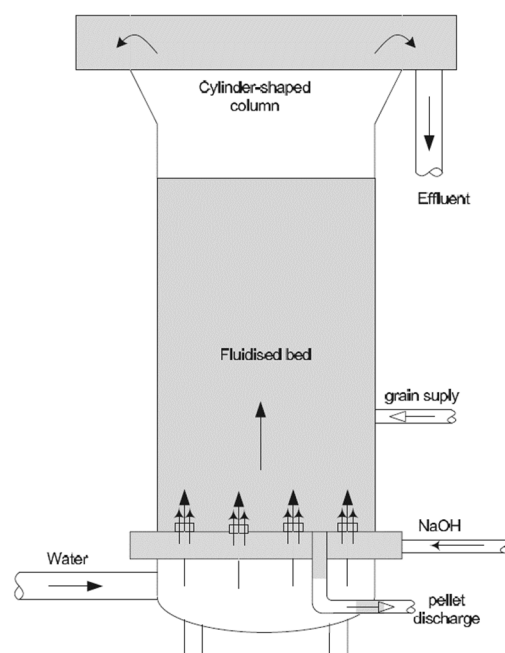


To carry out this process, it is possible to use the pellet reactor (Figure 6), which is especially used in the Netherlands [35]. Precipitation of calcium carbonate occurs on the particles used in the pellet reactor, where the liquid is passed upwards causing fluidized particles, while the reagents are dosed. Calcium carbonate will crystallise on the pellets, which are removed from time to time.

##### 4.2. Complexing Agents and Other Inhibitors of Precipitation

There are chemical substances such as phosphates, polyphosphates, and organophosphonates which can be used as scale inhibitors because they can prevent the precipitation of calcium carbonate and other ions as scale [36]. In different studies, the formation of unstable forms of calcium carbonate, such as vaterite and aragonite, occurs and therefore decreases the concentration of calcite, which is the main source of scale.

Calcium carbonate scale is inhibited with low concentrations of phosphonic copolymer of maleic anhydride and sodium *p*-styrene sulphonate [37]. An interesting observation was made in the presence of low phosphonic copolymer, when some vaterite was obtained. It was found that the thermodynamically unstable vaterite could be kinetically stabilized in the presence of low phosphonic copolymer.



**Figure 6.** Structure of a fluidized bed reactor [35].

Recently, so-called green inhibitors are being developed because they are biodegradable, non-toxic, and environmentally friendly, for example recent studies with quercetin (3,3',4',5,7-pentahydroxyflavone), a flavonoid present in plants as a secondary metabolite. It was observed that, in the absence of an inhibitor, crystals with rhombohedral (calcite) and needle (aragonite) morphology appeared, while in the presence of quercetin, the aragonite fraction increased slightly [38]. As previously mentioned, aragonite has a higher density than calcite and is less prone to produce scale [14]. It was also observed that low concentrations of quercetin were needed to block the growth-germination of calcium carbonate as calcite. As commented, these studies determine that the presence of scale inhibitors can stabilize the most unstable forms of calcium carbonate, and therefore decrease the concentration of calcite. Furthermore, it was observed that the precipitation of  $\text{CaCO}_3$  in solution it was totally inhibited with 2 mg/L of quercetin.

Studies have been carried out where plant extracts such as *Paronychia arabica* (PA) are applied as antiscalants. It was observed that the presence of the extract reduces the amount of scale deposited on the entire surface of the electrode. This inhibitor can be used for groundwater in conventional electrochemical cells with three electrodes, where the water temperature can reach 32 °C. It was observed that, at concentrations of 80 ppm of the PA extract, there is a partial inhibition of the  $\text{CaCO}_3$  deposition and when the concentration of the inhibitor was increased to 150 ppm, no scale was formed [39].

On the other hand, addition of acids such as sulphuric acid to the fluid during the water pre-treatment process in refrigeration systems is another technique which prevents scale precipitation because it converts calcium bicarbonate into more stable and soluble calcium sulphate; it also contributes to the formation of  $\text{CO}_2$  [40]. Other techniques based on the addition of compounds with metals are no longer used, such as molybdate, which reacts with other organic and inorganic compounds. These inhibitors are restricted by legislation due to their toxic effects on the environment [41].

#### 4.3. Electrochemical Treatments

Redox processes are one of the most recent procedures implemented for the treatment of water hardness. These processes cause water circulation through an electrolyser, with a set of electrodes to treat the water, and calcium carbonate will deposit on the surface of the cathode plates. These deposits fall spontaneously or are forced by mechanical action. Once carbonate has accumulated in the bottom, it can be removed and, in some cases, revalued.



The formation of deposits on the cathode plates causes the deactivation of this electrode and an increase in the electrical resistance if the deposit does not separate. Figure 7 shows the schematic of an ERCA<sup>2</sup> electrolyser.

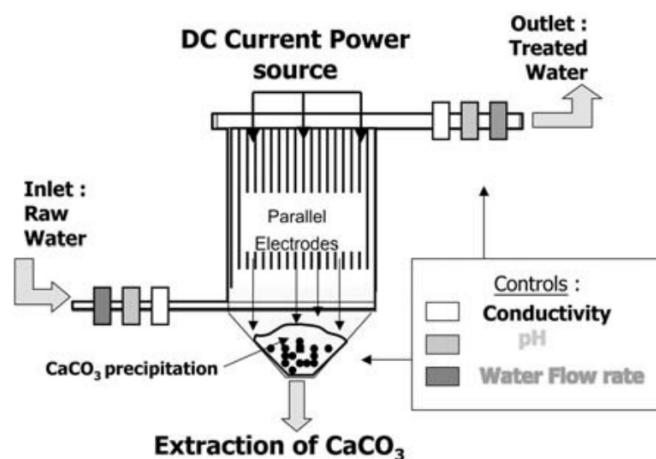
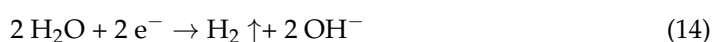


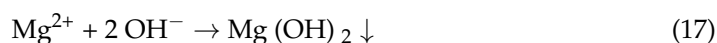
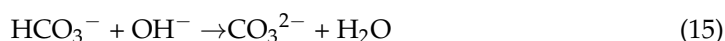
Figure 7. Scheme of the ERCA<sup>2</sup> electrolyser [42].

The speed of the cathode accumulation depends on various factors, such as the morphology of the crystal or the type of structure (calcite, aragonite, or vaterite). One of the advantages of this process is that it does not require chemical substances that can be toxic to drinking water [42].

The electrochemical process is based on the generation of a high pH around the cathode by the following cathode reactions (13) and (14) [43]:



Alternatively, the precipitation process occurs due to the following reactions (15)–(17) [43]:



The key factors to ensure the efficiency of this process are the type of precipitate and the type of material chosen for the electrode and the surface (stainless steel has the best cost-efficiency ratio). Other important factors are the operating conditions and the composition of the water to be treated. When determining the efficiency of the technique, for instance, it was observed that calcium is eliminated better than magnesium [44]. There must be a certain level of alkalinity ( $\text{HCO}_3^-$ ) for removal of calcium in the form of calcium carbonate. The presence or absence of certain elements in the water, as well as their concentrations, are key factors when determining the size of the crystals, their porosity, and their composition, among others.

The industrial application of this technology is quite restricted due to limitations such as the need for a large area by the cathode, the existence of a limit current density, and the periodic cleaning of the cathode surface for the process to continue working [45]. With respect to regular cleaning to maintain efficiency, Jin et al. [43] demonstrated the effectiveness of polarity reversal in removing depositions on the cathode. This system eliminates incrustations with more efficient reduction in the hardness of the water, as well as being more energy efficient.

This technique can also be used to treat tap water, using different settings, obtaining a low pH zone and a higher pH zone with low salinity. Mixing the treated water of these

two configurations could produce tap water with the desired pH. Calcium removals of between 73–86% were observed by precipitation [46].

Yu et al. [47] carried out comparative studies between conventional electrochemical reactors and multistage electrochemical precipitation reactors, when the latter presented a clear superiority maintain a stable softening efficiency after a long time operation, were the hardness removal efficiency was 18.7–21.6%.

Combined electrochemical treatments have been developed to try to increase effectiveness in reducing water hardness, for instance conventional electrocoagulation and electrochemical precipitation. Flocs formed in the electrocoagulation cell, which could provide more electrostatic attraction and precipitation surface for hardness species in electrochemical precipitation cell [48].

#### 4.4. Cationic Exchange

A common technique in water softening is ion exchange with application for domestic and municipal use. This technique involves an exchange between ions from water of similar charge to the resin, maintained by electrostatic forces in charged functional groups located on a solid. The exchange occurs between multivalent ions, such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , found in the feed water with a cation trapped in the resin, which is usually  $\text{Na}^+$  [49]. Depending on the type of resin used, a wide variety of elements can be removed such as radium, barium, nickel, vanadium, nitrates, chromates, arsenates, etc. With removal rates of up to 98% using selective resins [34,50].

The most used material for this process are synthetic resins, networks of hydrocarbon radicals that form a three-dimensional matrix to which soluble ionic functional groups are attached [51]. Recycled materials have been proposed for the manufacture of the resins, which can help to make this technique a little more ecological. Bekri-Abbes et al. [52] developed a technique to recycle polystyrene residues from coffee cups to generate cation exchange resins. Calcium removals of up to 0.93 mmol/g were observed after 4 h of treatment at 40°.

