THEORETICAL STUDY OF ELECTRICAL CHARGE INFLUENCE ON AGGREGATION RATE OF NANOPARTICLES OF ZERO VALENT IRON*

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Introduction

Nanoparticles of zero valent iron are particles with diameter about 50 nm and with large specific surface. Particles have remedial properties, they can adsorb pollutants on their surface or can change oxidation state of contaminant. Chemical and physical reactions with iron can imply decrease of mobility, toxicity, or solubility of the contaminants. Moreover, nanoparticles are mobile and can drift to the contaminated area and this way increase efficiency of remediation activity. However, the nanoparticles aggregate and form bigger superparticles which decreases or makes impossible their further transport. Aggregation in natural medium is supposed to be irreversible. The rate of aggregation is supposed to be proportional to probability of collision of two particles. The main processes influencing probability of collision are Brownian movement, drifting in water, and sedimentation. Derivation of mass transport coefficients quantifying the aggregation rate for the mentioned three processes was published e.g. in [1]. The mentioned derivation was done for uncharged particles. Here, we are presenting expansion of derivation of mass transport coefficients for uniformly electrically charged particles.

For simulation using derived mass transport coefficients we should understand aggregates of various sizes as different substances. It makes any realistic simulation impossible as it would need to calculate reactions among millions of substances. Because of that we used an idea of clustering published e.g. in [6]. We divided the aggregates into sections according to their size. We modified the coefficients of transport and other parameters important for transport of particles for these sections. The system of clustering is another part of our presentation. Due to this system the simulation can deal with reactions among several size sections only.

Aggregation of nanoparticles

We suppose that if centres of two particles get as close as or closer than to the sum of their radii, they aggregate. Diameter of observed aggregates is up to 5 μm. The speed of clustering and the amount of created aggregates are represented by the rate of aggregation. We derived rate of aggregation from equilibrium of forces between two particles in form of mass transport coefficients β [m^3/s] as they were defined in [1]:

$$P_{ij}=(\tilde{\beta}_{ij}^{3el}+\tilde{\beta}_{ij}^{2el}+\tilde{\beta}_{ij}^{1el})\, n_i\, n_j$$

Probability of aggregation of particle i with particle j is proportional to the molar concentration of particles i (n_i), molar concentration of particles j (n_j), and sum of mass transport coefficients expressing the contributions of sedimentation ($\tilde{\beta}_{ij}^{3el}$), velocity gradient ($\tilde{\beta}_{ij}^{2el}$), and Brownian movement ($\tilde{\beta}_{ij}^{1el}$), all of them with respect to the electrical charge of particles. Saying particle i, we mean the aggregate created from i elemental nanoparticles. We suppose that the surface charge of all particles in the same electrolyte has the same polarity which is most frequent case.

The resulting formulas for computation of mass transport coefficients are:

$$\beta_{ij}^{1el}=\frac{2k_BT}{3\eta}\frac{(d_i+d_j)^2}{d_id_j}-\frac{\pi d_i^2d_j^2\sigma_i\sigma_j}{3\eta\varepsilon_0(d_i+d_j)}$$

$$\tilde{\beta}_{ij}^{1el}=max(0,\beta_{ij}^{1el})$$

$$\beta_{ij}^{2el}=\frac{1}{6}G(d_i+d_j)^3-\frac{\pi d_i^2d_j^2\sigma_i\sigma_j}{12\eta\varepsilon_0}\left|\frac{1}{d_i}+\frac{1}{d_j}\right|$$

$$\tilde{\beta}_{ij}^{2el}=max(0,\beta_{ij}^{2el})$$

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

$$-\frac{\pi d_i^2d_j^2\sigma_i\sigma_j}{12\eta\varepsilon_0}\left|\frac{1}{d_i}+\frac{1}{d_j}\right|,\quad \tilde{\beta}_{ij}^{3el}=max(0,\beta_{ij}^{3el}).$$

Where d_i is diameter of particle i, k_B is Boltzmann constant, T is temperature, η is medium viscosity, ε_0 is medium permittivity, σ_i is surface charge of particle i, G is the velocity gradient, ρ_p is mass density of particles, ρ is mass density of medium, and g is gravitational acceleration.

The derivation is done in [3] and [7].

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Clustering of the particle sizes

The simulate aggregation of nanoparticles we should understand aggregates of different sizes as different species. Aggregation is then analogous to chemical interactions among such species. Because aggregates can be composed of 1 to 10^6 elemental nanoparticles, such a simulation deals with millions of species. Such a computation is not possible for a real-world-size problem. Because of that we had to generate a system for the clustering of particles into several sections according to their size. We reformulated the mass transport coefficients so they correspond to the probabilities of particle aggregation between the sections. The choice of cluster size is not arbitrary, but the rule of geometric limitation has to be satisfied:

$$k_l \geq 2\, k_{l+1}$$

where k_l is the amount of nanoparticles that create the largest aggregate in the section l. It means that aggregate created by the collision of two particles from a section pertains into the same or immediate following section.

Let us denote N_l the concentration of particles from the section l:

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

Time change of N_l is equal to

$$\frac{\mathrm{d}N_l(t)}{\mathrm{d}t} = \frac{1}{2}\sum_{r=1}^{l-1}\sum_{p=1}^{l-1} {}^{1}\beta^{+}_{r,p,l} N_r N_p - \sum_{r=1}^{l-1} {}^{2}\beta^{-}_{r,l} N_r N_l$$

$$- \frac{1}{2}{}^{3}\beta^{-}_{l,l} N_l N_l - \sum_{r=l+1}^{m} {}^{4}\beta^{-}_{r,l} N_r N_l,$$

where the first term at the right hand side expresses increase of particles in l^{th} section due to aggregation of particles from lower sections, the second, third, and fourth terms stand for decrease due to aggregation with particles from lower sections, the same section, and higher sections respectively. The following table shows the formulas for respective betas:

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

Function Θ stands for the characteristic function of the condition in its brackets (its value is either 1 or 0, if the condition holds or does not). Symbols α and λ in the table are useful when we are interested in the change of the surface of particles (important for reactivity) or in the change of the volume of particles (good for accuracy verification as it must not change due to mass conservation law). For calculation of change of number of particles in the section l set α=1 and λ=0; for change of volume set α=1 and λ=0; for change of particle surface set $\alpha=\sqrt[3]{36\pi}$ 1 and λ=2/3.

Conclusion

We developed a theoretical model of aggregation of electrically charged iron nanoparticles during their transport through the porous medium. It allows us simulate transport and aggregation of particles using the derived parameters. It is useful for simulation of processes that occur during remediation of groundwater and soil using zero valent iron nanoparticles. The derived parameters determine the rate of aggregation. Knowing this rate, we can estimate the distribution of particle size and then the ability of particles to travel through the porous medium.

In this paper the derivation of the mass transport coefficients with the influence of electrostatic forces is presented. Furthermore the system of clustering of particles into section according to their size is shown.

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