

Magnetic Water Treatment for a Less Tenacious Scale

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This paper discusses the mechanism for magnetic water treatment, which has been used practically for over a century but is still not completely understood. Modified crystallization and agglomeration, which produce a less tenacious scale, retain this property for hours following treatment. It is considered to be a result of magnetically modified hydration and Lorentz force effects of magnetic devices. In treated water, as a complex solution/dispersion system, they affect the kinetics of processes at solution/solid interfaces. Which effect prevails depends on the treatment regime and water composition.

INTRODUCTION

Scale formation on pipe walls and heat exchange equipment is a serious problem encountered in almost all water processes. Typical scale deposits are composed of minerals that become less soluble with increasing temperature, calcium carbonate and sulfate being the most common. They usually form hard to remove linings, which reduce water flow capacities. When they build up on the heat exchangers' surfaces, heat transfer efficiency is reduced because of their low thermal conductivity.

Antiscale water treatment using traditional reagent chemical methods changes the solution chemistry and can be very expensive. The reagent methods for water conditioning are economically and ecologically charged especially under conditions of high circulation flow rates characteristic for large nuclear and thermal power plants. In some other areas, such as the food and drink industries, there are strict requirements for water quality.

Thus, environmental protection and economic considerations are two strong motivations for developing various types of physical antiscale methods, among which are ultrasonic, ultraviolet radiation, electric, and magnetic treatment.

Dalas et al. observed strong retardation of calcium carbonate (calcite) crystallization using all four types of treatment, when operational parameters of treatment were adjusted properly. The mechanism of crystallization was not influenced because the order of growth was practically unchanged. However the rate constant was lowered, which indicates the possibility that the dehydration step of the growth units or the migration step of the dehydrated growth units to the active sites is affected.^{1–4}

A MAGNETIC WATER TREATMENT MECHANISM

Magnetic water treatment (MWT) is a method, where supplied or circulated water is simply exposed to a magnetic field. This method has a long and controversial history but

is reported to have been effective in numerous instances. Its main effect is to either reduce scale deposit or remove existing scale or produce a softer and less tenacious scale.^{5–9}

The mechanism is still unclear, although MWT has been practically used for over half a century. Understanding how the magnetic field of relatively low densities precisely modifies the precipitation of low magnetic minerals is still being developed because the treatment differs from well-known magnetic separations of high magnetic materials by strong magnetic fields. Iron-containing components have some influence on calcium carbonate precipitation¹⁰—more as a heteronucleator although it is still unclear how the activation by magnetic field occurs.¹¹

Recent worldwide research has shown that under the influence of a magnetic field, larger particles of calcium carbonate and sulfate are usually crystallized or aggregated. A higher ratio of aragonite/calcite was found.^{12–17} Aragonite is a low adhesive calcium carbonate crystal phase consisting of needlelike crystals, while the latter form of calcium carbonate consists of rhombic crystals and is able to adhere to compact scale, which is hard to remove. Such particles remain in a suspended form rather than adhere to the equipment walls and also offer a better basis for crystal growth than the equipment walls, when conditions for precipitation arise.¹⁸

The experiments and theory in this field lead us to the conclusion that the MWT mechanism is complex, consisting of certain processes very sensitive to small changes in water composition and magnetic treatment regime. Although it is almost certain that there are influential factors that are unrecognized at the present time, it can be summarized that the following types of effects most probably affect dispersion stability and crystallization: (1) *magnetically modified hydration of ions and solid surfaces* and (2) *Lorentz force effects on ions and dispersed particles*.

Which effect would prevail depends on the magnetic treatment regime (e.g. static/dynamic) and on the composition of the treated system. The major effect is expected at the solution/solid interfaces of dispersed mineral particles, where any long-lasting changes could occur due to selective adsorption or incorporation of ions into the crystal net.