A problem associated with the use of these systems is the sodium concentration increase in the water, released from the resin and during the resin regeneration. In some cases, this increase can be very high and may have negative effects on health and the environment [49]. Due to these problems in countries such as the United States, legislative measures have been taken against the discharge of water from ion exchange treatments [53]. To try to reduce the effects associated with excess sodium, different alternatives have been proposed, for example, replacing NaCl from resins with KCl. This is because a controlled increase in potassium does not produce negative effects for health and the environment [54].

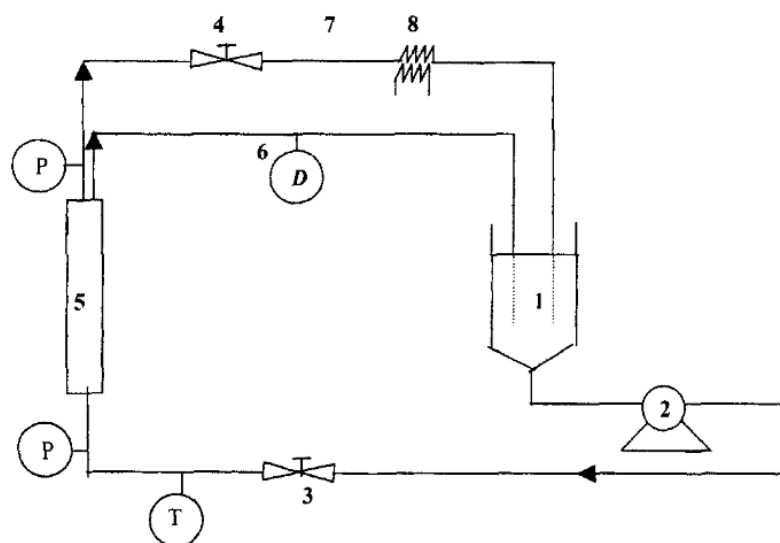
#### 4.5. Membrane Treatment

Separation of ions, which contributes to scale formation, can be obtained with membrane techniques, but it is a less common treatment used to reduce water hardness.

Different kind of membranes can be used, and the cation removal depends on porous measure or other mechanism and coupled process. Ultrafiltration membranes alone are inefficient at reducing hardness, with removals of around 15%. However, if the treatment is supplemented with a Fluidized Bed Pellet Reactor, the removal rates can be around 85%. Reducing water hardness with an integrated membrane and fluidized bed reactor has been shown to be very effective [55].

It has been observed that nanofiltration processes allow elimination of multivalent ions of around 90% and monovalent ions of between 60–70%. In the case of calcium, a rejection greater than 90% was observed, depending on the conditions [56], and removal rates of around 96–98% for calcium and magnesium using a commercial spiral-wound nanofiltration membrane [57]. Dependence between nanofiltration treatment and pressure were analysed, with low (0.5, 1, and 2 bar) and high (4–16 bar) pressures. Rates of retention reached 50% for  $\text{Ca}^{2+}$ , 63% for  $\text{Mg}^{2+}$  and 40% for  $\text{HCO}_3^-$  at strong pressures, and 34% for

$\text{Ca}^{2+}$ , 40% for  $\text{Mg}^{2+}$  and 30% for  $\text{HCO}_3^-$  at low pressures. Figure 8 shows the scheme of the nanofiltration system used [58].



**Figure 8.** Diagram of the nanofiltration pilot. 1 tank, 2 feed pump, 3 and 4 pressure regulation, valves, 5 nanofiltration module, 6 permeate recirculation, 7 retentate recirculation, 8 heat exchanger. D, flow meter; P, pressure sensor; T, temperature sensor [58].

New membranes with layers, or with better self-cleaning systems, are being developed that improve the performance of the process. For example, a nanofiltration membrane made of nanocomposite polyamide layer with nanoparticles of MOF (metal-organic frameworks), based on phthalic acid and aluminium nitrate to improve the function of the thin-composed membrane. After the study, a significant improvement in water flow and rejection of multiple compounds ( $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ) for water softening was observed [59].

In studies with reverse osmosis membranes, hardness removal of around 95% was obtained. It was observed that removal efficiency depends on the raw water conditions [60].

#### 4.6. Other Treatments

New techniques and treatments have been developed to combat the effects of hard water and, in severe cases, by combining two or more removal processes.

New self-cleaning filters have also been developed using spark-generated shock waves. These filters avoid filter replacement after fouling and are more efficient than self-cleaning backwash filters. The spark discharges, generated from short electrical pulses, produced shock waves that propagated towards the filter surface. This shock wave produced enough force to dislodge the calcium carbonate particles deposited on the filter surface, decreasing the pressure drop across the filter [61].

In small communities in semi-arid regions that have problems with highly calcareous waters and do not have access to conventional treatments, materials such as *Moringa oleifera* seeds are used as adsorbents with good results to soften water in combination with the dosage of coagulants [62].

Adsorbent based on natural polymers can also be an effective procedure in reducing the hardness of water. Spherical antibacterial hydrogel beads were synthesized and employed to remove calcium and magnesium ions and reduce the hardness of water. The sorption capacity under optimal adsorption conditions was  $162 \text{ mg g}^{-1}$  for  $\text{Mg}^{2+}$  and  $114 \text{ mg g}^{-1}$  for  $\text{Ca}^{2+}$ . The beads were also found to be reusable with a negligible decrease in removal efficiency, even after four cycles. On the other hand, a good antimicrobial effect was observed against Gram positive and negative bacteria thanks to the  $\text{Ag}^0$  nanoparticles [63].

Microbial Desalination Cells (MDC) can remove hardness and heavy metals from water in an environmentally friendly and low power consumption process. MDCs consist of three compartments: the anode, the cathode, and a salt compartment, which is located between the anode and the cathode. Up to 90% reduction in water hardness was observed in the treated samples, and between 90–99% of four types of heavy metals (arsenic, copper, mercury, and nickel) were removed [53].

Some authors propose combining other techniques, such as ultrasound, with ion exchange to increase the efficiency of the process. It was observed that the sorption capacity and the removal speed of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were higher in the presence of ultrasound than with the classical method, especially in the early stages [64].

#### 4.7. Advantages and Disadvantages of Classical Water Softening Techniques and Comparative

All these techniques, usually used to reduce the hardness of water, present a series of advantages and disadvantages in their application. Table 2 summarizes the advantages and disadvantages of these classical techniques used for water softening.

**Table 2.** Advantages and disadvantages of classical water softening techniques (own elaboration).

Treatment	Advantages	Disadvantages
Chemical softening and inhibitors	<ul style="list-style-type: none"> <li>- Cheap treatment</li> <li>- Highly effective</li> </ul>	<ul style="list-style-type: none"> <li>- Add new compounds</li> <li>- Downgrade water quality</li> <li>- Water not suitable for all uses</li> </ul>
Electrochemical	<ul style="list-style-type: none"> <li>- No chemicals are added</li> <li>- Revaluation of precipitates</li> </ul>	<ul style="list-style-type: none"> <li>- Limitations in industrial applications</li> <li>- Periodic cleaning</li> <li>- Downgrade water quality</li> </ul>
Cation exchange	<ul style="list-style-type: none"> <li>- A wide variety of compounds can be removed</li> <li>- High efficiency</li> <li>- Resins from recycled materials</li> </ul>	<ul style="list-style-type: none"> <li>- Increase <math>\text{Na}^+</math> harmful to the environment and health</li> <li>- Maintenance of resins</li> <li>- Downgrade water quality</li> </ul>
Membrane	<ul style="list-style-type: none"> <li>- High efficiency</li> </ul>	<ul style="list-style-type: none"> <li>- Not all membranes are useful</li> <li>- High cost related with high efficiency</li> <li>- Membrane maintenance</li> <li>- Downgrade water quality</li> </ul>

All these techniques are very effective in reducing or eliminating calcium carbonate deposits in systems that work with water. It is difficult to select one of them as the most effective, since each one has different fields of application and has some limitations.

Chemical precipitation and the application of inhibitors are effective and widely used techniques. However, they add new compounds to water, affecting its quality, so the resulting water is not suitable for all uses. Electrochemical processes are one of the most recently implemented procedures for the treatment of water hardness, although it has some technical limitations in industrial applications, such as the need for periodic cleaning. Ion exchange is also a widely used technique, especially in domestic and municipal contexts. One of the main drawbacks is the increased concentration of ions such as sodium in the outlet water, which can cause harmful effects on health and the environment. On the other hand, membrane treatments are less used in water softening. Osmosis membranes and nanofiltration membranes are the most efficient, although other types of membranes can be used if they are combined with other techniques. However, there are problems associated with fouling of the membranes. Among the new techniques, those associated with adsorption processes present very good prospects, especially in places with fewer resources.

Although new, more environmentally friendly and less polluting materials and compounds are being used in many cases, so it is difficult to avoid the possible drawbacks of these techniques.

## 5. Application of Magnetic and Electromagnetic Techniques to Prevent the Effects of Water Hardness

As mentioned, the treatments presented above reduce the formation of carbonate precipitates, by reducing water hardness, through different techniques that prevent the formation of incrustations in pipes and heating systems. However, these techniques have some disadvantages, as has been seen. Alternatively, magnetic and electromagnetic techniques prevent the effects of water hardness without adding or removing compounds and minimize scale deposits. However, the different equipment which is being commercialized is not complete in effectiveness in several cases, and its effectiveness is not easily demonstrated in domestic devices with analytical procedures.

Below is an exhaustive review of the magnetic and electromagnetic treatment techniques that aims to know the state of the art of these techniques and their possible applications.

### 5.1. Magnetic Techniques

References to the application of magnetic treatment are older than those to electromagnetic treatments. Gruber and Carda [65] proposed different installation configurations of permanent magnets (Figure 9), with different orientations of the magnetic field, in intrusive and non-intrusive systems. In those of class I and IV, the applied field is parallel to the direction of the flow, while in those of class II and III, the field is orthogonal to the flow.

