METHOD OF SIMULATION OF MAGNETIC NANOPARTICLE AGGREGATION WITH USING CLUSTERING SYSTEM

Dana ROSICKA, Jan SEMBERA

Technical University of Liberec, Liberec, Czech Republic, EU, dana.rosicka@tul.cz

Abstract

Nanoparticles and colloids in the ground aggregate. In case of simulation of nanoparticle and colloid transport and reactions, dynamics of the aggregation is necessary to be described. Most important causes of the nanoparticle aggregation are heat fluctuation, sedimentation, and drifting of nanoparticles in the medium. In the ground, particles moving in electrolyte may have a nonzero surface charge that affect the rate of particle aggregation. In case of magnetic nanoparticles, attractive magnetic forces have great importance in assessment of the particle aggregation rate.

In the paper, it is presented how to simulate the aggregation of nanoparticles in case of magnetic nanoparticles with nonzero surface charge. Influence of magnetic and electrostatic forces is derived, dynamics is describe by the help of mass transport coefficients giving the probability of aggregation, and the mass transport coefficients are modified for nanoparticle size clusters. That helps to compute reactions among all aggregates during aggregation process.

Keywords: magnetic nanoparticles, magnetic force, electrostatic force, mass transport coefficient, aggregation, clustering system

1. INTRODUCTION

In case of some colloids or nanoparticles, simulation of transport of the nanoparticles is needed. In environmental science, experiments and simulations with zero-valent iron nanoparticles (nZVI) are done. Iron nanoparticles are magnetic nanoparticles used for decontamination of groundwater and soils, especially for decontamination of organic pollutants such as halogenated hydrocarbons [1.]. During a remedial intervention, transport of the iron nanoparticles is slowed down due to rapid aggregation of them. Since the particles are made of iron, the aggregation is caused mainly by the long range attractive magnetic forces [2.-6.]. In electrolyte, a surface charge is established on the surface. Zero-valent iron provides alkaline reaction in water and that induces mainly negative value of the ζ potential of nZVI [7.]. That is why the repulsive electrostatic forces and attractive magnetic forces had to be added into the aggregation model. In our previous papers, the model based on a limit distance between aggregates was presented [8.]. In the submitted paper [9.], mass transport coefficients giving rate of aggregation are modified with use of the limit distance. In this contribution, method of using of the mass transport coefficients for simulation of magnetic nanoparticle aggregation is presented. Aggregates (particles) are divided into groups (clusters) with similar size and transport properties. Mass transport coefficients are modified to describe aggregation dynamics between clusters. That allows us to simulate the aggregation of magnetic nanoparticles during a migration.

2. METHODS AND MODELS

2.1. Model of aggregation of nanoparticles

The particles in groundwater aggregate easily. They create clumps of particles up to the size of several μm [5.] that cohere and decrease the possibility of migration of particles through pores of the ground. The aggregation of the particles is caused by processes that generally occur during a particle migration. The decreasing of mobility can be formulated by a rate of aggregation given by mass transport coefficients β

$[m^3 s^{-1}]$ [10., 11.]. The coefficients give a probability P_{ij} of creation of aggregate from particle i and particle j with concentrations n_i, n_j of particles i, j, respectively (1). Particle (aggregate) i means the aggregate created from i elementary nanoparticles.

$$P_{ij} = \beta_{ij} n_i n_j, \tag{1}$$

$$\beta_{ij} = \beta_{ij}^1 + \beta_{ij}^2 + \beta_{ij}^3. \tag{2}$$

The coefficient (2) is given by sum of mass transport coefficients of Brownian diffusion β_{ij}^1, velocity gradient β_{ij}^{21}, and sedimentation β_{ij}^3. The notation is adopted from [10.]. The mass transport coefficients are equal to:

$$\beta_{ij}^1 = \frac{2k_B T}{3\eta} \cdot \frac{(d_i + d_j)^2}{d_i d_j}, \tag{3}$$

$$\beta_{ij}^2 = \frac{1}{6} \cdot G(d_i + d_j)^3 \tag{4}$$

$$\beta_{ij}^3 = \frac{\pi g}{72\eta}(\rho_p - \rho)(d_i + d_j)^2 |d_i^2 - d_j^2|, \tag{5}$$

where k_B stands for Boltzmann constant, T denotes absolute temperature, η is viscosity of medium, d_i is diameter of particle i, G is an average velocity gradient in a pore, g is gravity acceleration, ρ is density of medium, and ρ_p is density of aggregating particles.