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The first hypothesis, *magnetically modified hydration* of ions and solid surfaces, was proposed based on changes in the physicochemical habits of water solutions and dispersions, which were observed during static magnetic exposure.^{15,19–26}

Higashitani et al. have conducted comprehensive experiments. Calcium chloride and sodium carbonate solutions were separately exposed to a static magnetic field with a density of 0.3 T for 10 min and after 120 h mixed into supersaturated solution, in which the nucleation frequency was suppressed but the growth of particles was accelerated and the portion of aragonite was raised. The effect was attributed mainly to the magnetic exposure on sodium carbonate.¹⁵

Static magnetic field exposure raised the fluorescence emission of alkyl-chain probes in water, postulating that the magnetic field orders the structure of water molecules around the hydrophobic chains.²³

Static magnetic field exposure also reduced the mass transfer rate at the ion-exchange process when the exposure time was greater than 25 min and the exchanging ions were water structure-disordering K^+ and Cs^+ , but there was no effect in the case of structure-ordering ions Li^+ and Na^+ ions.²⁶

The results suggest intensified hydration on solid surfaces of ion-exchanging resins,²⁶ polystyrene latex,^{21,22} and silicon dioxide particles in KCl solution.²⁵ The effects decayed when raising the temperature or alcohol concentration in the solution.^{23,24,26} At most experiments, the effects existed even for several days.

Second, most commercial magnetic devices for scale control are of dynamic type, where treated water flows through a perpendicular magnetic field.

At Krylov's laboratory experiments,^{12,13} the magnetic destabilization of calcium carbonate dispersion is caused by water flow. The effect was increasing with water velocity¹³ and magnetic field density.¹²

Theoretically, in addition to the modified hydration effect, *Lorentz forces effect* can occur also. Lorentz force acts on every electrical charged particle, when it is moving through the applied magnetic field. Charged particles in the solution/dispersion system are as follows: (1) ions in the bulk of the solution, (2) ions in the electric double layer, and (3) dispersed particles.

Tombacz et al. studied the behavior of the hematite sol in dynamic and static magnetic water treatment systems. The aggregation effect was observed in the dynamic magnetic systems, while little effect on aggregation state was observed in the static magnetic systems and the flowing systems without the magnetic field. These effects were discussed in terms of Lorentz interactions.²⁷

Lorentz force effect on collision probability of dispersed particles is essential in the entire particle size interval, when particles are highly electrical charged. When the Lorentz flow of dispersed particles is essential, an induced electric potential and a resulting ponderomotive force occur. In the case of laminar water flow with parabolic profile, this ponderomotive force flattens the profile.²⁸

Lorentz force effect on ions in the bulk of the solution is negligible in comparison to the thermal collision probability;

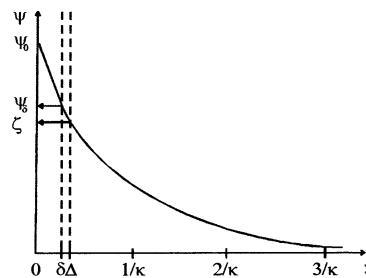


Figure 1. Scheme of electric double layer at dispersed particle: Potential-determining ions are directly adsorbed on solid surface or incorporated into crystal lattice (at normal distance $x = 0$) electrically charging the particle (ψ_0 = surface electric potential). Stern layer is the first, thin and condensed neutralization layer, which consists of (hydrated) counterions attracted to solid surface by strong electrostatic and van der Waals forces reducing electric potential to ψ_δ at normal distance $x = \delta$. Gouy–Chapman layer is the second, wider and scattered layer as a result of weaker electrostatic forces to the surface and thermal motions of ions reducing the potential practical to zero at distance $x = 3/\kappa$.

however, it is essential in the electric double layer at the solid surfaces, where it could enhance coagulation and modify crystallization processes.^{29–32}

Most water dispersions are meta-stable due to their slow coagulation. Namely, highly charged particles have strong electric repulsion, when their electric layers are overlapping. For successful collisions, the electric layer needs to be condensed to some extent. Shifting the ions toward surface of dispersed particles under the action Lorentz force could be an explanation for enhanced coagulation.