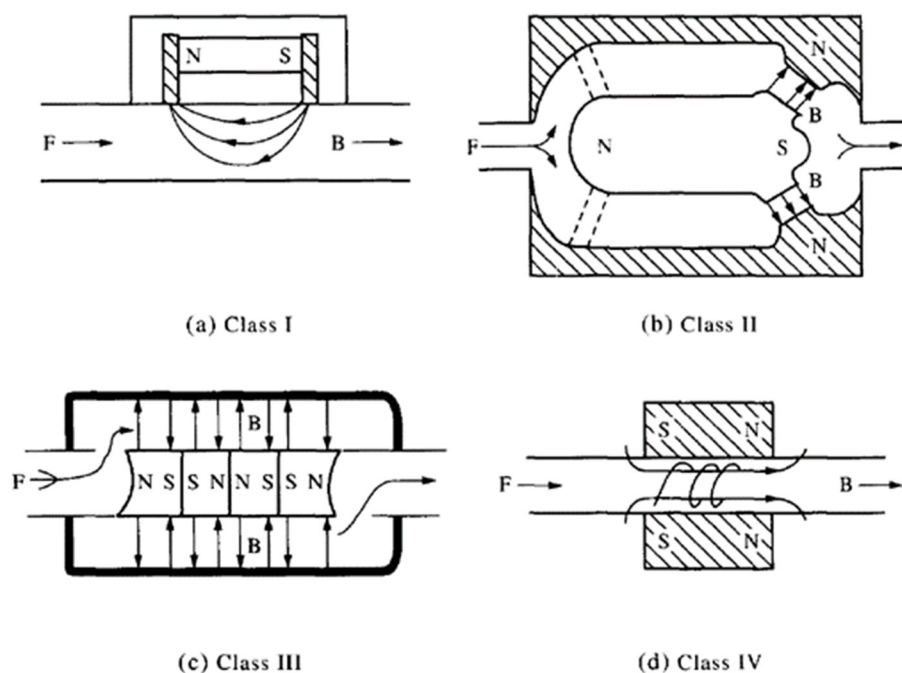


Figure 9. Configurations of magnetic assemblies [65].

Although currently, magnetic techniques are less used than electromagnetic techniques, magnetic techniques continue to be studied. This is the case of the Alomari [66] study in which the efficiency of the application of magnetic fields in the formation of encrustations in groundwater is tested. Permanent neodymium magnets were used to generate the magnetic field and groundwater was heated in a beaker at 95 °C to obtain the incrustations. The good results achieved are attributed to the magnetic field reducing both the dissolved CO<sub>2</sub> content and the surface tension, thus reducing the amount of temporary hardness. An alteration was seen in the shape and size of the calcium carbonate crystals that prevent their adhesion to the substrate by forming hard scales. There is a great variety of assemblies for applying magnetic fields to water.

Table 3 shows some of those found in the bibliography. In the equipments used in the literature, the magnetic field intensities applied to water range from 0.007 to 1 T,

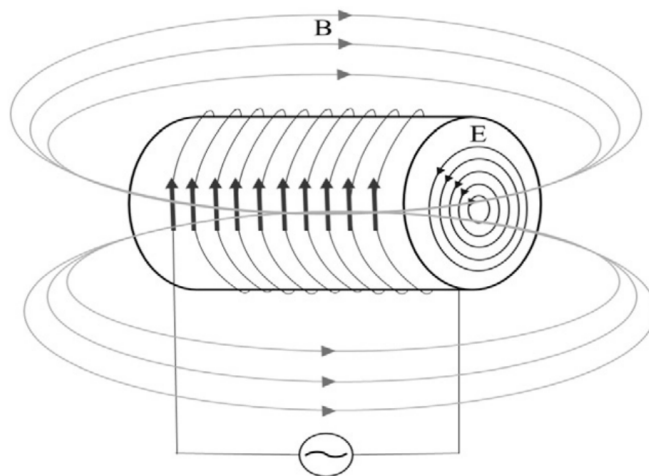
mainly ferrite or neodymium magnets being used. Electromagnetic fields are applied to a multitude of solutions ranging from groundwater to synthetic solutions with pollutants. In turn, there are many applications studied with special emphasis on the effect on calcium carbonate. Reductions in hardness and fouling of between 15–45% are observed, depending on the case. In addition, it is also observed, in some papers, that the application of the treatment increases the formation of aragonite instead of calcite. Apart from these effects, modifications are also observed in the properties of the water that can be very interesting due to its different applications.

In summary, it is observed how the application of magnetic fields to water generates various effects on the formation of scale (modifications in hardness, prevention of scale formation, variation in crystalline structures . . . ), and in the properties of water. Other effects have also been reported, such as the increase in the adsorption rate of heavy metals that should be studied in more depth.

### 5.2. Electromagnetic Techniques

Electromagnetic techniques have been developed in recent years to a greater extent than magnetic techniques, as another way of applying magnetic treatments to water. There are many studies that show the effect of these techniques, in addition to the comments of users who observe the effects of the multiple commercial electromagnetic equipment at domestic and industrial levels [78].

This research line has shown good results, as demonstrated by simulation studies such as Kozic et al. [79], which support the interest and effectiveness of these techniques. They used equipment consisting of a nickel-galvanized iron casing and an inner steel plate. The electromagnetic coil is a solenoid with rectified alternating currents which produces a pulsating field. A computer simulation verified the efficiency of electromagnetism equipment in reducing the formation of carbonate deposits. Figure 10 shows one of the most common designs for the generation of electromagnetic fields, a solenoid to which an electric current is passed [80].



**Figure 10.** Electromagnetic field generator system [80].

Table 4 includes EM equipment commercials from research studies. In them it is observed that the frequencies used range from 0.05 to 400 kHz, and the equipment used is based mainly on solenoids to which an electric current is passed. On the other hand, the solutions used are also very broad, from synthetic hard water to sea water. It is also observed that the effects analysed are varied.



**Table 3.** Magnetic equipment used in the literature (own elaboration).

Reference	Magnetic Equipment	Intensity (T)	T (°C)	Solution	Volume (L)	Velocity (m/s)	Effects Studied and Results
Alomari, 2019 [66]	Neodymium magnets	0.5	-	Groundwater	20	-	Hardness and scale formation (39% reduction in temporary hardness, 2% in permanent hardness and 9% in total hardness)
Rajczykowski & Loska, 2018 [67]	Neodymium magnets N38	0.517	-	Heavy metal solutions	0.4	-	Adsorption of heavy metals on activated carbon (The effectiveness of the process with respect to copper is increased by more than 40% and a summary molar removal was increased by 11%)
Wang et al., 2018 [68]	MWD-1 magnetizing equipment	0.28	25–70	Tap water	-	0.8	Specific heat (Treatment can decrease it), evaporation (Increases by 39%), and boiling point (Reduction of around 2 °C)
Han et al., 2016 [69]	Permanent magnets	0.08–0.18	20	Purified water and KCl solutions	-	-	Properties of water and KCl solutions
Latva et al., 2016 [70]	Bauer Water Ltd.PJ-20iHS	0.026	21.1–21.5	Tap water	60	-	Calcium carbonate precipitation (Reduction by 15%) and corrosion of pipes (Corrosion rates of 1–50 mils/year were obtained using chemical inhibitors, with corrosion rates of 0.0 mils/year obtained for the magnetically treated water)
Mahmoud et al., 2016 [71]	Permanent magnets GMX 8000	0.8	27.3–27.9	Hard water	1	-	Calcium carbonate precipitation with a rapid controlled precipitation test (Antiscaling efficiency was approximately 45%)
Silva et al., 2015 [72]	Permanent magnets	1	24	Ba, Sr, Ca, Ag and Na solutions	0.05	0.992	Control of sulfate scales (The particle size distributions obtained for the treated solutions are in a smaller range than the untreated ones)
Liu et al., 2010 [73]	Own equipment	0.01–0.04	20	Synthetic water	60	0.5	Effect on the structure of calcite and aragonite (Changes in morphology are observed after application of the treatment)
Tai et al., 2008 [74]	MagneGen 1000 and 100	0.007–0.102	25	Na <sub>2</sub> CO <sub>3</sub> and CaCl <sub>2</sub>	-	0.047	Calcite and aragonite growth rates (Reductions of up to 37% were observed in the growth rate of calcite. When treating for 24 h before nucleation, more than 50% aragonite appeared. When treating for 48 h, the calcite disappeared, and the aragonite was the predominant form)

Table 3. Cont.