2.2. Magnetic and electrostatic properties of iron nanoparticles

Every nanoparticle has a nonzero vector of magnetization. For TODA iron nanoparticles, the saturation magnetization and average diameter was measured [5.]: saturation magnetization $570\ \mathrm{kA/m}$, average diameter $40\ \mathrm{nm}$. For simplicity we suppose the same magnitude of vector of polarization for all nanoparticles. Our model of magnetic field around the iron nanoparticle is based on the model of magnetic field around a magnet. [12.]

The magnetic force between the source of the intensity of magnetic field and a permanent magnet of volume $\vec{V}$ with the vector of polarization $\vec{M}$ at the point $\vec{r}$ is equal to

$$\vec{F}(\vec{r}) = \int_{\vec{V}} (\vec{M}_0 \cdot g\vec{r}\vec{a}d) g\vec{r}\vec{a}d \left(\int_V \frac{\vec{M}\vec{R}}{R^3} dV \right) dV, \tag{6}$$

where $\vec{M}$ is the vector of magnetic polarization at the point dV, the vector $\vec{R}$ is the difference between the source of magnetic field dV and the point $\vec{r}$, R is the length of $\vec{R}$.

Electrostatic forces among iron particles are given by the surface charge. The surface charge density of particle σ_p is related to the potential Ψ as follows [13.]

$$\sigma_p = \sqrt{8RT\varepsilon\varepsilon_0 c 10^3} \sinh\left(\frac{Z\Psi F}{2RT}\right). \tag{7}$$

R is molar gas constant, T is absolute temperature, ε is dielectric constant of water, c is molar concentration of electrolyte, Z is charge number, F is Faraday's constant, and I is ionic strength.

We calculated the limit distance for the surface charge $10^{-6}\ \mathrm{Cm}^{-2}$ which corresponds to value of ζ potential $1.25\ \mathrm{mV}$ and for the surface charge $2.5 \cdot 10^{-5}\ \mathrm{Cm}^{-2}$ which corresponds to value of ζ potential $30\ \mathrm{mV}$. For the value $1.25\ \mathrm{mV}$, surface charge of particles is close to the iso-electric point, electrostatic forces have small influence, and the particles aggregate. For the value of $30\ \mathrm{mV}$, surface charge causes stabilization of aggregating particles.

2.3. Limit distance

The influence of magnetic forces on the rate of aggregation was assessed by one number – the limit distance L_D. This dimension expresses a range of magnetic forces between particles. The definition of this quantity follows: up to this distance from centre of an aggregate, attractive magnetic forces cause the aggregation between the aggregate and a particle placed in the range. Hence, in a range larger than the limit distance, other forces outweigh the magnetic forces.

The limit distance L_D can be defined as the distance of the point in which gravitation F_g and magnetic forces F_{mg} effecting on the aggregate are equal

$$F_g = F_{mg}(L_D). \tag{8}$$

The limit distance has the form

$$L_{D,0} = \sqrt[4]{\frac{F_{mg}(R_0)}{F_g}}R_0. \tag{9}$$

Magnetic force between two single magnetic nanoparticles falls with the power of 4. In the case of aggregates, the fall depends on the structure of aggregates and the iteration of limit distance computation is needed [14.].

$$L_{D,1} = \sqrt[4]{\frac{F_{mg}(L_{D,0})}{F_g}}L_{D,0}. \tag{10}$$

Including electrostatic forces, we define the limit distance as the distance where the repulsive magnetic forces is equal to the sum of attractive forces F_{mg} and F_C.

