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## Does Magnetic Treatment of Water Change Its Properties?

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Some properties and functions of water treated under magnetic field were examined. No change in properties of pure water distilled from ultrapure water in vacuum was observed by magnetic treatment. However, when the same magnetic treatment was carried out after the distilled water was exposed to O<sub>2</sub>, water properties such as vibration modes and electrolytic potential were changed. The degree of magnetic treatment effect on water was quantitatively evaluated by contact angle.

Curious effects of magnetic-field-treated water (MT water), so-called "magnetized" water, on scale formation in boilers, dying of strings and cloths, growth of plants, etc. are widely known.1 Many kinds of devices for magnetic field treatment (MT) of tap and industrial waters are sold commercially worldwide and installed into boiler piping of factories and pipes of buildings. Scientific journals and literature have repeatedly reported various findings of the MT effects<sup>2-10</sup> on water containing ionic species. However, it seems still to be doubtful, because the reported results are apt to have not only low reproducibility but also inconsistencies. Since magnetized water, in most cases, was made of natural and tap waters in air, some people are suspect of the MT effects because of so many uncontrollable factors such as magnetic impurities, magnetohydrodynamic effects, etc. Other sophisticated people, who believe there is no reason that pure water would be changed by MT, have claimed the existence of magnetized water, especially magnetized water made of pure water and its memory keeping the MT effects after MT. Notwithstanding, we report the remarkable results that even pure water was affected markedly by MT if dissolved O<sub>2</sub> or air. When pure water was prepared by distillation in vacuum, MT did not modify its properties at all. We here show that the degree of "magnetization" of water can be quantitatively and easily evaluated by contact angle, along with other sensitive methods.

In the beginning, to evaluate the effects of magnetic field treatment on water, we surveyed suitable methods for water treatment based on steady magnetic fields and for quantitative evaluation of the degree of "magnetization" of water. We have adopted measurements of contact angle  $\theta$  of water on a Pt plate from several candidates as the critical method. <sup>11</sup> Two methods for MT of water were chosen from scientific and practical viewpoints: One (MT1) for pure water is based on reciprocating motion of water in a sealed flask in steady magnetic fields in order to avoid a contamination and control an atmosphere in the flask, another (MT2) is based on circulation (0.20 m s<sup>-1</sup>) of pure water under air with a tubing pump having two flow

lines that run through and out of a 6 T magnetic field at the same time. 6 T was enough for obtaining MT effects.<sup>11</sup>

Our first question is whether pure water is "magnetized" by MT. If not, then a second question is whether there is "magnetized" water. Therefore, we conducted air-free experiments in which all procedures (distillation, MT1 and contact angle measurements) were carried out under vacuum. For this purpose, two sets of greaseless Pyrex distillation flasks with a vacuum valve were made, which were separable in order to connect to the vacuum chamber for contact angle measurements. The flasks were connected to a vacuum line (1 mPa) with greaseless glass joints. Using ultrapure water (Milli-Q water; 18  $M\Omega$ ) in a reservoir placed in the vacuum line, the water was degassed by repeating a freezing-pumping-melting cycle for more than five times, followed by distillation due to temperature difference under vacuum. After distillation, in some cases O<sub>2</sub> (purity: 99.99%) of various pressures or air (1 atm) was introduced through the vacuum line. One of the flasks containing the distilled water was treated by reciprocating motion of 30 times/min in the region of more than 2 T across the center (6 T) of a steady magnetic field of a superconducting magnet at 298 K for 2.5 h. Another flask was also treated by the same procedures at a zero field and the same conditions. The two flasks containing the distilled water were connected to the chamber with greaseless flanges without invasion of air, and water droplets were gently dropped down from each flask on a solid plate in vacuum, O2, or air. The contact angle of both MT and non-MT (NMT; reference) water was measured at the same time for both sides of several drops with a CCD camera system.

The contact angle of the distilled water on a Pt plate (purity 99.98%), washed with acetone by ultrasonication, was measured in the vacuum chamber. It took approximately 20 min after each MT1 to finish measuring the contact angle. Figure 1 shows that the contact angle of the vacuum-distilled (or deaerated) water was unchanged by MT, demonstrating that the distilled water in vacuum was not magnetized.