Reference	Magnetic Equipment	Intensity (T)	T (°C)	Solution	Volume (L)	Velocity (m/s)	Effects Studied and Results
Coey and Cass, 2000 [14]	Ferrite ring magnets and Nd-Fe-B magnets	0.1	-	Groundwater and mineral water	0.5–1	0.04–1.2	Structure of calcium carbonate and persistence of the treatment (A lower amount of Aragonite (7%) is observed in the untreated samples and 54% in the treated samples. A memory effect of more than 200 h was observed)
Wang et al., 1997 [75]	Neodymium-iron-boron magnets	0.2	25–30	Na <sub>2</sub> CO <sub>3</sub> and CaCl <sub>2</sub>	0.005	-	Nucleation of a supersaturated solution (The application of the treatment generates a faster precipitation, with smaller and more irregular crystals)
Kronenberg, 1985 [76]	Ferrite type ring magnets	0.1	-	Tap water	$2 \times 10^{-5}$ – $1 \times 10^{-4}$	-	Crystal morphology and formation of precipitates (An increase in crystallization nuclei and a reduction in crystals attached to the substrate are observed)
Martynova et al., 1969 [77]	Undetermined	0.9	-	CaSO <sub>4</sub> , CaSiO <sub>3</sub> , BaSO <sub>4</sub> , Ca(HCO <sub>3</sub> ) <sub>2</sub> solutions	-	0.1	Scale formation (The dimensions of the crystals decrease, and their number increases as the intensity of the magnetic field increases)

**Table 4.** Electromagnetic equipment used in the literature (own elaboration).

Reference	Electromagnetic Equipment	Frequency (kHz)	T (°C)	Solution	Volume (L)	Flow (L/h)	Velocity (m/s)	Effects Studied
Gimeno Amorós et al., 2019 [9]	TK3K equipment	1	21–29	Tap and synthetic water	4	600	-	Calcium carbonate precipitation and structure (The evaporation of water with temperature generates almost 100% aragonite in the samples. The Meigen test is useful for the identification of crystalline forms, but it has many interferences)
Jiang et al., 2019 [81]	HydroFLOW S38 and HS48	150	21–37	Groundwater	-	1362	-	Scale in reverse osmosis membranes and effect on the permeate (The decreasing rate of the normalized water permeability with treatment improved by 38.3% and 14.3% compared to permeate flow without treatment)
Hachicha et al., 2018 [82]	Aqua-4D system	1–10	-	Saline water	0.005	-	-	Effect of saline water on seed germination of corn and potato crop (The treatment of saline irrigation water increased the germination rate of corn seeds, absorption of the nutrients (K, N and P) by the potatoes and decreased the ion toxicity for the crop by decreasing the Na <sup>+</sup> contents in the plants)
Piyadasa et al., 2017 [83]	Pulsed electromagnetic field (PEMF) devices	100	27–40	Na <sub>2</sub> CO <sub>3</sub> and CaCl <sub>2</sub>	0.002–0.01	-	-	Calcium carbonate precipitation and structure (Effects were observed on the CaCO <sub>3</sub> precipitation profile and on the characteristics of the precipitate, but only with one of the two equipment analysed)
Piyadasa et al., 2018 [84]	Pulsed electromagnetic field (PEMF) devices	100	25–27	Water with bacteria	2	5.52–27.6	-	Effects on microorganisms (Negative and positive adaptive responses are observed in the growth rate after the application of the different equipment. These responses are highly dependent on the interaction of numerous factors and parameters)
Verdú, 2016 and Gonzálvez, 2017 [29,85]	Antical RF equipment	20–200	25–75	Tap and pond water	50	1000–500	-	Calcium carbonate precipitation and effect on microorganisms (The Meigen test is useful for the identification of crystalline forms. Colony reduction percentages of up to 67% were observed in <i>Escherichia coli</i> and up to 78% in <i>Enterococcus faecalis</i> )
Mercier et al., 2016 [86]	Aqua-4D system	1–10	20–25	River water	0.05	25	-	Formation of biofilms (Reductions of up to 39.9% in maximum biofilm thickness were observed with treatment after 45 days)
Rouina et al., 2016 [80]	Copper solenoid with a flow of alternating electrical current	0.05	28–35	Calcium carbonate solution	25	-	1.8–4.8	Membrane performance, fouling and permeate (The rejection increased by 5.3% after the application of the electromagnetic fields. In the presence of the treatment, the permeate flow rate increased by 30% compared to the case in which no treatment was applied)

Table 4. Cont.

Reference	Electromagnetic Equipment	Frequency (kHz)	T (°C)	Solution	Volume (L)	Flow (L/h)	Velocity (m/s)	Effects Studied
Zhao et al., 2014 [87]	Magnetoelectric coordinated water processor	0.05–0.3	30–90	Cooling water	-	-	0.334–0.669	Calcium carbonate precipitation and structure (The application of electromagnetic fields under favourable conditions can have a significant anti-scaling effect with 68.95% of anti-scaling ratio. It was also observed that the appearance and growth of aragonite is favoured and its transition to calcite is slowed)
Xuefei et al., 2013 [88]	Electromagnetic signal generator	66–400	25	Synthetic hard water	40	-	0.8	Cooling water scale (Conductivity it was reduced by 17% with treatment, compared to 31% for the untreated case. A smaller particle size was also observed with treatment, as well as looser structures, unlike without treatment, the crystalline structures were more compact)
Stojiljkovic et al., 2011 [89]	Solenoid around a pipe.	0.2–4	60	Geothermal water	-	54	-	Scale formation (A decrease in deposit of up to 78 times was achieved using a variable frequency electromagnetic field)
Catli, 2009 [90]	Hydronic equipment	0.5–6	80	Company's water trial system	-	-	-	Modification of scale and effect on the water molecule (A modification of the crystalline phase is observed after the application of the treatment, favouring the formation of aragonite. The field strongly "polarizes" water, lining up the charges in the molecules)
Shahryari and Pakshir, 2007 [91]	MEF generating coil.	1–5	30	Cooling water	-	-	0.5–1.3	Effect on fouling of a heat exchanger ( $\text{Ca}^{2+}$ decreases in the water of 23%, 11.5% and 7% were observed at water velocities of 0.5, 0.8 and 1.3 $\text{ms}^{-1}$ , respectively)
Xiaokai et al., 2005 [92]	Electromagnetic anti-fouling device	6–22	-	$\text{Na}_2\text{CO}_3$ and $\text{CaCl}_2$	50	-	-	Crystal nucleation and fouling (The resistance to fouling obtained with the treatment was between 50–72% lower than that observed without treatment. It was also observed that the growth of the particles was promoted by a coagulation process and not by a nucleation growth.)

Reductions in scale formation of up to 70%, alterations in the crystals formed and in the form of nucleation have been reported after the application of electromagnetic fields. Apart from the reduction in calcium carbonate scale, a multitude of effects have been observed in other very interesting fields of application. Improvements have been reported in the permeate of the membrane treatment after the application of electromagnetic fields, as well as reductions in the formation of biofilms of between 40–70%. Alterations in bacterial growth rates have also been observed after the application of electromagnetic fields, as well as variations in germination rates and nutrient absorption by different crops using electromagnetically treated water.

In conclusion, a great variety of effects of the application of electromagnetic fields have been reported in various fields apart from the reduction in calcium carbonate deposits. These effects include the improvement of permeate, the effect on the formation of biofilms, and the alteration of bacterial growth, as this shows that the application of electromagnetic fields can be very beneficial in many fields.

## 6. Studies of the Effects of Magnetic and Electromagnetic Fields on the Water Hardness

The effect by which the application of magnetic and electromagnetic fields prevents scale formation is not fully defined. There are two main theories on which these techniques are based: a modification of the crystalline structure of calcium carbonate between calcite and aragonite and the formation of crystals within the fluid not bound to the surfaces of the pipes.

### 6.1. Identification of Crystalline Forms

#### 6.1.1. Formation of Calcite and Aragonite in Scale

Current references report that magnetic and electromagnetic techniques influence the crystalline formation of calcium carbonate precipitates that produce scale. In absence of treatment, precipitation occurs in the form of calcite, while magnetic and electromagnetic techniques cause a less compact scale formation, probably as a consequence of the crystallization of calcium carbonate as aragonite [14]. In some studies, after the application of the magnetic and electromagnetic field, an increase in the concentration of aragonite, with a needle shape, and a lower presence of calcite crystals, with rhombohedral structure, is observed in scale [70].

Aragonite is a mineral whose precipitation produces less scale in pipes. These deposits, less compact and more easily eliminated, were also observed in other studies after applying magnetic treatment [73]. In this study, SEM was used to distinguish between treated and untreated samples of scale deposits. Aragonite was observed mainly in the treated samples and calcite mainly in the untreated samples.

#### 6.1.2. Reversion of Aragonite to Calcite

Coey and Cass [14] observed in the experiments that aragonite crystals return to calcite after some time, and the effect of magnetism on the crystals could extend to more than 200 h before the reversion occurred. On the other hand, the experiments of Botello-Zubiate et al. [93] obtained a much smaller effect at the same time range. Botello-Zubiate et al. states that these differences could be related to the chemical composition of the samples (Table 5), since the samples contain higher amounts of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$ , and concentrations of  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Zn}^{2+}$  were also different from those of Coey and Cass.

#### 6.1.3. Formation of Calcite and Aragonite Induced by Evaporation

Changes have been found in the calcite/aragonite ratio produced in deposits after water evaporation, before (80%/20%) and after (20%/80%) treatment. However, this occurred under certain conditions which were not specified and not in all experiments [94].

The SEM technique was also used in the studies of Catli [90] when the crystalline structure of calcite and aragonite formed on the water surface after the application of electromagnetism was analysed, observing clear morphological differences. In this case,

the waste produced without and with treatment was analysed, with calcite and aragonite appearing, respectively.

