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MODIFIED SCALE CRYSTALLIZATION AND DISPERSION STABILITY IN MAGNETIC WATER TREATMENT

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The effects of magnetic water treatment (MWT) devices are discussed with the emphasis on modified dispersion stability and modified $CaCO_3$ crystallization. MWT mechanism, most probably consisting of several interacting effects, is strongly dependent on water composition, solid phase presence and working conditions.

Keywords: water treatment, magnetic hydrodynamics, water dispersion systems

Introduction

MWT is an alternative method of water conditioning for scale control. It has also become important for amelioration in other industrial dispersion areas. MWT equipment has had practical application for over half a century.

Working experience has shown it to be a cheap and non – polluting application for hard scale prevention, and the improvement of dispersion separation [1-4].

Several empirically – based designs of MWT devices have been produced. However, their mechanism, how a magnetic field precisely acts in a treated water system, still remains uncertain. A precise theoretical understanding is crucial when designing reliably efficient equipment for specific technological systems because of the delicate dependency on water composition and operational conditions.

Certain theoretical conclusions have been reached from widespread laboratory research. These state that the process of modified scale crystallization and dispersion destabilization most probably consists of three parallel interacting steps:

- magnetically modified hydration of ions and solid / solution interfaces,
- Lorentz force effect on water dispersion systems and
- concentration effects in working channels of MWT devices.

These three hypotheses are being developed. Firstly, there is a theoretical possibility of magnetic resonance of two neighbouring protons in hydration net during magnetic treatment, which could cause spin transition from a ground state (anti – parallel orientation of spins) into an agitated state (parallel orientation). This would indirectly lead to weakening of the hydrogen bond [5].

Secondly, during the use of the dynamic MWT type, the Lorentz force, F_L (Eq.1), occurs on ions in the solution causing them to shift towards the surfaces of the dispersed particles (Eq.2). Therefore, the stability of water dispersion could be affected [6].

$$\vec{F}_L = e\vec{v}\times\vec{B} \tag{1}$$

$$\Delta x_i = \frac{e_0}{6\pi\eta}\frac{z_i}{r_i}(B\tau v) \tag{2}$$

where parameters are:

B = magnetic field density,
e = electric charge,
e_0 = electron charge = $1{,}6\cdot10^{-19}$As,
r_i = ion radius,
v = flow velocity of dispersion through the channel of MWT device,
Δx_i = Lorentz shift of ion,
z_i = ion valence,
η = water viscosity,
τ = retention time of dispersion in channel of MWT device.

The $B\tau v$ product is known as the technical module and is an important criterion for the practical efficiency of MWT devices.

Thirdly, concentration effects partially explain the aggregation of fine, already destabilized, particles into

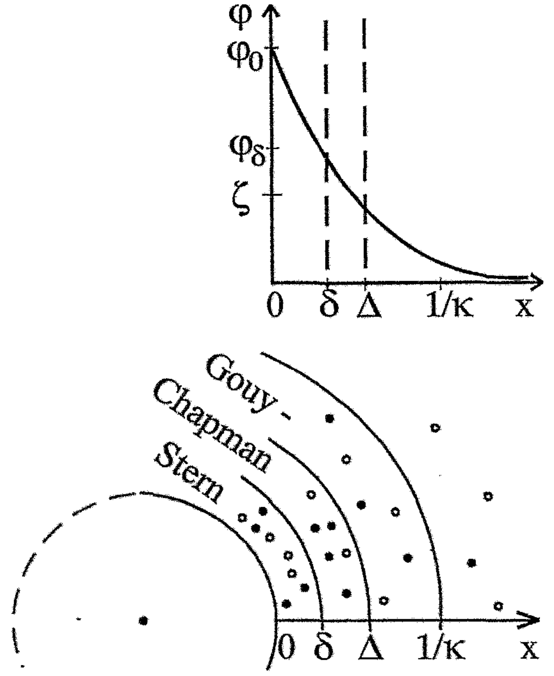

Fig.1 Scheme of electric layer and adherent electrical potential

bigger ones, whilst modified crystallization and destabilization of dispersed scale forming components are better explained by the first two hypotheses.

Which mechanism prevails, depends on water composition and treatment conditions. The MWT mechanism's action on dispersed particles will be discussed here.

Possible explanations for magnetic destabilization of water dispersions

It is well known that dispersed particles are essentially electrically charged on their surfaces even at very low solution concentration of electrolytes due to both the dissociation of the solid surface in contact with water molecules, and the selective adsorption of electrolytes from bulk solution. The ions which are adsorbed on solid surfaces are named co –ions. In the surrounding water layer, so called counter-ions are concentrated for the neutralization of the charged solid surface. The double electrical layer theory (Voyutski [7], 1979; Hunter [8], 1996) describes the concentration distribution of counter – ions and adherent electrical potentials, as is shown *in Fig. 1*.