As influence of electrostatic forces fall with power of 2, inclusion of electrostatic forces into equilibrium of force can be done by following way [14.]

$$L_{D,0} = \sqrt{\frac{\sqrt{F_C^2(R_0) + 4F_g\ F_{mg}(R_0)} - F_C\ (R_0)}{2F_g}}R_0, \tag{11}$$

$$L_{D,1} = \sqrt{\frac{\sqrt{F_C^2(L_{D,0}) + 4F_g\ F_{mg}(L_{D,0})} - F_C\ (L_{D,0})}{2F_g}}L_{D,0}. \tag{12}$$

The values of the magnetization vector and surface charge were selected the following way: $M = 570\ \mathrm{kA/m}$; $\sigma = 2.5 \cdot 10^{-5}\ \mathrm{Cm}^{-2}$. We used these selected values for all the computations of interaction energy and mass transport coefficients.

2.4. Inclusion of the limit distance into mass transport coefficients

Inclusion of the limit distance into mass transport coefficients was done in the submitted paper [9.]. The basic model of aggregation in the section 2.1 indicates rate of aggregation caused by collision of particles (in proximity, attractive forces outweigh the repulsive ones).

Mass transport coefficients (3), (4), (5) were derived on the basis of flux of nanoparticles trough observed volume or circle area around a particle. The area had radius equal to sum of radii of both particles. That means that particles collide and aggregate.

In the section 2.3, the limit distance in which attractive forces outweigh the repulsive ones is established. The magnetic forces attract particles close to each other and then they aggregate due to attractive van der Waals forces. According to this idea, the particles do not have to be in proximity to aggregate when attractive magnetic forces acting between them. Therefore, the mass transport coefficients are computed as flux trough sphere or circle area around a particle with diameter equal to limit distance:

$$\beta_{ij}^{1,mg} = \frac{4k_B T}{3\eta} \cdot \left(\frac{1}{d_i} + \frac{1}{d_j}\right) L_{D,1}, \tag{13}$$

$$\beta_{ij}^{2,mg} = \frac{4}{3} \cdot G \cdot {L_{D,1}}^3 \tag{14}$$

$$\beta_{ij}^{3,mg} = \frac{\pi g}{18\eta} (\rho_p - \rho) |d_i^2 - d_j^2| L_{D,1}^2, \tag{15}$$

where $\beta_{ij}^{1,mg}$, $\beta_{ij}^{2,mg}$, $\beta_{ij}^{3,mg}$, stand for mass transport coefficient of Brownian motion, velocity gradient, and sedimentation, respectively, with inclusion of magnetic forces among particles.

3. RESULTS AND DISCUSSION

In this section, it is shown how to use derived mass transport coefficients (13), (14), (15) for simulation of magnetic nanoparticle transport. In the transport solvers that compute reactions between species in water, aggregation can be seen as reaction between aggregates, since two particles interact and one new particle (aggregate) arises. During the aggregation process, millions of different sizes of aggregates with different transport properties should be considered. Because it is not possible to compute the reactions among millions species, we generated a system for the clustering of particles into several sections according to their size.

3.1. Clustering of nanoparticle sizes

System of clustering of nanoparticles according to their size is based on splitting of aggregates into groups (clusters) containing aggregates with similar size and transport properties. Solver of transport then computes reaction among the clusters instead of among the aggregates. That gives the dynamics of aggregation during transport processes and helps to predict worsening transport possibilities of nanoparticles in time with ongoing aggregation.

The mass transport coefficients had to be reformulated so that they correspond to probabilities of particle aggregation between the clusters. The choice of cluster size is not arbitrary, but the rule of geometric limitation has to be satisfied: $k_i \geq k_{i-1}$, where k_i is an amount of nanoparticles that create the largest aggregate in the cluster i. It means that aggregate created by the collision of particles from a cluster pertains into the same or immediate following cluster.

Probabilities of aggregation of particles are divided according to the final cluster of created aggregate. It depends on the sizes of aggregating particles, whether the created aggregate stays in the cluster of larger aggregating particle or pertains to the following cluster.