**Table 5.** Comparative analysis of the waters used in the studies (own elaboration).

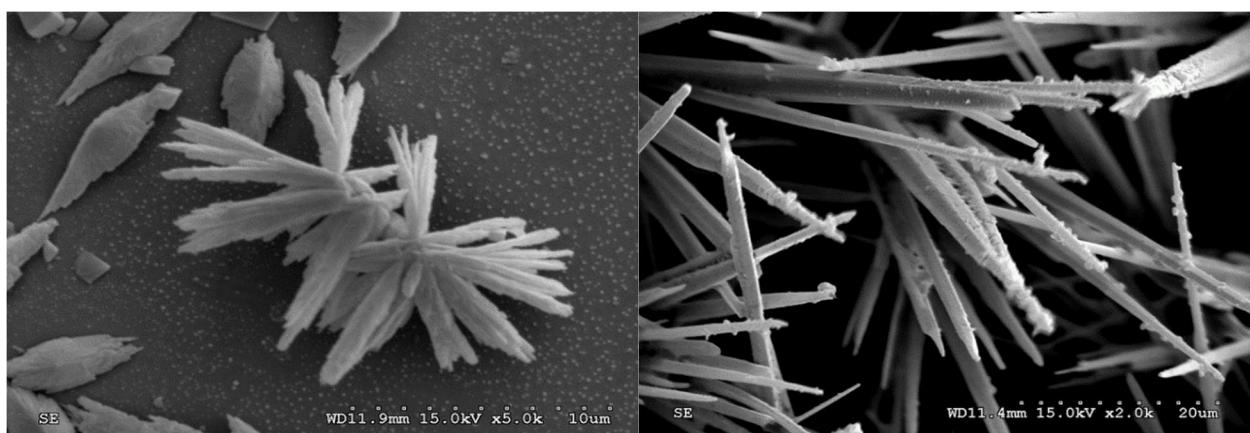
	Botello-Zubiate et al., (2004) [93]	Coey and Cass (2000) [14]
Na <sup>+</sup> (mg/L)	163	6
Ca <sup>2+</sup> (mg/L)	229	132
K <sup>+</sup> (mg/L)	12	1
Fe <sup>2+</sup> (mg/L)	0.32	2.49
Mn <sup>2+</sup> (mg/L)	1.23	0.46
Zn <sup>2+</sup> (mg/L)	0.95	0.04

Although it has usually been observed that magnetic and electromagnetic treatment promotes the formation of aragonite, some studies have observed that the formation of calcite is favoured in waters supersaturated with calcium hydroxide [95].

Different studies have been carried out at the University of Alicante on the application of electromagnetic fields in waters, focusing on reducing the hardness of tap water. The studies used 2 types of electromagnetic equipment, Antical RF and TK3K, which emit low frequency radio-electromagnetic waves (20–200 kHz) through the water. The Meigen Test and the SEM technique were used to differentiate between calcite and aragonite, obtained after evaporation in controlled temperature [29]. It should be noted that to apply this techniques, solid mineral phases are needed, so to study liquid samples they must be previously evaporated. When the crystals are generated, the conditions of the sample are altered, and transformation between calcite and aragonite occurs, masking the results produced by the electromagnetic treatment [9].

#### 6.1.4. Orientation of Aragonite Crystals

From the results obtained in the studies carried out with the TK3K and Antical RF equipment, it was observed that electromagnetic treatment seems to generate a small crystal, with orientation and agglomeration that does not occur without the treatment, as can be seen in the SEM analyses (Figure 11). This may be due to the influence of the electromagnetic field, which causes the crystals formation with a certain orientation and agglomeration [9].



**Figure 11.** SEM image of aragonite crystals with and without electromagnetic treatment [29].



## 6.2. Liquid Phase Studies

### 6.2.1. Crystal Formation within the Fluid

Other theories state that the effect of magnetic treatment is not related to the type of crystal formed, but rather it consists in promoting the formation of crystals within the fluid rather than in the pipes, so that scale does not form [96]. This can be seen by studying the Tyndall effect in the solution. When these crystals are formed, they will scatter and block an incident laser beam, reducing the photoenergy received by an optical sensor. In this way, the speed and intensity of the crystallization process can be analysed [75].

A relationship has also been observed between the application of electromagnetic techniques and the alteration of the hydrodynamics of the fluid flow. These techniques can increase or decrease turbulence in the fluid, promoting the aggregation or disaggregation of ferromagnetic and diamagnetic colloids [97].

In other papers, it has also been seen that the anti-scaling properties of the treated water persist for some time after the magnetic treatment, producing a kind of memory effect [71]. With these results, there may be a great dependence on the time after exposure and the chemical composition of the water, with respect to the effectiveness of the treatment.

### 6.2.2. Effects on Water Properties

In the study of Han et al. [69] with highly purified water, it was observed that magnetic fields cause displacement and polarization of molecules and atoms, change the distribution of molecules and electrons, change the dipole-moment transition and vibrational states of molecules, and vary the transition probability of electrons, but no alteration was observed in the constitution of molecules and atoms.

According to the studies of Wang et al. [68], there was a decrease in the specific heat and boiling point of water after magnetic application, as well as an increase in evaporation. A 39% increase in evaporation of treated water was observed compared to untreated, and the optimal magnetizing condition was determined as the magnetic field strength (MFS) of 300 mT. This effect can be of great benefit in the field of energy efficiency because this technique would help reduce the energy required to bring water to the boiling point necessary in many applications.

The influence of an electromagnetic field on the pH of the solution has been observed as an initial reduction in the pH that directly affected scale growth. It was also observed that the effects of magnetic treatment on scale formation are eliminated when pH is controlled [98]. This paper attributes the variations in pH to the effect of the electromagnetic field, but it could also be influenced by water agitation eliminating CO<sub>2</sub> and thus reducing pH, which directly affects the growth of lime scale.

## 7. Other Magnetic and Electromagnetic Applications

The most important magnetic and electromagnetic application is the treatment of water hardness, but it is not the only one. There are other less studied applications, but with very interesting results.

### 7.1. Combining with Other Treatments

Rajczykowski and Loska [67] studied the effect of magnetism on the adsorption of heavy metals such as copper, nickel, or cadmium. They demonstrated that the application of magnetic fields increased the efficiency of the adsorption process, and it is possible to accelerate and increase adsorption of heavy metals in aqueous solution, maintaining adequate conditions.

In the studies of Guo et al. [99] the magnetic field is beneficial to the membrane separation by reverse osmosis of brine from seawater, focusing mainly on the effect on sodium, magnesium, and calcium. After the study, it was observed that the concentrations of brine separated from the magnetically treated solutions are usually higher than those of the untreated ones. It was also observed that, after the application of the treatment, the

diffusion coefficients of the sodium, magnesium, and calcium ions increased, and those of the anions decreased.

### 7.2. Microbiological Effects

Mercier et al. [86] observed an increase in the appearance of planktonic microorganism after applying electromagnetic fields in fluvial waters, leading to a reduction in microbiological contamination of water and a decrease in the concentration of sessile microorganisms in the biofilm formations. In this study, the application of electromagnetism affected the population structure, producing changes in the classes of Proteobacteria during the formation of the biofilm. A modulation in biofilm formation occurred after the application of low frequency electromagnetic fields.

In the experiments of Piyadasa et al. (2018) [84], it was observed that electromagnetic fields generate a great variety of positive or negative adaptive responses of different microorganisms, under various conditions. The interactions of some factors such as the type of microorganism, the specifications of the device generating the electromagnetic field (waveform, frequency, intensity, etc.), flow rate, exposure time, etc., are responsible for these responses. The dependence of these parameters on the precipitation of calcium carbonate and the formation of deposits was also observed.

A possible bactericidal effect was observed in a study carried out at the University of Alicante, after the application of the Antical RF device. The redox potential measurement showed that prolonged use of the equipment generates a disinfecting effect in the water by increasing the oxidation-reduction potential, with a decrease in the formation of bacterial colonies [85].

## 8. Conclusions

It is well known that hardness produces negative effects in hot water systems in both domestic and industrial heat exchange devices. Interest in topics such as water hardness, scale prevention, and others related with water softening has grown, especially during the 2000s, since 2008. This increase in interest is driven by the need to prevent calcium carbonate scale for more efficient heat exchange systems and reduced energy consumption.

Calcium and magnesium are the most common elements involved in the scale precipitation, and carbonate minerals are the most abundant in the nature, thus calcium carbonate formation is very common. This compound has different tendency to other minerals since the solubility product decreases as the temperature increases, giving calcium carbonate precipitation. This system is influence of atmospheric  $\text{CO}_2$ , since an increase in  $\text{CO}_2$  affects the dissolution of  $\text{CaCO}_3$ , and the removal of  $\text{CO}_2$  causes the precipitation of  $\text{CaCO}_3$ . Calcium carbonate is one of the main compounds in the formation of scale, being able to crystallize as calcite, aragonite, or vaterite. Aragonite has a higher density than calcite and is less prone to produce scale. Scale samples from domestic water systems, has a higher presence of calcite in samples from taps and pipes; however, a greater amount of aragonite was found in samples inside heaters. Therefore, at higher temperatures the formation of aragonite is favoured over calcite.

To determine the presence of the mineral phase, colorimetric tests, SEM, and X-ray diffraction can be applied. Colorimetric tests are fast and cheap; however, they can have many interferers that can complicate the identification of minerals, but they can be a complement to the XRD and SEM techniques. However, a solid phase must be obtained with evaporation of the water sample, complicating identification as a consequence of the transformation of calcite into aragonite at high temperatures than 40 °C.

There is a great variety of technologies to try to prevent the effects of water hardness. The classical techniques, such as chemical softening, precipitation inhibitors, electrochemical treatments, ion exchange, and membrane separation are highly efficient in the elimination and reduction in calcium carbonate scale, making it difficult to stand out one over the other. Therefore, each application case must be analysed individually in order to select the most efficient technique. However, these techniques present some problems such as the

modification of the composition of the water or the generation of waste. To try to reduce these effects, these processes are being modified with new materials and more ecological and less polluting compounds are being used.