The electric double layer at the dispersed particle is expressed by eqs 1–3³³ and represented in Figure 1. The more condensed and thinner the layer is, the more the particles are able to aggregate.

$$\psi_\delta = \psi_0 - \sigma_\delta \delta / \epsilon \quad (1)$$

$$\tanh\left(\frac{zF\psi}{4RT}\right) = \tanh\left(\frac{zF\psi_\delta}{4RT}\right) \exp(-\kappa(x - \delta)) \quad (2)$$

$$\kappa = \sqrt{\frac{F^2 \sum_i z_i^2 c_{i\infty}}{RT\epsilon}} \quad (3)$$

The electrical potential of the Stern layer, ψ_δ , depends on its composition, which is specific for each solution/dispersion system. A determination of the precise ψ_δ value is difficult. Usually, the empirical parameter ζ -electrokinetic potential at slipping plane Δ is taken as an approximation for ψ_δ . The possible mechanism for magnetic destabilization could be predicted by measuring electrical conductivity, pH , and ζ -potential. Theoretical possibilities are schematically shown in Figure 2.

The intensified hydration in the Stern layer shifts the slipping plane aside from the solid surface (Δ_2 to Δ_1 in Figure 2a), which would lead into lowered ζ -potential (ζ_2 to ζ_1). Intensively hydrated counterions have less neutralization abilities, which stabilize the particles. Namely, the raised dielectricity, ϵ , lowers the value of Debye–Hückel parameter, κ (eq 3), and raises the value of ψ_δ (eq 1), which gives less intensive decreasing of the $\psi(x)$ curve (eq 2).

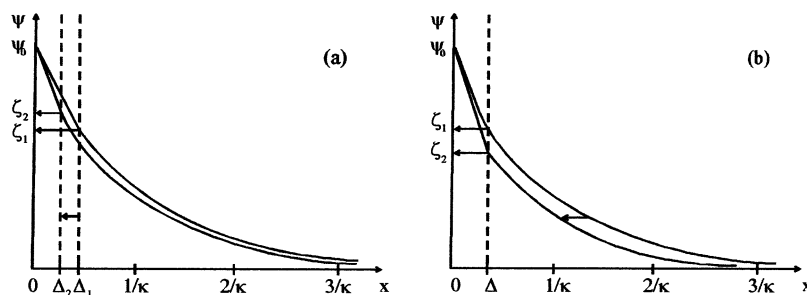


Figure 2. Theoretical possibilities for magnetic destabilization of water dispersion: The weakened hydration in the Stern layer. The condensation of the Stern layer by Lorentz ion shifts.

According to this, Higashitani et al.^{21,22} experimentally observed that the static magnetic treatment stabilizes colloidal polystyrene latex despite ζ -drop and postulated that the decreased coagulating rate and ζ -drop are attributed to thickening of the Stern layer.

Figure 2b is constructed for a theoretical model of the Stern layer condensation caused by shifts of counterions from the Gouy–Chapman layer toward the solid surface under the action of Lorentz force. The resulting lack of ions in the Gouy–Chapman layer is considered to be recovered by thermal motion of ions from the bulk of the solution, and ψ_δ would remain essentially reduced for an essential time.

A LORENTZ FORCE MECHANISM

Minerals dispersed in natural waters are usually positively charged on their surfaces. For instance, CaCO_3 particles have Ca^{2+} and CaHCO_3^+ potential-determining ions.³⁴ If the disperse medium is distilled water, this positive charge is partially neutralized by the Stern layer consisting of HCO_3^- to electrokinetic potential from 5 to 6 mV.¹²

If the dispersion medium is natural water solution higher surface potential is expected but is also more neutralized by present indifferent electrolytes. For the following estimation of Lorentz effect, the electrokinetic potential from 20 to 100 mV will be taken.

Ions in solution are hydrated. The hydration intensity depends on electron configuration and radius of ions. At similar electron configuration, it decreases with increasing radius. Anions have bigger radius and therefore weaker hydration (0–2 water molecules), while cations can be associated with 4–6 water molecules.³⁵

Mg^{2+} and Fe^{2+} , which are smaller than Ca^{2+} , are more strongly hydrated than Ca^{2+} ions. When they are moving, it seems they have a higher radius than when in crystal form (Table 1).

