#### **Technical University of Liberec**

Faculty of Mechatronics, Informatics and Interdisciplinary Studies Institute of Novel Technologies and Applied Informatics

## An Investigation of Aggregation Models of Magnetic, Zero-valent Iron Nanoparticles

Model agregace magnetických nanočástic nulmocného železa

by

### Dana Rosická

supervisor: doc. Ing. Jan Šembera, Ph.D.

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#### ABSTRACT

This work focuses on an investigation into the aggregation mechanisms of unstable, nanoscale particles in flowing groundwater. A study and a description of the process of aggregation help to simulate the transport of unstable undissolved nanoparticles. This could be useful when one needs to know how the nanoparticles behave in transit. In the following example a knowledge of this process is helpful. Some contaminants, such as halogenated hydrocarbons, are remediable by zero-valent iron nanoparticles. These are very unstable particles but still have a high potential in remediation field. Thanks to their (nano)size, they can migrate through the ground and are able to decontaminate wide areas. However, they aggregate into microsized entities and lose their migratory ability. Simulation of the transport of iron nanoparticles and their aggregation could be useful in predicting the success of decontamination interventions. The mathematical derivation of iron nanoparticle aggregation is so complex and difficult that this work is focused mainly on them.

This work is mainly theoretical. First, an aggregation model is described. The model is based on aggregation due to the heat fluctuation of nanoparticles and due to their different velocities during sedimentation and drifting in groundwater. This model is then extended to include the impact of repulsive electrostatic and attractive magnetic forces that affect the rate of aggregation of magnetic nanoparticles with non-zero surface charge. The coefficients of aggregation are recalculated in order to compute the aggregation not only between single nanoparticles, but also between aggregates of nanoparticles (more simply called "particles"). A study of the possible aggregate structures was performed to be able to compute their mutual reactions. Extended coefficients of aggregation between particles were converted to coefficients of aggregation between "sections" of nanoparticles with similar size and properties. This enabled the simulation of aggregation in real time. The subsequent part of this work is dedicated to the computational aspects of aggregation in order to make the computation faster, but with a small error. At the end of the work, simulations of aggregation and transport of different types of nanoparticles are presented. Technická univerzita v Liberci Fakulta mechatroniky, informatiky a mezioborových studií

#### ABSTRAKT

Tato práce se zabývá procesem agregace nestabilních nanočástic s nenulovým povrchovým nábojem a magnetizací, unášených vodou. Motivací pro tuto práci byla potřeba simulovat transport zejména následujícího typu nestabilních nanočástic. Pro sanační účely jsou používány nulmocné železné nanočástice. Jde o velmi reaktivní nanočástice s velkým měrným povrchem schopné dekontaminovat například halogenové uhlovodíky. Nančástice však zároveň ve velké míře agregují, což vede k omezení migračních schopností nanočástic. I přes to jde o velmi ceněné sanační činidlo. Porozumění agregaci železných nanočástic může být užitečné pro simulaci jejich transportu potažmo pro odhad účinnosti sanačního zásahu. Odvození agregace těchto částic je velmi komplexní a komplikovaný problém, proto je tato práce zaměřena zejména na ně.

Tato práce je především teoretická. Nejprve je zde popsán obecný model agregace založený na Brownově pohybu a na různých rychlostech částic při sedimentaci a migraci v proudu vody. Tento model je zde rozšířen o vliv odpudivých elektrostatických sil a přitažlivých magnetických sil. Koeficienty určující agregaci jsou přeformulovány tak, aby byla počítána agregace nejen mezi jednotlivými nanočásticemi, ale také mezi agregáty nanočástic. Zároveň jsou zde zkoumány struktury, které nanočástice v agregátech nejpravděpodobněji zaujímají. Pro všechny další výpočty je pak vybrána jedna struktura agregátů. Z důvodu výpočetní náročnosti agregace mezi všemi různě velkými agregáty je zde představen model klastrování, kdy částice (agregáty) jsou rozděleny do klastrů podle velikosti a agregace je počítána pomocí reakcí mezi těmito klastry. Ze stejného důvodu je dále zkoumána možnost zrychlení výpočtů agregace průměrováním agregátů. Na závěr jsou představeny některé simulace transportu nanočástic a jejich agregace.

## Prohlášení

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Ing. Dana Rosická

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# Nomenclature

a	$[\mathbf{m}]$	radius
$a_a$	[m]	radius of sand grain
$a_n$	[m]	radius of pore
A	[1]	number of nanoparticles in the averaged aggregate from a section $Se$
В	$[m^3/s]$	average probability of collision of particle in sections
c	[g/L]	concentration
d	[m]	diameter of a particle
D	$[m^2/s]$	diffusion coefficient
E	[1]	limit difference between two iteration steps
f	[kg/s]	friction coefficient
F	[C/mol]	Faraday constant
$F_{buo}$	[N]	buoyant force
$F_c$	[N]	electrostatic (Coulomb's) force
$F_{fric}$	[N]	frictional force
$F_{g(rav)}$	[N]	gravitational force
$F_{mg}$	[N]	magnetic force
g	$[m/s^2]$	gravity acceleration
G	[1/s]	velocity gradient
h	[1]	number of sections
i,j	[1]	number of nanoparticles in an aggregate
Ι	[M]	ionic strength
j	$[1/m^2/s]$	flux density
$j_{adv}$	$[1/m^2/s]$	advection flux density
$j_{dif}$	$[1/m^2/s]$	diffusion flux density
J	[1/s]	flux of particles
k	[1]	number of particles limiting section
$k_R$	[L/g/s]	rate constant of kinetic reaction
$k_B$	[J/K]	Boltzmann constant
K	[m/s]	coefficient of permeability
l, r, p	[-]	observed sections
$L_d$	[m]	limit distance
m	[kg]	weight

M	[A/m]	magnetization (magnetic polarization)
n	$[1/m^{3}]$	number of particles in one $m^3$ (particle concentration)
$n_{Re}$	[1]	number of different types of reactions
$n_{Se}$	[1]	number of particle size sections
N	[1]	number of particles in section
$N_n$	[1]	number of nanoparticles
$N_p$	[1]	number of particles
0	[1]	reaction order
Р	$[1/m^3/s]$	frequency of aggregation
$P_I$	[1]	number of parts of the section $r$
q	[1/s]	flow
Q	[C]	charge
r	[m]	location (variable distance)
$r_c$	[1]	retardation coefficient
R	[m]	distance
$R_m$	[J/mol/K]	molar gas constant
s	[1]	number of iterations
S	$[m^2]$	area
$S_R$	[1]	stoichiometry
$S_I$	[1]	size of parts of the section $r$
t	$[\mathbf{s}]$	time
T	[K]	absolute temperature
U	[1]	probability of no aggregation
v	[m/s]	velocity of transport
$v_b$	[m/s]	theoretical Brownian velocity
$v_r$	[g/L/s]	rate of change of kinetic reaction
V	$[m^3]$	volume
w	[1/s]	frequency of collisions
W	[1]	probability of aggregation
Ζ	[1]	charge number
$\alpha, \lambda$	[1]	symbols for definition of computed change of number, surface, or volume
eta	$[m^3/s]$	mass transport coefficient
$\beta^1$	$[m^3/s]$	mass transport coefficient for Brownian motion
$\beta^2$	$[m^3/s]$	mass transport coefficient for velocity gradient
$\beta^3$	$[m^3/s]$	mass transport coefficient for sedimentation
$\beta^+$	$[m^3/s]$	total probability of collision of particles from sections
$\beta^{-}$	$[m^3/s]$	decrease of particles in the section
ε	[1]	dielectric constant of solution
$\varepsilon_0$	[F/m]	vacuum permittivity
$\eta$	$[Pa \cdot s]$	dynamic viscosity

$\kappa$	[1/m]	Debye parameter
$\varrho$	$[\mathrm{kg}/\mathrm{m}^3]$	density of solution
$\varrho_p$	$[\mathrm{kg}/\mathrm{m}^3]$	density of an aggregating particle
$\sigma$	$[C/m^2]$	surface charge density
$\phi$	[1]	porosity
$\psi~(\zeta)$	[V]	surface charge potential
L		Litre $(dm^3)$
$\mathrm{mL}$		milliLitre ( $cm^3$ )
CL		in Czech Language
DLS		Dynamic Light Scattering
DLVO theory		theory named after Derjaguin, Landau, Verwey, Overbeek
ELS		Electrophoretic Light Scattering
$\operatorname{FP}$		Particle in a Flux of particles
GL		in German Language
IEP		Iso-Electric Point
LDE		Laser Doppler Electrophoresis
LDV		Laser Doppler Velocimetry
MTC		Mass Transport Coefficient
nZVI		Zero-Valent Iron Nanoparticle
OP		Observed Particle
OS		Observed Sphere
OV		Observed Volume
PSS		Particle Size Section
Re		Reaction type label
RNIP		Reactive Nanoscale Iron Particles
Se		label of particle size Section
SEM		Scanning Electron Microscope
SQUID		Superconducting Quantum Interference Device
TEM		Transmission Electron Microscope
TUL		Technical University of Liberec
XRD		X-Ray Diffraction
ZVI		Zero-Valent Iron Nanoparticle

### Chapter 1

### Introduction

#### **1.1** Problem Statement

Many types of nanoparticles and colloidal particles occur in groundwater. Some of the particles are formed naturally; others are generated synthetically and put into the ground by human activity. It may be necessary to know both the reactivity of the nanoparticles in the ground and their migratory properties for simulation of their behaviour in the ground. That is the reason why the processes of mutual nanoparticle reactions (aggregation) during their transport through the ground are examined in this work. Studies of the problem of particle aggregation have been published before [1-3], but are insufficient for a description of the interactions between nanoparticles with non-zero surface charge and/or magnetic moment. These types of nanoparticles are examined at the Technical University of Liberec (TUL) where experiments and simulations of nanoscale zero-valent iron (nZVI) reactivity and transport are performed. nZVI describes iron nanoparticles used for water and soil treatment. They are able to migrate in groundwater through contaminated areas and remediate polluted soils and water [4]. The properties of nZVI depend on their production method which can be carried out in many ways [5–7]. This work mainly deals with RNIP and NANOFER nZVI described in Section 2. However, the derived models in this work are general and can be used for the computation of aggregation of migrating nanoparticles with/without magnetic and/or electrostatic mutual interactions.

#### **1.2** Motivation and Challenges

To be able to simulate the migration of magnetic nanoparticles with non-zero surface charge a knowledge of how they behave during migration was required. A lot of experiments concerning nZVI transport through a porous medium have been performed at TUL [8] (in Czech language (CL)). Hence, it was possible to describe the mutual interactions between nZVI nanoparticles and to verify the new model of aggregation on the results of the transport experiments. The basis was an aggregation model of unstable nanoparticles derived from these articles: [1–3], and specified in the author's diploma thesis [9](CL). The aim was to include the effects of electrostatic and magnetic forces on the old aggregation model and make the model more general. The old commonly used aggregation model with mass transport coefficients [3,10] describing aggregation is based on collisions between nanoparticles caused by heat fluctuation and the different velocities of nanoparticles during settlement and drifting. This model does not include a reduction in the aggregation rate due to repulsive electrostatic forces which themselves occur due to the electric double-layer which forms on the nanoparticle surfaces [11]. Furthermore, in the case of magnetic nanoparticles, the aggregation is rapidly accelerated by attractive magnetic forces between nanoparticles [5, 12–15]. Therefore the aggregation model had to be extended and a more accurate model of aggregation of iron nanoparticles in water could be achieved.

#### **1.3** Contributions

The main contribution of this work is that it enables the computation of aggregation dynamics of general nanoparticles where the effect of electrostatic and magnetic forces can be included. This was achieved by carrying out the following actions.

- The mass transport coefficients (MTC) were extended to include the impact of repulsive electrostatic forces and attractive magnetic forces between particles. Mass transport coefficients give the frequency of collisions between nanoparticles or aggregates of nanoparticles (particles). Magnetic forces were added by creating a "limit distance" which gives the critical distance between aggregates in which magnetic forces attract particles and cause aggregation.
- The probable structures of aggregates created from nanoparticles were assessed. The effect of magnetic forces on the aggregation rate of some probable structures was computed and a comparison was made of the experimental results. Next, the interaction energies between nanoparticles in aggregates were computed. These are the interactions which produce the most stable structures of aggregates of magnetic nanoparticles.
- Computation of all reactions between every single nanoparticle and aggregate is very time-consuming. Therefore, a system of clustering the particles into "sections" with similar properties according to their sizes was derived based on the work: [16]. The aggregation model was then adapted to compute the reactions between the particle size sections (PSS). That accelerated the computation of the

mass transport coefficient and enabled the transformation of the mass transport coefficient into kinetic reactions between sections of particles. That enabled the new aggregation model to be used in a variety of simulation software.

- The possibility of averaging the PSS and their acting forces was examined in order to accelerate the aggregation computation. The influence of averaging the magnetic force computation on computational error was analyzed and when it is suitable to use the averaging model was assessed.
- The extended aggregation model of iron nanoparticles was converted into a kinetic form of the aggregation between PSS and included into a formula for particle transport in groundwater. This can be used to simulate the transport of iron nanoparticles and to predict the efficiency of a remedial intervention. That could be useful when proposing an optimal remedial intervention which would enable the decontamination of an affected area efficiently and economically.

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The work in this thesis has been published in part or in full in the following publications:

#### Journal:

- Rosická D., Šembera J.: Changes in the nanoparticle aggregation rate due to the additional effect of electrostatic and magnetic forces on mass transport coefficients, Nanoscale Res. Lett. 2013, 8(20).
- Rosická D., Šembera J.: Influence of structure of iron nanoparticles in aggregates on their magnetic properties, Nanoscale Res. Lett. 2011, 6(527).
- Szilágyi I., Rosická D., Hierrezuelo J., Borkovec M.: Charging and stability of anionic latex particles in the presence of linear poly(ethylene imine), J. Colloid Interface Sci. 2011, 360(2):580-5.
- Šembera J., Rosická D.: Computational Methods for Assessment of Magnetic Forces Between Iron Nanoparticles and Their Influence on Aggregation, Adv. Sci. Eng. Med. 2011, 3(1-2):149-154(6).
- Rosická D., Šembera J.: Assessment of Influence of Magnetic Forces on Aggregation of Zero-valent Iron Nanoparticles, Nanoscale Res Lett 2011, 6(10).

#### Conference:

- Rosická D., Šembera J.: Method of simulation of magnetic nanoparticle aggregation with using clustering system, 4th International Conference NANOCON 2012, Brno 2012 (October 23rd - 25th 2012), Conference Proceedings Book, in print.
- Rosická D., Šembera J.: Inclusion of Electrostatic Forces to Assessment of Rate of Magnetic Forces Impact to Iron Nanoparticle Aggregation, 3th International Conference NANOCON 2011 in Olomouc (September 21st-23rd 2011), Conference Proceedings Book (ISBN 978-80-87294-27-7), 387–392.
- Rosická D., Šembera J., Maryška J.: Theoretical study of electrical charge influence on aggregation rate of zero valent iron, 18th Annual International Conference on Composites/Nano Engineering (ICCE -18) 2010 in Anchorage, Alaska (July 4-10, 2010), Book of Abstracts, 641–642.

#### 1.4 Outline of the Thesis

This prelude has introduced the idea of deriving an aggregation model of nanoparticles with non-zero surface charge and magnetic moment.

Chapter 2 provides a basic understanding of zero-valent iron nanoparticles (nZVI). The properties of nZVI are listed as well as statistics that support the assumption that the particles are ferromagnetic. The main result in this chapter concerns their high reactivity and rapid aggregation rate.

Chapter 3 describes the aggregation model based on Brownian motion and different velocities of particles during sedimentation and drifting in groundwater. There is a comparison of the importance of these processes on the rate of aggregation for different types of interacting particles (the word "particle" includes both nanoparticles and aggregates).

Chapter 4 presents the impact of including electrostatic forces into the aggregation model from Chapter 3. Electrostatic forces between particles occur because of the electric double-layer that forms around a particle in an electrolyte. The electrostatic forces are added into the mass transport coefficient calculations giving the frequency of collisions between particles. Measurement of the zeta-potential of nZVI depending on the pH of the solution is also presented here. The surface charge is quantifiable from the measured zeta-potential. The effect of including the surface charge in the model of the aggregation rate is considered at the end of this chapter.

Chapter 5 is concerned with a sectional model of the computation of aggregation between particles. The aggregation can be viewed as first-order kinetic reactions when two particles collide and result in one particle. A huge number of reactions would have to be computed to describe an aggregation between every different nanoparticle and aggregate. Therefore, the particles are categorized into "sections" according to their size. The reactions between these sections are calculated instead of between the individual particles. Modified mass transport coefficients for this computation are defined in this chapter. Using these modified mass transport coefficients, a time variation in particle size sections (PSS) can be computed and the dynamics of particle aggregation over time can be seen. The computation was very time-consuming so an average was taken of the mass transport coefficients of PSS to compute changes in the number, volume, or surface area of particles in every PSS. The surface area and number of particles change over time but the overall volume of the particles is constant. Computation of the sum of changes in the volume of all the PSS acts as verification of the computation.

Chapter 6 describes the magnetic forces between magnetic iron nanoparticles. First, the magnetic forces between two single nanoparticles are derived, then, the magnetic field around an aggregate of magnetic nanoparticles is examined. The magnetic force between particles strongly depends on the structure that the nanoparticles take in the aggregates. The quantity "Limit distance" is introduced in this chapter. This quantity is an instrument for the estimation of the magnitude of the effect of a magnetic force on the aggregation rate.

Chapter 7 studies the aggregate structures that nanoparticles in the aggregate are likely to take. Unstructured models of aggregates were examined where the positions of nanoparticles are random and also structured models of aggregates where nanoparticles in the aggregates form a pattern or "constellation", such as a chain or a cube, etc. For all the chosen cases the sizes of the magnetic forces were calculated and a decision was made as to whether it was a realistic value or not. Another way of judging a structure of an aggregate that was researched was a computation of the interaction energies between nanoparticles in different constellations of aggregates. The results of the research are summarized in this chapter.

Chapter 8 presents a study of how to accelerate these computations. Computation of the magnetic force between two aggregates is time-consuming because the overall magnetic force is computed as a sum of the magnetic forces between every single nanoparticle from the first aggregate and every single nanoparticle from the second aggregate. A computation of the magnetic force between two "average aggregates" is proposed where the magnetic moment vector of the averaged aggregate is given by the sum of magnetic vectors of all the nanoparticles creating the aggregate. The results generated using the accurate summation method were compared against the faster averaging method. Thus when it is possible to use the averaging method without incurring a large error was estimated.

Chapter 9 provides an overview of computing the limit distance depending not only on the magnetic field around aggregates, but also on the electrostatic field. It is another way of computing the effect of electrostatic forces between particles on the aggregation rate. This way is better when particles are magnetic and have a non-zero surface charge. Repulsive electrostatic forces and attractive magnetic forces act between these particles and the strength of repulsion or attraction depends on the distance between the particles. The limit distance gives a distance from a particle at which the repulsive and attractive forces are equal.

Chapter 10 describes inclusion of the limit distance computation into the mass transport coefficients (MTC) that give the frequency of collisions between particles. Now, the MTCs compute the aggregation rate between particles that oscillate, settle, drift in water, attract each other due to magnetic forces and repulse each other due to their surface charge. A comparison of MTC computations using the old model without the inclusion of electrostatic and magnetic forces and using the new model including the forces is described here.

Chapter 11 is concerned with the conversion of the aggregation model into first-order reactions which are usable in particle transport software. The reactions describe collisions of particles from two sections (either different or the same one) that lead to a single particle formation (that falls into the larger of the two sections or into the section immediately following). Changes in the number of particles in sections leads to a change in particle transport.

Chapter 12 gives some simulations of nanoparticle transport and aggregation in order to verify the theoretical aggregation models. Firstly, the model from Chapter 4 is verified. The model describes the aggregation of nanoparticles caused by their oscillation, different velocities during sedimentation and drifting in water, and their mutual repulsion due to electrostatic forces. Bentonite colloidal nanoparticles were chosen as an example of non-magnetic nanoparticles with non-zero surface charge. Secondly, simulation of migration experiments of one-dimensional nZVI particles were performed. This simulation served to verify the aggregation model with inclusion of both magnetic and electrostatic forces. Thirdly, simulations of a real migration of nZVI in the ground were examined, when the nanoparticles were used for remediation of a real area.

Chapter 13 provides a review of the overall contributions of this thesis and provides some ideas for future work.

### Chapter 2

# Characterization and properties of nZVI

#### 2.1 nZVI characterization

Zero-valent iron nanoparticles (nZVI) are spherical particles with size in tens and hundreds of nanometers. They have become quite a popular choice for the treatment of hazardous and toxic waste and for the remediation of contaminated sites. nZVI technology is widely used, mainly in North America and Europe [17]. In the U.S. alone, more than 20 projects have been completed since 2001. In Europe, nZVI was first used in the Czech Republic in 2004. Since then, research groups all over the world have been examining nZVI synthesis, reactivity, stabilization, etc.

Many studies have demonstrated the effect of zero-valent iron nanoparticles for the transformation of halogenated organic contaminants and heavy metals [18–21]. In addition, several studies have demonstrated that zero-valent iron is effective in stabilizing or destroying the hosts of pollutants due to its highly reducing character [22]. Therefore, zero-valent iron (ZVI) is used as one of the most reactive materials in permeable reactive barrier (PRB) technology [23]. At nanoscales, ZVI usability extends even further. The specific surface area of nZVI increases dramatically and so the surface reactivity is higher [24]. Laboratory studies have confirmed that nZVI can destroy, stabilize or transform halogenated hydrocarbons, carbon tetrachloride, polychlorinated biphenyls (PCBs), chlorinated organic solvents, organochlorine pesticides and many more pollutants [4,6,25–28].

#### 2.2 nZVI synthesis

nZVI can be prepared in many ways. A nice summary of nZVI preparation was published in [5, 22]. There are two general strategies for preparing nanoscale particles. One is to start with larger size (i.e., granular or microscale) materials and generate the nanoparticles by mechanical and/or chemical steps including milling, etching, and/or machining. The other is to "grow" the nanostructures atom-by-atom or molecule-by-molecule via chemical synthesis, self-assembly, positional assembly, etc. Both approaches have been successfully applied in the preparation of nZVI nanoparticles. For example, nZVI has been prepared by the reduction of goethite and hematite particles using hydrogen gas at elevated temperatures [29], and also by the reduction of ferric (Fe(III)) or ferrous (Fe(II)) salts using sodium borohydride in an aqueous media [11]. Transmission electron microscopy (TEM) images of different iron nanoparticles are shown in Fig. 2.1.



FIGURE 2.1: Transmission electron microscopy (TEM) images of different iron nanoparticles

(A) nZVI synthesized by the reduction of aqueous  $Fe^{2+}$  using sodium borohydride [30]; (B) nanoscale magnetite, purchased from SigmaAldrich (PubChem Substance ID: 24882829) [31]; (C) NANOFER STAR, purchased from NANO IRON, s.r.o. [32]; (D) nZVI synthesized by the carbothermal reduction of aqueous  $Fe^{2+}$  [33]; (E) nZVI synthesized by the reduction of aqueous  $Fe^{2+}$  using green tea polyphenols [34]; and (F) nZVI synthesized by the reduction of aqueous  $Fe^{2+}$  using sodium borohydride then annealed under vacuum (at least 10-6 mbar) at 500 C for 24 h [35]. Source: [36].

At the Technical University of Liberec (TUL), two types of nZVI are used for experiments: RNIP (Reactive Nanoscale Iron Particles) produced by Toda Kogyo Corp. (Onoda, Japan) [6] and nanoparticles NANOFER, produced by NANO IRON s.r.o. (Rajhrad, Czech Republic) [7]. Toda RNIP is a crystalline form of nanoiron made from the gas phase reduction of FeOOH. It has an average size of 70 nm with a surface area of 29 m<sup>2</sup>/g. The nanoparticles are coated with polymaleic or polyacrylic acid [6]. A TEM

image of RNIP that has been published in [6] is shown in Fig. 2.2. NANOFER are nZVI produced from nanosized ferrihydrite. The nanoparticles are stored in an inert atmosphere before surface coating with different chemicals. NANOFER 25 is an extremely reactive aqueous dispersion of Fe(0) nanoparticles stabilized solely by an inorganic modifier. The product exhibits an extremely high reactivity but is characterized by a higher degree of aggregation and faster sedimentation. It has an average size of approximately 50 nm with a surface area of 25 m<sup>2</sup>/g. The product is stored and delivered in the form of an aqueous dispersion [37]. TEM image of RNIP published in [37] is in Fig. 2.3.