Electromagnetic and magnetic techniques are a good alternative to classic water hardness reduction treatments because these non-invasive and cheap techniques do not need chemicals added to the water. There are various theories about the effects of these techniques. For instance, it seems that the application of magnetic and electromagnetic techniques favours the formation of aragonite (non-encrusting) instead of calcite (encrusting). Different papers support this effect; it is even stated that the effect of electromagnetism on the crystals could extend up to more than 200 h before the reversion from aragonite to calcite. Other papers affirm that an electromagnetic field favours the formation of crystals within the fluid instead of in the pipes, and for this reason, scale would not form. These techniques can increase or decrease turbulence in the fluid, promoting the aggregation or disaggregation of ferromagnetic and diamagnetic colloids. In addition, studies conducted at the University of Alicante have seen an orientation of the crystals formed after the application of electromagnetic treatment that did not occur without treatment. It has also been observed in other studies that after the application of the magnetic treatment, the diffusion coefficients of the sodium, magnesium, and calcium ions increased and those of the anions decreased.

Different applications of electromagnetic and magnetic techniques are being studied. One of them are the possible bactericidal effects observed after the application of electromagnetic treatments, since it has been observed that electromagnetic fields generate a great variety of positive or negative adaptive responses from different microorganisms, under different conditions, or other lesser known effects such as elimination of pollutants through adsorption processes, possible changes in water properties such as specific heat and boiling point, among others, have been reported.

In summary, classical water hardness treatment techniques are highly efficient, and each case must be analysed for their installation. However, they have a series of disadvantages that must be taken into account when applying them. As an alternative, magnetic and electromagnetic techniques are presented, so it is important to continue studying their possibilities in different fields and to continue delving into domestic and industrial installations, because the effectiveness of these treatments is not easily demonstrable in all cases. Therefore, a large number of variables must be taken into account for each water composition, and the device must be verified and tested under the experimental conditions of each water installation.

**Author Contributions:** Conceptualization, methodology, software, validation, formal analysis, investigation, resources, data curation, writing—original draft preparation, writing—review and editing, visualization, supervision, project administration, funding acquisition, S.M.M. and N.B.B. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Generalitat Valenciana (FEDEGENT/2018/005), the company ECOTÉCNICA ENERGY SYSTEMS S.L (ECOTECNICA1-18Y) and the facilities of the University Institute of Chemical Process Engineering and the University Institute of Water and Environmental Sciences of the University of Alicante.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** This study was carried out thanks to the financial support of the Generalitat Valenciana (FEDEGENT/2018/005), the company ECOTÉCNICA ENERGY SYSTEMS S.L (ECOTECNICA1-18Y) and the facilities of the University Institute of Chemical Process Engineering and the University Institute of Water and Environmental Sciences of the University of Alicante.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Ghizellaoui, S.; Euvrard, M.; Ledion, J.; Chibani, A. Inhibition of scaling in the presence of copper and zinc by various chemical processes. *Desalination* **2007**, *206*, 185–197. [\[CrossRef\]](#)
2. Eaton, A.D.; Clesceri, L.S.; Rice, E.W.; Greenberg, A.E.; Franson, A.M.H. *Standard Methods for the Examination of Water and Wastewater*, 21st ed.; American Public Health Association: Washington, DC, USA, 2005.
3. Kirk, R.E.; Othmer, D.F.; Grayson, M.; Eckroth, D. *Encyclopedia of Chemical Technology*, 4th ed.; Wiley: New York, NY, USA, 1998.
4. Kiely, G. *Ingeniería Ambiental: Fundamentos, Entornos, Tecnologías y Sistemas de Gestión*; McGraw-Hill/Interamericana de España, S.A.: Madrid, Spain, 1999; ISBN 9788448121518.
5. Elsevier, B. Scopus Database. 2020. Available online: <https://www.scopus.com/search/form.uri?display=basic#basic> (accessed on 20 August 2021).
6. Appelo, C.A.J.; Postma, D. Geochemistry, groundwater and pollution. *Geochem. Groundw. Pollut.* **1993**. [\[CrossRef\]](#)
7. de Leeuw, N.H.; Parker, S.C. Surface Structure and Morphology of Calcium Carbonate Polymorphs Calcite, Aragonite, and Vaterite: An Atomistic Approach. *J. Phys. Chem. B* **1998**, *102*, 2914–2922. [\[CrossRef\]](#)
8. Pedersen, O.; Colmer, T.; Sand-Jensen, K. Underwater Photosynthesis of Submerged Plants—Recent Advances and Methods. *Front. Plant Sci.* **2013**, *4*, 140. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Gimeno Amorós, M.; Martínez Moya, S.; Boluda Botella, N. *Tratamiento de Agua Por Electromagnetismo: Aplicación de Técnicas de Identificación de Calcita y Aragonito*; Repositorio Institucional de la Universidad de Alicante: Alicante, Spain, 2020.
10. Blanco-Gutiérrez, V.; Demourges, A.; Jubera, V.; Gaudon, M. Eu(III)/Eu(II)-doped (Ca<sub>0.7</sub>Sr<sub>0.3</sub>)CO<sub>3</sub> phosphors with vaterite/calcite/aragonite forms as shock/temperature detectors. *J. Mater. Chem.* **2014**, *2*, 9969–9977. [\[CrossRef\]](#)
11. Chen, Z.; Xin, M.; Li, M.; Xu, J.; Li, X.; Chen, X. Biomimetic synthesis of coexistence of vaterite-calcite phases controlled by histidine-grafted-chitosan. *J. Cryst. Growth* **2014**, *404*, 107–115. [\[CrossRef\]](#)
12. Tucker, M.; Wright, P. *Carbonate Sedimentology*; Blackwell Scientific Publications: Oxford, UK; London, UK, 1990.
13. Wang, H.; Huang, W.; Han, Y. Diffusion-reaction compromise the polymorphs of precipitated calcium carbonate. *Particuology* **2013**, *11*, 301–308. [\[CrossRef\]](#)
14. Coey, J.M.D.; Cass, S. Magnetic water treatment. *J. Magn. Magn. Mater.* **2000**, *209*, 71–74. [\[CrossRef\]](#)
15. Raisen, E. The control of scale and corrosion in water systems using magnetic fields. In Proceedings of the International Corrosion Forum Devoted Exclusively to the Protection and Performance of Materials, New Orleans, LA, USA, 2–6 April 1984; National Association of Corrosion Engineers: New Orleans, USA, 1984.
16. Herzog, R.E.; Shi, Q.; Patil, J.N.; Katz, J.L. Magnetic Water Treatment: The Effect of Iron on Calcium Carbonate Nucleation and Growth. *Langmuir* **1989**, *5*, 861–867. [\[CrossRef\]](#)
17. Kobe, S.; Dražić, G.; Cefalas, A.C.; Sarantopoulou, E.; Stražisar, J. Nucleation and crystallization of CaCO<sub>3</sub> in applied magnetic fields. *Cryst. Eng.* **2002**, *5*, 243–253. [\[CrossRef\]](#)
18. Martínez Moya, S.; Boluda Botella, N.; García Quiles, J. Effect of electromagnetic water treatment on carbonate scale. Determination of calcite and aragonite by the Meigen test. In Proceedings of the 14th Mediterranean Congress of Chemical Engineering, Barcelona, Spain, 16–20 November 2020.
19. Van, H.T.; Huong, L.; Nguyen, V.D.; Hoan, X. Characteristics and mechanisms of cadmium adsorption onto biogenic aragonite shells-derived biosorbent: Batch and column studies. *J. Environ. Manag.* **2019**, *241*, 535–548. [\[CrossRef\]](#) [\[PubMed\]](#)
20. Sibony-nevo, O.; Pinkas, I.; Farstey, V.; Baron, H.; Addadi, L.; Weiner, S. The Pteropod *Creseis acicula* Forms Its Shell through a Disordered Nascent Aragonite Phase. *Cryst. Growth Des.* **2019**, *19*, 2564–2573. [\[CrossRef\]](#)
21. Raz, S.; Hamilton, P.C.; Wilt, F.H.; Weiner, S.; Addadi, L. The transient phase of amorphous calcium carbonate in sea urchin larval spicules: The involvement of proteins and magnesium ions in its formation and stabilization. *Adv. Funct. Mater.* **2003**, *13*, 480–486. [\[CrossRef\]](#)
22. Kong, J.; Liu, C.; Yang, D.; Yan, Y.; Chen, Y.; Huang, J.; Liu, Y.; Zheng, G.; Xie, L.; Zhang, R. Al<sub>v</sub> Protein Plays Opposite Roles in the Transition of Amorphous Calcium Carbonate to Calcite and Aragonite during Shell Formation. *Cryst. Growth Des.* **2018**, *18*, 3794–3804. [\[CrossRef\]](#)
23. Friedman, G.M. Identification of Carbonate Minerals by Staining Methods. *SEPM J. Sediment. Res.* **1959**, *29*, 87–97. [\[CrossRef\]](#)
24. Tamer, A. Chemical staining methods used in the identification of carbonate minerals. *Bull. Miner. Res. Explor. Inst. Turk.* **1965**, *65*, 133–147.
25. Pueyo, J.J.; Alonso, R. *Génesis de Formaciones Evaporíticas: Modelos Andinos e Ibéricos*; Universitat de Barcelona: Barcelona, Spain, 1991; ISBN 84-7875-666-3.
26. Togari, K.; Togari, S. Conditions Controlling the Crystal from of Calcium Carbonate Minerals (I) (On the Influences of the Temperature and the Presence of Magnesium Ion). *J. Fac. Sci. Hokkaido Univ.* **1955**, *9*, 55–65.
27. Salzer, H. Eine einfache Reaktion zur Unterscheidung von Calcit und Aragonit. *Speläologisches Jahrb.* **1936**, 76–79. Available online: <http://www.xray.cz/xray/csa/kol2011/kurs/dalsi-cteni/connolly-2005/01-xrd-intro.pdf> (accessed on 20 August 2021).
28. Jirová, D. Modifications of CaCO<sub>3</sub> in the shells of foraminifera. *Časopis Pro Mineral. A Geol.* **1956**, *1*, 101–104.
29. Verdú, D. *Efecto del Electromagnetismo Sobre la Dureza del Agua*; Repositorio Institucional de la Universidad de Alicante: Alicante, Spain, 2016.
30. Feigl, F. *Qualitative Analysis by Spot Tests. III*; Elsevier Publishing Company: New York, NY, USA, 1947.
31. Goldstein, J.I. *Scanning Electron Microscopy and X-ray Microanalysis*; Springer: New York, NY, USA, 2013.