Let the cluster l be the observed cluster. An aggregate created from particles i and j from clusters r and p which are smaller than or equal to l will belong to the cluster l if the sum of particle sizes is greater than the lower limit k_{l-1} of the cluster l and lower than or equal to the upper limit k_l of the cluster l. Total probability of collision of particles from clusters r and p that create a particle from cluster l per one second with unit concentration of particles from clusters r and p is

$$\beta^{+}_{r,p,l} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{p-1}+1}^{k_p} \frac{\beta_{ij}\theta(k_{l-1} < i+j \le k_l)}{(k_r - k_{r-1})(k_p - k_{p-1})}, \tag{16}$$

where the function θ stands for a condition. If it is fulfilled, the value of the condition is 1, otherwise it is 0. Decrease of particles from the cluster l is given by aggregation of two particles whereof at least one particle is from the cluster l. The average probability of collision of a particle from cluster l with a particle from cluster r per one second and unit concentration of particles is

$$B_{r,l} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{l-1}+1}^{k_l} \frac{\beta_{ij}}{(k_r - k_{r-1})(k_l - k_{l-1})} \tag{17}$$

and consequently the decrease of particles in the cluster l due to collisions with particles from cluster r is

$$\beta^{-}_{r,l} = B_{r,l} - \beta^{+}_{r,l,l}. \tag{18}$$

An overview of all the formulas for computation of these coefficients is presented in Tab.1.

Tab. 1: Summary of the mass transport coefficient for clusters of aggregates in the discrete form

$r < l, p < l$	$^{1}\beta^{+}_{r,p,l} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{p-1}+1}^{k_p} \frac{\beta_{ij}\theta(k_{l-1} < i+j \le k_l)(i+j)^{\lambda}}{(k_r - k_{r-1})(k_p - k_{p-1})\alpha i^{\lambda} j^{\lambda}}$
$r < l, p = l$	$^{2}\beta^{-}_{r,l} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{l-1}+1}^{k_l} \frac{\beta_{ij} j^{\lambda}}{(k_r - k_{r-1})(k_l - k_{l-1})\alpha i^{\lambda} j^{\lambda}} - \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{l-1}+1}^{k_l} \frac{\beta_{ij}\theta(i+j \le k_l)(i+j)^{\lambda}}{(k_r - k_{r-1})(k_l - k_{l-1})\alpha i^{\lambda} j^{\lambda}}$
$r = l, p = l$	$^{3}\beta^{-}_{r,l} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{l-1}+1}^{k_l} \frac{\beta_{ij}(i^{\lambda} + j^{\lambda})}{(k_r - k_{r-1})(k_l - k_{l-1})\alpha i^{\lambda} j^{\lambda}} - \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{l-1}+1}^{k_l} \frac{\beta_{ij}\theta(i+j \le k_l)(i+j)^{\lambda}}{(k_r - k_{r-1})(k_l - k_{l-1})\alpha i^{\lambda} j^{\lambda}}$
$r > l, p = l$	$^{4}\beta^{-}_{r,l} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{l-1}+1}^{k_l} \frac{\beta_{ij} j^{\lambda}}{(k_r - k_{r-1})(k_l - k_{l-1})\alpha i^{\lambda} j^{\lambda}}$

We usually observe a change of numbers of particles in clusters. Symbols α and λ in Tab.1 are useful when we are interested in change of the surface of particles (important for reactivity) or in change of the volume of particles. The change of volume of particles should be equal to zero because of mass conservation law, so it could be good method for verification of calculation accuracy. For computation of change of number of

particles in the cluster l: $\alpha = 1, \lambda = 0$; for change of volume: $\alpha = 1, \lambda = 1$; for change of particle surface: $\alpha = \sqrt[3]{\pi}\sqrt[3]{6^2}, \lambda = \frac{2}{3}$.

Let us denote N_l the concentration of particles from the cluster l

$$N_l(t) = \sum_{i=k_{l-1}+1}^{k_l} n_i(t), \tag{19}$$

The change of N_l in time is equal to

$$\frac{dN_l}{dt} = \frac{1}{2}\sum_{r=1}^{l-1}\sum_{p=1}^{l-1} {}^1\beta^+_{r,p,l} N_r N_p - \sum_{r=1}^{l-1} {}^2\beta^-_{r,l} N_r N_l - \frac{1}{2} {}^3\beta^-_{r,l} N_l N_l - \sum_{r=l+1}^{m} {}^4\beta^-_{r,l} N_r N_l \tag{20}$$

$l = 1,2,\ldots,m$, where m is the number of clusters.

