



# Magnetic water treatment

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## Abstract

Carbonates formed by heating water containing  $\approx 120$  mg(Ca)/l are characterized by X-ray diffraction and electron microscopy. Tests on 32 pairs of samples establish, at the 99.9% probability level, that drawing water through a static magnetic field ( $B \approx 0.1$  T,  $\nabla B \approx 10$  T/m) increases the aragonite/calcite ratio in the deposit. There is an incubation period of several hours, and memory of magnetic treatment extends beyond 200 h. © 2000 Elsevier Science B.V. All rights reserved.

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The limescale problem in hard water arises because the solubility of  $\text{CaCO}_3$  decreases with increasing temperature [1]. Huge amounts of energy are wasted because hard scale forms in boilers, heat exchangers and domestic hot-water systems. Various magnetic, electromagnetic and electrostatic devices purporting to control limescale formation are sold worldwide for domestic and industrial applications. Typical products incorporate arrangements of permanent magnets; large magnet structures are in daily use in industries ranging from brewing to hydro-electric power generation. Belief in the beneficial effects of magnetic fields on water has led to the sale of millions of magnetic cups in China.

Despite its ubiquity, there is relatively little scientific literature on magnetic water treatment. It is not clear how, or even if, it works. Unlike chemical water softening, magnetic treatment should have no direct effect on water chemistry (unless the magnets are in contact with the water); yet, it is claimed to alter the morphology and adhesion of calcium carbonate scale. Published data are often contradictory. For example, there is some dispute as to whether the deposits of calcium carbonate from magnetically treated water are predominantly calcite or aragonite. These are the two common natural forms of

$\text{CaCO}_3$ , with rhombohedral and orthorhombic crystal structures, respectively. Aragonite has the higher density, and it is less prone to form hard scale. The efficacy of magnetic treatment is reported to last from tens of minutes to hundreds of hours. There is a review of the literature by Baker and Judd [2].

These, and similar claims of a field effect on precipitation of other salts, coagulation of colloids and wax formation from crude oil, have been met with considerable scepticism, mainly because there is no obvious way for a magnetic field to influence any of these processes. Much of the irreproducibility of the data, and possibly the effect itself, may result from inadequate control of experimental conditions. Here, we set out to establish whether or not any effect exists. We conducted blind tests using identically treated pairs of samples, with and without magnetic field. There is considerable variability in the results, but our method allows us to answer the key question, and to identify some relevant variables.

Two groups of experiments were conducted, each using different water and a different magnetic device. The first was on groundwater drawn from a well sunk in limestone in West County Dublin, Ireland. The water could either be drawn through a plastic filter assembly containing a stack of Teflon-coated ferrite ring magnets<sup>1</sup>, or bypass the magnet assembly. The water was sealed in

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<sup>1</sup> Manufactured by D-Fluid, Milan.

Table 1

Analyses of untreated water (mg/l). The only significant changes after magnetic treatment are shown in square brackets

	Well water	Mineral water		Well water	Mineral water
Na	6	15	SO <sub>3</sub>		15
Mg	24	16	NO <sub>2</sub>	0.05	
K	1	3	NO <sub>3</sub>	< 0.01	9
Ca	132	114	Cl	23	
Fe	2.49 [1.39]	< 0.01	pH	7.2	6.9
Mn	0.46 [0.37]	< 0.01	$\sigma$ (mS/m)	64.8	
Zn	0.04				

1-l polythene bottles, and all tests were conducted blind. The experimenter (SC) was unaware whether a particular sample had been drawn through the magnetic device, or through the bypass valve. The second group of experiments was conducted on a commercial still mineral water, which was simply poured out of its 500 ml bottle with or without a 20 mm split-ring collar containing Nd–Fe–B magnets<sup>2</sup> fitted around the neck of the bottle. In each case the water was exposed to a maximum field of  $\approx 0.1$  T, and a field gradient of  $\approx 10$  T/m. Analyses of the water are given in Table 1. The only discernible difference after magnetic treatment was a decrease in Fe and Mn content of the well water, shown in square brackets.