FIGURE 2.2: TEM images of RNIP

(A) Low magnification image of as-received sample. (B) Higher resolution image of irregularly shaped metal particle. (C) Higher resolution image of oxide shell around metal particle. (D) Low resolution image of flash-dried sample. Source: [6].



FIGURE 2.3: TEM images of nanoparticles of NANOFER 25 stabilized by nanostructural inorganic shell Source: [37].

#### 2.3 nZVI interaction

The nZVI are valuable for their high reactivity with pollutants. However, the nZVI particles are very unstable and that leads to rapid aggregation (Fig. 2.4) as a result of attractive magnetic and van der Waals forces [6]. Furthermore, the size and/or surface



(a) One iron nanoparticle

(b) Aggregated nanoparticles

FIGURE 2.4: TEM scan of one iron nanoparticles Source: [11].

charge of the aggregates result in a very high deposition on porous media grains, which severely limits its transport in porous media [14, 38]. Surface modification of nZVI in order to preserve its transportability is the subject of many studies [39–42]. Stabilization by polyelectrolytes, polymers and surfactants that provides steric and electrostatic stabilization acting against the particle-particle attractive forces significantly improves its migration through porous media [38, 39, 43]. The ionic strength of groundwater may influence the extent of particle-particle electrostatic interactions and influence transport [44–46] as might high concentrations of particles in groundwater [14].

The iron particles corrode in groundwater which causes a change in the surface charge as well as a change in the rate of aggregation of nZVI [47]. In [48], XRD (X-ray diffraction) and SEM results revealed that nZVI gradually converts to magnetite/maghemite corrosion products. The particles have a core-shell structure (Fig. 2.5) where the core is zero-valent iron and the shell consists of iron oxides. This significantly affects the rate of aggregation [5, 12–14]. For simplicity, it was supposed that the iron particle is ferromagnetic in this work. In [14], RNIP, that are used in TUL experiments, turned out to behave as single-domain magnetic particles. NANOFER particles were measured by magnetometer MPMS XL, a piece of equipment based on the SQUID effect (Superconducting quantum interference device), owned by the Palacký University Olomouc, Czech Republic. The iron particles were ferromagnetic. A hysteresis loop of the iron particles measured by SQUID is shown in Fig. 2.6.

In summary, nZVI are reactive iron nanoparticles used for remediation. The particles corrode, aggregate, and settle in groundwater because of the high particle-particle and particle-collector electrostatic, magnetic and van der Waals interactions.



FIGURE 2.5: Schematic diagram of nZVI core-shell structure Source: [49].



FIGURE 2.6: Hysteresis loop of the zero-valent iron nanoparticles for temperature of 300 K Data was obtained by magnetometer MPMS XL by Jiří Tuček at the Palacký University Olomouc.

### Chapter 3

### Aggregation of nZVI

#### 3.1 Particle size distribution measurement

The particles in groundwater aggregate easily. They create clumps of particles up to the size of several  $\mu$ m [14] that cohere so reduce migration of particles through pores in the ground. The aggregation of particles is proven by experiments described in many articles. In [11], particle size, size distribution and surface composition were characterized by transmission electron microscopy (TEM), X-ray diffraction, high-resolution X-ray photoelectron spectroscopy, X-ray absorption near the edge of the structure, and acoustic/electroacoustic spectrometry. In [6], characterization of iron nanoparticles using TEM according to methods of its preparation was performed. In [14], the type of aggregation according to the initial concentration of iron nanoparticles is studied using dynamic light scattering, optical microscopy, and sedimentation measurements (Fig. 3.1).

Measurement of size distribution over time is a good indicator of nZVI instability. At TUL, a piece of equipment called Zetasizer Nano ZS (Malvern Instruments Inc, UK) was used for such measurements [50]. The Zetasizer uses dynamic light scattering (DLS) to



FIGURE 3.1: In-situ micrographs with a light microscope illustrating aggregation kinetics of the dispersion of RNIP

Measured at 60 mg/L (pH 7.4,  $\Phi = 10^{-5.02}$ ): (a) time (t)=1 min; (b) t = 3.75 min; (c) t = 9 min; and (d) t = 30 min. Scale bar = 25  $\mu m$ . Source: [14].

measure size distribution and electrophoretic light scattering (ELS) for measuring zeta potential. The specification of ELS methodology is in Section 4.2. The specification of DLS for measuring nZVI size distribution (Tab. 3.1, 3.2), follows.

Concentration	Time	$d_p$ I.	$d_p$ II.	$d_p$ III.
[mg/L]	[minute]	[nm]	[nm]	[nm]
1	0	88	-	-
	6	221	-	-
	17	149	750	-
	34	71	385	4940
10	0	122	-	-
	6	142	-	-
	17	127	521	-
	46	161	444	5405
100	0	519	-	-
	6	704	-	-
	29	158	877	5356
	46	719	-	-
300	0	492	-	-
	6	793	-	-
	17	145	1142	-
	46	481	5321	-

TABLE 3.1: RNIP size distribution over time  $d_p$  refers to the averaged hydrodynamic diameter. Values were measured using Zetasizer Malvern equipment. Source: [8].

Particles in dispersion undergo Brownian motion due to random collisions between the solvent molecules and the particles. As a consequence of this particle motion, light scattering from the particle ensemble fluctuates with time. In DLS, the autocorrelation of these temporal fluctuations in scattered light intensity is evaluated to determine the intensity weighted average diffusion coefficient  $D \, [m^2/s]$  of the particles [51]. The software of the Zetasizer equipment computes an averaged hydrodynamic diameter  $d_p$  using the Stokes-Einstein equation:  $D = k_B T/3\pi\eta d_p$ , where  $k_B$  is the Boltzmann constant, T is the absolute temperature, and  $\eta$  is the viscosity of the medium. However, the equipment is calibrated using latex particles that are monodisperse spherical particles with low sedimentation and reactivity (no attractive magnetic forces). Furthermore, the measurement is taken without flowing - in a closed static cell. That allows sedimentation of the large aggregates while measuring over time. Therefore, the measurements of size distribution are useful for observing the trend in changes in particle size. Absolute values of particle sizes are not relevant.

At TUL, two types of nZVI were measured using the Zetasizer Malvern equipment: RNIP (type 10E) and NANOFER (type 25S). The measured values of particle size dispersion of nZVI have already been published in J. Nosek's Thesis [8]. In this work, there is a table of measured data for both types (Tables 3.1, 3.2). An example of the measured
Concentration	Time	$d_n$ I.	$d_{n}$ II.	$d_n$ III.
[mg/L]	[minute]	[nm]	[nm]	[nm]
5	0	85	-	-
	6	137	-	-
	40	267	5200	-
	46	148	386	-
10	0	122	-	-
	6	195	461	-
	29	187	469	-
	46	114	363	-
100	0	106	-	-
	14	88	1028	-
	31	108	998	-
	42	121	906	-
300	0	495	-	-
	6	94	1090	-
	23	123	1016	5383
	46	111	507	-

TABLE 3.2: NANOFER size distribution in time

Symbol  $d_p$  stands for averaged hydrodynamic diameter. Values were measured by Zetasizer Malvern equipment. Source: [8].

data of RNIP size distribution with concentration of 1 mg/L over time is given in Fig. 3.1.

It is hard to say which type of nZVI is better in terms of size distribution. According to the results of the size distribution measurement (Tab. 3.1, 3.2), the NANOFER appears to be slightly better when values of concentrations of 10 and 100 mg/L are compared. However, the reason almost no big aggregates were recorded may be due to faster sedimentation (in this case, RNIP would be better in terms of size distribution).

## 3.2 Mathematical model of aggregation

This chapter was presented in [9].

The aggregation of particles is caused by many processes that generally occur during particle migration. The decrease in mobility can be formulated by a rate of aggregation given by the mass transport coefficients (MTC)  $\beta$  [m<sup>3</sup>/s]. These coefficients represent a frequency of collisions between particles. Due to the attractive Van der Waals forces, collisions lead to aggregation of the particles (the particles remain adherent). Models of aggregation of small particles have been published in many articles (e.g. [3,10,52]). These are mostly based on the publications [1], [2](GL).



FIGURE 3.2: Behaviour of RNIP size distribution over time Source: [8].

The coefficients give a probability  $P_{ij}$  of the creation of an aggregate from particle iand particle j together with numbers  $n_i$ ,  $n_j$  of particles i and particles j in one m<sup>3</sup> (3.1).  $n_i$  can be also called particle concentration in this work. The probability means a frequency of collision between i and j particles. Particle i means the aggregate created from i elementary nanoparticles. It was published in [3].

$$P_{ij} = \beta_{ij} \, n_i \, n_j, \tag{3.1}$$

$$\beta_{ij} = \beta_{ij}^1 + \beta_{ij}^2 + \beta_{ij}^3. \tag{3.2}$$

Coefficient  $\beta_{ij}^1$  is the mass transport coefficient of heat fluctuation, coefficient  $\beta_{ij}^2$  is the mass transport coefficient for velocity gradients, and the coefficient  $\beta_{ij}^3$  is the mass transport coefficient of aggregation caused by gravity. The concept is adopted from [3]. A detailed derivation summary of the MTC was presented in author's diploma thesis [9]. The goal of this thesis is to present an unified text, therefore the derivation of MTC is presented here, too.

#### 3.2.1 Brownian motion

In the case of small iron nanoparticles (< 100 nm) [53], the temperature fluctuation of particles has a significant effect on particle aggregation [54]. Brownian diffusion causes a random movement of the particles and it facilitates aggregation. Brownian diffusion of particles in a fluid causes irregular movement of the particles - the higher the temperature, the faster the random movement and the higher the probability of particle aggregation. The probability of aggregation is derived from a flux of particles (FP is a particle in the flux) around one observed particle (OP). The observed area around OP is a sphere with radius equal to the sum of radii  $a_{fp}$  and  $a_{op}$  of particles FP and OP, respectively:  $R = a_{fp} + a_{op}$ .

We assess the probability of aggregation of particles FP and OP from the flux J of FP through an observed volume (OV) around the OP with the radius R.

$$J = \int_{S} \vec{j} d\vec{S}, \tag{3.3}$$

where flux density  $\vec{j}$  is equal to

$$\vec{j} = D \cdot \nabla n. \tag{3.4}$$

The diffusion coefficient D is equal to [54]

$$D = \frac{k_B T}{f},\tag{3.5}$$

where f is the friction coefficient,  $k_B$  is the Boltzmann constant, and T is the temperature. Smoluchowski [2] derived the value of  $\nabla n$  assuming a symmetrical distribution of FP concentration in time  $\tau$  and zero concentration of FP  $n_i$  inside the OV. On the surface of OV, where r = R, is  $\nabla n$  equal to:

$$\frac{\partial n(\tau)}{\partial r} = n_i \left[ \frac{1}{R} + \frac{1}{\sqrt{\pi D\tau}} \right]. \tag{3.6}$$

From eq. (3.3), (3.4), (3.5), (3.6):

$$J(\tau) = \frac{k_B T}{f} S \frac{n_i}{R} \left[ 1 + \frac{R}{\sqrt{\pi D\tau}} \right], \qquad (3.7)$$

where S is the surface of OV:

$$S = 4\pi R^2. \tag{3.8}$$

The number  $N_p$  of particles FP passing through the OS over time t:

$$N_p = \int_0^t J(\tau) d\tau.$$
(3.9)

After substituting the equations (3.7), (3.8) into eq. (3.9) and integration:

$$N_p = 4\pi R D n_i \left[ t + \frac{2R\sqrt{t}}{\sqrt{D\pi}} \right].$$
(3.10)

On the condition  $t \gg \frac{R^2}{D}$ , the last term in the expression can be neglected (3.10). Then

$$N_p \cong 4\pi R D n_i t.$$

For very small  $n_i$  is  $N_p \ll 1$ . Then  $N_p$  can be understood as the probability of a collision of one OP with any FP. Probability of a collision of any OP with any FP can be expressed as the product of  $N_p$  and OP concentration  $n_j$ . The same collision can appear as a collision of any FP with any OP depending on the diffusion coefficient of OP. The frequency of collisions of particles FP and OP adjusting for time is:

$$P_{ij} = 4\pi R (D_i + D_j) n_i n_j, (3.11)$$

where  $D_i$  is the diffusion coefficient of FP and  $D_j$  is the diffusion coefficient of OP. We can define the mass transport coefficient for Brownian motion by comparing eq. (3.11) and (3.1):

$$\beta_{ij}^1 = 4\pi R (D_i + D_j). \tag{3.12}$$

The distance R can be expressed as  $\frac{d_i+d_j}{2}$ , where  $d_i$  is the diameter of the particle i (FP). The friction coefficient is according to Stokes' law (for the frictional force exerted on spherical objects with very small Reynolds numbers in a continuous viscous fluid):

$$f_i = 3\pi\eta d_i,\tag{3.13}$$

where  $\eta$  is the dynamic viscosity of the medium. From eq. (3.5), (3.12), (3.13), the mass transport coefficient for Brownian diffusion [3] giving the probability that one FP is situated in the observed volume around one OP is:

$$\beta_{ij}^{1} = \frac{2k_B T}{3\eta} \frac{(d_i + d_j)^2}{d_i d_j}.$$
(3.14)

Fig. 4.6(a) represents the MTC of Brownian motion depending on aggregated particles size.

### 3.2.2 Velocity gradients

Another process causing aggregation is the drifting of nanoparticles in water. Water flowing through a pore of soil has a velocity profile. In the middle of the pore the velocity of water is highest. Since the particles have different velocities, according to their location in the flow, the particles can move close together and create an aggregate.

Again, we will chose a particle (OP) with smaller velocity of drifting and observe number of particles (FP) in flux around OP. The observed volume (OV) is a sphere around the OP with radius  $R = a_{fp} + a_{op}$ . Sketch of OP, FP, and observed sphere is in Fig. 3.3.



FIGURE 3.3: Sketch of observed and in flux particles for derivation of MTC of velocity gradients

Velocity of OP is V. FP is in distance z normal to the flow. Velocity of FP is then  $v + \frac{\partial v}{\partial n}z$ . Frequency of collision of OP with FP is equal to the flux q of FP proportional to number of FP  $n_i$ .

$$q = S \cdot \Delta v \cdot n_i,$$

where  $\Delta v = \frac{\partial v}{\partial n} z$  supposing  $\frac{\partial v}{\partial n}$  nearly constant for small dS:

$$dq = dS \cdot \Delta v \cdot n_i,$$
$$dS = ldz,$$
$$l = 2\sqrt{(R^2 - z^2)},$$

The flux of particles dq is integrated over two identical semicircles that represent a section of the observed volume.

$$q = \int_0^R \frac{\partial v}{\partial n} z \cdot 2\sqrt{(R^2 - z^2)} dz.$$
$$q = \frac{4}{3} \frac{\partial v}{\partial n} R^3.$$
(3.15)

Let us denote  $\frac{\partial v}{\partial n}$  as G representing the velocity gradient of the liquid [1].

The mass transport coefficient for the velocity gradients of particles [3] is

$$\beta_{ij}^2 = \frac{1}{6} G \left( d_i + d_j \right)^3. \tag{3.16}$$

Fig. 4.7(a) represents the MTC of the velocity gradients depending on the aggregated particles size.

#### 3.2.3 Sedimentation

Particles settle due to gravitational forces. The velocity of the sedimentation varies for different aggregates depending on their size, so particles can move closer together and aggregate. Gravitational force  $F_{grav}$ , buoyant force  $F_{buo}$ , and frictional force  $F_{fric}$  act on the particle during sedimentation.

$$F_{grav} = m_j g; \tag{3.17}$$

$$F_{buo} = \varrho V_j g; \tag{3.18}$$

$$F_{fric} = 6\pi \eta a_j v_j, \tag{3.19}$$

where  $m_j$  is the weight of particle j, g is the gravitational acceleration,  $\rho$  is density of the liquid,  $V_j$  is the volume of the particle j,  $\eta$  is the viscosity of the liquid,  $a_j$  is the radius of the particle j ( $a_j = d_j/2$ ),  $v_j$  is the velocity of the particle j. Again, there is a flux of particles falling around the observed particle. The OV is again a sphere around the OP with radius  $R = a_{fp} + a_{op}$ . A sketch of OP, FP, and the observed sphere is shown in Fig. 3.4.



FIGURE 3.4: Sketch of the observed and influx particles for the derivation of MTC of sedimentation

FIGURE 3.5: The balance of forces acting on particles during sedimentation

Derivation of MTC is based on the flux q of FP around OP. Collision of OP with FP is equal to the flux q of FP proportional to the FP concentration  $n_i$ .

$$q = S \cdot \Delta v \cdot n_i, \tag{3.20}$$
$$\Delta v = v_j - v_i,$$

,

Using the balance of powers (Fig. 3.5) and eq. (3.17), (3.18), and (3.19):

$$m_i g = \varrho V_i g + 6\pi \eta a_i v_i,$$
$$\Delta v = v_i - v_j = \frac{g}{18\eta} (\varrho_p - \varrho) |d_i^2 - d_j^2|$$

where  $\rho$  is the density of the medium, and  $\rho_p$  is the density of the aggregating particles.

After substitution in the equation (3.20) and expressing of surface area and radius of the observed sphere, the mass transport coefficient for the sedimentation [3] is

$$\beta_{ij}^3 = \frac{\pi g}{72 \eta} \left( \varrho_p - \varrho \right) \left( d_i + d_j \right)^2 |d_i^2 - d_j^2|.$$
(3.21)

Fig. 4.8(a) represents the MTC of sedimentation depending on aggregated particles size.

#### 3.2.4 Comparison of MTC

A statistical assessment of the importance of particular processes to the creation of aggregates was carried out. MTC were computed using eq. (3.14), (3.16), (3.21), with the following values: the radius of one nanoparticle a = 25 nm, the density of particles  $\rho_p = 6700 \text{ kg/m}^3$ , the temperature T = 300 K, the dynamic viscosity of water  $\eta = 10^{-3}$  Pa·s, the density of water  $\rho = 1000 \text{ kg/m}^3$ , velocity gradient  $G = 50 \text{ s}^{-1}$ .

The velocity gradient G was computed as the average value  $\langle G \rangle$  supposing the circular symmetry of the velocity profile in a pore cross-section.

$$\langle G \rangle = \frac{1}{S} \int_{S} \frac{\partial v}{\partial r} dS,$$
 (3.22)

where  $\frac{\partial v}{\partial r}$  is the velocity gradient in the radial direction r, S is the area of the pore cross-section:

$$S = \pi R^2, \ dS = 2\pi r dr.$$
 (3.23)

The instantaneous value of G is derived from the parabolic profile of the velocity of flowing water.

$$v = v_{max} \left[ 1 - \left(\frac{r}{R}\right)^2 \right], \qquad (3.24)$$

where  $v_{max}$  is the maximal velocity in the centre of the pore:  $v(0) = v_{max}$ , v(R) = 0.

$$\frac{\partial v}{\partial r} = -\frac{2v_{max}}{R^2}r.$$
(3.25)

From the eq. (3.22), (3.23), (3.25):

$$\langle G \rangle = \frac{1}{\pi R^2} \int_R^0 -\frac{2v_{max}}{R^2} r 2\pi r dr = \frac{4}{3} \frac{v_{max}}{R}.$$
 (3.26)

Usually the average velocity or the flow in a porous medium is known.  $v_{max}$  can be calculated from the average velocity  $\langle v \rangle$  again assuming the circular symmetry of the velocity profile in the pore cross-section:

$$\langle v \rangle = \frac{1}{S} \int_0^R v dS. \tag{3.27}$$

From the eq. (3.27), (3.23), (3.24):

$$\langle v \rangle = \frac{2v_{max}}{R^2} \int_0^R \left[ 1 - \left(\frac{r}{R}\right)^2 \right] dS = \frac{v_{max}}{2}.$$
 (3.28)

If we denote the radius of the pore  $a_p$ , then the average velocity gradient  $\langle G \rangle$  is

$$\langle G \rangle = \frac{8}{3} \frac{\langle v \rangle}{a_p} = \frac{8}{3} \frac{q}{\phi S a_p},\tag{3.29}$$

where  $\langle v \rangle$  is the average velocity of dispersion, q is the flux of the dispersion through a normal area of the section S.

The radius of the pore is unknown but an approximate value can be computed using the interpolation formula giving the relation between radius of a sand grain  $a_g$  and radius of a pore  $a_p$  derived in [55]:

$$a_p = (1.1969 \cdot \phi - 0.1557)a_q, \tag{3.30}$$

where  $\phi$  is the porosity of the soil. According to [56], the average size of the sand grains (radius)  $a_g = 0.0625-2$  mm. The pore diameter of a sand porous medium is computed by the eq. (3.30)  $a_p = 19-622 \ \mu\text{m}$ . The velocity gradient is calculated using the values of flux  $q = 2.75 \cdot 10^{-6} \text{ m}^3/\text{s}$ , porosity  $\phi = 0.39$ , and section  $S = 7.5 \cdot 10^{-3} \text{ m}^2$ , which are the real values of an nZVI transport experiment through a sand column, described in [8] (CL) or in the section 12.2. The average magnitude of the velocity gradient is then G $= 4-132 \text{ s}^{-1}$ . The value  $G = 50 \text{ s}^{-1}$  is taken as it corresponds to the fine sand grains for consequent computations.

i [1]	j [1]	$\beta_{ij}^{1}  [\mathrm{m^{3}s^{-1}}]$	$\beta_{ij}^2  [{\rm m}^3 {\rm s}^{-1}]$	$\beta_{ij}^3  [{\rm m}^3 {\rm s}^{-1}]$
1	1	$1.0 \cdot 10^{-17}$	$2.2 \cdot 10^{-20}$	0
1	10	$1.3 \cdot 10^{-17}$	$8.8 \cdot 10^{-20}$	$5.9 \cdot 10^{-22}$
1	$10^{2}$	$1.9 \cdot 10^{-17}$	$5.0 \cdot 10^{-19}$	$1.0 \cdot 10^{-20}$
1	$10^{3}$	$3.3 \cdot 10^{-17}$	$3.7 \cdot 10^{-18}$	$2.0 \cdot 10^{-19}$
1	$10^{4}$	$6.5 \cdot 10^{-17}$	$3.2 \cdot 10^{-17}$	$3.8 \cdot 10^{-18}$
1	$10^{5}$	$1.3 \cdot 10^{-16}$	$3.0 \cdot 10^{-16}$	$7.9 \cdot 10^{-17}$
1	$10^{6}$	$2.8 \cdot 10^{-16}$	$3.0 \cdot 10^{-15}$	$1.7 \cdot 10^{-15}$
1	$10^{7}$	$6.0 \cdot 10^{-16}$	$2.8 \cdot 10^{-14}$	$3.5 \cdot 10^{-14}$
10	10	$1.1 \cdot 10^{-17}$	$2.2 \cdot 10^{-19}$	0
$10^{2}$	$10^{2}$	$1.3 \cdot 10^{-17}$	$8.8 \cdot 10^{-19}$	$1.2 \cdot 10^{-20}$
$10^{3}$	$10^{3}$	$1.1 \cdot 10^{-17}$	$2.2 \cdot 10^{-17}$	$5.9 \cdot 10^{-18}$
$10^{4}$	$10^{4}$	$1.3 \cdot 10^{-17}$	$8.8 \cdot 10^{-17}$	0

TABLE 3.3: The MTC of Brownian diffusion, velocity gradients, and sedimentation, for different sizes of aggregates

The Table 3.3 shows that Brownian diffusion is most significant for the smallest particles. Sedimentation is most significant when the difference between sizes of the aggregates is largest. It is a consequence of the fact that the difference between the velocities of the particles is largest. The velocity gradients depend on the pore size. When the size of pores is small, aggregation is most influenced by the velocity gradient, if the difference between the particles is large. The mass transport coefficient for the velocity gradients can be quantified for the case of a small pore size and a large flux, for example G = 50 s<sup>-1</sup>,  $q = 2.75 \cdot 10^{-6}$  m<sup>3</sup>/s,  $\phi = 0.39$ . In other cases, the mass transport coefficient would be much smaller than the others.

## Chapter 4

## Inclusion of Electrostatic forces into MTC

This chapter was derived in author's diploma thesis [9] and submitted to [57].