In the equation (20), the first and the third term are multiplied by $\frac{1}{2}$ because the double sums add the same reactions twice.

4. CONCLUSION

We developed a theoretical model of aggregation of electrically charged magnetic nanoparticles during their transport through a porous medium. This model gives probability of aggregation between two aggregates (particles). For efficiency of computation of aggregation among all aggregates, simplification had to be done. Clustering model divided aggregates into groups and aggregation is computed between these groups. For this system, mass transport coefficients giving the probability of aggregation had to be modified.

In this paper, the theoretical model of aggregation of electrically charged magnetic nanoparticles is presented. The system of clustering of particles into section according to their size is shown, as well as computation of aggregation rate with using the clustering system.

ACKNOWLEDGEMENTS

This work was supported by the research project FR-TI1/456 "Development and implementation of the tools additively modulating soil and water bioremediation" - Programme MPO-TIP supported by Ministry of Industry and Trade and by the Ministry of Education of the Czech Republic within the project no. 7822 of the Technical University in Liberec.

LITERATURE

[1.] Zhang W-x: *Nanoscale Iron Particles for Environmental Remediation: an Overview*, J. Nanopart. Res. 5, 3-4 (2003)

[2.] Li L., Fan M., Brown R. C., Van Leeuwen J. (H.), Wang J., Wang W., Song Y., Zhang P.hang: *Synthesis, Properties, and Environmental Applications of Nanoscale Iron-Based Materials: A Review*, Crit. Rev. Env. Sci. Technol. 36, 405-431 (2006)

[3.] Horak D, Petrovsky E, Kapicka A, Frederichs T: *Synthesis and Characterization of Magnetic Poly(Glycidyl Methacrylate) Microspheres*, Journal of Magnetism and Magnetic Materials 500-506 (2007)

[4.] Masheva V, Grigorova M, Nihtianova D, Schmidt JE, Mikhov M: *Magnetization Processes of Small $\gamma-Fe_2O_3$ Particles in Non-Magnetic Matrix*, Phys. D: Appl. Phys. 32, 1595-1599 (1999)

[5.] Phenrat T ,Saleh N, Sirk K, Tilton RD, Lowry GV: *Aggregation and Sedimentation of Aqueous Nanoscale Zerovalent Iron Dispersions*, Environ. Sci. Technol. 41(1), 284-290 (2007)

[6.] Zhang LY, Wang J, Wei LM, Liu P, Wei H, Zhang YF: *Synthesis of Ni nanowires via a hydrazine reduction route in aqueous ethanol solutions assisted by external magnetic fields*, Nano-Micro Lett. 1, 49-52 (2009)

[7.] Sun Y-P, Cao J, Zhang W-x, Wang H P: *Characterization of zero-valent iron nanoparticles*, Advances in Colloid and Interface Science 120, 47-56 (2006)

[8.] Rosicka D, Sembera J: *Inclusion of electrostatic forces to assessment of rate of magnetic forces impact to iron nanoparticle aggregation*, proceedings of conference Nanocon 2011, Brno

[9.] Rosicka D, Sembera J: *Modification of nanoparticles aggregation rate by addition of effect of electrostatic and magnetic forces among them into mass transport coefficients*, submitted in Nanoscale Res. Lett.

[10.] Buffle J, Van Leeuweh H, (EDS.): *Environmental Particles*, Lewis publishers 2, 353--360 (1993).

[11.] Smoluchowski M v: *Test of a mathematical theory of coagulation kinetics of colloid solutions* [in German], Zeitschrift f. physik. Chemie, XCII, 129--168 (1916).

[12.] Votrubik V, Editor, *Theory of the electromagnetic field* [in Czech], Czechoslovak Academy of Science Publication, Praha (1958)

[13.] Stumm W, Morgan JJ: *Aquatic Chemistry*, A Wiley-Interscience Publication, New York, (1996)

[14.] Sembera J, Rosicka D: *Computational Methods for Assessment of Magnetic Forces Between Iron Nanoparticles and Their Influence on Aggregation*, Adv. Sci. Eng. Med. 3, 149-154 (2011)