The ion mobility in the Stern layer strongly depends on hydration of the solid surface and on the way of hydrating of the ions.²⁶ If we assume the mobility depends only on the ion hydration and radius, we can get an estimated ion radius (r_{hyd}) from the diffusion coefficient, D , in an infinite diluted solution. The estimation is made by the Einstein equation for thermal moving: For the following analysis, we

$$r_{\text{hyd}} = k_B T / 6\pi\eta D \quad (4)$$

take values z/r_{hyd} from 6 to 15/nm. In practical MWT devices, water flows with velocity v_w (with values in the range of

Table 1. Comparison of the Radius for Some Major Cations in Crystal and Solute Form at 20 °C

ion	r_{cryst} (10^{-10} m) ³⁶	D (10^{-9} m ² /s) ³⁶	r_{hyd} (10^{-10} m)
Ca^{2+}	$1.0 \div 1.3$	1.584	1.3
Mg^{2+}	$0.6 \div 0.9$	1.412	1.5
Fe^{2+}	$0.6 \div 0.9$	1.438	1.5
Li^+	$0.6 \div 0.9$	1.029	2.1
Na^+	$1.0 \div 1.2$	1.334	1.6

0.5–2 m/s) through a perpendicular magnetic field of density B (0.05–1 Vs/m²). The result is Lorentz force acting on dispersed particles and ions:

$$\vec{F}_L = e \cdot \vec{v}_w \times \vec{B} \quad (5)$$

When magnetic lines are perpendicular to the direction of water flow, F_L is $ev_w B$.

The electrical charge, e , is for dispersed particles $4\pi a^2 \sigma_\delta$, where radius of the particle, a , will be taken from 0.01 to 1 μm . Surface charge density on the Stern plane, σ_δ , can be estimated as $\epsilon \kappa \zeta$,³³ ranging in the interval $7 \cdot 10^{-3}$ – $35 \cdot 10^{-3}$ As/m².

The electrical charge of ions is ze_0 , where z is ions' valence and e_0 is electron charge.

When charged particles are moving through the liquid medium by the act of Lorentz force, a viscosity force, F_{vis} , retards them:

$$F_{\text{vis}} = 6\pi\eta r v \quad (6)$$

Parameter η is solution viscosity, and v is the velocity of the motion through the liquid medium $= \Delta x / \tau$. Parameter Δx is the shift, and τ is the exposure time in the magnetic field. In commercial MWT devices, the time τ is of order 10^{-1} s in a homogeneous magnetic field, 10^{-2} s at an alternating magnetic field, and approximately 10^{-3} s at a rotating magnetic field.²⁵

Newton's equation gives force balance (7). Integrating it, we get the expression (8) in which the exponential term is negligible as early after time t is 10^{-10} – 10^{-6} s for dispersed particles and 10^{-13} s for ions.

$$ev_w B - 6\pi\eta r v = m \frac{dv}{dt} \quad (7)$$

$$v = \frac{ev_w B}{6\pi\eta r} \left(1 - \exp\left(\frac{-6\pi\eta r}{m} t\right) \right) \quad (8)$$

The motion can be considered as uniform. From $F_L = F_{\text{vis}}$,

we can simply express the shifts as

$$\Delta x(\text{ion}) = \frac{e_0 z (\tau B v_w)}{6 \pi \eta r} \quad (9)$$

$$\Delta x(\text{particle}) = \frac{2 a \sigma_\delta (\tau B v_w)}{3 \eta} \quad (10)$$

According to previously quoted values of parameters B , v_w , a , and σ_δ ; $r = r_{\text{hyd}}$ and τ for the homogeneous magnetic field, we obtain that the ions' shifts range from 0.2 to 10 nm and particles' shifts from 0.2 nm to 2 μm , which is comparable to the thickness of the electric double layer (some nm at $\kappa = 500/\mu\text{m}$, for instance).