## 4.1 Electrostatic properties of iron nanoparticles

Particles in an electrolyte have a surface charge density  $\sigma$  with dimension [C/m<sup>2</sup>], depending on the pH and ionic strength of water. If all particles have the same polarity, the particles repel each other due to the repulsive electrostatic forces between them. This affects the rate of aggregation of the particles. The aggregation model based on the sedimentation, velocity gradients and Brownian diffusion is not sufficient for the description of nZVI aggregation. Therefore, the influence of electrostatic forces was added into the calculation of the mass transport coefficients (section 4.3).

According to conventional DLVO (Derjaguin, Landau, Verwey, Overbeek) theory [58,59], the net interaction energy between particles is the sum of Van der Waals attraction and electrostatic double layer repulsion. The electric double layer is the layer surrounding a particle in the dispersed phase and including the ions adsorbed onto the particle surface and a film of the counter-charged dispersion medium (Fig.4.1) [60].

When a colloidal particle moves in a dispersion medium, a layer of the surrounding liquid remains attached to the particle. The boundary of this layer is called the slipping plane (shear plane). The value of the electric potential at the slipping plane is called the zeta potential, which is a measurable parameter and helps to determine the surface charge of particles. Particles with zeta potential values greater than +30 mV and less than -30 mV are considered stable. The closer the zeta potential value is to the PZC (point of zero charge), the less stable the particles are and more likely to aggregate [61].



FIGURE 4.1: Electric double layer schema Source: [60].

The surface charge density  $\sigma$  can be determined by zeta potential (potential  $\Psi$  in the equation) as follows [62]:

$$\sigma = \sqrt{8RT\varepsilon\varepsilon_0 c10^3} \sinh\frac{Z\Psi F}{2R_m T},\tag{4.1}$$

where  $R_m$  is the molar gas constant, T is the absolute temperature,  $\varepsilon$  is the dielectric constant of water,  $\varepsilon_0$  is the permittivity of the free space, c is the molar concentration of the electrolyte, Z is the charge number, F is Faraday's constant. When the potential is low, the last equation is approximately

$$\sigma = \varepsilon \varepsilon_0 \kappa \Psi, \tag{4.2}$$

where

$$\kappa = \sqrt{\frac{2F^2 I 10^3}{\varepsilon \varepsilon_0 R_m T}}.$$
(4.3)

I is the ionic strength and  $\kappa$  is Debye parameter.

Measurements of the zeta potential of nZVI are presented in the next section.



FIGURE 4.2: Zeta potential of nZVI as a function of solution pH Source: [11].

## 4.2 Zeta potential measurement

The zeta potential of nZVI has been measured and published in many research papers, e.g. in [11], where the zeta potential, iso-electric point (IEP, the point where zeta potential is equal to zero), and solution Eh and pH were presented (Fig. 4.2). It was shown that IEP is independent of particle concentration (when no inert electrolyte was added).

However, nZVI differs according to the process of production. Therefore we also measured the zeta potential of particles in dispersion as a function of dispersion pH. In order to measure the zeta potential, the Zetasizer Nano ZS equipment (Malvern Instruments Inc, UK) was used. The Zetasizer utilizes electrophoretic light scattering (ELS), also known as laser Doppler electrophoresis (LDE) or laser Doppler velocimetry (LDV), to measure zeta potential.

When an electric field is applied across the dispersion, charged particles in the dispersion will move toward the electrode of the opposite polarity. This phenomenon is called electrophoresis. If a laser beam is passed through the sample undergoing electrophoresis, the scattered light from the moving particles will be frequency shifted. By measuring the frequency shift, electrophoretic mobility can be determined given the laser wavelength and the scattering angle. The zeta potential is then calculated using the Smoluchowski equation

$$\zeta = \frac{\eta \mu_e}{\varepsilon \varepsilon_r}$$

where  $\zeta$  is the zeta potential,  $\eta$  is the dynamic viscosity of the liquid,  $\mu_e$  is the electrophoretic mobility,  $\varepsilon$  is the dielectric constant of the liquid, and  $\varepsilon_0$  is the permittivity of the free space [51].

The dependence of  $\zeta$  potential on the pH of the RNIP (Toda) dispersion was measured and is recorded in Fig. 4.3. A point of zero charge for the TODA particles is between pH



FIGURE 4.3: Zeta potential of nZVI as a function of solution pH, measured by Malvern Zetasizer

6 and 7. Zero-valent iron resulted in an alkaline reaction in water, so the measurement was taken using higher pH values only.

The pH of dispersion was prepared by adding of HCl or NaOH. The measured values of zeta potential of nZVI are shown in Tab. 4.1. It can be seen that the addition of nZVI changes the pH of dispersion in the table, as well as the oxidation/reduction potential. The table also shows the surface charge density computed by using the measured zeta potential.

Sample	pH before nZVI	pH after nZVI	Redox	Zeta potential	Surface charge
number	application [-]	application [-]	potential [mV]	[mV]	density $[C/m^2]$
1	1.9	7.2	-345	-6.5	$-4.7 \cdot 10^{-06}$
2	2.9	8.2	-404	-13.7	$-1.0 \cdot 10^{-05}$
3	3.6	10.4	-490	-24.8	$-1.8 \cdot 10^{-05}$
4	6.3	10.6	-480	-29.4	$-2.2 \cdot 10^{-05}$
5	6.3	10.6	-480	-29.4	$-2.2 \cdot 10^{-05}$
6	10.9	11.1	-477	-33.0	$-2.4 \cdot 10^{-05}$
7	12.1	11.9	-487	-47.2	$-3.5 \cdot 10^{-05}$
8	13.0	12.8	-614	-30.0	$-2.5 \cdot 10^{-05}$

TABLE 4.1: The measured values of pH, zeta potential, oxidation/reduction potential of nZVI  $\,$ 

For consequent computations, surface charge density values were calculated from chosen values of the zeta potential: 1.25 mV corresponding to  $\sigma = 10^{-6}$  Cm<sup>-2</sup> and 30 mV

corresponding to  $\sigma = 2.5 \cdot 10^{-5} \text{ Cm}^{-2}$ . These values are two extremes. For the value of 1.25 mV, the surface charge of the particles is close to the IEP, electrostatic forces have little influence and the particles aggregate. For the value of 30 mV, the surface charge causes stabilization of aggregating particles.

## 4.3 A Modification of the Mass transport coefficients

The magnitude of the surface charge density gives a long-range repulsive electrostatic force between particles. We added the force into the mass transport coefficients for all three processes ( $\beta^1$  (3.14),  $\beta^2$  (3.16), and  $\beta^3$  (3.21)). The electrostatic force  $F_c$  is given by Coulomb's law

$$F_c = \frac{1}{4\pi\varepsilon_0\varepsilon} \frac{Q_i Q_j}{R^2} \tag{4.4}$$

where  $\varepsilon$  is the dielectric constant of the liquid,  $\varepsilon_0$  is the vacuum permittivity, R is the distance between the centres of gravity of the particles i and j,  $Q_i$  is the charge of the particle i [C]. Particle charge  $Q_i = \sigma_i S_i$ , where  $S_i$  is the surface of particle i.

$$Q_i = \sigma_i \pi d_i^2;$$

$$F_c = \frac{\pi}{4\pi\varepsilon_0\varepsilon} \frac{\sigma_i \sigma_j d_i^2 d_j^2}{R^2}.$$
(4.5)

#### 4.3.1 Brownian motion

Brownian diffusion (motion) is the oscillation of particles dependent on temperature. The derivation of the mass transport coefficient of Brownian diffusion starts from the advection-diffusion equation

$$\frac{\partial n}{\partial t} + \nabla \cdot (\vec{v} \, n) - \nabla \cdot (D \vec{\nabla} n) = 0, \qquad (4.6)$$

where D is the coefficient of diffusion, v is the velocity of transport, and n is the concentration of the transported matter. Based on Einstein [54], the diffusion coefficient is equal to

$$D = \frac{k_b T}{f},\tag{4.7}$$

where  $k_b$  is the Boltzman constant, T is the absolute temperature, and f is the friction coefficient [2]. Let us denote the advection flux density  $\vec{j}_{adv}$  and the diffusion flux density  $\vec{j}_{dif}$ :

$$\vec{j}_{adv} = \vec{v} \, n, \tag{4.8}$$

$$\vec{j}_{dif} = D \cdot \vec{\nabla} n. \tag{4.9}$$

To evaluate particle velocity caused by Brownian motion, we express the diffusion flux density as equivalent to the Brownian advection density caused by a theoretical Brownian velocity  $v_b$  as follows:

$$\vec{j}_{adv} = \vec{v_b} \, n = \vec{j}_{dif} = D \cdot \vec{\nabla} n. \tag{4.10}$$

For the spherical observation volume (OV)

$$v_b = \frac{|\vec{j}_{dif}|}{n} = D \,\frac{\partial n}{\partial r} \,\frac{1}{n}.\tag{4.11}$$

On the surface of the OV, the distance r is equal to R. Now, let us evaluate the equilibrium of forces from frictional force  $F_{fric}$  and Coulomb's force  $F_c$ :

$$0 = F_{fric} + F_c. \tag{4.12}$$

The frictional force can be expressed as a frictional coefficient f multiplied by relative velocity, that is the difference between the particle velocity v and the medium velocity represented by the theoretical Brownian velocity  $v_b$ :

$$0 = (v - v_b) f + \frac{1}{4\pi\varepsilon_0} \frac{Q_i Q_j}{R^2}.$$
 (4.13)

Hence, the velocity of the particle is

$$v = v_b - \frac{1}{4\pi\varepsilon_0} \frac{Q_i Q_j}{R^2 f},\tag{4.14}$$

and the flux density of the particle is

$$\vec{j} = \vec{v}n. \tag{4.15}$$

After substituting of eq. (4.14) and (4.11) into eq. (4.15):

$$\vec{j} = D \,\frac{\partial n}{\partial r} - \frac{F_c}{f} \,n. \tag{4.16}$$

From this point, the derivation is similar to the one in sec. 3.2.1. We assess the probability of aggregation of particles FP (particle in flux of particles, having the concentration  $n_i$ ) and OP (observed particle with the concentration  $n_j$ ) from the flux J of FP through OV around the OP with the radius  $R = a_{op} + a_{fp}$ .

$$J = \int_{S} \vec{j} d\vec{S}, \tag{4.17}$$

Number  $N_p$  of particles FP passing through the OS over time t:

$$N_p = \int_0^t J(\tau) d\tau. \tag{4.18}$$

After substituting of the equations (4.17), (3.8), (4.15) into eq. (4.18) and integration:

$$N_{p} = 4\pi R D n_{i} \left[ t + \frac{2 R \sqrt{t}}{\sqrt{D\pi}} \right] - 4\pi R^{2} \frac{F_{c}}{f} n_{i} t.$$
(4.19)

Assuming  $t \gg \frac{R^2}{D}$ , we neglect the middle term in the expression (4.19). Then

$$N_p \cong 4\pi R \left( D - R \frac{F_c}{f} \right) n_i t.$$
(4.20)

For very small  $n_i$  is  $N_p \ll 1$ . Then  $N_p$  can be understood as the probability of a collision of one OP with an FP. The probability of a collision of an OP with an FP can be expressed as the product of  $N_p$  and OP concentration  $n_j$ . The frequency of an collision between particles FP and OP adjusting for time is

$$P_{ij} = 4\pi R \left( D - R \frac{F_c}{f} \right) n_i n_j.$$
(4.21)

Here

$$f = 3\pi\eta (d_i + d_j), \tag{4.22}$$

where  $\eta$  is the dynamic viscosity of the medium,  $d_i$  is the diameter of FP,  $d_j$  is the diameter of OP. Having expressed the diffusion coefficient (4.7), the frictional coefficient (4.22), and Coulomb's force (4.5), the final mass transport coefficient with electrostatic forces for Brownian diffusion can be presented as follows

$$\beta_{ij}^{1,el} = \frac{2 \, k_B \, T}{3 \, \eta} \, \frac{(d_i + d_j)^2}{d_i \, d_j} - \frac{\pi \, d_i^2 \, d_j^2 \, \sigma_i \sigma_j}{3 \, \eta \, \varepsilon_0 \, (d_i + d_j)},\tag{4.23}$$

$$\tilde{\beta}_{ij}^{1,el} = \max(0, \beta_{ij}^{1,el}).$$
(4.24)

The probability of particle collision decreases quadratically with the quantum of the surface charge of particles.

#### 4.3.2 Velocity gradients

Again, the mass transport coefficients are derived for velocity gradients including the impact of electrostatic forces from equilibrium forces. Only the derivation in the case of 1D space is presented here, because the derivation in 2D space is more complicated and the difference between the resulting values is insignificant.

The equilibrium of resistance force  $F_{fric}$  and the Coulomb's force  $F_c$  is in this case

$$F_{fric} + F_c = 0,$$
 (4.25)



FIGURE 4.4: Equilibrium of forces for two particles in flowing fluid

where

$$F_{fric} = 3\pi \eta \, d_i \, (v_i - v_{i \, water}), \qquad (4.26)$$

and  $F_c$  is the same as before (4.4).

To derivate the mass transport coefficient, it is necessary to express the difference between velocities of the particles i and j again. From (4.4), (4.25), and (4.26)

$$v_i = v_{i\,water} - \frac{1}{12\,\pi^2\,\eta\,\varepsilon_0\,d_i}\,\frac{Q_i\,Q_j}{R^2},\tag{4.27}$$

$$v_j = v_{j \,water} - \frac{1}{12 \,\pi^2 \,\eta \,\varepsilon_0 \,d_j} \,\frac{Q_i \,Q_j}{R^2}, \tag{4.28}$$

$$\Delta v = \frac{\partial v}{\partial n} z - \frac{Q_i Q_j}{12 \pi^2 \eta \varepsilon_0 R^2} \left| \frac{1}{d_i} + \frac{1}{d_j} \right|, \qquad (4.29)$$

where  $v_{iwater}$  and  $v_{jwater}$  stand for water velocity in the position of particles *i* and *j*, respectively,  $\frac{\partial v}{\partial n}$  refers to the derivative of water velocity field in the direction normal to mean flow, and *z* is the distance of the two particles in the direction normal to mean flow (see Fig. 4.4).

The mass transport coefficient  $\beta_{ij}^{2el}$  is given by the flow density of FP around OP. It can be evaluated as an integral of particle velocity difference  $\Delta v$  over a half of the surface of the OV which is a sphere of radius  $R = a_{fp} + a_{op}$  around the OP. This is equal to the integral of the velocity difference over the normal cross-section S of the OV:

$$\beta_{ij}^{2,el} = \int_{S} \triangle v \, dS = 2 \left( \int_{0}^{R} \frac{\partial v}{\partial n} z \, 2\sqrt{R^2 - z^2} dz \right)$$

$$- \int_{0}^{R} \frac{Q_i Q_j}{12\pi^2 \eta \, \varepsilon_0 R^2} \left| \frac{1}{d_i} + \frac{1}{d_j} \right| 2\sqrt{R^2 - z^2} dz \right).$$

$$(4.30)$$

So the mass transport coefficient for the velocity gradients  $G = \frac{\partial v}{\partial n}$  including the impact of electrostatic forces takes the form

$$\beta_{ij}^{2,el} = \frac{1}{6} G \left( d_i + d_j \right)^3 - \frac{\pi \, d_i^2 \, d_j^2 \, \sigma_i \sigma_j}{12 \, \eta \, \varepsilon_0} \left| \frac{1}{d_i} + \frac{1}{d_j} \right|. \tag{4.31}$$

The probability of coagulation decreases quadratically with increasing surface charge. If a component that reduces the mass transport coefficient is bigger than the mass transport coefficient excluding the influence of electrostatic forces, the probability of particles i and j colliding will be zero. That is why again

$$\tilde{\beta}_{ij}^{2,el} = \max(0, \beta_{ij}^{2,el}).$$
(4.32)

#### 4.3.3 Sedimentation

The mass transport coefficient for sedimentation was derived from the force equilibrium. We added the Coulomb's law (4.4) into the equilibrium of forces. The derivation is presented here in 1D space only.



FIGURE 4.5: Equilibrium of forces for two particles during sedimentation

The force equilibrium has this form (see Fig. 4.5):

$$F_{qrav} = F_c + F_{fric} + F_{buo}, \tag{4.33}$$

where  $F_{grav}$  is the gravitational force,  $F_{buo}$  is buoyancy force,  $F_{fric}$  is frictional force and  $F_c$  is Coulomb's force. After expression of these parts of equation on the basis of gravitational law (3.17), Coulomb's law (4.4), Stokes law (3.19), and Archimedes principle (3.18), the equilibrium can be expressed as follows

$$\rho_p V_i g = \frac{1}{4\pi\varepsilon_0} \frac{Q_i Q_j}{R^2} + 6\pi\eta a_i v_i + \rho V_i g.$$
(4.34)

Here  $\eta$  is the viscosity of the medium,  $a_i$  is the radius of the particle i ( $a_i = d_i/2$ ),  $v_i$  is the velocity of the particle i,  $\rho$  is the density of the medium,  $\rho_p$  is the density of the aggregating particles,  $V_i$  is the volume of the particle i, and g is acceleration due to gravity.

The mass transport coefficient is equal to the flux of FP through OV around an OP. The OV is a sphere with the radius equal to the sum of the radii of the FP and OV  $R = a_{fp} + a_{op}$ . Without loss of generality we assume that the particle *i* is the FP and particle *j* is the OP. It follows that the mass transport coefficient is the area of the cross-section of OV  $S = \pi R^2$  multiplied by the difference between the velocities of the particles  $\Delta v = v_i - v_j$ :

$$\beta_{ij}^{3,el} = S \,\Delta v. \tag{4.35}$$

From (4.34)

$$v_i = V_i g \left( \varrho_p - \varrho \right) \frac{1}{3 \pi \eta \, d_i} - \frac{1}{4 \pi \, \varepsilon_0} \, \frac{Q_i \, Q_j}{R^2 \, 6 \, \pi \, \eta \, a_i}. \tag{4.36}$$

Then from (4.35) and (4.36)

$$\beta_{ij}^{3,el} = \frac{\pi g}{72 \eta} \left( \varrho_p - \varrho \right) \left( d_i + d_j \right)^2 \left| d_i^2 - d_j^2 \right| - \frac{\pi d_i^2 d_j^2 \sigma_i \sigma_j}{12 \eta \varepsilon_0} \left| \frac{1}{d_i} - \frac{1}{d_j} \right|, \tag{4.37}$$

where  $\sigma_i$  and  $\sigma_j$  stand for the surface charge on particle *i* and particle *j*, respectively.  $\beta_{ij}^{3el}$  is the mass transport coefficient including the impact of electrostatic forces on sedimentation. The probability of coagulation decreases quadratically with the increasing charge. If a component that reduces the mass transport coefficient is bigger than the mass transport coefficient excluding the impact of electrostatic forces, the probability of particles *i* and *j* colliding will be zero. That is why

$$\tilde{\beta}_{ij}^{3,el} = \max(0, \beta_{ij}^{3,el}).$$
(4.38)

## 4.4 The effect of including the surface charge on the aggregation rate

A comparison of MTC values for different values of surface charge density is shown in Tab. 4.2. The MTC value is the sum of the MTC of Brownian motion, velocity gradients and sedimentation. The MTC values are calculated between two nanoparticles, where the values used for the computation are: the diameter of one nanoparticle a = 50 nm, the density of particles  $\rho_p = 6700$  kg/m<sup>3</sup>, the temperature T = 300 K, the dynamic viscosity of water  $\eta = 10^{-3}$  Pa·s, the density of water  $\rho = 1000$  kg/m<sup>3</sup>, velocity gradient G = 50 s<sup>-1</sup>.

$\beta_{ij}  [\mathrm{m^3 s^{-1}}]$
$1.11 \cdot 10^{-17}$
$1.11 \cdot 10^{-17}$
$1.11 \cdot 10^{-17}$
$1.10 \cdot 10^{-17}$
$9.44 \cdot 10^{-18}$
0

TABLE 4.2: A comparison of MTC values for different values of surface charge density of nZVI

A value of the surface charge density  $\sigma = 0 \text{ C/m}^2$  means that no electrostatic forces act between the nanoparticles. A value of MTC  $\beta = 0 \text{ m}^3 \text{s}^{-1}$  means that repulsive electrostatic forces between the nanoparticles are so strong that the probability of aggregation is zero.

The probability of collision between particles i and j is determined by the density of these particles and by the sum of the mass transport coefficients (from (3.1) and (3.2)).

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

$$(4.39)$$

Mass transport coefficients were calculated corresponding to a pH of water 6. This value of pH changes the surface charge density to the value of  $\sigma = 10^{-6} \text{ C/m}^2$ . For simplicity, the surface charge density of all particles in dispersion are taken to be the same value. On Fig. 4.6, 4.7, and 4.8, it is possible to see how the particles are unstable and that the aggregation occurs. The surface charge density would have to be 4 times larger to prevent the particles from aggregating.



(a) Excluding the influence of elstat. forces

(b) Including the influence of elstat. forces, surface charge density  $\sigma$  =  $10^{-6}~{\rm C/m^2}$ 

FIGURE 4.6: The mass transport coefficient of the particles for Brownian diffusion



(a) Excluding the influence of elstat. forces

(b) Including the influence of elstat. forces, surface charge density  $\sigma = 10^{-6}~{\rm C/m^2}$ 

FIGURE 4.7: The mass transport coefficient of the particles for the velocity gradients



(a) Excluding the influence of elstat. forces



(b) Including the influence of elst at. forces, surface charge density  $\sigma = 10^{-6}~{\rm C/m^2}$ 

FIGURE 4.8: The mass transport coefficient of the particles for sedimentation The mass transport coefficient for Brownian diffusion is limited by the surface charge effect especially for large aggregates. The mass transport coefficient for the velocity gradients is limited by the surface charge only when there is a larger surface charge. The mass transport coefficient for sedimentation is not in the logarithmic scale because a large part of the graph is equal to the zero. The aggregation for sedimentation is limited especially for the small particles.

## Chapter 5

## Sectional aggregation model

This chapter was described in the diploma thesis [9].

## 5.1 Clustering of the particle sizes

Gen-tran is the software used at the Technical University of Liberec to compute reactions between entities in water. Here, it was required to compute reactions between the aggregates (particles), describing collisions of two aggregates leading to the creation of one aggregate. There are over a million of aggregates with different sizes and different transport properties in a dispersion of unstable particles. It is not possible to compute reactions between the millions of entities, therefore it was necessary to generate a system for clustering particles into several categories, which are here called "sections", according to their size. Particles with similar size have similar transport properties. We can observe migration of the particle size sections (PSS) instead of observing every single aggregate. Thereafter, we can estimate a distribution of the sections in the media and their percentage giving a good insight into how the dispersion would migrate in the medium.

We based the clustering model on the sectional representations for simulating aerosol dynamics published in the paper [16]. This chapter describes the sectional model.

The choice of section size is not arbitrary, but the rules of geometric limitation have to be satisfied:

$$k_i \ge 2\,k_{i-1},\tag{5.1}$$

where  $k_i$  is the number of nanoparticles that create the largest aggregate in the section i. It means that an aggregate created by the collision of particles from a section belongs to the same or subsequent section.

The main problem was the reformulation of the mass transport coefficients so that they corresponded to the probabilities of particle aggregation between the sections. We split the probabilities of aggregation of particles according to the final section of aggregate created. It depends on the sizes of aggregating particles as to whether the created aggregate stays in the same section where to larger aggregate belonged or pertains to the following section.

For example, section l. An aggregate created from particles i and j from sections r and p, respectively, which are smaller than or equal to l, will belong to section l if the sum of particle sizes of i and j is greater than the lower limit  $k_{l-1}$  of section l and lower than or equal to the upper limit  $k_l$  of section l. The overall probability of a collision of particles from sections r and p that create a particle belonging to section l per one second and unit concentration of particles from sections r and p is given by

$$\beta_{r,p,l}^{+} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{p-1}+1}^{k_p} \frac{\beta_{ij} \Theta(k_{l-1} < i+j \le k_l)}{(k_r - k_{r-1})(k_p - k_{p-1})},$$
(5.2)

where the function  $\Theta$  represents a condition. If it is fulfilled, the value of the condition will be 1, otherwise 0.

Next we consider a reduction of particles from the section l, so we are interested in the aggregation of particles where at least one particle is from section l.