When the MT was carried out after  $O_2$  was dissolved in the water at  $0.2 \sim 700$  Torr, the contact angle (65°) decreased

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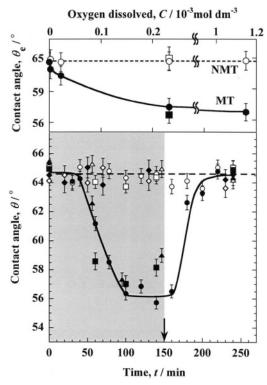


Figure 1. (lower) Contact angle  $\theta$  of the vacuum-distilled water on a Pt plate was measured in the vacuum chamber under vacuum, various  $O_2$  pressures, and air as a function of time treated under magnetic field. (upper) Contact angle  $\theta_e$  averaged in the range 90-150 min as a function of  $O_2$  concentration dissolved in distilled water. The water was prepared with the vacuum distillation flask in vacuum and then treated in vacuum or after introduction of  $O_2$  and air by reciprocating motion at 30 cycle/min for 2.5 h at a zero field (NMT; open symbols) and in the region of more than 2 T across the center (6 T) of a steady magnetic field of a superconducting magnet (MT; solid symbols) at 298 K. Atmosphere in treating the distilled water and measuring contact angle: diamond, vacuum; triangle, 140 Torr  $O_2$ ; square, 700 Torr  $O_2$ ; circle, air (1 atm).

markedly to reach a stationary value, e.g., 57.5° at 700 Torr after a dead time of approximately 30 min, indicating that the MT may promote water to wet the solid surfaces.<sup>11</sup> The upper figure shows that the MT effect was promoted with O2 concentration and enhanced by air (1 atm) down to 56°. The existence of O2 may be a dominant factor for magnetization of water. It is noteworthy to point out that the addition of electrolytes (10 mM) such as NaCl, KCl, and CaCl2 to the distilled water caused no MT effects as long as there was no  $O_2$ , which is different from most reports that ioninc species brought about MT effects to pure water, because the Lorentz force or current during MT would be presumed. Moreover, when the water containing air stood silently in a 10 T steady magnetic field, a little change (<2°) in contact angle was observed. It seems that magnetic flux should be changed over water for effective MT effects.

The contact angle  $\theta^i$  of water treated (H) and untreated (0) under magnetic fields is expressed by

$$\gamma_{\rm sg}^{\ i} = \gamma_{\rm sl}^{\ i} + \gamma^{i} \cos \theta^{i} (i = 0 \text{ or H})$$
 (1)

where  $\gamma_{sg}^i$  is the solid/gas interfacial tension,  $\gamma_{sl}^i$  is the solid/water interfacial tension, and  $\gamma$  is the surface tension of water. Since we may assume  $\gamma_{sg}^0 \approx \gamma_{sg}^H$  and the experiment demonstrated  $\gamma^0 \approx \gamma^H (\gamma^0/\text{mNcm}^{-1} = 72.0 = \gamma^H + 0.6 \text{ at } 298 \text{ K})$ , the change  $(\Delta \gamma_{sl}^H)$  of the interfacial energy of the water/Pt

interface due to MT,

$$\Delta \gamma_{sl}^{H} \equiv \gamma_{sl}^{H} - \gamma_{sl}^{0} \approx \gamma^{0} (\cos \theta^{0} - \cos \theta^{H})$$
 (2)

is estimated  $-15 \text{ mJ cm}^{-2}$ . The large, negative  $\Delta \gamma_{sl}^{H}$  demonstrates that the MT water is stabilized at a Pt surface; in other words, a hydrated layer on a Pt surface may develop. The increase in the thickness was estimated to be approximately 200 nm, using the heat of melting of ice 6.0 kJ mol<sup>-1</sup>. Since such layer thickness seems to be too thick, the hydration energy near solid surface should be enhanced. The interaction modification might arise from clathrate-like hydrates, although the O2 clathrate in bulk water is formed only over 109.2 atm at -1.0°C.12 Hallbrucker and Mayer reported that an oxygen clathrate hydrate from vapor-deposited amorphous solid water was unexpectedly stable; the clathrate hydrate decomposed only close to the melting point of ice. 13 Higashitani et al. 8-10 persisted that the hydration layer around ions and colloids in aqueous solutions under air should be thickened by a MT. Ozeki et al. 14-16 inferred from the promotion in water adsorption and the lower pressure shift of the capillary condensation onset that the water/solid interaction in vacuum ( $\gamma_{sl}$ ) should be enhanced even by steady magnetic fields.

The following experiments, shown in Figure 2, were carried out after checking the contact angle (on a Pt plate) of water used, whose changes are given as MT ( $\Delta\theta$ ). The contact angle of aerated water on a Cu plate (purity 99.96%) decreased by 10 degrees by MT1 ( $\Delta\theta = -7.4^{\circ}$ ).