32. Connolly, J.R. Introduction to X-ray Powder Diffraction. 2007, pp. 1–9. Available online: [https://www.google.com.hk/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwjbdS08NjyAhWHO3AKHSR\\_CW0QFnoECAIQAQ&url=http%3A%2F%2Fwww.xray.cz%2Fxd%2Ffscs%2Fkol2011%2Fkrs%2Fdalsi-cteni%2Fconnolly-2005%2F01-xrd-intro.pdf&usg=AOvVaw1PRd7YZi4ZI3dWNOKGmZZz](https://www.google.com.hk/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwjbdS08NjyAhWHO3AKHSR_CW0QFnoECAIQAQ&url=http%3A%2F%2Fwww.xray.cz%2Fxd%2Ffscs%2Fkol2011%2Fkrs%2Fdalsi-cteni%2Fconnolly-2005%2F01-xrd-intro.pdf&usg=AOvVaw1PRd7YZi4ZI3dWNOKGmZZz) (accessed on 20 August 2021).
33. Bunaciu, A.A.; UdrişTioiu, E.; Aboul-Enein, H. X-Ray Diffraction: Instrumentation and Applications. *Crit. Rev. Anal. Chem. CRC* **2015**, *45*. [CrossRef] [PubMed]
34. Letterman, R.D. *Calidad y Tratamiento del Agua*; McGraw Hill: Madrid, Spain, 2002.
35. Van Schagen, K.M.; Babuška, R.; Rietveld, L.C.; Veersma, A.M.J. Model-based dosing control of a pellet softening reactor. *IFAC Proc. Vol.* **2009**, *7*, 267–272. [CrossRef]
36. Rahmani, K.; Jadidian, R.; Haghtalab, S. Evaluation of inhibitors and biocides on the corrosion, scaling and biofouling control of carbon steel and copper–nickel alloys in a power plant cooling water system. *Desalination* **2016**, *393*, 174–185. [CrossRef]
37. Wang, C.; Li, S.; Li, T. Calcium carbonate inhibition by a phosphonate-terminated poly(maleic-co-sulfonate) polymeric inhibitor. *Desalination* **2009**, *249*, 1–4. [CrossRef]
38. Ghizellaoui, S.; Boumagoura, M.; Rhouti, S.; Cheap-Charpentier, H.; Horner, O. Inhibition of CaCO<sub>3</sub> growth in hard water by quercetin as green inhibitor. *Water Environ. J.* **2019**, 1–10. [CrossRef]
39. Karar, A.; Henni, A.; Namoune, F.; Rosei, F. Inhibition of nucleation and crystal growth of calcium carbonate in hard waters using Paronychia arabica in an arid desert region. *Water Environ. J.* **2020**, 1–9. [CrossRef]
40. Hu, R.; Huang, T.; Wang, T.; Wang, H.; Long, X. Application of chemical crystallization circulating pellet fluidized beds for softening and saving circulating water in thermal power plants. *Int. J. Environ. Res. Public Health* **2019**, *16*, 4576. [CrossRef]
41. Tour, R.; Dkhireche, N.; Ebn Touhami, M.; Lakhrissi, M.; Lakhrissi, B.; Sfaira, M. Corrosion and scale processes and their inhibition in simulated cooling water systems by monosaccharides derivatives. Part I: EIS study. *Desalination* **2009**, *249*, 922–928. [CrossRef]
42. Gabrielli, C.; Maurin, G.; Francy-Chausson, H.; Thery, P.; Tran, T.T.M.; Tlili, M. Electrochemical water softening: Principle and application. *Desalination* **2006**, *201*, 150–163. [CrossRef]
43. Jin, H.; Yu, Y.; Zhang, L.; Yan, R.; Chen, X. Polarity reversal electrochemical process for water softening. *Sep. Purif. Technol.* **2019**, *210*, 943–949. [CrossRef]
44. Sanjuán, I.; Benavente, D.; Expósito, E.; Montiel, V. Electrochemical water softening: Influence of water composition on the precipitation behaviour. *Sep. Purif. Technol.* **2019**, *211*, 857–865. [CrossRef]
45. Hasson, D.; Shemer, H.; Semiat, R. Removal of scale-forming ions by a novel cation-exchange electrochemical system—A review. *Desalin. Water Treat.* **2016**, *57*, 23147–23161. [CrossRef]
46. Clauwaert, P.; De Paepe, J.; Jiang, F.; Alonso-Fariñas, B.; Vaiopoulou, E.; Verliefde, A.; Rabaey, K. Electrochemical tap water softening: A zero chemical input approach. *Water Res.* **2020**, 169. [CrossRef]
47. Yu, Y.; Jin, H.; Quan, X.; Hong, B.; Chen, X. Continuous Multistage Electrochemical Precipitation Reactor for Water Softening. *Ind. Eng. Chem. Res.* **2019**, *58*, 461–468. [CrossRef]
48. Zhi, S.L.; Zhang, K.Q. Hardness removal by a novel electrochemical method. *Desalination* **2016**, *381*, 8–14. [CrossRef]
49. Birnhack, L.; Keller, O.; Tang, S.C.N.; Fridman-Bishop, N.; Lahav, O. A membrane-based recycling process for minimizing environmental effects inflicted by ion-exchange softening applications. *Sep. Purif. Technol.* **2019**, *223*, 24–30. [CrossRef]
50. Al-Jaser, Z.A.; Hamoda, M.F. Removal of nickel and vanadium from desalination brines by ion-exchange resins. *Desalin. Water Treat.* **2019**, *157*, 148–156. [CrossRef]
51. Weber, W.J.J. *Control de la Calidad del Agua Procesos Físicoquímicos*; Reverte: Barcelona, Spain, 1979; ISBN 978-84-291-7522-6.
52. Bekri-Abbes, I.; Bayoudh, S.; Baklouti, M. The removal of hardness of water using sulfonated waste plastic. *Desalination* **2008**, *222*, 81–86. [CrossRef]
53. Brastad, K.S.; He, Z. Water softening using microbial desalination cell technology. *Desalination* **2013**, *309*, 32–37. [CrossRef]
54. Wist, W.; Lehr, J.H.; McEachern, R. *Water Softening with Potassium Chloride: Process, Health, and Environmental Benefits*; Wiley: Hoboken, NJ, USA, 2009.
55. Li, C.W.; Jian, J.C.; Liao, J.C. Integrating membrane filtration and a fluidized-bed pellet reactor for hardness removal. *J. Am. Water Work. Assoc.* **2004**, *96*, 151–158. [CrossRef]
56. Schaep, J.; Van Der Bruggen, B.; Uytterhoeven, S.; Croux, R.; Vandecasteele, C.; Wilms, D.; Van Houtte, E.; Vanlerberghe, F. Removal of hardness from groundwater by nanofiltration. *Desalination* **1998**, *119*, 295–301. [CrossRef]
57. Izadpanah, A.A.; Javidnia, A. The ability of a nanofiltration membrane to remove hardness and ions from diluted seawater. *Water* **2012**, *4*, 283–294. [CrossRef]
58. Ghizellaoui, S.; Chibani, A.; Ghizellaoui, S. Use of nanofiltration for partial softening of very hard water. *Desalination* **2005**, *179*, 315–322. [CrossRef]
59. Kianfar, F.; Kianfar, E. Synthesis of Isophthalic Acid/Aluminum Nitrate Thin Film Nanocomposite Membrane for Hard Water Softening. *J. Inorg. Organomet. Polym. Mater.* **2019**, *29*, 2176–2185. [CrossRef]
60. Kumara, K.M.S.; Kularathne, K.A.M.; Ranathunga, P.G.K.B.; Upeka, S.A.C.; Herath, D.C.; Weragoda, S.K. Hardness and Fluoride Removal Efficiency of Groundwater: Use of Physiochemical Methods in Water Purification at Anuradhapura District Dry Zone in Sri Lanka. In *ICSBE 2018*; Dissanayake, R., Mendis, P., Eds.; Springer: Singapore, 2020; pp. 171–182.