The average probability of a collision of a particle from section l with a particle from section r per one second and unit concentration of particles is

$$B_{r,l} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{l-1}+1}^{k_l} \frac{\beta_{ij}}{(k_r - k_{r-1})(k_l - k_{l-1})}.$$
(5.3)

Consequently, the reduction in the number of particles in section l due to collisions with particles from section r is

$$\beta_{r,l}^{-} = B_{r,l} - \beta_{r,l,l}^{+}.$$
(5.4)

An overview of all the formulas for computation of these coefficients is presented in Table 5.1.

Usually the change in the number of particles is observed.  $\alpha$  and  $\lambda$  in Table 5.1 are useful when the change of the surface area of particles (important for reactivity) or the change in the volume of particles are the subjects of interest. The change in the volume of particles should be zero according to the Law of mass conservation, so it could be a good method for verifying the accuracy of the calculation. When calculating the change in the number of particles in section l, we should use  $\alpha = 1$  and  $\lambda = 0$ ; for the change of volume we should set  $\alpha = 1$  and  $\lambda = 1$ ; for the change of particle surface area we set  $\alpha = \sqrt[3]{\pi}\sqrt[3]{6^2}$  and  $\lambda = \frac{2}{3}$ .

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

 TABLE 5.1: Summary of the mass transport coefficient for sections of aggregates in the discrete form

## 5.2 Time variation of aggregate sections

Let  $N_l$  be the concentration of particles from section l:

$$N_l(t) = \sum_{i=k_{l-1}+1}^{k_l} n_i(t).$$
(5.5)

The change of  $N_l$  over time is equal to

$$\frac{dN_l}{dt} = \frac{1}{2} \sum_{r=1}^{l-1} \sum_{p=1}^{l-1} {}^{1}\beta_{r,p,l}^{+} N_r N_p - \sum_{r=1}^{l-1} {}^{2}\beta_{r,l}^{-} N_r N_l \qquad (5.6)$$

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

l = 1, 2, ..., h, where h is the number of sections. In the equation (5.6), the first and the third term are multiplied by  $\frac{1}{2}$  because the double sums add the same reactions twice.

## 5.3 Averaging of discrete sections

The sections of aggregates were derived and mass transport coefficients were modified for the sections. However, computation of MTC is still computed for every particle i and every particle j in the sections. The number of reactions is still the same so the discrete sections are averaged. Every section is split into a number of equally large parts. In every part, the median size is specified. The MTC in discrete form 5.1 are integrated over the parts of the sections. The integration differs for the computation of changes in the number, volume, and surface area of aggregates during aggregation. Again, the collision of particles i from section r and particle j from section p that create a particle from section l is examined. The parts of section r are labelled I and the parts of section p are labelled J:

$$I=1,\ldots,P_I$$

$$J=1,\ldots,P_J.$$

 ${\cal P}_I$  and  ${\cal P}_J$  are the number of parts of section r and p respectively.

$$S_I = \frac{(k_r - k_{r-1})}{P_I},$$
  
 $S_J = \frac{(k_p - k_{p-1})}{P_J},$ 

where  $S_I$  and  $S_J$  are the sizes of the parts of section I and J respectively.

#### 5.3.1 Number of particles

In this section, equations (5.2), (5.3) and (5.4) are modified.

$$\beta_{r,p,l}^{+} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{p-1}+1}^{k_p} \frac{\beta_{ij} \Theta(k_{l-1} < i+j \le k_l)(i+j)^{\lambda}}{(k_r - k_{r-1})(k_p - k_{p-1}) \alpha i^{\lambda} j^{\lambda}},$$
(5.7)

When we calculate the change in the number of particles in section l, we use  $\alpha = 1$  and  $\lambda = 0$ .

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

$$= \frac{1}{(k_r - k_{r-1})(k_p - k_{p-1})} \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left[ \sum_{i=k_{i,I-1}+1}^{k_{i,I}} \sum_{j=k_{j,J-1}+1}^{k_{j,J}} \beta_{ij} \Theta(k_{l-1} < i+j \le k_l) \right].$$

Inner sums are replaced by approximate solution using integrals.

$$\hat{\beta}_{r,p,l}^{+} \cong \frac{1}{(k_{r}-k_{r-1})(k_{p}-k_{p-1})} \cdot \sum_{I=1}^{P_{I}} \sum_{J=1}^{P_{J}} \left[ \beta_{I_{M}J_{M}} \cdot \Theta(k_{l-1} < I_{M} + J_{M} \le k_{l}) \int_{i=k_{i,I-1}+1}^{k_{i,I}} \int_{j=k_{j,J-1}+1}^{k_{j,J}} 1 dj di \right].$$

$$\hat{\beta}_{r,p,l}^{+} \cong S_{I} \cdot S_{J} \cdot \sum_{I=1}^{P_{I}} \sum_{J=1}^{P_{J}} \left[ \frac{\beta_{I_{M}J_{M}} \cdot \Theta(k_{l-1} < I_{M} + J_{M} \le k_{l})}{(k_{r} - k_{r-1})(k_{p} - k_{p-1})} \right].$$
(5.8)

 $\beta_{I_M J_M}$  is the mass transport coefficient between aggregates  $I_M$  and  $J_M$  representing parts of sections I and J. We choose middle aggregate.

Equation (5.3) is modified in a similar way:

If 
$$r = l$$

$$B_{l,l} = \sum_{i=k_{l-1}+1}^{k_l} \sum_{j=k_{l-1}+1}^{k_l} \frac{\beta_{ij}(i^{\lambda}+j^{\lambda})}{(k_l-k_{l-1})(k_l-k_{l-1}) \alpha i^{\lambda} j^{\lambda}}.$$
(5.9)

$$\hat{B}_{l,l} = \frac{1}{(k_l - k_{l-1})(k_l - k_{l-1})} \sum_{i=k_{l-1}+1}^{k_l} \sum_{j=k_{l-1}+1}^{k_l} 2\beta_{ij}$$

$$= \frac{1}{(k_l - k_{l-1})(k_l - k_{l-1})} \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left[ \sum_{i=k_{i,I-1}+1}^{k_{i,I}} \sum_{j=k_{j,J-1}+1}^{k_{j,J}} 2\beta_{ij} \right].$$

$$\hat{B}_{l,l} \cong \frac{1}{(k_l - k_{l-1})(k_l - k_{l-1})} \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left[ \beta_{I_M J_M} \int_{i=k_{i,I-1}+1}^{k_{i,I}} \int_{j=k_{j,J-1}+1}^{k_{j,J}} 2djdi \right].$$
$$\hat{B}_{l,l} \cong 2 \cdot S_I \cdot S_J \cdot \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left[ \frac{\beta_{I_M J_M}}{(k_l - k_{l-1})(k_l - k_{l-1})} \right].$$
(5.10)

If  $r \neq l$ 

$$B_{r,l} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{l-1}+1}^{k_l} \frac{\beta_{ij} \, j^{\lambda}}{(k_r - k_{r-1})(k_l - k_{l-1}) \, \alpha i^{\lambda} j^{\lambda}}.$$
 (5.11)

$$\hat{B}_{r,l} \cong S_I \cdot S_J \cdot \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left[ \frac{\beta_{I_M J_M}}{(k_r - k_{r-1})(k_l - k_{l-1})} \right].$$
(5.12)

As before,

$$\hat{\beta}_{r,l}^{-} = \hat{B}_{r,l} - \hat{\beta}_{r,l,l}^{+}.$$
(5.13)

## 5.3.2 Volume of particles

Equations (5.7), (5.3), and (5.11) are modified again. In the case of observing volume change,  $\alpha = 1$  and  $\lambda = 1$ . Inner sums are replaced by integrals in the same way as in section 5.3.1.

$$\hat{\beta}_{r,p,l}^{+} \cong \frac{1}{(k_r - k_{r-1})(k_p - k_{p-1})} \cdot \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left[ \beta_{I_M J_M} \cdot \Theta(k_{l-1} < I_M + J_M \le k_l) \int_{i=k_{i,I-1}+1}^{k_{i,I}} \int_{j=k_{j,J-1}+1}^{k_{j,J}} \left(\frac{1}{i} + \frac{1}{j}\right) dj di \right].$$

$$\hat{\beta}_{r,p,l}^{+} \cong \sum_{I=1}^{P_{I}} \sum_{J=1}^{P_{J}} \sum_{J=1}^{(5.14)} \left\{ \left[ S_{I} \cdot ln\left(\frac{k_{p}}{k_{p-1}+1}\right) + S_{J} \cdot ln\left(\frac{k_{r}}{k_{r-1}+1}\right) \right] \frac{\beta_{I_{M}J_{M}} \cdot \Theta(k_{l-1} < I_{M} + J_{M} \le k_{l})}{(k_{r} - k_{r-1})(k_{p} - k_{p-1})} \right\}.$$

If r = l

$$\hat{B}_{l,l} \cong \frac{1}{(k_l - k_{l-1})(k_l - k_{l-1})} \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left[ \beta_{I_M J_M} \int_{i=k_{i,I-1}+1}^{k_{i,I}} \int_{j=k_{j,J-1}+1}^{k_{j,J}} \left(\frac{1}{i} + \frac{1}{j}\right) dj di \right],$$
$$\hat{B}_{l,l} \cong \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left\{ \left[ S_I \cdot ln \left(\frac{k_l}{k_{l-1}+1}\right) + S_J \cdot ln \left(\frac{k_l}{k_{l-1}+1}\right) \right] \frac{\beta_{I_M J_M}}{(k_l - k_{l-1})(k_l - k_{l-1})} \right\}.$$
(5.15)

If  $r \neq l$ 

$$\hat{B}_{r,l} \cong \frac{1}{(k_r - k_{r-1})(k_l - k_{l-1})} \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left[ \beta_{I_M J_M} \int_{i=k_{i,I-1}+1}^{k_{i,I}} \int_{j=k_{j,J-1}+1}^{k_{j,J}} \frac{1}{i} dj di \right],$$
$$\hat{B}_{r,l} \cong \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left\{ \left[ S_J \cdot ln \left( \frac{k_r}{k_{r-1}+1} \right) \right] \frac{\beta_{I_M J_M}}{(k_r - k_{r-1})(k_l - k_{l-1})} \right\}.$$
(5.16)

## 5.3.3 Surface of particles

To compute a change in the particle surface area,  $\alpha = \sqrt[3]{\pi}\sqrt[3]{6^2}$  and  $\lambda = \frac{2}{3}$ .

$$\hat{\beta}_{r,p,l}^{+} \cong \frac{1}{\sqrt[3]{\pi}\sqrt[3]{6^{2}}(k_{r}-k_{r-1})(k_{p}-k_{p-1})} \cdot \sum_{I=1}^{P_{I}} \sum_{J=1}^{P_{J}} \left[ \beta_{I_{M}J_{M}} \int_{i=k_{i,I-1}+1}^{k_{i,I}} \int_{j=k_{j,J-1}+1}^{k_{j,J}} \left( \frac{(i+j)^{\frac{2}{3}}}{i^{\frac{2}{3}} \cdot j^{\frac{2}{3}}} \right) djdi \right].$$

However, we did not find the analytical solution of the integral

$$\int_{i=k_{i,I-1}+1}^{k_{i,I}} \int_{j=k_{j,J-1}+1}^{k_{j,J}} \left(\frac{(i+j)^{\frac{2}{3}}}{i^{\frac{2}{3}} \cdot j^{\frac{2}{3}}}\right) dj di.$$

Therefore, the integral was replaced by its one-point quadrature:

$$\hat{\beta}_{r,p,l}^{+} \cong \sum_{I=1}^{P_{I}} \sum_{J=1}^{P_{J}} \left\{ \left[ \left( \frac{1}{I_{ap}} + \frac{1}{J_{ap}} \right)^{\frac{2}{3}} \cdot S_{I} \cdot S_{J} \right] \frac{\beta_{I_{M}J_{M}}}{\sqrt[3]{\pi}\sqrt[3]{6^{2}}(k_{r} - k_{r-1})(k_{p} - k_{p-1})} \right\}, \quad (5.17)$$
where  $I_{ap} = \frac{k_{r-1} + 1 + k_{r}}{2}, J_{ap} = \frac{k_{p-1} + 1 + k_{p}}{2}.$ 

If r = l

$$\hat{B}_{l,l} \cong \frac{1}{\sqrt[3]{\pi}\sqrt[3]{6^2}(k_l - k_{l-1})(k_l - k_{l-1})} \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left[ \beta_{I_M J_M} \int_{i=k_{i,I-1}+1}^{k_{i,I}} \int_{j=k_{j,J-1}+1}^{k_{j,J}} \left( \frac{1}{i^{\frac{2}{3}}} + \frac{1}{j^{\frac{2}{3}}} \right) dj di \right],$$

$$\hat{B}_{l,l} \cong \sum_{I=1}^{P_I} \sum_{J=1}^{P_J}$$
 (5.18)

$$\frac{\left[3 \cdot S_{I}\left(k_{l}^{\frac{1}{3}} - (k_{l-1}+1)^{\frac{1}{3}}\right) + 3 \cdot S_{J}\left(k_{l}^{\frac{1}{3}} - (k_{l-1}+1)^{\frac{1}{3}}\right)\right]}{\beta_{I_{M}J_{M}}}.$$
(5.19)

$$\sqrt[3]{\pi\sqrt[3]{6^2}(k_l-k_{l-1})(k_l-k_{l-1})}$$
.

If  $r \neq l$ 

$$\hat{B}_{r,l} \cong \frac{1}{\sqrt[3]{\pi}\sqrt[3]{6^2}(k_r - k_{r-1})(k_l - k_{l-1})} \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left[ \beta_{I_M J_M} \int_{i=k_{i,I-1}+1}^{k_{i,I}} \int_{j=k_{j,J-1}+1}^{k_{j,J}} \left(\frac{1}{i^{\frac{2}{3}}}\right) dj di \right],$$

$$\hat{B}_{r,l} \simeq \sum_{I=1}^{P_I} \sum_{J=1}^{P_J} \left\{ \left[ 3 \cdot S_J \left( k_r^{\frac{1}{3}} - (k_{r-1}+1)^{\frac{1}{3}} \right) \right] \frac{\beta_{I_M J_M}}{\sqrt[3]{\pi} \sqrt[3]{6^2} (k_r - k_{r-1}) (k_l - k_{l-1})} \right\}.$$
 (5.20)

Again, the relation (5.13) holds. With this model, it is possible to compute a change in particle number, volume and surface area, and to estimate a rate of aggregation over time. An example is given in Fig. 5.1, where a change in the number of particles in sections is expressed. The number of particles is expressed as a percentage ratio of the starting value. The results were computed using Matlab R2009a. The values of number changes were computed for three sections including particles with radii according to the label in Fig. 5.1. The starting value of particle number was  $2.17 \cdot 10^{17}$  nanoparticles in 1 L, radius of one nanoparticle is 20 nm, surface charge density is  $2.5 \cdot 10^{-5}$  Cm<sup>-2</sup>, density of particles is 6700 kg/m<sup>3</sup>, temperature is 300 K, dynamic viscosity of water is  $10^{-3}$  Pa·s, density of water is 1000 kg/m<sup>3</sup>, velocity gradient is 50 s<sup>-1</sup>.



FIGURE 5.1: Computed change of number of particles caused by the aggregation in 30 time steps

## Chapter 6

# Magnetic nanoparticle aggregation

Parts of this chapter were published in [63] and [68].

nZVI exposed to water acquires an oxide shell. For example, RNIP particles manufactured by Toda Kyogo, Japan, have a  $Fe^0$  core and a magnetite (Fe<sub>3</sub>O<sub>4</sub>) shell [6, 28]. Both  $Fe^0$  and  $Fe_3O_4$  are magnetic so magnetic attractive forces between particles may also affect the dispersion stability [64]. The influence of the magnetic properties of iron nanoparticles on their aggregation is apparent under an applied magnetic field, where ferromagnetic or paramagnetic dispersions form chain-like aggregates in which the dipoles are oriented in a head-tail configuration along the direction of the field [14]. Hence, an nZVI dispersion might undergo dipole-dipole attraction between the magnetic moments of the particles which may affect their size and dispersion stability.

Moreover, the results of the aggregation computation using a collision frequency factor based on Brownian motion and different velocities during sedimentation suggest that the aggregation model excludes the strong attractive forces between the particles. A comparison of aggregation kinetics of RNIP is shown in Fig. 3.1 and in Tab. 3.1 (from section 3.1) with the results of the aggregation kinetics computation.

Comparing Fig. 3.1 with Tab. 6.1, the measured aggregation is much faster than the computed. In Tab. 6.1, there are no aggregates larger than 500 nm in the dispersion in 10 minutes. Whereas in Fig. 3.1, aggregates larger than 1  $\mu$ m occur in the first few minutes.

Comparing Tab. 3.1 with Tab. 6.2, the measured aggregation is also faster than the computed. In Tab. 6.2, aggregates larger than 200 nm start to occur in the dispersion in 10 minutes. Whereas in Tab. 3.1, aggregates have an average size of 200 nm within 6 minutes.

% rate of starting particle concentration			Time
Section0 [%]	Section1 [%]	Section2 [%]	[min]
50 - 200  nm	$200-500~\mathrm{nm}$	> 500  nm	
100.0	0.0	0.0	0
99.7	0.3	0.0	1
99.3	0.7	0.0	2
99.0	1.0	0.0	3
98.7	1.3	0.0	4
98.4	1.6	0.0	5
98.0	2.0	0.0	6
97.7	2.3	0.0	7
97.4	2.6	0.0	8
97.1	2.9	0.0	9
96.8	3.2	0.0	10

TABLE 6.1: Changes in sections for comparison with Fig. 3.1 The concentration of particles is 60 mg/L, the radius of one nanoparticle is 25 nm, the density of particles is 6700 kg/m<sup>3</sup>, the temperature is 300 K, the dynamic viscosity of water is  $10^{-3}$ Pa·s and the density of water is 1000 kg/m<sup>3</sup>.

% rate of starting particle concentration			Time
Section0 [%]	Section1 [%]	Section2 [%]	[min]
50-200  nm	$200-500~\mathrm{nm}$	> 500  nm	
100.0	0.0	0.0	0
100.0	0.0	0.0	1
100.0	0.0	0.0	2
100.0	0.0	0.0	3
100.0	0.0	0.0	4
100.0	0.0	0.0	5
100.0	0.0	0.0	6
100.0	0.0	0.0	7
100.0	0.0	0.0	8
99.9	0.1	0.0	9
99.9	0.1	0.0	10

TABLE 6.2: Changes in sections for comparison with Tab. 3.1

The concentration of particles is 1 mg/L, the radius of one nanoparticle is 25 nm, the density of particles is 6700 kg/m<sup>3</sup>, the temperature is 300 K, the dynamic viscosity of water is  $10^{-3}$  Pa·s and the density of water is 1000 kg/m<sup>3</sup>.

Thus it was decided to include the impact of magnetic forces between particles into the common model of particle aggregation.

## 6.1 Analytical model of magnetic forces between two magnets

The iron particles are composed of iron oxides, especially when they are already partly reacted. RNIP nanoparticles have a significant layer of magnetite around their zero-valent core. Therefore, we assume that the iron particle is ferromagnetic. Remanent magnetization, saturation magnetization and coercivity were measured using SQUID for RNIP particles in the work [14]. A ratio of remanent and saturation magnetization was 0.13 and coercivity was 12.6 mT. Based on these measurements, it was deduced that the RNIP are pseudo-single domain (when the ratio of remanent and saturation magnetization is between 0.1 - 0.5 and the coercivity between 10 - 15 mT [14]. Hence, the saturation magnetization can be used to estimate the magnitude of the magnetic attractive force between the particles [65,66]. The value of the saturation magnetization of RNIP as published in [14] was 570 kA/m.

An attempt was made to include the influence of the magnetic forces between particles to the model of aggregation of the particles. However, it is a very complicated process which cannot be described analytically. Still, it is possible to derive a magnetic force equation between two nanoparticles.

According to [67], the electromagnetic potential at the point  $\vec{r}$  near a permanent magnet is equal to

$$\phi(\vec{r}) = \int_{V} \frac{\vec{M}\vec{R}}{R^3} dV, \qquad (6.1)$$

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

The intensity of the magnetic field  $\vec{H}$  can be subsequently computed as

$$\vec{H}(\vec{r}) = -g\vec{rad}(\phi(\vec{r})). \tag{6.2}$$

Finally, the magnetic force between the source of the intensity of the magnetic field  $\vec{H}$ and a permanent magnet with the magnetization  $\vec{M}_0$  at the point  $\vec{r}$  is equal to

$$\vec{F}(\vec{r}) = -\int_{V} (\vec{M_0} \cdot g\vec{rad}) \vec{H}(\vec{r}) dV.$$
(6.3)

## 6.2 Magnetic forces between two spherical iron nanoparticles

The scalar potential of the magnetic field around one homogeneous spherical iron nanoparticle with radius a located at the point [0, 0, 0] was determined to be:

$$\phi(\vec{r}) = M \int_0^{2\pi} \int_0^{\pi} \int_0^a \frac{(x_3 - r'\cos(\theta))r'^2\sin(\theta)}{\sqrt[3]{(x_1^2 + x_2^2 + x_3^2 - r'^2)^2}} dr' d\theta d\varphi,$$
(6.4)

where a is the radius of the nanoparticle and  $[x_1, x_2, x_3]$  are the coordinates of the point  $\vec{r}$ . The direction of the magnetization vector  $\vec{M}$  is set to the direction  $x_3$  and M is the magnitude of the vector  $\vec{M}$ .

After integration, the magnetic potential around a ferromagnetic sphere is obtained:

$$\phi(\vec{r}) = 4 M \frac{\pi x_3 \left(a - \arctan\left(\frac{a}{\sqrt{x_1^2 + x_2^2 + x_3^2 - a^2}}\right) \sqrt{x_1^2 + x_2^2 + x_3^2 - a^2}\right)}{\sqrt{x_1^2 + x_2^2 + x_3^2 - a^2}}.$$
 (6.5)

According to (6.2), the components of the vector of intensity of the magnetic field around a spherical ferromagnetic particle is

$$H_{i}(\vec{r}) = \delta_{i3} \left[ \frac{-4\pi}{C(\vec{r})} \left( a - \arctan\left(\frac{a}{C(\vec{r})}\right) C(\vec{r}) \right) \right] - \frac{4\pi x_{3}}{C(\vec{r})} \left( \frac{ax_{i}}{\vec{r} \cdot \vec{r}} - \frac{x_{i}}{C(\vec{r})} \arctan\left(\frac{a}{C(\vec{r})}\right) \right) + \frac{4\pi x_{3} x_{i}}{C(\vec{r})^{3}} \left( a - \arctan\left(\frac{a}{C(\vec{r})}\right) C(\vec{r}) \right),$$

$$(6.6)$$

where  $\delta_{i3}$  is the Kronecker delta and i = 1, 2, 3.  $C(\vec{r})$  replaces

$$C(\vec{r}) = \sqrt{x_1^2 + x_2^2 + x_3^2 - a^2}.$$
(6.7)

and

$$\vec{F}(\vec{r}) = -\int_{V} (\vec{M_0} \cdot g\vec{rad}) \vec{H}(\vec{r}) dV.$$
(6.8)

The derived formula for the size of the magnetic forces between two iron nanoparticles is very extensive and it is not presented here.

That we are able to compute a magnetic force between two nanoparticles is shown in Fig. 6.1. This is only an example of the numerical result, where a visualization of a part of the vector field of the magnetic forces between a nanoparticle in an arbitrary point near a nanoparticle with radius a is sketched. The reference particle is touching the center of the upper right of the figure. The figure is created by Mathematica 5 software, copyrighted by Wolfram Research, Inc.



 FIGURE 6.1: Visualization of the vector field of the magnetic forces between two spherical particles of nZVI
 Mathematica 5 software, copyrighted by Wolfram Research Inc., was used. One nanoparticle is at an arbitrary point near a nanoparticle with radius a which is touching the centre of the upper right side of the figure.

## 6.3 Magnetic field around an aggregate

An aggregate of iron nanoparticles is in fact a clump of many permanent magnets. It is impossible to establish an analytical model of the interaction between two such aggregates. To analyze statistically the influence of the magnetic forces on aggregation of two nanoparticle aggregates, a script was prepared to examine the most extreme possibility (the largest forces) and the averaged possibility of influencing the aggregation by the magnetic forces.

The statistical model of aggregation assumes that the volume of the aggregate is filled by uniformly distributed nanoparticles (small homogeneous magnets) with randomly uniformly distributed direction of magnetization (an assessment of the real structures of an aggregate is in Chapter 7). The magnitude of the magnetization vector of all nanoparticles is the same. The magnetic potential of the aggregate is then the sum of the magnetic potentials of all nanoparticles creating the aggregate:

$$\phi(\vec{r}) = \sum_{i=1}^{N_p} \phi_i(\vec{r} - \vec{r}_i), \qquad (6.9)$$

where  $\phi_i$  is the potential of the magnetic field of the nanoparticle *i* located at the point  $\vec{r_i}$ ,  $N_p$  is the number of nanoparticles in the aggregate.