The neutralization layer consists of two layers: the Stern layer – the first, thin and condensed layer due to the strong electrostatic and adsorption attractions of counter – ions to solid surface, and of the Gouy – Chapman layer – the second, wider and scattered layer due to weaker electrostatic attractions and the thermal motion of the ions. The distribution of counter – ions in the Stern layer is quantitatively similar to Langmuir adsorption (represented by equation (4), whilst the distribution in the Gouy – Chapman layer is determined by the Boltzmann equation (5). The electrical potential as a function of distance to solid surface (equation (6) is derived from the Poisson equation (8) together with equation (5). Parameters in these equations are defined in the nomenclature.

$$\varphi_\delta \approx \varphi_0 - \delta\sigma_\delta/\varepsilon \qquad (3)$$

$$\sigma_\pm = \frac{c_\infty \sigma_{\max}}{c_\infty + \exp((\theta_\pm \pm ZF\varphi_\delta)/RT)} \qquad (4)$$

$$c_\mp = c_\infty \exp\left(\pm ZF\varphi/RT\right) \qquad (5)$$

$$\tanh\left(\frac{ZF\varphi}{4RT}\right) = \tanh\left(\frac{ZF\varphi_\delta}{4RT}\right)\exp(-\kappa(x-\delta)) \qquad (6)$$

$$\kappa = \sqrt{\frac{2F^2 \sum_i Z_i{}^2 c_{i\infty}}{RT\varepsilon}} \qquad (7)$$

$$\frac{d^2\varphi}{dx^2} = -zF\left(c_+ - c_-\right)/\varepsilon \qquad (8)$$

Characteristic parameters of dispersion stability are φ_δ – electrical potential on the Stern border and κ – Debye – Hückel parameter. Namely, in most stable dispersions, the failure of particle collisions due to electrostatic repulsion in an overlapped electric layer, is responsible for very slow coagulation. The more condensed and thinner the layer is, the more particles are neutralized and able to aggregate. The electrical potential of the Stern layer – φ_δ depends on its composition, which is specific for each solution / dispersion system. A determination of the precise φ_δ – value is difficult. Usually, the empirical parameter ζ – electrokinetical potential of slipping plane, is taken as an approximation for φ_δ.

The possible mechanism for magnetic destabilization could be predicted by measuring electrical conductivity, *pH* and ζ – potential. Theoretical possibilities are schematically shown in Fig. 2.

Alternatively, the abundant precipitation of aragonite could be explained by Lorentz ion shifts, which have an influence on the value of k_0 and on the concentration of crystal – forming ions at the growing surface. Surfaces of $CaCO_3$ particles in natural waters, which are commonly neutral or slightly acid, are charged positively, therefore, Ca^{2+} ions could be considered as co – ions. Table 1 shows that shifts of Ca^{2+} are by a factor of 3.8 longer than the HCO_3^-, which drastically alters the relative concentrations of crystal – forming ions on the growing surface and accelerates the $CaCO_3$ growth according to Eq. (9).

Table 1 Lorentz ion shifts and relaxation times at Bv = 0,2 V/m and $\tau = 0,1$ s for some ions at room temperature

I	Na^+	Mg^{2+}	Ca^{2+}	HCO_3^-	SO_4^{2-}
$r_i\,(10^{-10}m)$	0.95	0.65	0.99	1.85	2.3
z_i	+1	+2	+2	-1	-2
$\Delta x_i(nm)$	1.8	5.3	3.4	0.9	1.5

Threshold inhibitors (i.e.Mg^{2+}, Fe^{2+}, Zn^{2+}) of the calcite growth have smaller radii than Ca^{2+}. Their incorporation into active calcite sites and their more intensive hydration than Ca^{2+}– ions retards the calcite growth and gives priority to the aragonite growth. This is more favourable from the viewpoint of hard scale prevention due to its lower adhesivety. Table 1 shows that shifts of Mg^{2+} are by a factor of 1.5 longer than that of Ca^{2+}. This leads to a concentration rise of Mg^{2+} – ions on the growing surface, lowers the value of k_0 in Eq.(9) for calcite and gives priority to the aragonite formation.

Conclusion

The key to MWT effectiveness in hard scale prevention is the forming of modified large crystals, which in supersaturation conditions serve as a basis for scale precipitation in a suspended form.

The MWT mechanism could be considered as complex, strongly linked with the presence of solid surfaces and consisting of several phenomena.

The modified hydration could essentially affect water dispersions and solutions even under static magnetic treatment. However, the most successful MWT devices are of the dynamic type (with the flowing of supplied water through static or pulsated magnetic fields) where the Lorentz effect on solid surfaces could become more noticeable and prevail under the effects of hydration.

SYMBOLS

B	Magnetic field density, Vs/m^2
c_{i_∞}	i – counter – ion concentration in bulk solution, mol/m^3
e	Electrical charge, As
e_0	Electron charge = $1,6\cdot10^{-19}$As
ΔE_{dehyd}	Activation energy for dehydration of crystal – forming ions, J/mol
$f(I)$	Factor of ionic strength – I, dimensionless
F	Faraday constant = $9,6\cdot10^4$As/mol
F_L	Lorentz force, N
k_0	Empiric parameter of water impurities, m/smol
K_s	Solubility product of $CaCO_3$, mol^2/m^6
r_i	Ion radius , m
R	general gas constant = 8,3J/molK
S	Crystal surface, m^2
t	Time, s
T	absolute temperature, K
x	radial coordinate, m
Δx_i	Lorentz shift of ion, m
z_i	i – ion valence, dimensionless

Greek Symbols

ε	dielectric constant of fluid, As/Vm
η	water viscosity, Ns/m^2
φ	electrical potential, V
φ_0	φ on solid surface ($x = 0$), V
φ_δ	φ on Stern border ($x = \delta$), V
κ	Debye – Hückel parameter, defined by (6), 1/m
θ	adsorption energy, J/mol
σ	surface electric charge density, As/m^2
τ	retention time of dispersion in channel of MWT device, s
ζ	electrokinetical potential at slipping plane ($x = \Delta$), V

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