61. Yang, Y.; Gutsol, A.; Fridman, A.; Cho, Y.I. Removal of  $\text{CaCO}_3$  scales on a filter membrane using plasma discharge in water. *Int. J. Heat Mass Transf.* **2009**, *52*, 4901–4906. [\[CrossRef\]](#)
62. Muniz, G.L.; Duarte, F.V.; Rakocevic, M. Assessment and optimization of carbonated hard water softening with moringa oleifera seeds. *Desalin. Water Treat.* **2020**, *173*, 156–165. [\[CrossRef\]](#)
63. Mohammadian, M.; Sahraei, R.; Ghaemy, M. Synthesis and fabrication of antibacterial hydrogel beads based on modified-gum tragacanth/poly(vinyl alcohol)/Ag<sub>0</sub> highly efficient sorbent for hard water softening. *Chemosphere* **2019**, *225*, 259–269. [\[CrossRef\]](#) [\[PubMed\]](#)
64. Entezari, M.H.; Tahmasbi, M. Water softening by combination of ultrasound and ion exchange. *Ultrason. Sonochem.* **2009**, *16*, 356–360. [\[CrossRef\]](#) [\[PubMed\]](#)
65. Gruber, C.E.; Carda, D.D. *Performance Analysis of Permanent Magnet Type Water Treatment Devices*; Final Report Issued to the Water Quality Association; South Dakota School of Mines and Technology: Rapid City, SD, USA, 1981.
66. Alomari, A.A. Effect of magnetic treatment on temporary hardness of groundwater. *Asian J. Chem.* **2019**, *31*, 1017–1021. [\[CrossRef\]](#)
67. Rajczykowski, K.; Loska, K. Stimulation of Heavy Metal Adsorption Process by Using a Strong Magnetic Field. *Water Air Soil Pollut.* **2018**, *229*. [\[CrossRef\]](#)
68. Wang, Y.; Wei, H.; Li, Z. Effect of magnetic field on the physical properties of water. *Results Phys.* **2018**, *8*, 262–267. [\[CrossRef\]](#)
69. Han, X.; Peng, Y.; Ma, Z. Effect of magnetic field on optical features of water and KCl solutions. *Optik* **2016**, *127*, 6371–6376. [\[CrossRef\]](#)
70. Latva, M.; Inkinen, J.; Rämö, J.; Kaunisto, T.; Mäkinen, R.; Ahonen, M.; Matilainen, J.; Pehkonen, S. Studies on the magnetic water treatment in new pilot scale drinking water system and in old existing real-life water system. *J. Water Process Eng.* **2016**, *9*, 215–224. [\[CrossRef\]](#)
71. Mahmoud, B.; Yosra, M.; Nadia, A. Effects of magnetic treatment on scaling power of hard waters. *Sep. Purif. Technol.* **2016**, *171*, 88–92. [\[CrossRef\]](#)
72. Silva, I.B.; Queiroz Neto, J.C.; Petri, D.F.S. The effect of magnetic field on ion hydration and sulfate scale formation. *Colloids Surf. A Physicochem. Eng. Asp.* **2015**, *465*, 175–183. [\[CrossRef\]](#)
73. Liu, C.Z.; Lin, C.H.; Yeh, M.S.; Chao, Y.M.; Shen, P. Surface Modification and Planar Defects of Calcium Carbonates by Magnetic Water Treatment. *Nanoscale Res. Lett.* **2010**, *5*, 1982–1991. [\[CrossRef\]](#) [\[PubMed\]](#)
74. Tai, C.Y.; Wu, C.K.; Chang, M.C. Effects of magnetic field on the crystallization of  $\text{CaCO}_3$  using permanent magnets. *Chem. Eng. Sci.* **2008**, *63*, 5606–5612. [\[CrossRef\]](#)
75. Wang, Y.; Babchin, J.; Chernyi, L.T.; Chow, R.S.; Sawatzky, R.P. Rapid onset of calcium carbonate crystallization under the influence of a magnetic field. *Water Res.* **1997**, *31*, 346–350. [\[CrossRef\]](#)
76. Kronenberg, K.J. Experimental evidence for effects of magnetic fields on moving water. *IEEE Trans. Magn.* **1985**, *21*, 2059–2061. [\[CrossRef\]](#)
77. Martynova, O.I.; Gusev, B.T.; Leont'ev, E.A. Concerning the mechanism of the influence of a magnetic field of aqueous solutions of salts. *Uspekhi Fiz. Nauk* **1969**, *98*, 195–199. [\[CrossRef\]](#)
78. Martinez, S.; Boluda, N.; García, J. Técnicas electromagnéticas para el tratamiento de aguas y diseño de una planta piloto con dispositivo TK3K. In *Congreso Nacional del Agua 2019: Innovación y Sostenibilidad*; Universitat d'Alacant: Alacant, Spain, 2019; pp. 1003–1014; ISBN 978-84-1302-034-1.
79. Kozic, V.; Kropce, J.; Lipus, L.C.; Ticar, I. Magnetic field analysis on electromagnetic water treatment device. *Hung. J. Ind. Chem.* **2006**, *34*, 51–54. [\[CrossRef\]](#)
80. Rouina, M.; Kariminia, H.R.; Mousavi, S.A.; Shahryari, E. Effect of electromagnetic field on membrane fouling in reverse osmosis process. *Desalination* **2016**, *395*, 41–45. [\[CrossRef\]](#)
81. Jiang, W.; Xu, X.; Lin, L.; Wang, H.; Shaw, R.; Lucero, D.; Xu, P. A pilot study of an electromagnetic field for control of reverse osmosis membrane fouling and scaling during brackish groundwater desalination. *Water* **2019**, *11*, 1015. [\[CrossRef\]](#)
82. Hachicha, M.; Kahlaoui, B.; Khamassi, N.; Misle, E.; Jouzdan, O. Effect of electromagnetic treatment of saline water on soil and crops. *J. Saudi Soc. Agric. Sci.* **2018**, *17*, 154–162. [\[CrossRef\]](#)
83. Piyadasa, C.; Yeager, T.R.; Gray, S.R.; Stewart, M.B.; Ridgway, H.F.; Pelekani, C.; Orbell, J.D. The influence of electromagnetic fields from two commercially available water-treatment devices on calcium carbonate precipitation. *Environ. Sci. Water Res. Technol.* **2017**, *3*, 566–572. [\[CrossRef\]](#)
84. Piyadasa, C.; Yeager, T.R.; Gray, S.R.; Stewart, M.B.; Ridgway, H.F.; Pelekani, C.; Orbell, J.D. Antimicrobial effects of pulsed electromagnetic fields from commercially available water treatment devices—controlled studies under static and flow conditions. *J. Chem. Technol. Biotechnol.* **2018**, *93*, 871–877. [\[CrossRef\]](#)
85. Gonzálvez, N. *Efecto del Electromagnetismo Sobre la Dureza, Bacterias y Algas en Agua*; Repositorio institucional de la Universidad de Alicante: Alicante, Spain, 2017.
86. Mercier, A.; Bertaux, J.; Lesobre, J.; Gravouil, K.; Verdon, J.; Imbert, C.; Valette, E.; Héchard, Y. Characterization of biofilm formation in natural water subjected to low-frequency electromagnetic fields. *Biofouling* **2016**, *32*, 287–299. [\[CrossRef\]](#)
87. Zhao, J.-D.; Liu, Z.-A.; Zhao, E.-J. Combined effect of constant high voltage electrostatic field and variable frequency pulsed electromagnetic field on the morphology of calcium carbonate scale in circulating cooling water systems. *Water Sci. Technol.* **2014**, *1074*–1082. [\[CrossRef\]](#)



88. Xuefei, M.; Lan, X.; Jiapeng, C.; Zikang, Y.; Wei, H. Experimental study on calcium carbonate precipitation using electromagnetic field treatment. *Water Sci. Technol.* **2013**, *67*, 2784–2790. [[CrossRef](#)] [[PubMed](#)]
89. Stojiljkovic, D.T.; Mitić, N.C.; Šmelcerović, A.A.; Kalićanin, B.M.; Tasić-Kostov, M.Z.; Djurović-Petrovi, M.D. Effect of variable frequency electromagnetic field on deposit formation in installations with geothermal water in Sijarinjska spa, Serbia. *Therm. Sci.* **2011**, *15*, 643–648. [[CrossRef](#)]
90. Catli, Y. *Studying Electric Field Effect on Water by Analysing the Instrument “Hydronic”*; University of Trento: Trento, Italy, 2009. Available online: <http://www.hydroniconline.it/pdf/tesidimaster.pdf> (accessed on 20 August 2021).
91. Shahryari, A.; Pakshir, M. Influence of a modulated electromagnetic field on fouling in a double-pipe heat exchanger. *J. Mater. Process. Technol.* **2007**, *3*, 389–395. [[CrossRef](#)]
92. Xiaokai, B.X.; Chongfang, M.; Yongchang, C. Investigation on the Electromagnetic Anti-Fouling Technology for Scale Prevention. *Chem. Eng. Technol.* **2005**, 1540–1545. [[CrossRef](#)]
93. Botello-Zubiate, M.E.; Alvarez, A.; Martínez-Villafañe, A.; Almeraya-Calderon, F.; Matutes-Aquino, J.A. Influence of magnetic water treatment on the calcium carbonate phase formation and the electrochemical corrosion behavior of carbon steel. *J. Alloy. Compd.* **2004**, *369*, 256–259. [[CrossRef](#)]
94. Donaldson, J.D. Scale prevention and descaling. *Tube Int.* **1988**, *7*, 39–49.
95. Ellingsen, F.T.; Vik, E.A. A revue of scale formation with emphasis on magnetic water treatment. In Proceedings of the 14th World Congress of the International Water Supply Association, Zurich, Switzerland, 6–10 September 1982; pp. 12–25.
96. Zavaleta, M.; Rivas, E.; Mendoza, A.; Tinoco, S. Efecto del Campo Magnético en el Tratamiento de Aguas Duras. *Inst. Fis. Glew Wataghim* **1998**, *8*, 3–8.
97. Busch, K.W.; Busch, M.A. Laboratory studies on magnetic water treatment and their relationship to a possible mechanism for scale reduction. *Desalination* **1997**, *109*, 131–148. [[CrossRef](#)]
98. Parsons, S.A.; Wang, B.-L.; Judd, S.J.; Stephenson, T. Magnetic treatment of calcium carbonate scale. Effect o pH control. *Water Res.* **1997**, *31*, 339–342. [[CrossRef](#)]
99. Guo, B.; Han, H.B.; Chai, F. Influence of magnetic field on microstructural and dynamic properties of sodium, magnesium and calcium ions. *Trans. Nonferrous Met. Soc. China* **2011**, *21* (Suppl. 2), s494–s498. [[CrossRef](#)]