The magnetic force between two aggregates is the sum of magnetic forces between all pairs of nanoparticles from the two aggregates (between every nanoparticle from the first aggregate and every nanoparticle from the second aggregate):

$$\vec{F}_A(\vec{r}) = \sum_{i=1}^{N_{p,1}} \sum_{j=1}^{N_{p,2}} \vec{F}_{ij}, \qquad (6.10)$$

where  $\vec{F}_A$  is the magnetic force between two aggregates,  $\vec{F}_{ij}$  is the magnetic force between *i*-th nanoparticle in the first aggregate and *j*-th nanoparticle in the second aggregate,  $N_{p,1}$ ,  $N_{p,2}$  is the number of nanoparticles in the first and second aggregate respectively.

This way we can express the strength of the magnetic attraction between two aggregates depending on their relative position. The magnetic force magnitude is largest when opposite sign dipoles of aggregates are pointing towards each other. Conversely, dipole-dipole repulsion could reduce the rate of aggregation. However, this is not thought to happen. Firstly, particles in liquid rotate easily, the turning motion tends to line up the magnetic moment of one aggregate with the magnetic field of the next aggregate. Secondly, even though same sign dipoles of two aggregates cause repulsion, the aggregates can get closer to other aggregates and may aggregate.

The main question was how to add the effect of attractive magnetic force into the aggregation model. The aggregation model gives the frequency of collisions between particles leading to the cohesion of the particles. Magnetic forces act over relatively long distances, so particles can be attracted and aggregate also when they seem to have non-collision trajectories. The approach was to extend the observed volume around the observed particle described in section 3.2. The frequency of collisions between the observed particle and other particles is derived from the flux of particles in the observed sphere volume (OS) around the observed particle. The aggregation rate is increased by extending the radius of the observed sphere.

The value of the OS radius depends on the forces affecting particle-particle interaction. The limit of the OS radius is the distance from centre of the OP in which attractive magnetic and repulsive forces are equal. At shorter distances than this limit, the magnetic force between particles causes attraction and the particles collide. We called this point the "Limit distance". Using this value, it is possible to estimate the desired distance between particles in dispersion. Having a uniformly distributed dispersion of nZVI, the computed limit distance may serve to assess the optimum concentration value for the desirable aggregation rate.
#### 6.4 Limit distance

The influence of magnetic forces in comparison to the gravitational forces was investigated. It was also possible to compare it with other acting forces but gravitation force was chosen due to the small number of variables involved. The effect of magnetic forces was assessed using the value limit distance. Up to this distance from the centre of an aggregate, the attractive magnetic forces cause the aggregation of the aggregate and a particle placed inside this range. In ranges larger than the limit distance, other forces outweigh the magnetic forces. The limit distance value gives the loci in which the gravitational and magnetic forces affecting the aggregate are equal (6.11). Figure 6.2 represents two interacting aggregates, a larger one and a smaller one. The limit distance is specified based on the computed magnetic force between the two aggregates. In the figure, the limit distance is identified by the black line around the bigger aggregate. If the distance between the bigger and smaller aggregate is shorter than the limit distance, the particles will aggregate. If it is further, the particles do not aggregate due to attractive magnetic forces (in this case, the particles would probably aggregate due to sedimentation).



FIGURE 6.2: An illustration of the comparison between the attractive magnetic force and the counteracting gravitational force At the limit distance, the two forces are balanced.

$$F_q = F_{mq}(L_d), \tag{6.11}$$

where  $F_{mg}(L_d)$  is the magnetic force computed at the distance  $L_d$  from the centre of the observed particle.

If two interacting nanoparticles are compared, the magnetic force decreases by the power of 4, as is shown in Table 6.3. Hence, we computed the magnetic force  $F_{mg}$  of two single nanoparticles at a distance  $R_0$  which is equal to the sum of the radii of both nanoparticles. We estimated the limit distance using the equation:

$$L_d = \sqrt[4]{\frac{F_{mg}(R_0)}{F_g}} R_0.$$
 (6.12)

The magnetic forces between the two single domain magnetic nanoparticles are listed in Tab. 6.3. Values of  $F_{mg}$  were computed using a value of magnetization vectors 570 kA/m with head-tail orientation of dipoles. In the case of aggregates, the fall depends

Distance [m]	$F_{mg}$ [N]
$4.0 \cdot 10^{-8}$	$7.22 \cdot 10^{-11}$
$4.0 \cdot 10^{-7}$	$3.15 \cdot 10^{-15}$
$4.0 \cdot 10^{-6}$	$3.13 \cdot 10^{-19}$
$4.0 \cdot 10^{-5}$	$3.13 \cdot 10^{-23}$
$4.0 \cdot 10^{-4}$	$3.13 \cdot 10^{-27}$
$4.0 \cdot 10^{-3}$	$3.13 \cdot 10^{-31}$
$4.0 \cdot 10^{-2}$	$3.12 \cdot 10^{-35}$
$4.0 \cdot 10^{-1}$	$3.44 \cdot 10^{-39}$

TABLE 6.3: Table of magnetic forces between two nanoparticles depending on their distance

It shows that the magnetic force decreases almost precisely with the power of four.

on the structure of the aggregates and a correction to the limit distance computation is needed.

#### 6.4.1 Correction of the limit distances between aggregates

In the case of interacting aggregates, the magnetic force does not decrease with distance precisely to the power of 4 as in the case of two interacting nanoparticles. If the second aggregate is moved further from the first aggregate, the distances between single nanoparticles in the two aggregates changing in different ways. The nanoparticles of the second aggregate which are closer to the first aggregate move relatively less and they have a relatively bigger influence on the magnetic force. Conversely, the nanoparticles with less influence move relatively more. Overall, the magnetic force decreases with higher than power of four as it is expected in (6.12). An example of this is presented in Table 6.4. The number called "Aggregate" in Table 6.4 refers to the number of nanoparticles constituting each of the aggregates. The power P is computed as a common logarithm of the ratio of the magnetic forces of aggregates close to each other (at distance  $R_0$ ) and the same aggregates ten times further apart (at distance  $10 \cdot R_0$ ):

$$P = \log\left(\frac{F_{mg}(R_0)}{F_{mg}(10 \cdot R_0)}\right). \tag{6.13}$$

If the decrease in the magnetic force was biquadratic, the power P should be equal to 4. It can be seen from the Table 6.4 that the power P generally increases with the size of the aggregate and it is always higher than 4.

Aggregate [1]	P[1]
1	4.2
10	4.3
100	4.5
1000	6.0
10000	5.8
100000	6.3
1000000	7.0

TABLE 6.4: Table of power P of the decrease in the magnetic force  $F_{mg}$  at very short distances between the aggregates

Therefore, the iteration for the correction of  $L_d$  was proposed as follows: The limit distance is estimated using (6.12) as a starting distance for the next iteration.

$$L_{d,0} = \sqrt[4]{\frac{F_{mg}(R_0)}{F_g}} R_0.$$
(6.14)

The next computation of  $L_{d,s+1}$  applies to particles placed at distance  $L_{d,s}$  and uses the magnetic force computed with the corrected value of the distance  $F_{mg}(L_{d,s})$ , where  $s = 0, \ldots s_{max}$  is the number of iteration,  $s_{max}$  is chosen maximum number of iterations or the last iteration step when a chosen condition is satisfied.

$$L_{d,s+1} = \sqrt[4]{\frac{F_{mg}(L_{d,s})}{F_g}} L_{d,s}.$$
(6.15)

for s = 0:

$$L_{d,1} = \sqrt[4]{\frac{F_{mg}(L_{d,0})}{F_g}} L_{d,0}.$$
(6.16)

Table 6.5 shows the difference between the first estimation of the limit distance  $L_{d,0}$ and the corrected value  $L_{d,s_{max}}$ . The  $L_d$  values are expressed as a multiple of  $R_0$ . The values are computed for magnetic forces between one single nanoparticle and aggregates of different sizes. Our condition to terminate the iteration was E < 10%, where

$$E = \left| \frac{L_{d,s+1}}{R_0} - \frac{L_{d,s}}{R_0} \right|$$

for  $s = s_{max}$ . Again, the value of magnetization was 570 kA/m with the same direction of magnetization of all nanoparticles in spherical aggregates.

	i [1]	$L_{d,0}/R_0$ [1]	$L_{d,s}/R_0 \ [1]$	$L_{d,s}$ [µm]	s [1]
	1	75.54	75.54	3.06	0
	10	41.01	43.08	2.72	3
	100	17.97	20.55	2.32	3
	1000	5.79	12.96	2.85	6
	10000	4.40	5.08	2.29	7
	100000	3.96	2.11	2.00	8
ĺ	1000000	2.64	1.50	3.04	7

TABLE 6.5: A comparison of the first estimation of the limit distance and the corrected value computed by iteration

The limit distance is expressed as a multiple of the sum of the radii of the aggregate and the nanoparticle  $R_0$ , *i* is number of nanoparticles creating the aggregate and *s* is the step of the iteration.

According to the results of the limit distance between particles in Tab. 6.5, particles should have a distance larger than 3  $\mu$ m between each other, which corresponds to the concentration of 8 mg/L of particles, in order not to aggregate due to the relatively long-range attractive magnetic forces. However, it must be taken into account that the value of the concentration was computed in the case of direct dipole-dipole interaction (the largest possible magnetic force between particles) and that the particles would have to be perfectly dispersed with no sedimentation etc.

## Chapter 7

## Structure of Aggregates

This chapter was published in [69].

Because of the composition of nanoparticles, every nanoparticle has a non-zero vector of magnetization. According to [14], nZVI with diameter of 40 nm has a saturation magnetization of 570 kA/m. This is the value of the nanoparticles composed of 14.3% of Fe<sup>0</sup> and 85.7% of Fe<sub>3</sub>O<sub>4</sub>. This data is used for the model. Therefore, it is assumed that all nanoparticles have the same magnitude of magnetization vector. However, the structure that nanoparticles form in the aggregate is not known - that is, the position of the nanoparticles in the aggregate and the direction of their magnetization vector. This knowledge is crucial in order to compute the magnetic forces between aggregates. In the next sections, various aggregate structures are examined and assessed.

#### 7.1 An unstructured model of aggregates

An unstructured model of an aggregate  $A(n, \vec{R})$  composed of n nanoparticles with its centre at position  $\vec{R}$  is a set of n nanoparticles so that all of the nanoparticles are spheres of constant radius a and constant saturation magnetization M and their centres  $\vec{r}_i$   $(i \in \{1, \ldots, n\})$  are uniformly randomly distributed inside the sphere with centre at  $\vec{R}$  and radius  $\sqrt[3]{na}$ , and the directions of the saturation magnetization vectors  $\vec{M}_i$  are uniformly randomly (Fig. 7.1) or equally (Fig. 7.2) distributed in the individual sphere.

These two models of aggregate structure were compared by computing the magnetic force and the corrected limit distance between one single nanoparticle and aggregates of different sizes. The result of the computation is in Tab. 7.1. The comparison of  $L_d$  for different aggregate sizes is shown in Fig. 7.3.

As it was expected, when nanoparticles have the same direction of magnetization, the attractive magnetic force of the aggregate created by the nanoparticles have a longer



FIGURE 7.1: An unstructured model of an aggregate with randomly directed vectors of magnetization of nanoparticles creating the aggregate



FIGURE 7.2: An unstructured model of an aggregate with the same direction of vectors of magnetization of nanoparticles creating the aggregate

		Same direc	Same direction of $\vec{M}$		ection of $\vec{M}$
i [1]	$F_g$ [N]	$F_{mg}(R_0)$ [N]	$L_{d,0}/R_0$ [1]	$F_{mg}(R_0)$ [N]	$L_{d,0}/R_0$ [1]
1	$2.02 \cdot 10^{-18}$	$6.58 \cdot 10^{-11}$	75.7	$1.20 \cdot 10^{-11}$	49.3
10	$2.02 \cdot 10^{-17}$	$8.28 \cdot 10^{-11}$	43.9	$7.45 \cdot 10^{-12}$	24.6
100	$2.02 \cdot 10^{-16}$	$2.57 \cdot 10^{-12}$	24.0	$3.96 \cdot 10^{-11}$	21.1
1000	$2.02 \cdot 10^{-15}$	$3.12 \cdot 10^{-11}$	11.9	$1.98 \cdot 10^{-11}$	10.0
10000	$2.02 \cdot 10^{-14}$	$2.99 \cdot 10^{-11}$	6.1	$6.52 \cdot 10^{-12}$	4.3
100000	$2.02 \cdot 10^{-13}$	$2.28 \cdot 10^{-11}$	3.8	$6.08 \cdot 10^{-13}$	1.8
1000000	$2.02 \cdot 10^{-12}$	$8.41 \cdot 10^{-12}$	2.2	$4.98 \cdot 10^{-12}$	1.4

 

 TABLE 7.1: Computed magnetic forces and limit distances of structured aggregates with the same and with random magnetization direction

range than when the nanoparticles have randomly directed magnetization. A significant attribute of the unstructured model of the aggregate is the size of the magnetic force in comparison with the size of the other forces affecting the aggregate movement. The computed magnetic forces are bigger than the counteracting gravitational force and the aggregation rate increases.

#### 7.2 A structured model of aggregates

The alternative aggregate structure is that the nanoparticles arrange themselves in a structured order in the aggregate. Vectors of magnetization of the nanoparticles adhere to the structure. According to the observed behaviour of spherical magnets, the magnets create sections with the minimum of energy. With a small number of magnets, most sections are created in circles composed of chains. Other structured models of aggregates were also considered - namely, cubic and honeycomb. The directions of vectors of magnetization of nanoparticles in these models of structured aggregates are shown in Fig. 7.4.



FIGURE 7.3: Comparison of unstructured model with the same and random magnetization direction

The magnetic force values are computed between one single nanoparticle at a fixed point and aggregates of different sizes under the nanoparticles on which the gravitational force acts.



FIGURE 7.4: Diagram of the structure of nanoparticles creating an aggregate with schematic directions of magnetization vectors of the nanoparticles

According to observed behaviour of spherical magnets, the magnets create sections with less energy in which the vectors of magnetization cancel each other out and the final vector of magnetization approaches zero. Consequently, in the case of a structured order of nanoparticles, the magnetic forces among the particles have negligible influence on the aggregation of the particles. The following table presents the magnitude of the magnetic force between a nanoparticle and a cubic aggregate attached to each other. The directions of magnetization of nanoparticles in the aggregate are set according to Fig. 7.6(d). The results show that the magnetic force between structured particles approaches zero. The results for a cubic structure can be seen in Table 7.2.

Even though the distance between the particles is the smallest possible, the magnetic

i [1]	$ F_{\rm mg} $ [N]	$ F_g $ [N]
1	$2.4 \cdot 10^{-38}$	$2.0 \cdot 10^{-18}$
8	$4.1 \cdot 10^{-38}$	$1.6 \cdot 10^{-17}$
125	$6.6 \cdot 10^{-40}$	$2.5 \cdot 10^{-16}$
1,000	$7.7 \cdot 10^{-41}$	$2.0 \cdot 10^{-15}$
10,648	$8.4 \cdot 10^{-42}$	$2.2 \cdot 10^{-14}$
97,336	$5.7 \cdot 10^{-42}$	$2.0 \cdot 10^{-13}$
1,000,000	$5.0 \cdot 10^{-42}$	$2.0 \cdot 10^{-12}$

TABLE 7.2: Magnetic forces between one nanoparticle and cubic aggregate

The particles are attached to each other. *i* refers to the number of nanoparticles in a cubic aggregate,  $|F_{\rm mg}|$  is the magnitude of the magnetic force between the nanoparticle and the aggregate and  $|F_g|$  refers to the magnitude of the gravitational force between the nanoparticle and the aggregate.

forces between the particles are negligible in comparison with the gravitational forces. For structured aggregates with magnetization of nanoparticles adhering to the structure, the magnetic forces have an insignificant influence on the rate of aggregation of the particles. That does not match the observations [14]. Therefore, on the basis of the results in this section, it was decided not to study more structured forms. The structure of real aggregates was assumed to be damaged.

## 7.3 Structure of aggregate on the basis of interaction energy

Another way to assess the most probable structures of aggregates is by computing the interaction energy E between nanoparticles which make up the aggregate. According to [70]:

$$E = -\vec{m} \cdot \vec{B}.\tag{7.1}$$

E is the potential energy that a magnetic moment  $\vec{m}$  has in an externally-produced magnetic field  $\vec{B}$ . Again, it is assumed that all nanoparticles in the aggregate have the same value of magnetization vectors (570 kA/m [14]). Positive interaction energy signifies repulsion of one magnetic moment from the magnetic field by another magnetic moment, whereas negative interaction energy means attraction of the dipoles. One can assess the probability of stability of different aggregate structures (the higher negative interaction energy, the higher the probability of the structure) by summation of the interaction energies between every pair of nanoparticles in an aggregate.

The interaction energy results are shown in Fig. 7.5. The computed interaction energies are displayed for different aggregate structures (according to schemes from Fig.7.6). The figure is in a logarithmic scale. The exact values of the interaction energies for different aggregate structures and the varying number of nanoparticles which make up

the aggregate are in Tab. 7.3. The absolute values are not relevant, but a comparison of the values of different structures is. According to Fig. 7.5, the most probable structure for small aggregates is chains and for bigger aggregates is spherical sections with the same direction of magnetization vectors of nanoparticles creating the aggregate.





(the larger the negative energy, the higher the probability of the structure)



FIGURE 7.6: Scheme of structure of nanoparticles creating an aggregate with schematic directions of magnetization vectors of the nanoparticles

In the article [14], aggregates of nanoscale zero-valent iron particles were measured using dynamic light scattering, optical microscopy and sedimentation measurements. According to their results, at first nanoparticles create sections, subsequently these aggregates assemble themselves into fractal, chain-like sections. We believe that is due to the high concentrations of nanoparticles that they used, which lead to very fast aggregation first into chains then into sections, which in turn lead to the measurement of only larger sections in [14]. The presumption is that with a larger number of nanoparticles, spherical

Interaction energies				
Number of nanoparticles [1]	Structure	Energy/ $\mu$ [eV]		
2	chain	273		
3	chain	588		
8	cube	903		
8	sphere	1449		
8	circle	2184		
8	chain	2688		
27	chain	3780		
27	sphere	8400		
29	cube	8400		
343	cube	56700		
343	chain	109200		
343	sphere	184800		

TABLE 7.3: Interaction energies of a variety of aggregate structures The computed interaction energies divided by a permittivity constant for a variety of aggregate structures (according to schemes 7.6) and for different numbers of nanoparticles creating the aggregates.

sections are created, which leads to the supposition that with very high concentration of particles, spherical structured aggregates only attach to each other, without changing their structure. This corresponds with the observations of [14]: that in high concentrations, first nanoparticles aggregate into sections, then these created sections aggregate into doublets or triplets, and finally into chain-like fractal aggregates.

In this work, it is assumed that larger aggregates are composed from more than just ten nanoparticles, therefore aggregates are assumed to be spherical in subsequent computations. It is suggested that future work could focus on the division of aggregates according to their size and possible structure.

## Chapter 8

# Methods of computing magnetic forces

This chapter was published in [68].

The magnetic field around an aggregate depends on the aggregate structure and on the structure of the particles constituting the aggregate. It is assumed that the magnitude of the magnetization vector of each single particle is the same and they differ only in the direction of their vector of magnetization. The magnetic field of aggregates is computed on the basis of the magnetization vectors of the nanoparticles in the aggregates. This computation is very time-consuming. Therefore, a faster method to compute the magnetic forces between particles is proposed. The more accurate, time-consuming method and the less accurate, faster method are compared for the case of an unstructured model of aggregate with random direction of magnetization (see section 7.1).

According to [14], the radius of the nanoparticles is set to a = 20 nm and all the nanoparticles in the model have the same magnitude of magnetization  $M_0 = 570 \text{ kA/m}$ .

The magnetic forces interacting between two aggregates can be computed in two ways. The more correct one called summation and the more rapid one called averaging.

#### 8.1 Method of summation

The method of summation has already been described in sec. 6.3 and is based on the accurate computation by the summation of magnetic forces between every nanoparticle in the first aggregate and every nanoparticle in the second aggregate: The magnetic field around the first aggregate  $A(n_1, \vec{0})$  is computed as the sum of the magnetic fields

of every single nanoparticle creating the aggregate:

$$\tilde{\phi}(\vec{r}) = \sum_{i=1}^{n_1} \phi(\vec{r} - \vec{r}_{1i}, \vec{M}_{1i}, a), \tag{8.1}$$

where  $\phi$  is computed using the formula (6.4) rotated to the direction of magnetization  $M_{1i}$ ,  $\vec{r}_{1i}$  is the location of the centre of the *i*-th nanoparticle in the first aggregate, and  $\vec{M}_{1i}$  is the magnetization vector of the *i*-th nanoparticle in the first aggregate.

The magnetic force acting on the second aggregate  $A(n_2, \vec{R})$  is then computed as the sum of the magnetic forces acting on every single nanoparticle in the second aggregate:

$$\vec{F} = \sum_{j=1}^{n_2} \tilde{V}(\vec{M}_{2j} \cdot g\vec{rad})g\vec{rad}\tilde{\phi}(\vec{r}_{2j})$$
(8.2)

where  $\tilde{V} = \frac{4}{3}\pi a^3$  is the volume of a nanoparticle,  $\vec{r}_{2j}$  is the location of the centre of the *j*-th nanoparticle in the second aggregate and  $\vec{M}_{2j}$  is the magnetization vector of the *j*-th nanoparticle in the second aggregate.

For faster computation we approximate the magnetic force by the formula

$$\vec{F} \doteq \sum_{j=1}^{n_2} \tilde{V}(\vec{M}_{2j} \cdot g\vec{rad})g\vec{rad}\tilde{\phi}(\vec{R})$$
(8.3)

where  $\vec{R}$  is the position of the centre of the second aggregate  $A(n_2, \vec{R})$ .

#### 8.2 Method of averaging

The *method of averaging* works with aggregates with averaged magnetization vector according to the following formula:

$$\vec{M}_{A} = \frac{\sum_{i=1}^{n} \vec{M}_{i}}{n}.$$
(8.4)

where  $\vec{M}_A$  is the averaged magnetization vector of the aggregate A and  $\vec{M}_i$  is the vector of magnetization of the i-th nanoparticle from the aggregate A. The magnetic force between  $A(n_1, \vec{0})$  and  $A(n_2, \vec{R})$  is approximated by the formula

$$\vec{F} \doteq V_2(\vec{M}_{2A} \cdot g\vec{rad})g\vec{rad}\phi(\vec{R}, \vec{M}_{1A}, \sqrt[3]{n_1}a)$$
(8.5)

where  $\vec{M}_{1A}$  and  $\vec{M}_{2A}$  are the averaged magnetization vectors of the aggregates  $A(n_1, \vec{0})$ and  $A(n_2, \vec{R})$  respectively,  $V_2 = \sqrt[3]{n_2 a}$  is the volume of the second aggregate and  $\phi(\vec{R}, \vec{M}, V)$  is the electromagnetic potential of the averaged aggregate computed analogously to (6.1):

$$\phi(\vec{R}, \vec{M}, V) = \int_{V} \frac{\vec{M}\vec{R}}{R^3} dV.$$
(8.6)

## 8.3 A comparison of the averaging and summation methods

The magnetic force values computed by averaging and summation method were compared. Tab. 8.1 shows that the magnetic force values between one single nanoparticle and the aggregates with different sizes when attaching to each other (at distance  $R_0 = a_i + a_j$ ). The plotted data can be seen in Fig. 8.1.

i [1]	Averaged $F_{\rm mg}$ [N]	Deviation [N]	Summed $F_{\rm mg}$ [N]	Deviation [N]
1	$1.4 \cdot 10^{-9}$	$2.5 \cdot 10^{-9}$	$6.3 \cdot 10^{-9}$	$1.1 \cdot 10^{-9}$
10	$4.4 \cdot 10^{-10}$	$1.9 \cdot 10^{-10}$	$6.3 \cdot 10^{-9}$	$8.4 \cdot 10^{-9}$
100	$7.2 \cdot 10^{-11}$	$2.7 \cdot 10^{-11}$	$4.6 \cdot 10^{-9}$	$5.4 \cdot 10^{-9}$
1,000	$1.1 \cdot 10^{-11}$	$3.0 \cdot 10^{-12}$	$7.4 \cdot 10^{-8}$	$1.1 \cdot 10^{-7}$
10,000	$1.9 \cdot 10^{-12}$	$6.0 \cdot 10^{-13}$	$5.9 \cdot 10^{-8}$	$7.0 \cdot 10^{-8}$
1,000,000	$2.8 \cdot 10^{-13}$	$1.1 \cdot 10^{-13}$	$8.7 \cdot 10^{-9}$	$1.0 \cdot 10^{-8}$
1,000,000	$5.4 \cdot 10^{-14}$	$2.2 \cdot 10^{-14}$	$3.0 \cdot 10^{-8}$	$4.9 \cdot 10^{-8}$

TABLE 8.1: The magnetic forces of particles at distance  $R_0$  computed by the averaging and the summation methods

Symbol i refers to the number of nanoparticles in the aggregate. The deviation is an averaged value of absolute deviations of data points from their mean value. Each line results from 1000 computations with randomly generated directions of magnetization vectors.