More than 100 samples were examined using a simple protocol. Water was stored for a time  $t_i$  before heating in open 500 ml beakers at 80° to form limescale. Scale was collected on a fresh microscope slide at the bottom of the beaker. All samples were examined by X-ray diffraction using Cu K <sub>$\alpha$</sub>  radiation, and 14 of them were selected for scanning electron microscopy and microprobe analysis. The ratio of calcite to aragonite was evaluated by measuring the ratio of three X-ray reflections in the region  $25^\circ < 2\theta < 30^\circ$ . The peaks are calcite 104 and aragonite 111 and 102. The quantity

$$A = (I_{111} + I_{102}) / (I_{104} + I_{111} + I_{102})$$

gives an estimate of the fraction of calcium carbonate present as aragonite.

The incubation time  $t_i$  was varied from 0 to 200 h, and the speed of flow of water through the magnets was varied from 0.04 to 1.2 m/s.  $A$  ranged from 0% to 100%. No systematic influence of flowrate could be discerned, but the data suggest a maturing effect when  $A$  increases with  $t_i$  for several hours, and that a significant increase in  $A$  persists for as long as 200 h after magnetic treatment (Fig. 1). Electron micrographs of carbonate deposits from

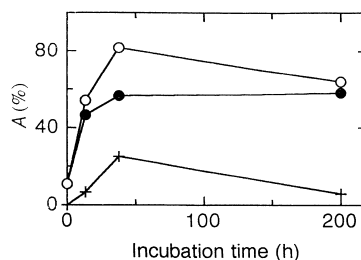


Fig. 1. A set of data showing evolution of the aragonite ratio  $A$  with incubation time  $t_i$  in untreated water (+), treated water (O) and the difference (●).

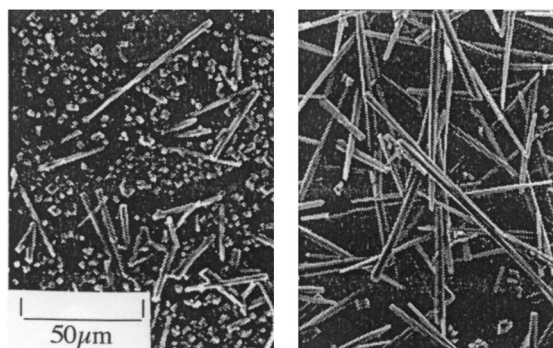


Fig. 2. Electron micrographs of carbonate deposits from untreated (left) and magnetically treated (right) mineral water.

untreated ( $A = 7\%$ ) and treated ( $A = 54\%$ ) mineral water are shown in Fig. 2. The long, acicular crystals ( $\approx 30 \times 3 \times 3 \mu\text{m}^3$ ) are identified as aragonite [3], whereas the equiaxed crystals ( $\approx 4 \mu\text{m}$ ) are calcite. Typical microanalyses are shown in Table 2. The main difference in composition is that the acicular crystals contain less Mg and no Mn. Neither contains detectable amounts of Fe ( $< 0.1$  wt%).

A comparison of  $A$  for 32 pairs of samples, each including an untreated control is summarized in Table 3. It is

<sup>2</sup> Manufactured by San Huan, Peking.

Table 2

Typical microprobe analyses of calcite and aragonite from mineral water and well water (at%)

	Well water		Mineral water	
	Calcite	Aragonite	Calcite	Aragonite
Na	1.5	2.8	3.1	0.8
K	0.3	0.2	1.0	0.1
Mg	3.7	1.0	3.0	–
Ca	90.7	95.8	90.7	99.1
Mn	3.2	–	–	–
Cl	–	–	1.7	–
S	0.6	0.2	0.5	–

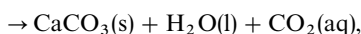
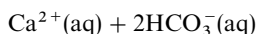
Table 3