The result for dispersed particles is comparable to the result in Tombacz's calculation.²⁷

Particles in dispersed system are *rotating thermally*. Their average angle velocity ω can be estimated from energy eq 11, where J is the rotation moment for spherical shape $2\pi a^2/5$ and ρ is the mass density of the mineral.

$$k_B T = J \omega^2 / 2 \quad (11)$$

$$\omega = \sqrt{\frac{15 k_B T}{4 \pi \rho a^5}} \quad (12)$$

Taking the rotation time $2\pi/\omega$, a dispersed particle in the homogeneous magnetic field ($\tau \approx 10^{-1}$ s) rotates at least 1000 times, in the alternating field (during one impulse is $\tau \approx 10^{-2}$ s) at least 100 times, and in the rotating field (during one impulse is $\tau \approx 10^{-3}$ s) at least 10 times in average. It is expected that the condensation occurs uniformly on the entire sphere.

Ions and colloid particles have *thermal translation movement* comparable to the movement of the water flow. The average thermal velocity can be estimated from energy eqs 13 and 14, where M is molar mass of ions. As they are hydrated they move slightly slower; therefore, we took 80–140 g/mol for hydrated ions.

$$v_{\text{ther}}(\text{ion}) = \sqrt{3RT/M} \quad (13)$$

$$v_{\text{ther}}(\text{particle}) = \sqrt{\frac{3k_B T}{4\pi\rho a^3}} \quad (14)$$

The thermal velocity for hydrated ions is 220–300 m/s and for dispersed particles 10^{-3} to 1 m/s. Ions have thermal velocities essentially higher than water flow velocity, while for dispersed particles, they are comparable only at radius of some 0.01 μm .

Thermal motion can be considered as a random motion. Particle (or ion) moves in one direction until it collides with another particle (ion). The average time for one direction motion is much smaller than the retention time of water in the magnetic device, and the shifts are too small to have any effect on the aggregation state.

CONCLUSION

One example of recently used physical methods for reducing scale formation in heat exchange equipment is the fine-dispersed suspension method, where fine powder is

added to supplied water to stimulate the crystal nucleation of hardness, forming salts directly on suspended powder. The crystallization nuclei passing through a heat exchanger accepts the scale and consequently reduces the precipitation on the heat exchanger's surfaces. The MWT method could be, in principle, similar to this method.

Two leading hypotheses were discussed: magnetically modified hydration of ions and solid surfaces and Lorentz force effects on ions and dispersed particles. Which effect would prevail depends on the magnetic treatment regime and on the composition of the treated system.

Estimated shifts due to Lorentz force considering thermal translation velocities are negligible in comparison to the thickness of electric double layer for ions and also for particles. Therefore, experimentally observed magnetic field effects on static water solutions and dispersions^{15,19–26} are attributed to the modified hydration.

On the other hand, when treated water is flowing through the magnetic field, Lorentz force causes essential shifts of ions and particles, which can affect the aggregation and crystallization processes.

Abbreviations. a , particle radius, m; B , magnetic field density, T = Vs/m²; c_∞ , molar concentration of electrolytes in the bulk of the solution, mol/m³; D , diffusion coefficient, m²/s; e , electrical charge, As; e_0 , electron charge = $1.6 \cdot 10^{-19}$ As; F , Faraday constant = $9.6 \cdot 10^4$ As/mol; F_L , Lorentz force, N; F_{vis} , viscosity force, N; k_B , Boltzmann constant = $1.38 \cdot 10^{-23}$ J/K; m , mass, kg; M , molar mass, kg/mol; r , ion radius, m; R , universal gas constant = 8.3 J/mol K; T , absolute temperature, K; v , velocity, m/s; v_{ther} , velocity of thermal motion, m/s; v_w , flow velocity of dispersion through the channel of MWT device, m/s; x , normal coordinate, m; Δx , shift of ion, m; z , ion valence, dimensionless; δ , thickness of Stern layer, m; Δ , slipping plane, m; ϵ , absolute dielectricity of water, As/Vm; η , water viscosity, Ns/m²; κ , Debye–Hückel parameter, 1/m; ρ , mass density of mineral, kg/m³; σ_δ , surface charge density at Stern plane, As/m²; τ , retention time of dispersion in channel of MWT device, s; ω , angle velocity of rotation, rad/s; ψ , electrical potential, V; ψ_0 , electrical potential on particle surface, V; ψ_δ , electrical potential at Stern plane, V; $\psi_{\delta 1/2}$, electrical potential at Stern plane before/after MWT, V; ζ , electrokinetic potential, V.

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