In close proximity, the position and magnetization vector of individual nanoparticles in the aggregates have a significant effect on the final magnetic force value. It is therefore assumed that the difference between the averaging and the summation methods will be less significant at larger distances between particles  $r \gg R_0$ . Hence, the magnetic force values between particles at distance  $1000 \cdot R_0$  were computed and the results compared in Tab. 8.2. The plotted data is in Fig. 8.2.

This work mainly presents results of the interactions between one single nanoparticle and different aggregates. It is only to maintain the clarity of the results (2D-graphs, smaller tables). An example of the results of a comparison between averaging and summation methods of  $F_{mg}$ ,  $L_d$  computation for different interacting aggregates is displayed in Fig. 8.3.



FIGURE 8.1: The magnetic forces of particles at distance  $R_0$  computed by the averaging and the summation methods

i $[1]$	Averaged $F_{\rm mg}$ [N]	Deviation [N]	Summed $F_{\rm mg}$ [N]	Deviation [N]
1	$2.0 \cdot 10^{-20}$	$1.0 \cdot 10^{-20}$	$3.1 \cdot 10^{-20}$	$5.5 \cdot 10^{-21}$
10	$3.3 \cdot 10^{-21}$	$2.3 \cdot 10^{-21}$	$6.5 \cdot 10^{-21}$	$4.0 \cdot 10^{-21}$
100	$4.7 \cdot 10^{-22}$	$2.8 \cdot 10^{-22}$	$5.9 \cdot 10^{-22}$	$2.2 \cdot 10^{-22}$
1,000	$4.7 \cdot 10^{-23}$	$1.7 \cdot 10^{-23}$	$5.1 \cdot 10^{-23}$	$3.0 \cdot 10^{-23}$
10,000	$7.9 \cdot 10^{-24}$	$4.0 \cdot 10^{-24}$	$1.5 \cdot 10^{-23}$	$8.5 \cdot 10^{-24}$
100,000	$1.1 \cdot 10^{-24}$	$5.6 \cdot 10^{-25}$	$1.5 \cdot 10^{-24}$	$1.1 \cdot 10^{-24}$
1,000,000	$1.4 \cdot 10^{-25}$	$7.1 \cdot 10^{-26}$	$4.1 \cdot 10^{-25}$	$2.0 \cdot 10^{-25}$

TABLE 8.2: The magnetic forces of particles at distance  $1000 \cdot R_0$  computed by averaging and summation methods

i refers to the number of nanoparticles in the aggregate. The deviation is an averaged value of absolute deviations of data points from their mean value. Each line results from 1000 computations with randomly generated directions of magnetization vectors.

#### 8.4 Assessment of the suitability of the averaging method

By assumption, the averaging method for computing magnetic forces is inadvisable in the case of small distances between particles. However, in the case of large distances between particles, the error of the method is negligible. Where is the limit for the usefulness of the averaging method? Tab. 8.3 compares the magnetic force between an aggregate and a nanoparticle as computed by averaging and summation for various dimensions of aggregates and various distances of interacting particles. The distances are expressed in multiples of corresponding  $R_0$ . As can be seen from the table, the results of the two methods differ only for small distances between the aggregate and the nanoparticle.



FIGURE 8.2: The magnetic forces of particles at distance  $1000 \cdot R_0$  computed by averaging and summation methods



FIGURE 8.3: The limit distances of two interacting aggregates computed by the averaging and the summation methods

On the left side of the graph, gravity affects the smaller aggregates, on the right side, gravity affects the bigger aggregates.

The computed magnetic forces depending on distances between particles are compared in Fig. 8.4, 8.5. In Fig. 8.4, the distance between particles is expressed as total value in metres, in Fig. 8.5, the distance between particles is expressed as a multiple of the smallest possible distance  $R_0$ . In this figure, a relation of averaging of computation as a function of distance between particles can be seen. The larger the aggregate, the bigger

Aggregate composed of 10 nanoparticles				
Distance/ $R_0$ [1]	averaged $F_{mg}$ [N]	summed $F_{mg}$ [N]		
1	$1.6 \cdot 10^{-11}$	$2.6 \cdot 10^{-11}$		
10	$1.4 \cdot 10^{-15}$	$1.3 \cdot 10^{-15}$		
100	$6.7 \cdot 10^{-20}$	$6.8 \cdot 10^{-20}$		
1000	$3.9 \cdot 10^{-24}$	$3.9 \cdot 10^{-24}$		

Aggregate composed of $10^3$ nanoparticles			
Distance/ $R_0$ [1]	averaged $F_{mg}$ [N]	summed $F_{mg}$ [N]	
1	$9.8 \cdot 10^{-13}$	$1.4 \cdot 10^{-11}$	
10	$1.9 \cdot 10^{-17}$	$1.3 \cdot 10^{-17}$	
100	$6.6 \cdot 10^{-21}$	$6.7 \cdot 10^{-21}$	
1000	$1.1 \cdot 10^{-24}$	$1.1 \cdot 10^{-24}$	

Aggregate composed of $10^6$ nanoparticles			
1188108400	composed of 10 m		
Distance/ $R_0$ [1]	averaged $F_{mg}$ [N]	summed $F_{mg}$ [N]	
1	$2.9 \cdot 10^{-15}$	$6.9 \cdot 10^{-12}$	
10	$5.9 \cdot 10^{-19}$	$6.6 \cdot 10^{-19}$	
100	$7.7 \cdot 10^{-23}$	$7.6 \cdot 10^{-23}$	
1000	$2.2 \cdot 10^{-27}$	$2.2 \cdot 10^{-27}$	

TABLE 8.3: A comparison of magnetic force computation for different distances between particles

The computation is performed using the summation and the averaging methods. Different sized aggregates interact with one single nanoparticle.

the error of the averaging method for particles being close together. However, from the distance of  $10 \cdot R_0$ , the averaging method can be used to compute magnetic forces.



FIGURE 8.4: Magnetic forces computed by the averaging and the summation methods as a function of the distance between particles expressed in metres



FIGURE 8.5: Magnetic forces computed by the averaging and the summation methods as a function of the distance between particles expressed as a multiple of  $R_0$ 

## Chapter 9

# Inclusion of electrostatic forces in the computation of the limit distance

This chapter was published in [71].

The effect of electrostatic forces on the aggregation rate was derived for the case where the interacting particles are attached (the distance between particles is equal to the sum of their radii  $R_0 = a_i + a_j$ ). The derivation was described in Chapter 4.

However, due to long-range attractive magnetic forces, forces acting on the particles not only in close proximity  $R_0$  but also in further distances are of interest. The question is how large the repulsive electrostatic force is at the limit distance  $L_d$  and how it affects the attraction of particles.

The magnitude of the electrostatic force is a function of the distance between particles as well as the strength of the magnetic force. Therefore, we decided to include computation of the effect of the electrostatic force once more directly into the limit distance computation. There is another way to compute the effect of electrostatic forces between particles but more suitable for the case of particles upon which the long-range forces act.

#### 9.1 Limit distance extended by electrostatic forces

The extension of  $L_d$  by electrostatic forces was published in [71].

The extension was achieved by adding Coulomb's law  $F_c$  (4.5) into the equilibrium equation of the forces acting on the aggregating particle (Fig. 9.1). In this case, the equation was expressed in terms of attractive magnetic force on one side and counteracting gravitational force on the other (6.11). By including the repulsive electrostatic force, the limit distance that expresses the border of particle mutual attraction leading to aggregation of particles is reduced depending on the surface charge density of the particles.



FIGURE 9.1: An illustration of a comparison of the attractive magnetic forces and counteracting gravitational and electrostatic forces

At the limit distance, the forces are balanced. When the electrostatic force effect is included in the limit distance computation, the long-range attractive magnetic force has a smaller effect depending on the surface charge density of the interacting particles.

As in Chapter 4, surface charge density  $\sigma$  of the particles was used to evaluate the magnitude of the electrostatic force between particles.

$$F_c = \frac{\pi}{4\pi\varepsilon_0\varepsilon} \frac{\sigma_i \sigma_j d_i^2 d_j^2}{R^2},\tag{9.1}$$

where  $\varepsilon$  is the dielectric constant of the liquid,  $\varepsilon_0$  is the vacuum permittivity, R is the distance between the centres of gravity of the particles i and j,  $\sigma_i$  is the surface charge density of particle i and  $d_i$  is its diameter.

Because the magnetic force decreases to the power 4 and Coulomb's force to the power 2, the equilibrium equation of forces takes the form:

$$F_g + F_c \frac{R_0^2}{L_d^2} - F_{mg} \frac{R_0^4}{L_d^4} = 0.$$
(9.2)

After solving of this quadratic equation

$$F_g(L_d^2)^2 + F_c R_0^2 L_d^2 - F_{mg} R_0^4 = 0, (9.3)$$

we obtain the extended formula for the limit distance with the inclusion of electrostatic forces:

$$L_d^{el} = \sqrt{\frac{\sqrt{F_c^2 + 4F_g F_{mg}} - F_c}{2F_g}} R_0.$$
(9.4)

The magnetic force  $F_{mg}$  was obtained from the formulas (6.1, 6.2, and 8.2).

#### 9.1.1 Correction of the limit distance including the electrostatic forces

Electrostatic forces fall with the power of 2 and magnetic forces between two single domain magnetic nanoparticles fall with the power of 4. In the case of aggregates, the decrease depends on aggregate structure and iteration of the limit distance computation is needed [68]. A constant surface charge density of all nanoparticles and aggregates is assumed.

The iteration for the correction of  $L_d^{el}$  was proposed the same way as in section 6.4.1: the limit distance estimated by (9.4) is used as a starting distance for the next iteration.

$$L_{d,0}^{el} = \sqrt{\frac{\sqrt{F_c^2(R_0) + 4F_g F_{mg}(R_0)} - F_c(R_0)}{2F_g}} R_0.$$
(9.5)

The next computation of  $L_{d,s+1}^{el}$  is performed with particles placed at distance  $L_{d,s}^{el}$  and using the magnetic force and electrostatic force computed with the corrected value of distance  $F_{mg}(L_{d,s}^{el})$  and  $F_c(L_{d,s}^{el})$  respectively.

$$s=0,\ldots s_{max},$$

where s is the number of iteration,  $s_{max}$  is chosen maximum number of iterations or the last iteration step when a chosen condition is satisfied.

$$L_{d,s+1}^{el} = \sqrt{\frac{\sqrt{F_c^2(L_{d,s}^{el}) + 4F_g F_{mg}(L_{d,s}^{el})} - F_c(L_{d,s}^{el})}{2F_g}} L_{d,s}^{el}.$$
(9.6)

Table 9.1 shows the difference between the first estimation of the limit distance  $L_{d,0}^{el}$  and the corrected value  $L_{d,s_{max}}^{el}$ . The  $L_d$  values are expressed as multiples of  $R_0$ . The values are computed for the interaction between one single nanoparticle and aggregates with different sizes. The aggregate structure is the one where all the nanoparticles in the aggregate are randomly positioned and have the same direction of magnetization vector. Our condition to terminate the iteration was E < 10%, where

$$E = \left| \frac{L_{d,s+1}^{el}}{R_0} - \frac{L_{d,s}^{el}}{R_0} \right|$$

for  $s = s_{max}$ . Again, the value of magnetization was 570 kA/m with the same direction of magnetization of all nanoparticles in spherical aggregates and the value of the surface charge density was  $2.5 \cdot 10^{-5}$  Cm<sup>-2</sup>.

i [1]	$L_{d,0}^{el}/R_0$ [1]	$L_{d,s}^{el}/R_0 \ [1]$	$L_{d,s}^{el}$ [µm]	s [1]
1	27.00	27.00	1.12	0
10	21.76	19.88	1.25	3
100	9.30	14.70	1.66	5
1000	10.87	9.01	1.98	3
10000	5.40	4.45	2.01	13
100000	3.20	1.83	1.74	10
1000000	2.52	0.44	0.90	7

 TABLE 9.1: A comparison of the first estimation of the limit distance with electrostatic force inclusion and the corrected value computed by iteration

The limit distance is expressed as a multiple of the sum of the radii of the aggregate and the nanoparticle  $R_0$ , *i* is the number of nanoparticles creating the aggregate, *s* is the step of the iteration.

According to the results in Tab. 9.1, iteration of the limit distance values  $L_d^{el}$  is needed.

### 9.2 A comparison of the limit distances with and without the effect of electrostatic forces

Tab. 9.2 presents the differences between the computed values of the limit distance without electrostatic force inclusion  $L_d$  and the limit distance including the electrostatic force  $L_d^{el}$ . Iteration of the limit distance values has been used. The value of magnetization is 570 kA/m with the same direction of magnetization of all nanoparticles in spherical aggregates, the value of the surface charge density is  $2.5 \cdot 10^{-5}$  C/m<sup>2</sup> and the diameter of one nanoparticle is 50 nm.

Electrostatic force repulsion of particles has an impact especially in the aggregation of small particles. The larger the aggregate, the smaller the difference between the limit distance values with and without electrostatic forces, as is presented in Tab. 9.2. The magnetic forces decrease more quickly than the electrostatic forces. Hence, the larger the distance between particles, the smaller the influence that the magnetic forces have and the electrostatic force are more important.

A comparison between the computation of the limit distance with and without electrostatic forces is also in Fig. 9.2, 9.3. The limit distance was computed with the values: diameter of one nanoparticle is 50 nm, size of magnetization vector is 570 kA/m, surface charge of all particles is either  $10^{-6}$  or  $2.5 \cdot 10^{-5}$  C/m<sup>2</sup> (these values were chosen on the basis of the values ascertained for low and high effect of electrostatic forces between particles on the aggregation rate in Section 4.2). The unstructured model of aggregates

i [1]	$L_d/R_0$ [1]	$L_{d}^{el}/R_{0}$ [1]
1	75.54	27.00
10	43.08	19.88
100	20.55	14.70
1000	12.96	9.01
10000	5.08	4.45
100000	2.11	1.83
1000000	1.50	0.44

 TABLE 9.2: A comparison of the computed values of the limit distance with and without the inclusion of electrostatic forces

 $L_d$  is the limit distance without electrostatic force inclusion,  $L_d^{el}$  is the limit distance including electrostatic forces and *i* is the number of nanoparticles creating the aggregate. The limit

distance is expressed as a multiple of the sum of the radii of the aggregate and the nanoparticle  $R_0$ .

with the same direction of magnetization was used for the computation. The computed limit distances are shown in Fig. 9.2 and 9.3. The values of limit distances computed using equation (9.4) are compared with values of the limit distance computed by the equation excluding the effect of the electrostatic forces (6.12).



FIGURE 9.2: Limit distance values with and without electrostatic force inclusion The surface charge of particles is  $10^{-6}$  C/m<sup>2</sup>

In the graphs, the limit distance is not expressed in absolute values but as the ratio of the limit distance and the distance between the centres of the interacting particles attached to each other  $\frac{L_d}{R_0}$ . This represents how many times the distance between the centres of particles had to be increased in order not to aggregate due to magnetic forces. The comparison was performed for one nanoparticle interacting with aggregates of different sizes comprised of *i* nanoparticles.

It can be seen that in the case of higher  $\zeta$  potential, the limit distance of magnetic forces is decreased. Hence it is important to include the effect of electrostatic forces as well as



FIGURE 9.3: A comparison of limit distances with and without consideration of the effect of electrostatic forces with surface charge of particles  $2.5 \cdot 10^{-5} \text{ C/m}^2$ 

the effect of magnetic forces in the determination of the aggregation rate of particles.

## Chapter 10

## MTC extended by electrostatic and magnetic forces

This chapter was described in [72].

### 10.1 Inclusion of the limit distance into the computation of mass transport coefficients

The basic model of aggregation in Section 3.2 indicates the rate of aggregation caused by the collision of particles at distance  $R_0 = a_i + a_j$  apart, where  $a_i$  is the radius of the particle *i* and attractive forces outweigh the repulsive ones.

In the Sections 6.4 and 9.1, it was established that the limit distance is the distance inside of which attractive forces outweigh the repulsive ones (particles do not have to be distance  $R_0$  apart to aggregate). The magnetic forces attract the particles to each other and then they aggregate due to attractive van der Waals forces.

The mass transport coefficients (3.14), (3.16), (3.21) where derived on the basis of a flux of nanoparticles through an observed volume or spherical area around a particle. The area had radius  $R_0$  equal to the sum of radii of both particles. That means that particles collide and aggregate. According to arguments presented in this work, the particles do not have to be in contact to aggregate when attractive magnetic forces are acting between them. Therefore, the mass transport coefficients are computed as a flux through a sphere or circle area around a particle with diameter equal to the limit distance (6.15), (9.4).

If the particles are magnetic but have zero surface charge density, the mass transport coefficient (MTC) of particles i and j is equal to

$$\beta_{ij}^{mg} = \beta_{ij}^{1,mg} + \beta_{ij}^{2,mg} + \beta_{ij}^{3,mg}.$$
 (10.1)

$$\beta_{ij}^{1,mg} = \frac{4 \, k_B \, T}{3 \, \eta} \, \left(\frac{1}{d_i} + \frac{1}{d_j}\right) \, L_d,\tag{10.2}$$

$$\beta_{ij}^{2,mg} = \frac{4}{3} G \cdot L_d^3, \tag{10.3}$$

$$\beta_{ij}^{3,mg} = \frac{\pi g}{18\eta} \left( \varrho_p - \varrho \right) |d_i^2 - d_j^2| L_d^2.$$
(10.4)

If the particles have non-zero surface charge density and magnetization, the mass transport coefficient (MTC) of particles i and j is equal to

$$\beta_{ij}^{mg,el} = \beta_{ij}^{1,mg,el} + \beta_{ij}^{2,mg,el} + \beta_{ij}^{3,mg,el}.$$
(10.5)

$$\beta_{ij}^{1,mg,el} = \frac{4k_B T}{3\eta} \left(\frac{1}{d_i} + \frac{1}{d_j}\right) L_d^{el},$$
(10.6)

$$\beta_{ij}^{2,mg,el} = \frac{4}{3} G \cdot \left( L_d^{el} \right)^3, \tag{10.7}$$

$$\beta_{ij}^{3,mg,el} = \frac{\pi g}{18 \eta} \left( \varrho_p - \varrho \right) |d_i^2 - d_j^2| \left( L_d^{el} \right)^2.$$
(10.8)

The results of this change in the mass transport coefficients are discussed in the next section.

## 10.2 Comparison of MTC with and without the influence of electrostatic and magnetic forces

The comparison was performed for an extreme case with a spherical aggregate structure with the same direction of magnetization vectors of all nanoparticles creating the aggregates. This model of aggregate structure shows the highest possible aggregation rate. In Table 10.1 the mass transport coefficients  $\beta_{ij}$  computed by the model of particle aggregation at a distance of  $R_0$  (3.2) apart are compared with the mass transport coefficients of particles at distance  $L_d$  including magnetic forces  $\beta_{ij}^{mg}$  (10.1) and also with the mass transport coefficients computed at distance  $L_d^{el}$  including both magnetic forces and electrostatic forces  $\beta_{ij}^{mg,el}$  (10.5). Computation of  $L_d$  and  $L_d^{el}$  for the magnetic forces was performed using the method of averaging for particles with ratio  $L_d/R_0$  higher than 15, otherwise it was performed accurately using the method of summation (for more information see Section 8.4).

i [1]	i [1]	$\beta_{ii}$ [m <sup>3</sup> /s]	$\beta_{\cdots}^{mg}  [\mathrm{m}^3/\mathrm{s}]$	$\beta_{\cdot\cdot}^{mg,el}$ [m <sup>3</sup> /s]	$\frac{L_d^{el}}{2}$ [1]
1	<u> </u>	$\frac{110^{-17}}{110^{-17}}$	$\frac{\beta_{ij}}{3.1 \cdot 10^{-15}}$	$2.9 \cdot 10^{-15}$	$\frac{R_0}{78.9}$
1	10	$1.3 \cdot 10^{-17}$	$2.9 \cdot 10^{-15}$	$2.8 \cdot 10^{-15}$	50.6
1	100	$1.9 \cdot 10^{-17}$	$2.8 \cdot 10^{-15}$	$2.7 \cdot 10^{-15}$	28.4
1	1,000	$3.4 \cdot 10^{-17}$	$2.7 \cdot 10^{-15}$	$2.7 \cdot 10^{-15}$	14.6
1	10,000	$7.3 \cdot 10^{-17}$	$2.8 \cdot 10^{-15}$	$2.8 \cdot 10^{-15}$	7.1
1	100,000	$2.2 \cdot 10^{-16}$	$3.1 \cdot 10^{-15}$	$3.0 \cdot 10^{-15}$	3.4
1	1,000,000	$1.4 \cdot 10^{-15}$	$4.2 \cdot 10^{-15}$	$4.2 \cdot 10^{-15}$	1.6
10	10	$1.1 \cdot 10^{-17}$	$1.4 \cdot 10^{-14}$	$1.3 \cdot 10^{-14}$	65.6
10	100	$1.3 \cdot 10^{-17}$	$1.3 \cdot 10^{-14}$	$1.3 \cdot 10^{-14}$	42.0
10	1,000	$2.0 \cdot 10^{-17}$	$1.3 \cdot 10^{-14}$	$1.3 \cdot 10^{-14}$	23.5
10	10,000	$4.2 \cdot 10^{-17}$	$1.3 \cdot 10^{-14}$	$1.3 \cdot 10^{-14}$	12.1
10	100,000	$1.6 \cdot 10^{-16}$	$6.9 \cdot 10^{-14}$	$6.8 \cdot 10^{-14}$	10.2
10	1,000,000	$1.3 \cdot 10^{-15}$	$2.5 \cdot 10^{-14}$	$2.5 \cdot 10^{-14}$	3.2
100	100	$1.2 \cdot 10^{-17}$	$7.1 \cdot 10^{-14}$	$6.9 \cdot 10^{-14}$	54.4
100	1,000	$1.5 \cdot 10^{-17}$	$7.1 \cdot 10^{-14}$	$7.0 \cdot 10^{-14}$	34.7
100	10,000	$3.0 \cdot 10^{-17}$	$7.2 \cdot 10^{-14}$	$7.1 \cdot 10^{-14}$	19.4
100	100,000	$1.4 \cdot 10^{-16}$	$7.0 \cdot 10^{-13}$	$7.0 \cdot 10^{-13}$	21.1
100	1,000,000	$1.3 \cdot 10^{-15}$	$1.9 \cdot 10^{-13}$	$1.9 \cdot 10^{-13}$	6.4
1,000	1,000	$1.5 \cdot 10^{-17}$	$4.0 \cdot 10^{-13}$	$3.9 \cdot 10^{-13}$	45.1
1,000	10,000	$3.2 \cdot 10^{-17}$	$4.0 \cdot 10^{-13}$	$4.0 \cdot 10^{-13}$	28.7
1,000	100,000	$1.5 \cdot 10^{-16}$	$4.1 \cdot 10^{-13}$	$4.1 \cdot 10^{-13}$	16.1
1,000	1,000,000	$1.4 \cdot 10^{-15}$	$1.3 \cdot 10^{-12}$	$1.3 \cdot 10^{-12}$	11.8
10,000	10,000	$5.4 \cdot 10^{-17}$	$2.2 \cdot 10^{-12}$	$2.2 \cdot 10^{-12}$	37.3
10,000	100,000	$2.2 \cdot 10^{-16}$	$2.3 \cdot 10^{-12}$	$2.3 \cdot 10^{-12}$	23.7
10,000	1,000,000	$1.8 \cdot 10^{-15}$	$2.4 \cdot 10^{-12}$	$2.4 \cdot 10^{-12}$	13.3
100,000	100,000	$4.4 \cdot 10^{-16}$	$1.3 \cdot 10^{-11}$	$1.3 \cdot 10^{-11}$	30.8
100,000	1,000,000	$2.7 \cdot 10^{-15}$	$1.3 \cdot 10^{-11}$	$1.3 \cdot 10^{-11}$	19.6

TABLE 10.1: A comparison of mass transport coefficients without and with inclusion of electrostatic and magnetic forces

A comparison of mass transport coefficients computed using the primary model, mass transport coefficients computed at distance  $L_d$  including magnetic forces and mass transport coefficients computed at distance  $L_d^{el}$  including both magnetic forces and electrostatic forces.  $\beta$  represents the sum of mass transport coefficients for Brownian motion, velocity gradient, and sedimentation. Computation of  $L_d$  and  $L_d^{el}$  for magnetic forces was performed using the averaging method for particles with ratio  $L_d/R_0$  higher than 15, otherwise it was preformed accurately using the summation method.