Effect of magnetic treatment; numbers of tests in which aragonite increased ( $\uparrow$ ), decreased ( $\downarrow$ ) or did not change ( $\leftrightarrow$ )

	#	$A\uparrow$	$A\leftrightarrow$	$A\downarrow$	$\langle A \rangle_{\text{un}}$	$\langle A \rangle_{\text{tr}}$
Well water	20	14	3	3	0.31	0.50
Mineral water	12	11	1	0	0.30	0.58
Total	32	25	4	3	0.31	0.53

evident that the average  $\langle A \rangle_{\text{tr}}$  tends to be greater in treated samples of both waters, although standard deviations are large because of the variability of the data being averaged (different flow rates and incubation times). The null hypothesis, that magnetic treatment has no effect on  $A$ , can be tested directly on the pairs of data on treated and untreated samples where all other conditions remained the same. The probability of this is 4% for the well water, and 0.3% for the mineral water. Taking both data sets together, we deduce that *magnetic treatment increases the amount of aragonite in the carbonate deposits*, at the 99.9% probability level (3.4  $\sigma$  confidence level).

In order to try to understand the mechanism, we recall that the reaction



has an associated Gibbs free energy  $\Delta G = -24$  kJ/mol, but the free energy difference between pure calcite and aragonite at 25°C at 1 bar is only  $-1$  kJ/mol ( $\approx 120$  K/ion) [1]. Calcite has the lower free energy under ambient conditions; aragonite has the lower en-

thalpy, but also the lower entropy. Despite its metastability, aragonite formation is favoured at lower evaporation rates and higher temperatures [4]. Minute concentrations of cations such as  $\text{Fe}^{2+}$  [5] and  $\text{Zn}^{2+}$  [6] can influence nucleation. Our data indicate that the magnetic field somehow promotes nucleation of aragonite as the water flows past the magnets; the nuclei are stable for hundreds of hours and they grow into the observed crystals when the water is heated to supersaturation. From the volume of the aragonite crystallites,  $\approx 3 \times 10^{-16}$  m<sup>3</sup>, the number of nuclei is estimated to be  $\approx 10^8$ /l.

The problem is to explain how a magnetic field influences nucleation, and why it favours aragonite. Conceivably, the field might:

(i) lower the energy of a nucleus because of a difference in susceptibility with the surroundings. Microprobe analysis found no iron or manganese in the aragonite crystals, but even assuming that  $S = \frac{5}{2}$  ions are present at the 1 at% level in nuclei, energies involved in a 0.1 T field are only of the order of  $10^{-2}$  J/mol.

(ii) influence clusters of iron or manganese hydroxide that act as heterogenous nucleation centres. For example,  $\delta'\text{FeOOH}$  has a plate-like morphology with a net moment when an odd number of ferromagnetic layers are coupled antiferromagnetically [7]. The energy ( $\frac{1}{2}$ )  $MB$  of superparamagnetic clusters will be of the order of 1 J/mol.

(iii) modify the local ionic concentrations via the Lorentz force  $q\mathbf{v} \times \mathbf{B}$ . By analogy with the Hall effect, assuming  $v = 1$  m/s and  $B = 0.1$  T, the nonelectrostatic field of 0.1 V/m is associated with a surface charge density of  $10^{-11}$  C/m<sup>2</sup>. This corresponds to an extra ionic concentration in the micromolar range, provided the charge is concentrated in a surface layer 1 nm thick. This is still three orders of magnitude less than the Ca concentration, but it is comparable to the concentrations of  $\text{OH}^-$  and  $\text{HCO}_3^-$ , which limit formation of the  $\text{CO}_3^{2-}$  ion [1]. Statistical fluctuations or turbulence may enhance it locally.

In conclusion, we have established that a magnetic field effect exists. Passing water through a magnetic field subsequently favours formation of aragonite rather than calcite in our experiments, and the influence of the treatment persists for more than two hundred hours. Further experiments on ultra-pure calcium carbonate solutions are needed to test the hypotheses regarding the mechanism by which the magnetic field produces the effect.

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