The Raman band of the distilled water appeared in the regions of 430 nm (1640 cm $^{-1}$ ), 462 nm (3360 cm $^{-1}$ ), and 602 nm (8400 cm<sup>-1</sup>) by irradiation of a 400 nm UV light using a fluorescence spectrophotometer at 298 K (Figure 2B). O2 exposure of the distilled water never changed the Raman spectrum, but when followed by the MT1 ( $\Delta\theta = -7.2^{\circ}$ ), all the Raman bands were markedly strengthened and a significant shoulder in the range  $480\sim540 \text{ nm}$  ( $4180\sim6480 \text{ cm}^{-1}$ ) appeared. The shoulder bands correspond to the overtones and combination bands of the bending and stretching modes of hydrogen bonded water, that again seem to be ascribed to O2 clathrate-like hydrates. After the contact angle recovered the initial value ( $\Delta\theta = 0^{\circ}$ ), the shoulder disappeared to give the initial spectrum. The appearance of the shoulder suggests that the forbidden transition in the Raman combination modes should be forgiven by symmetry changes of O<sub>2</sub>-containing water with the MT.

The electrolytic potential of the distilled water exposed to air,  $H_2O \rightarrow (1/2)O_2 + H_2$ , shifted by 0.28 V from 2.35 to 2.63 V by the MT1 ( $\Delta\theta = -6.2^{\circ}$ ), as seen in Figure 2C. Measuring the electrolytic potential after the contact angle recovered the initial value ( $\Delta\theta = 0$ ); no electrolytic potential shift was observed. Cyclic voltammetry also showed that the anodic reaction ( $H_2O \rightarrow (1/2)O_2 + 2H^+ + 2e$ ) shifted to the higher potential, suggesting that the oxidation of water may be affected by the MT. The higher potential shift is probably attributed to the overpotential of oxygen. The electrolytic potential of water, to which 0.05 mol dm<sup>-3</sup>  $H_2SO_4$  was added just before measurements, was measured using two platinized Pt electrodes at 298 K.

After stopping the MT, the low contact angle was maintained for about 20 min (Figure 1) and the MT memory left beyond 60 min with MT2. The memory was immediately lost by addition of ethanol, application of ultrasonication, and temperature rise (>323 K), suggesting that magnetization should relate closely to water structure. Since ethanol will interact strongly with water, no ethanol forms clathrate hydrate even when  $O_2$  coexists. To the contrary, it is well known that a second component may assist the clathrate formation. The fact that air

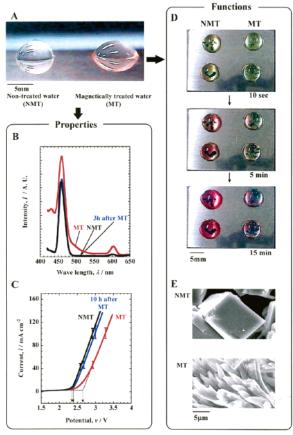


Figure 2. Magnetic treatment effects on aerated water at 298 K. All solutions were prepared by dilution of small amount of concentrated solutions with an MT1 water, which was checked by the contact angle before using. (A) The contact angle of water (MT1) on a Cu plate: left, NMT; right, MT. (B) The Raman bands of the aerated water by irradiation of a 400 nm UV light: black, NMT; red, MT1 ( $\Delta\theta = -7.2^{\circ}$ ); blue, 3 h ( $\Delta\theta = 0$ ) after MT1. (C) The electrolytic potential of the aerated water: black, NMT; red, MT1 ( $\Delta\theta = -6.2^{\circ}$ ); blue, 10 h ( $\Delta\theta$ = 0) after MT1. (D) A model corrosion system comprising two water droplets each containing K<sub>3</sub>Fe(CN)<sub>6</sub> and phenolphthalein on an Fe plate (purity 99.5%): left, NMT; right, MT( $\Delta\theta = -7.4^{\circ}$ ). (E) Changes in morphology of CaCO<sub>3</sub> due to MT1 ( $\Delta\theta = -7.4^{\circ}$ ).

brought about MT effects larger than O2 (Figure 1) suggests that something in air should assist a clathrate formation, although N<sub>2</sub> or CO<sub>2</sub> itself assisted no MT effects.

The three kinds of experiment for water properties presented above are, in our knowledge, the first observation to prove the existence of magnetized water. The magnetization of pure water required O2 or air and the relative motion of water against a magnetic flux and seems to be accompanied with formation of clathrate-like hydrate of O<sub>2</sub> and promotion of hydrogen bonded networks. Very recently, a few papers reported that some properties of pure water in air changed very slightly when the pure water stood in steady magnetic fields; 0.1% increase in the refractive index of pure water at 10 T,17 5 mK rise in the melting point of ice at 5 T,18 and 0.3% increase in the intensity of the near-infrared band of 1930 nm at 14 T.19 These magnetic field effects were attributed to hydrogen bond development. The values, however, are very small compared with the MT effects here, suggesting that the magnetic flux changes should affect strongly the structure or properties of aerated water.