The MTC values in Tab. 10.1 and Fig. 10.2 were computed using the following values: diameter of one nanoparticle is 50 nm, density of particles is  $6700 \text{ kg/m}^3$ , temperature is 300 K, dynamic viscosity of water is  $10^{-3}$  Pa·s, density of water is  $1000 \text{ kg/m}^3$ , velocity gradient is 50 s<sup>-1</sup>, size of magnetization vector is 570 kA/m and the surface charge of all particles is  $10^{-6}$  Cm<sup>-2</sup>.

The results of the size of the effect of magnetic forces were summarized and included into an analytical model of collisions between magnetic nanoparticles. Due to attractive magnetic forces, the aggregation rate is significantly higher and the repulsive electrostatic forces are almost negligible (Fig. 10.2). It is assumed that with other realistic choices of values of magnetization vector or surface charge, this trend would not change dramatically.



FIGURE 10.1: A comparison of MTC computed with and without the effect of electrostatic and magnetic forces

This modified model of aggregation better explains the rapid aggregation of zero-valent iron nanoparticles that is observed. This can help to simulate the migration of undissolved particles in groundwater.

## Chapter 11

# Adaptation of aggregation model to kinetic reactions

This chapter was derived in author's diploma thesis [9].

In chapter 5, the aggregation between particles was transformed to a model of aggregation between particle size sections (PSS) described by mass transport coefficient (MTC) giving the frequency of aggregation between particles from different sections (computable using equations (5.8), (5.10), (5.12) and (5.13)). The MTC gives the rate of aggregation between average particles in the PSS that are computable by the model (10.5) in the case of magnetic particles with non-zero surface charge.

The dynamics of aggregation correspond to a first-order reaction Re where two particles from different or the same sections aggregate (react) and a single particle is formed. Velocity of reactions is given by rate of change  $v_R$  which is proportional to rate constant  $k_R$  and concentrations of reacting species (concentrations  $c_r$  and  $c_p$  of aggregates from sections r and p respectively):

$$v_R = k_R c_p c_r.$$

The change in concentration of the particles in observed section l over time t is:

$$\frac{dc_l}{dt} = S_R(l) \cdot v_R = S_R(l)k_R c_p c_r, \qquad (11.1)$$

where  $S_R$  is the stoichiometry [1]. Here, the rate constant  $k_R$  has the unit [l/g/s].

Under the assumption of constant number of nanoparticles, the total volume of all particles in one section is equal to the total number of nanoparticles forming all the particles in the section multiplicated by the volume of a single nanoparticle. The change of total volume of a section can be evaluated as the change of number of all nanoparticles forming particles in the observed section. The change is given by aggregation of particles from smaller sections forming particles from larger sections. Because the change of volume of all nanoparticles in each section is being observed, reactions inside one section (both aggregating particles and also the resulting one belong into the same section) are not of interest. Reactions that give the change in the volume in sections are shown in Table 11.1 for aggregation between 2, 3, and 4 sections. In general, the number of different types of reactions  $n_{Re}$  depends on the number of the particle size sections  $n_{Se}$ :

$$n_{Re} = n_{Se}^2 - n_{Se}.$$
 (11.2)

(a) Reaction between 2 sections

Reaction
description
$r+p\rightarrow l$
$Se1+Se1 \rightarrow Se2$
$Se1+Se2 \rightarrow Se2$

(b) Reactions between 5 sections			
Reaction	Reaction		
label	description		
Re1	$Se1+Se1 \rightarrow Se2$		
Re2	$Se1+Se2 \rightarrow Se2$		
Re3	$Se1+Se2 \rightarrow Se3$		
Re4	$Se2+Se2 \rightarrow Se3$		
$\operatorname{Re5}$	$Se1+Se3 \rightarrow Se3$		
Re6	$Se2+Se3 \rightarrow Se3$		

Reactions between 3 sections

Reaction	Reaction
label	description
Re1	$Se1+Se1 \rightarrow Se2$
Re2	$Se1+Se2 \rightarrow Se2$
Re3	$Se1+Se2 \rightarrow Se3$
Re4	$Se2+Se2 \rightarrow Se3$
Re5	$Se1+Se3 \rightarrow Se3$
Re6	Se2+Se3→Se3
Re7	Se1+Se3→Se4
Re8	Se2+Se3→Se4
Re9	Se3+Se3→Se4
Re10	$Se1+Se4 \rightarrow Se4$
Re11	$Se2+Se4 \rightarrow Se4$
Re12	Se3+Se4→Se4

(c) Reactions between 4 sections

TABLE 11.1: A description of different reactions depending on the number of sections For example, reaction description  $Se1+Se2 \rightarrow Se2$  refers to a particle from Section1 aggregating with a particle from Section2 and creating an aggregate which still belongs to the Section2.

The aggregation rate can be given by MTC  $\hat{\beta}_{r,p,l}^+$  which is the mass transport coefficient of an increase of particles in the observed section l formed by the aggregation of the particles from sections r and p (see chapter 5.3.1). Reactions that are represented by the  $\hat{\beta}_{r,p,l}^+$  are listed in Tab. 11.1, where r, p and l correspond to the labels of sections Se (see Tab. 11.1(a)). A change in the particle concentration  $n_l$  in the section l follows:

$$\frac{dn_l}{dt} = \hat{\beta}^+_{r,p,l} n_p n_r. \tag{11.3}$$

The rate constant  $k_R$  can be calculated from the MTC  $\hat{\beta}_{r,p,l}^+$ . To have the aggregation in the form of first-order reactions, equations (11.1) and (11.3) are compared. Concentration of the particles  $c_l$  in section l reflects the weight of particles [g] from section l in one litre. Concentration  $n_l$  refers to the number of the particles from section l in one m<sup>3</sup>. The weight of a single nanoparticle is  $m_0$ , therefore the weight of the particles in section l can be computed if the number of the nanoparticles in section l is known. Thus, an average aggregate A was chosen in every section. The average aggregate  $A_l$  in section l represents all the aggregates in section l and its value refers to the average number of the nanoparticles creating the aggregates belonging to section l. Hence:

$$c_l = n_l m_0 A_l. \tag{11.4}$$

After substituting of eq. (11.4) into eq. (11.3), the change in particle concentration over time is:

$$\frac{dc_l}{dt} = \hat{\beta}^+_{r,p,l} \frac{1}{m_0} \frac{A_l}{A_r A_p} c_p c_r.$$
(11.5)

Thus, the rate constant  $k_R$  from eq. (11.1) is:

$$k_R = \frac{1}{S_R(l)} \hat{\beta}_{r,p,l}^+ \frac{1}{m_0} \frac{A_l}{A_r A_p}.$$
(11.6)

The value of  $A_l$  is not set by any theory, so the following choice of average aggregate size was chosen:  $A_l = \frac{k_l - k_{l-1}}{2}$  where  $k_l$  is the number of the nanoparticles which make up the largest possible aggregate belonging in section l (see chapter 5). The stoichiometry  $S_R$ has been also derived from the volume of the aggregates (number of the nanoparticles) in aggregating sections. By convention, the stoichiometries for reactants are negative and for products positive. An example reaction is shown below, where  $A_1$  is an average aggregate from section  $Se_1$ , characterized by the number of its nanoparticles.

Example reaction Se1+Se1
$$\rightarrow$$
Se2:  $S_R(Se1) = -2 \cdot A_1,$   
 $S_R(Se2) = +2 \cdot A_1.$ 

Now it is possible to transfer the mass transport coefficients  $\hat{\beta}^+_{r,p,l}$  into kinetics. Having chosen a representative aggregate for every PSS, the stoichiometry and the rate constant can be computed for every reaction representing aggregation between PSS.

#### 11.1 An example of transfer of MTC to kinetics

We chose three sections containing aggregates with size boundary according to Tab. 11.2. In the Table, the average aggregate from every section is chosen.

Section	Diameter of aggregates	Numbers of nanoparticles	Averaged aggregate
label	[nm]	of aggregates [1]	A [1]
Se1	50-200	1-64	16
Se2	200-500	64–1000	343
Se3	500-2000	1000-64000	15625

TABLE 11.2: Section size boundaries and its average aggregates The number A is the number of nanoparticles of the average aggregate from a section.

The stoichiometry of the reactions is shown in Tab. 11.3.

Reaction	Reaction	S S	Section	s
label	description	Se1	Se2	Se3
Re1	$Se1+Se1 \rightarrow Se2$	-32	32	0
Re2	$Se1+Se2 \rightarrow Se2$	-16	16	0
Re3	$Se1+Se2 \rightarrow Se3$	-16	-343	359
Re4	$Se2+Se2 \rightarrow Se3$	0	-686	686
Re5	$Se1+Se3 \rightarrow Se3$	-16	0	16
Re6	Se2+Se3→Se3	0	-343	343

TABLE 11.3: The stoichiometry of the kinetics of the reactions between 3 sections

In Tab. 11.4, the mass transport coefficients describing aggregation between sections are transformed into the rate constant of kinetics for every reaction between sections. The values are computed using eq. (11.6) with the following values: the radius of one nanoparticle a = 25 nm, the weight of one nanoparticle  $m_0 = 4.4 \cdot 10^{-19}$  kg, the temperature T = 300 K, the dynamic viscosity of water  $\eta = 10^{-3}$  Pa·s, the density of water  $\rho = 1000$  kg/m<sup>3</sup>, the velocity gradient G = 50 s<sup>-1</sup> and the size of magnetization vector  $M_0 = 570$  kA/m. The value of stoichiometry  $S_R(l)$  is taken from Tab. 11.3 (the one positive number of every reaction).

Reaction	Reaction	$\hat{\beta}^+_{r.p.l}$ (MTC)	$k_R$
label	description	$[m^3/s]$	[L/g/s]
Re1	$Se1+Se1 \rightarrow Se2$	$6.98 \cdot 10^{-16}$	70.4
Re2	$Se1+Se2 \rightarrow Se2$	$8.66 \cdot 10^{-17}$	0.79
Re3	$Se1+Se2 \rightarrow Se3$	0	0
Re4	Se2+Se2→Se3	$4.70 \cdot 10^{-16}$	0.2
Re5	Se1+Se3→Se3	$2.10 \cdot 10^{-19}$	0.0019
Re6	Se2+Se3→Se3	$2.09 \cdot 10^{-18}$	$4.0 \cdot 10^{-5}$

TABLE 11.4: The rate constants of kinetics computed from the MTC

The highest rate constant is for the reactions between small particles. It corresponds to the observation that smallest particles are the most reactive. In a dispersion of already aggregated particles, aggregation eventually stops.

## Chapter 12

# Simulation of transport of aggregating nanoparticles

## 12.1 Simulation of non-magnetic nanoparticles to verify the electrostatic aggregation model

Simulation of non-magnetic nanoparticles with non-zero surface charge serves to verify the electrostatic model of aggregation (Chapter 4).

## 12.1.1 A description of a simulation of bentonite migration and its results

For the purpose of simulation, an experiment involving the transport of bentonite colloid particles through a block of granite with a dominant sub-horizontal fracture was chosen [73]. The size of the granite block and fracture location is displayed in Figure 12.1 (scale is in millimetres).

In Figure 12.2, the mean fracture elevation and distribution of the boreholes net is shown with the injection well L1 and withdrawal well L4 highlighted.

The L1 and L4 boreholes, situated 380 mm from each other, were used for the migration of bentonite colloids. The measured volume of the fracture was 2.5 L, so the width of the fracture was set to 3 mm (constant across the whole area).

First, the geometry of the problem was designed for the whole granite block. However, the bentonite transport mainly occurred in the fracture and transport through the granite block is negligible. Therefore, the geometry of the problem was designed only in the fracture area. The computation was accelerated and it was possible to generate a more accurate model. The grid consists of 800 monolayer elements (Fig. 12.3). In the figure,



FIGURE 12.1: Figure of granite block with a dominant fracture and boreholes used for the bentonite transport experiment Dimensioning is in millimetres. Source: [73].

the elements representing injection well L1 (source) and withdrawal well L4 (sink) are highlighted. The pressure distribution on the upper layer of the fracture was computed (Fig. 12.3).

The porosity of the fracture model was set to 80%. This value was chosen because surface of the granite is not smooth. The value of hydrodynamic permeability was not measured during the experiment, therefore this value was calibrated in simulation together with the porosity value. The ionic strength of the solution was 0.001 mol/L, the pH of the solution was 7.5, the average velocities of water during the experiment were 0.4 m/h, 0.034 m/h, and 0.005 m/h. The results of the experiment with the velocity of 0.4 m/h are most readable, see Fig. 12.5. Hence, the simulation was done for these results.

Bentonite particles concentration was set according to the experiment B2 (Fig. 12.4). The input concentration was 40 mg/L. First, 380 - 453 mL of particle dispersion were injected, then water was injected. The size of the bentonite particles was 4–15 nm and 70 nm–1.5  $\mu$ m (Fig. 12.4). Therefore, the simulation was computed with three size sections of particles (4–15 nm, 15–70 nm, 70 nm–1.5  $\mu$ m). Changes of particle numbers in the size sections are caused by particle size changes. Sedimentation, velocity gradient and Brownian motion causes these changes. The size limits of each section and the number of particles in each section are recorded in Table 12.1. On the basis of size distribution in Fig. 12.4, it can be seen that no aggregation occurred in the dispersion before its injection. Otherwise, particles with size of 15–70 nm would be presented in the size distribution.

The duration of the experiment B2 was 7 hours. In this time, 3600 mL was withdrawn. The first bentonite particles were withdrawn after 500 mL of water. During the experiment, 30% of the particles were retained inside the granite block. A graph of particle



FIGURE 12.2: Mean fracture elevation In the experiment, the borehole L1 was used as an injection well and L4 as a withdrawal well. Source: [73].

	Concentration rate				
	Section1 Section2 Section3				
	$415~\mathrm{nm}$	15-70  nm	70 nm–1.5 $\mu {\rm m}$		
Experiment	$36\% C_0$	0%	$64\% C_0$		
Simulation	$36\% C_0$	0%	$64\% C_0$		

TABLE 12.1: The size limits of sections and the number of particles in the sections

concentration at the end of the transport system is shown in Figure 12.5, where the experiment B2 is represented by square marks.

#### 12.1.2 Simulation including electrostatic forces in the aggregation model

If the new electrostatic model is not considered, the changes to the sections are caused by aggregation between particles due to Brownian motion (3.14), velocity gradient (3.16) and sedimentation (3.21). The changes to the sections are described and computable using the model (5.6). The following values of bentonite colloidal particles properties were chosen: radius of one bentonite nanoparticle a = 4 nm; density of particles  $\rho_p =$ 2600 kg/m<sup>3</sup>; temperature T = 300 K; dynamical viscosity of water  $\eta = 8.90 \cdot 10^{-4}$  Pa · s;



FIGURE 12.3: Top view on the fracture grid, pressure distribution and boundary condition elements

Measurements of the area are in millimetres, the scale of pressures is in metres.

density of water  $\rho = 1000 \text{ kg/m}^3$  and duration of simulation t = 7 h (25200 s). Changes to the sections during the experiment are written in Table 12.2.

Original particle number rate			Time	Sum of particle
Section1 [%]	Section2 [%]	Section3 [%]	$[\mathbf{s}]$	number [% ]
36	0	64	0	100
6.5	29.5	64	2520	100
3.4	32.6	64	5040	100
2.2	33.8	64	7560	100
1.6	34.4	64	10080	100
1.2	34.8	64	12600	100
0.9	35.1	64	15120	100
0.8	35.2	64	17640	100
0.6	35.4	64	20160	100
0.5	35.5	64	22680	100
0.4	35.6	64	25200	100

TABLE 12.2: Changes to the sections during the experiment computed excluding the effect of surface charges

It can be seen that with the basic model of aggregation (excluding the effect of electrostatic forces), an aggregation of bentonite colloidal particles is expected to occur during


FIGURE 12.4: The size distribution of bentonite particles before injection Source: [73].

the experiment. However, according to the results of the experiments (Fig. 12.6, no particles were recorded in the middle Section2 with particle size between 15–70 nm.

This suggests that the repulsive electrostatic forces between bentonite particles have a significant effect on the aggregation rate of particles. During the experiment, the ionic strength of the solution was 0.001 mol/L and the pH of the solution was 7.5. On the basis of the experimental results [74] enumerating the dependence of surface charge density of a bentonite colloid on the pH and ionic strength of the solution (Fig. 12.7), 0.02 C/m<sup>2</sup> was chosen as the value of the bentonite surface charge density.

When considering the effect of electrostatic forces, the changes to the sections are computed from equations (4.23), (4.31) and (4.37). The changes to the sections are computable using the model (5.6). The values of bentonite colloid properties are the same as before, with a surface charge density of 0.02 C/m<sup>2</sup>. Computed values of changes to the sections due to aggregation are given in Table 12.3.

The value of the surface charge for the given pH and ionic strength is so high that no aggregation occurs during the experiment (the computed MTC values are equal to zero). Particles repel each other and stay stable. That corresponds to the experiment results.

#### 12.1.3 Results of simulation using a new aggregation model

During the experiment, 3600 mL of solution was withdrawn. After 500 mL of clear water, the first bentonite colloidal particles appeared at the end of the system. Over the



FIGURE 12.5: Withdrawn particle concentration over time Particle concentration is expressed at the rate of the original particle concentration. Source: [73].

Original particle number rate			Time	Sum of particle
Section1 [%]	Section2 [%]	Section3 [%]	$[\mathbf{s}]$	number [% ]
36	0	64	0	100
36	0	64	2520	100
36	0	64	5040	100
36	0	64	7560	100
36	0	64	10080	100
36	0	64	12600	100
36	0	64	15120	100
36	0	64	17640	100
36	0	64	20160	100
36	0	64	22680	100
36	0	64	25200	100

TABLE 12.3: Changes to the sections during the experiment computed including the effect of surface charges

7 hours of the experiment, 70 % of all injected bentonite particles were withdrawn. 30 % remained in the granite block.

In the simulation, a calibration was performed. The filtration coefficient was not a sensitive parameter with the given conditions, therefore its value was not calibrated and remained  $10^{-5}$  m/s. The retardation coefficient  $r_c$  gives the retardation of a substance (sections of particles in this case) with the velocity  $v_s$  compared with the velocity of



FIGURE 12.6: Particle concentration at withdrawal depending on time and size Particle concentration is expressed at the rate of the original particle concentration. Source: [73].

flowing water  $v_f$ :

$$v_s = r_c v_f. \tag{12.1}$$

Retardation expresses the ratio between the actual velocity of transported particle and the water flow velocity. Usually, the velocity of bigger particles (Section3) is smaller than velocity of smaller particles (Section1) and larger particle peak appears later than smaller particle peak. That did not happened during the experiment according to results in Fig. 12.6 where the peaks of all the particle sections appeared approximately at the same time. It was caused by the fact that the bentonite transport was mainly proceeded in the fracture and a transport through the granite block, where the large particle would remain, was negligible. Therefore, the sections have the retardation coefficient equal to 1 (no retardation).

During the experiment, 70 % of bentonite particles were recovered, during the simulation 84 % particles were recovered. Presumably, this is caused by a gradual colmatage of smaller fractures around the main fracture in the system. In the future, this phenomenon could be included in a simulation model (for example, by a dynamic change of the retardation coefficient).

The results of the simulation are displayed in Figure 12.8 representing the progress of bentonite colloid flux during the simulation between the injection and withdrawal boreholes. The figure has been produced using Gwsview software developed by the company Diamo s.p. It shows that the first particle concentration is in the withdrawal borehole



FIGURE 12.7: Surface charge density for the bentonite colloids as a function of the pH At different ionic strengths of 0.001, 0.01, and 0.1 M NaClO<sub>4</sub> respectively. Source: [74].

after approximately 500 mL, as in the experiment. After 7 hours of the simulation (after 3600 mL of withdrawn solution), a quantity of the bentonite colloid is retained in the fracture as in the experiment.

A development of the particle concentration at the withdrawal borehole should correspond to Figures 12.5 and 12.6. Therefore, particle concentration in the element representing the borehole during the simulation was observed. The results are shown in Figure 12.9.

The total concentration curve in Fig. 12.9 is comparable to the curve for the velocity of 0.4 m/h shown in Fig. 12.5. The curve with square marks in Fig. 12.9 is comparable to the curve with diamond marks in Fig. 12.6, and the curve with triangular marks in Fig. 12.9 is comparable to the total concentrations that are represented by the curves giving 70–1400 nm size in Fig. 12.6.

Including the effect of electrostatic forces into the aggregation model was important and effective, especially for particles with a wide size distribution. In general, particles of different size have different migration behaviour and it is important to know the aggregation dynamics between particles.



Volume = 2500 mL Volume = 3200 mL Volume = 3600 mL



# 12.2 1-D problem used to calibrate magnetic nanoparticle transport - A column experiment simulation

A column experiment is an experimental technique. The physical and chemical parameters of a substance migration through a porous medium are examined in a laboratory on a sample of soil from the area of interest. These experiments can be used to estimate the efficiency of a real remediation intervention. The simulation of the experiments helps to calibrate geophysical and chemical parameters of the problem.

#### 12.2.1 A description of column experiments and their results

Column experiment arrangement is shown in Figure 12.10. A dispersion was pumped into a column. The velocity of the injection of the dispersion can be controlled by a circulating pump. A measuring device at the output of the column monitors the properties of the output solution (pH, redox potential, conductivity, etc.). More details about column experiments are in the thesis: [8](CL).



FIGURE 12.9: A development of particle concentrations in every section, at the withdrawal element, over time



FIGURE 12.10: Column experiment arrangement Source: [8](CL).

A simulation of two column experiments named Column1 and Column2 is presented here. The experiments were done with RNIP iron nanoparticles (TODA). Glass cylindrical vessel used for soil sample had diameter of 6.5 cm and height of 31 cm. Quartz sand used as the soil samples had coefficient of permeability  $K = 10^{-3}$  m/s, at the bottom of the column was a 2–3 cm layer of gravel with effective porosity of 50 % and coefficient of permeability  $K = 10^{-2}$  m/s. Other input parameters that differ for the column experiments are in Table 12.4.

The results of the experiments are presented in Figure 12.11. It gives the total mass of iron nanoparticles in 3-cm slices after the end of the experiment in the column from

	Effective	Flow	Experiment duration	Total input
	porosity [% ]	$[m^3/day]$	[day]	concentration $[g/L]$
Column1	35	$1.0 \cdot 10^8$	0.2215	0.7
Column2	36	$1.2 \cdot 10^8$	0.189	1.8

TABLE 12.4: Parameter values of experiments used in the column experiment simulations

input to output. For clarity, a rotated image of a real column (Fig. 12.12) with a visible concentration of iron nanoparticles in the column (the iron dispersion is black) is shown under Figure 12.11.



FIGURE 12.11: Results of the experiments showing the mass of iron nanoparticles per a 3-cm slice of the column retained in the column after the end of the experiment Source: [8](CL).



FIGURE 12.12: A rotated image of a column after the end of the experiment

### 12.2.2 Simulation of a column experiment

A simulation of a column experiment was performed using flow software called Genflow and transport software called Gen-tran, provided by the company Diamo s.p. This software computes a flow model of the system and the transport of a substance in the system. In the software, retardation coefficients, dual porosity and aggregation dynamics as kinetic equations can be input. For more details about the software and its input files, please see [75] (CL).