Functions of the MT water will be illustrated below using two model systems for corrosion and scale formation. A corrosion system was constructed that water droplets containing both K<sub>3</sub>Fe(CN)<sub>6</sub> and phenolphthalein were settled on an Fe plate

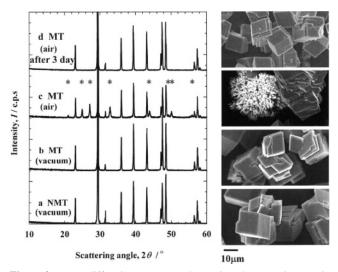


Figure 3. X-ray diffraction patterns and scanning electron microscopic images of CaCO<sub>3</sub> prepared by mixing CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> solutions at 298 K: (a) vacuum distilled water (NMT1); (b) vacuum distilled water treated by MT1( $\Delta\theta = 0^{\circ}$ ); (c) MT1( $\Delta\theta = -7.4^{\circ}$ ) after aeration of vacuum distilled water. (d) 3 days ( $\Delta\theta = 0^{\circ}$ ) after MT1. \* shows aragonite peaks.

(purity: 99.5%). Progress of the corrosion reactions, Fe  $\rightarrow$  Fe<sup>2+</sup> + 2e and  $H_2O + (1/2)O_2 + 2e \rightarrow 2OH^-$ , was visualized by appearance of Turnbull's blue and a pink region surrounding the blue precipitates, respectively. The pictures in Figure 2D were taken at 0.2, 5, and 15 min after the droplets of the distilled water, which was aerated and then treated (right) and untreated (left) by a 6 T magnetic field, were settled on the Fe plate. As the much later appearance of the color in the right droplets indicates, the MT1 ( $\Delta\theta = -7.1^{\circ}$ ) of aerated pure water brought about significant depression of corrosion. The OH<sup>-</sup> formation reaction in the MT water may be more difficult than that in the NMT water, as the electrolysis experiments suggested that the water oxidation should be depressed by the MT.

CaCO<sub>3</sub> formation was much affected by MT, as reported so far. 1,3,5,8 Figure 3 shows X-ray diffraction patterns and scanning electron microscopic images of CaCO<sub>3</sub> prepared by mixing CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> solutions at 298 K.

When the vacuum-distilled water was used, the MT1 ( $\Delta\theta$  = 0°) gave no effects on CaCO<sub>3</sub> (calcite) formation. Using after the water was exposed to O2 or air, the XRD pattern and SEM images of CaCO<sub>3</sub> were markedly changed by the MT1 ( $\Delta\theta$  =  $-7.4^{\circ}$ ), which indicated the aragonite formation. When the aerated MT water was used after its contact angle came back to the initial value ( $\Delta\theta=0^{\circ}$ ), the precipitates became calcite again. Such an effect of MT water on crystal formation also was observed in Cu2+ organocomplex formation, which gave a novel crystal.20

The results demonstrate obviously that the MT never modified properties and functions of water itself within the detection limitation of the employed techniques, but that aerated water was "magnetized" by the MT to reveal significant changes in various properties and functions of water. Thus, we may conclude that only when water dissolves O<sub>2</sub>, not ionic species, is the water magnetized by changing the magnetic flux over the water. Now, we believe there is a "magnetic-field affecting water" (MFA water), although the phenomena are still puzzling from the viewpoint of modern science. Since water structure changes dynamically, a structure formed by MT and thus "magnetization", if any, should be propagated or stand independent of thermal fluctuation. Such a process seems to be very difficult, even in O2-containing water. The electron transfer of triplet  $O_2$  to a water host cage might introduce small extent of multipole and spins to clathrate hydrates. Since the dispersion force between two bodies should depend on the magnetic susceptibility of a medium,  $^{21,22}$  a magnetic field may affect the interactions between hydrogen bonded clusters in the paramagnetic medium.

The MFA water may be regarded as a time-limited, novel material, different from "normal" water. The MFA water is a clean and safe solvent for preparing new materials or a reactant having new activity. To use practically the MFA water, it is indispensable to establish an easy, rapid, cheap, and reproducible method for quantitative evaluation of MFA water. We here propose to use the contact angle or Raman band intensity as a measure of progression of MT. The magnetic water treatment seems to be a promising technique, because a magnetic field is an ecologically clean and soft energy and has a strong power of material transmission. The devices for MFA water may be compact, comprising permanent magnets and thus are safe and cheap. Using MFA water, industrial and agricultural processing will change, and foods, cosmetics and sanitation, etc. might be improved.

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