The geometry of the column system consisted of one multi-element from three multinodes (Fig. 12.13) replacing the cylindrical column. The element was divided into 100 layers. A computation was performed as a one-dimensional flow through 100 elements (layers).



FIGURE 12.13: A schematic diagram of the grid of the column The column is composed of 100 layers.

On the lower face of the model, the Neumann boundary condition was set satisfying the flow velocities in Table 12.4. On the upper face, the Dirichlet boundary condition of atmospheric pressure was set. On all vertical faces, no flow boundary conditions were set. Zero concentration of iron nanoparticles in the column was set as the initial condition. All the input parameters were set according to the values from experimental measurements described in section 12.2.1.

# 12.2.3 A simulation including electrostatic and magnetic forces in the aggregation model

RNIP are very reactive nanoparticles. It is nearly impossible to have unreacted nanoparticles with homogeneous size at the beginning of the experiment. The experiments were performed with older iron nanoparticles of various sizes. Therefore the simulation was performed for three different size sections, similarly to the simulation described in chapter 12.1.1. Section1 represents the finest nanoparticles with small size and easily transportable, Section3 represents the big aggregates that migrate slowly and mostly remain as sediment. Division of particle size into the sections is shown in Table 12.5. The results of the calibration of the retardation coefficients in the simulation are given in Table 12.5 where the values of the concentrations and retardation coefficients of the sections in simulations of experiments Column1, Column2 are presented.

	Concentration [g/L]		Retardation coeff. [1]			
	Section1 Section2 Section3		Section1	Section2	Section3	
	40-400 nm	400-900 nm	900 nm-2 $\mu m$	40-400 nm	$400\text{-}900~\mathrm{nm}$	900 nm-2 $\mu \mathrm{m}$
Co1	5	7.5	14	0.0105	0.0038	0.0023
Co2	6	16	70.5	0.016	0.0095	0.0058

TABLE 12.5: The values of the calibrated parameters of simulations of column experiments "Co" is an abbreviation for Column

"Co" is an abbreviation for Column.

Using the equations (3.1), (10.2), (10.3) and (10.4), it is possible to compute a probability of aggregation between two aggregates (particles). The probability can be converted to first-order kinetics describing the reactions between entities (sections of particles, in our case). The reactions between sections, values of stoichiometry, and values of rate constants that were computed using Matlab2009R software are shown in Table 12.6. The reactions in Table 12.6 are described as follows: e.g. reaction Re1 represents the aggregation of two particles from Section1, an aggregate that they create belongs to Section2.

Reaction	Reaction	$\hat{\beta}^+_{r.n.l}$ (MTC)	$k_R$
label	description	$[m^3/s]$	[L/g/s]
Re1	$Se1+Se1 \rightarrow Se2$	$7.64 \cdot 10^{-16}$	0.087
Re2	$Se1+Se2 \rightarrow Se2$	$1.30 \cdot 10^{-17}$	$2.4 \cdot 10^{-4}$
Re3	$Se1+Se2 \rightarrow Se3$	0	0
Re4	$Se2+Se2 \rightarrow Se3$	$8.16 \cdot 10^{-16}$	$5.2 \cdot 10^{-4}$
Re5	Se1+Se3→Se3	$1.22 \cdot 10^{-17}$	$2.2 \cdot 10^{-4}$
Re6	Se2+Se3→Se3	$1.20 \cdot 10^{-16}$	$1.4 \cdot 10^{-5}$

TABLE 12.6: The reactions between sections, the values of MTC and the values of kinetic constants for nZVI

The chosen average aggregates from every section are displayed in Tab. 12.7.

Section	Diameter of aggregates	Number of nanoparticles	Averaged aggregate
label	[nm]	of aggregates [1]	A [1]
Se1	40-400	1-1000	500
Se2	400-900	1000-11390	6195
Se3	900-2000	11390-125000	68195

TABLE 12.7: The section size boundaries and their average aggregates of nZVI The number A refers to the number of nanoparticles of the average aggregate from a section.

Stoichiometries of the reactions are shown in Tab. 12.8.

Reaction	Reaction	Sections		
label	description	Se1	Se2	Se3
Re1	$Se1+Se1 \rightarrow Se2$	-1000	1000	0
Re2	$Se1+Se2 \rightarrow Se2$	-500	500	0
Re3	$Se1+Se2 \rightarrow Se3$	-500	-6195	6695
Re4	$Se2+Se2 \rightarrow Se3$	0	-12390	12390
Re5	Se1+Se3→Se3	-500	0	500
Re6	Se2+Se3→Se3	0	-6195	6195

TABLE 12.8: Stoichiometry of kinetics of reactions between 3 sections of nZVI The section values represent the numbers of nanoparticles in the aggregating particles, e.g. in Re1, two particles from Se1, that are composed of 500 nanoparticles, aggregate and fall into Se2.

The values for the rate constants are smaller than the ones computed in Chapter 11.1. This is due to different section boundaries being chosen. In this case, very wide boundaries were chosen for the first section where most of the aggregation occurs.

## 12.2.4 The results and discussion of the importance of the new aggregation model

The concentrations of iron nanoparticles in every layer of the multi-element were observed at the end of the simulation. A graph of nanoparticle concentration depending on location in the column was created for every section. The results were compared with the results of the experiment (that was converted to the same units (g/L) in order to be comparable). The comparisons are shown in Fig. 12.14.



FIGURE 12.14: The results of the simulation of iron nanoparticles transport in a column The result shows particle concentrations of every section of particles at the end of the simulation. For comparison, the results of the experiment are also presented.

In this section, a simulation of magnetic nanoparticles was presented. The particles were unstable and aggregated, however the particles were mostly aggregated before the experiment began. The kinetic reactions were specified, describing the aggregation dynamics during the simulation.

# 12.3 A real problem simulation - Usage of RNIP for the remediation of the Kurivody area

The Kurivody area in the Czech Republic is an area where real remediation interventions are taking place and where a durable impact of iron nanoparticles can be observed. Since 2004, a few pilot experiments with new remediation surfactant testing have been running. Iron nanoparticles were used as a final remediation method for testing. More information of the area, measurements and results of the application are available on request in the company AQUATEST a.s., Prague, Czech Republic.

An area of 10x10 m around an injection borehole PW-3 was chosen for a simulation of iron nanoparticle transport. Two monitoring boreholes MW-2 and MW-3 are situated in the area (Fig. 12.15).



FIGURE 12.15: Kurivody area with highlighted injection and monitoring boreholes and direction of groundwater flow Source: [76].

Development of iron nanoparticle concentration in monitoring boreholes after injection into injection borehole PW-3, depending on time, is recorded in Fig. 12.16.



FIGURE 12.16: The development of iron nanoparticle concentration in the boreholes over time Source: [76].

The results of the measurement of iron nanoparticle concentration in the boreholes are not very valuable, nevertheless, these measurements are the best documentation of a real remediation intervention using iron nanoparticles that we have at our disposal. It shows a trend of iron nanoparticle migration in monitored boreholes.

#### 12.3.1 A simulation of RNIP transport at Kurivody

A model of the geometry of the simulated area around the injection borehole is shown in Figure 12.17 [77]. The chosen area includes three geological areas of Kurivody two permeable aquifers and one almost impermeable aquitard between them. Under this area, there is another impermeable rock, which is represented as an impermeable boundary of the model. Hydraulic conductivities of all three layers of the model geometry are noted in Table 12.9.



FIGURE 12.17: The model geometry of a simulated area around an injection borehole PW-3 with marked geological layers

Layer	Hydraulic cond. in horizontal	Hydraulic cond. in vertical
description	direction [m/day]	direction $[m/day]$
Upper aquifer (A)	0.3260	0.0326
Central aquitard (B)	$1.7 \cdot 10^{-3}$	$1.7 \cdot 10^{-4}$
Lower aquifer (C)	0.1714	0.01714

#### TABLE 12.9: The hydraulic conductivities of geological layers of the chosen model geometry of Kurivody area Source: [77].

A grid of the model geometry is in Figure 12.18. The grid is made up of 3200 multielements that have three layers with different properties (as in Figure 12.17). Figure 12.18 shows a top view of the elements, highlighting the location of the injection borehole PW-3 and the monitoring boreholes MW-2 and MW-3.

Dirichlet boundary conditions were set on the boundaries of the layer based on [77] (CL). The pressure heads on the top of the permeable layers (upper and lower) are noted in Figure 12.19. A linear approximation in small regions around the critical points in the corners had to be done in order to satisfy compatibility of the boundary conditions.

A boundary condition for transport was defined in the volume of the element that represents the injection borehole. The condition means an injection of a constant concentration of iron nanoparticles. The real particle dispersion concentration used in the Kurivody area was 3300 g/m<sup>3</sup>. The duration of the first part of the simulation was 7.5 hours. 22 kg of iron nanoparticles were injected during the whole remediation intervention. A Neumann boundary condition representing the flow of iron nanoparticle dispersion was set so that 22 kg of iron nanoparticles was injected during the simulation. When the value of the Neumann boundary condition was 7 m<sup>3</sup>/m<sup>2</sup>/day, 22627 g of iron



FIGURE 12.18: A top view on a grid of the Kurivody model geometry Consisting of 3200 multi-elements, the multi-elements are highlighted in the location of the injection borehole PW-3 and the monitoring boreholes MW-2, MW-3. Measurements are given in metres.



FIGURE 12.19: Pressure head distribution in layers of the Kurivody model area In the figures, flow velocity vectors in elements are plotted.

nanoparticles were injected into the model. The porosity of all layers was set to 20 %. The second part of the simulation was without the boundary condition representing the injection of iron nanoparticles. The pressure head distribution in the model layers during nanoparticle injection is shown in Figure 12.20.

## 12.3.2 Simulation with inclusion of electrostatic and magnetic forces in aggregation model

Iron particles were divided into two sections according to their size - Section1 containing particles with size of 50-200 nm and Section2 containing particles with size larger than 200 nm. A surface charge  $\sigma = 2.5 \cdot 10^{-5} \text{ C/m}^2$  was chosen again. The aggregation



FIGURE 12.20: The pressure head distribution in layers of the Kurivody model area. The figures show flow velocity vectors in the elements and the location of a cross-section of the area.

of particles was computed again with the new aggregation model including the effect of electrostatic and magnetic forces (3.1), (10.2), (10.3) and (10.4). The results of the computation of iron nanoparticle aggregation with given concentration  $(3300 \text{ g/m}^3)$  and surface charge is given in Table 12.10.

Original partie	ele number rate	Time	Sum of particle
Section1 [%] Section2 [%]		[s]	number [% ]
100.0	0.0	0	100
0.0	100.0	1	100

 TABLE 12.10: Iron nanoparticle aggregation computed using the aggregation model including the effect of electrostatic and magnetic forces

Computed for a particle concentration of 3300 g/m<sup>3</sup> and a surface charge of  $2.5 \cdot 10^{-5}$  C/m<sup>2</sup>.

Aggregation is so rapid that all the particles aggregate in the first second. To judge how great the impact of the magnetic forces is on the rapid aggregation, the aggregation was also computed using the model of aggregation including the effect of electrostatic forces, but without the effect of magnetic forces (5.6), (4.23), (4.31) and (4.37). The results of this computation are shown in Table 12.11.

Even without the effect of attractive magnetic forces, iron nanoparticles aggregate very quickly. The iron nanoparticles aggregated in seconds. The iron nanoparticles very likely aggregated before being injected into the borehole. Therefore we did not simulate an aggregation of particles during the experiment simulation.

Original particle number rate		Time	Sum of particle
Section1 [%]	Section2 [%]	[s]	number [%]
100.0	0.0	0	100
71.5	28.5	1	100
56.9	43.1	2	100
47.7	52.3	3	100
41.2	58.8	4	100
36.4	63.6	5	100
32.6	67.4	6	100
29.6	70.4	7	100
27.1	72.9	8	100
25.0	75.0	9	100
23.2	76.8	10	100

 

 TABLE 12.11: Iron nanoparticle aggregation computed by an aggregation model including only the effect of electrostatic forces

Computed for a particle concentration of 3300 g/m<sup>3</sup> and a surface charge of  $2.5 \cdot 10^{-5}$  C/m<sup>2</sup>.

## 12.3.3 The results and discussion of the importance of the new aggregation model

An attempt was made to simulate a development of iron particle concentration in the monitored boreholes, MW-2 and MW-3. Despite the fact that the measurements of the Kurivody location are well documented and quite frequent, the results of the measurements of nanoparticle concentration are too sparse to perform a good simulation. The result of the particle concentration development in the elements representing the monitored boreholes are shown in Figures 12.21 and 12.22. The measured trends of concentrations in boreholes were added to compare the experiment and simulation results.



FIGURE 12.21: Comparison of measurement and simulation results of particle concentration development in borehole MW-2 and in the element representing the monitored borehole MW-2



FIGURE 12.22: Comparison of measurement and simulation result of particle concentration development in borehole MW-3 and in the element representing the monitored borehole MW-3

The concentration values in Figures 12.21 and 12.22 are in relative values in order to be comparable with the measurements. The maximum concentration in MW-2 borehole was measured after 2 months and simulated after 1.5 months. The maximum concentration in MW-3 borehole was measured after 1.5 months and simulated after 1 month.

The simulation of iron nanoparticle transport between the injection and monitoring boreholes gives quite good results. However, the calibration of the input values for the model, such as the retardation coefficient, is not effective. The available data for these measurements are so sparse that refinement of the model is not meaningful.

The benefits of a transport model including the effect of particle aggregation on transport are an improvement in the theoretical understanding of transport of unstable nanoparticles. This improvement could be useful for softwares which simulate the transport of aggregating particles, but only when the problems are well documented. It could also be useful when the aggregation of particles is crucial - for example, when computing the age of nanoparticles before their usage (how aggregated they are).

For this real-world problem of nZVI usage for remediation, the attachment of our detailed model of aggregation including the effects of electrostatic and magnetic forces to the transport model was not needed. Our model helped us to understand the reasons for very fast aggregation and justify adequacy of single transport model for solution of such a problem.

# Chapter 13

# Conclusions

Zero-valent iron nanoparticles are increasingly being used for water and soil treatment as a highly reactive, easily transportable, nontoxic remedial agent. However, it was found that the nanoparticles aggregate so rapidly that they quickly lose their high reactivity and transportability, which are the crucial parameters. This is caused mostly by the long-range attractive magnetic forces acting between the nanoparticles. This thesis has developed a theoretical model of aggregation of the migrating nanoparticles that includes the effect of repulsive electrostatic and the attractive magnetic forces acting between the particles. The model has then been modified for practical usage and is a proven improvement compared to the basic model of aggregation.

The benefits of the improved aggregation model are evident in the better theoretical understanding of the interactions between nanoparticles. The system of aggregation rate computation developed in this thesis can be used for the computation of the age of nanoparticles before their use which could lead to better utilization of the material and cost-saving. The transport model including the effect of particle aggregation on transport can be included into software which simulates the transport of aggregating particles, both for scientific and practical purposes. This concluding chapter summarizes the work presented in this thesis and suggests some future directions.

### 13.1 Summary of work

The aim of this thesis has been to research the interactions between magnetic nanoparticles with non-zero surface charge that are transported through a porous medium. We started with an aggregation model described by mass transport coefficients between particles computed on the basis of the heat fluctuation of particles and their different velocities during sedimentation and drifting in water. The coefficients gave a frequency of collisions between particles. The derivation of the coefficients is summarized in Chapter 3. Particles with high surface charge values repel each other and the rate of aggregation falls. We included the effect of electrostatic forces into the aggregation model in Chapter 4. In order to verify the new models, we modified a sectional model of aggregation, which allowed the computation of the reactions between particle size sections. Particles were divided into sections according to their size. Aggregation of particles does not have to be computed between each individual aggregate that occurs in the particle dispersion. The whole derivation of sectional model and modification of the mass transport coefficients for the model is detailed in Chapter 5.

The effect of magnetic forces on the aggregation rate was assessed in the Chapter 6. The magnitude of the magnetic force between two nanoparticles was derived as well as the magnetic field around an aggregate. The impact of the magnetic force on the aggregation rate was determined by using the value of the limit distance that gives the minimal distance between particles needed for particles not to aggregate due to their attractive magnetic forces.

In Chapter 7, the influence of the structure of nanoparticles in aggregates on the resulting magnetic field around the aggregates was examined. The parameters to be compare were the magnitude of the magnetic forces between particles and the limit distance. According to these two connected parameters, it was possible to estimate the degree of influence of the magnetic forces on the aggregation rate of particles. Then, the probable aggregate structure was examined on the basis of the interaction energy between the nanoparticles in an aggregate.

Since the computation of the magnetic forces is time consuming, two methods of estimating the magnetic forces are presented here – the simple and fast averaging of averaging and the more precise, but more time consuming summation method are discussed in Chapter 8. It was found that the best way to generalize the results is to relate the distance between two particles to the shortest possible distance  $R_0$ , which is the sum of radii of the investigated pair of aggregates. The limit where the averaging method could be used is the distance over  $10 \cdot R_0$  between particles. When the particles are closer to each other than  $10 \cdot R_0$ , the magnetic forces between the particles must be estimated using the slow, but more complex summation method. Otherwise, the averaging method can be used for computation.

Another way of including electrostatic forces into the aggregation model is examined in Chapter 9. The repulsive electrostatic forces are long-range as well as the attractive magnetic forces, therefore we added the electrostatic force effect directly in the limit distance model. In Chapter 10, the limit distance was used as an area around an aggregate in which the flux of other particles is observed. The mass transport coefficients are computed on the basis of this limit distance value that increases the aggregation rate. The model of aggregation computation was transferred to kinetics in Chapter 11. The aggregation between sections is calculated in the form of kinetic equations, which is useful for computing the transport of entities and the reactions between them in various software.

The aggregation model, with includes both electrostatic and magnetic forces was tested on simulations of particle transport in Chapter 12. First, the transport of non-magnetic particles with surface charge was simulated using the aggregation model from Chapter 4. Then, a one-dimensional model of the transport of magnetic nanoparticles with surface charge was simulated and the aggregation model from Chapter 10 was tested together with the transformation of mass transport coefficient into kinetics from Chapter 11. In the last section, the suitability of the aggregation model which includes electrostatic and magnetic forces was examined for the simulation of a real iron nanoparticle injection into ground.

### 13.2 Future work

A large part of this thesis has been concerned with the description of magnetic forces between iron nanoparticles and their inclusion in the aggregation model used for simulating the transport of aggregating particles. Whilst some progress has been made in describing aggregating particle transport, there is much scope for further investigation. In this section, some suggestions of possible themes for additional investigations are discussed.

In Chapter 7, the possible structure of aggregates that are important for the magnetic force of aggregates computation were examined. It was found out that firstly, a small chain of magnetic nanoparticles, then sections of nanoparticles are formed. At some point, the aggregated sections stop creating larger sections and they only attach to another chain of sections. This process should be taken into account. Our computations only account for spherical aggregates.

In Chapter 6, the limit distance is computed from the equilibrium equation of forces in which the only counteracting force against the magnetic force is gravity. For a more accurate description of the effect of magnetic forces, the others forces acting on the aggregating particles should be included in the equilibrium of forces and the limit distance computation.

Another simplification that was used was the presumption that the surface charge of all aggregates is constant and uniformly distributed on the surface of the aggregates. An investigation into the reality of the situation and its inclusion in the aggregation model could be another additional investigation. It is connected to the ageing of iron nanoparticles in a dispersion where the surface of the particle corrodes, changes and so do the properties of the particles, such as the surface charge, magnetization, etc. When we investigate the transport of reactive unstable particles, attachment of the particle to the pore surface should also be taken into account as a factor that slows down particle transport and prevents particle migration through the ground.

# Bibliography

- Camp TR, Stein PC: Velocity Gradients in Internal Work in Fluid Motion. MIT 1943.
- [2] Smoluchowski M: Versuch einer mathematischen Theorie der Koagulationskinetik kolloider Lösungen. Z. Phys. Chem. 1917, 92:129–168.
- [3] Buffle J, Leeuwen HPv: Environmental Particles. CRC Press, 1 edition 1992.
- [4] Zhang Wx: Nanoscale Iron Particles for Environmental Remediation: An Overview. Journal of Nanoparticle Research 2003, 5(3):323–332.
- [5] Li L, Fan M, Brown RC, Van Leeuwen JH, Wang J, Wang W, Song Y, Zhang P: Synthesis, Properties, and Environmental Applications of Nanoscale Iron-Based Materials: A Review. Critical Reviews in Environmental Science and Technology 2006, 36(5):405–431.
- [6] Nurmi JT, Tratnyek PG, Sarathy V, Baer DR, Amonette JE, Pecher K, Wang C, Linehan JC, Matson DW, Penn RL, Driessen MD: Characterization and properties of metallic iron nanoparticles: spectroscopy, electrochemistry, and kinetics. Environmental Science & Technology 2005, 39(5):1221–1230.
- [7] Filip J, Zboril R, Schneeweiss O, Zeman J, Cernik M, Kvapil P, Otyepka M: Environmental applications of chemically pure natural ferrihydrite. Environmental Science & Technology 2007, 41(12):4367–4374.
- [8] Nosek J: Laboratory research and modeling of nanoiron transport properties. *Dissertation thesis*, Technical University of Liberec, Liberec, Czech Republic 2009.
- [9] Pelikánová D: Nanoparticle aggregation model. *Diploma thesis*, Technical University of Liberec, Liberec, Czech Republic 2008.
- [10] Somasundaran P, Runkana V: Modeling flocculation of colloidal mineral suspensions using population balances. International Journal of Mineral Processing 2003, 72(1-4):33–55.

- [11] Sun Y, Li Xq, Cao J, Zhang Wx, Wang HP: Characterization of zero-valent iron nanoparticles. Advances in Colloid and Interface Science 2006, 120(1-3):47– 56.
- [12] Horak D, Petrovsky E, Kapicka A, Frederichs T: Synthesis and characterization of magnetic poly(glycidyl methacrylate) microspheres. Journal of Magnetism and Magnetic Materials 2007, 311(2):500–506.
- [13] Masheva V, Grigorova M, Nihtianova D, Schmidt JE, Mikhov M: Magnetization processes of small gamma-Fe<sub>2</sub>O<sub>3</sub> particles in non-magnetic matrix. Journal of Physics D: Applied Physics 1999, 32(14):1595–1599.
- [14] Phenrat T, Saleh N, Sirk K, Tilton RD, Lowry GV: Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions. *Environmental Sci*ence & Technology 2007, 41:284–290.
- [15] 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. *NanoMicro Letters* 2010, 1:49–52.
- [16] Gelbard F, Tambour Y, Seinfeld JH: Sectional representations for simulating aerosol dynamics. Journal of Colloid and Interface Science 1980, 76(2):541–556.
- [17] Elliott D, Li X, Zhang W: Zero-valent Iron Nanoparticles for Abatement of Environmental Pollutants. In Particulate Systems in Nano- and Biotechnologies. Edited by Ei-Shall H, Shah D, Sigmund W, Moudgil B, CRC Press 2008:309–329.
- [18] Chuang FW, Larson RA, Wessman MS: Zero-Valent Iron-Promoted Dechlorination of Polychlorinated Biphenyls. Environmental Science & Technology 1995, 29(9):2460-2463.
- [19] Hou M, Wan H, Zhou Q, Liu X, Luo W, Fan Y: The Dechlorination of Pentachlorophenol by Zerovalent Iron in Presence of Carboxylic Acids. Bulletin of Environmental Contamination and Toxicology 2009, 82(2):137–144.
- [20] Lackovic JA, Nikolaidis NP, Dobbs GM: Inorganic Arsenic Removal by Zero-Valent Iron. Environmental Engineering Science 2000, 17:29–39.
- [21] Kanel SR, Greneche JM, Choi H: Arsenic(V) removal from groundwater using nano scale zero-valent iron as a colloidal reactive barrier material. Environmental Science & Technology 2006, 40(6):2045–2050.
- [22] Yuvakkumar R, Elango V, Rajendran V, Kannan N: Preparation and characterization of zero valent iron nanoparticles. *Digest Journal of Nanomaterials* and Biostructures 2011, 6(4):1771–1776.

- [23] Çelebi O, Üzüm c, Shahwan T, Erten H: A radiotracer study of the adsorption behavior of aqueous Ba<sup>2+</sup> ions on nanoparticles of zero-valent iron. Journal of Hazardous Materials 2007, 148(3):761–767.
- [24] Ponder SM, Darab JG, Mallouk TE: Remediation of Cr(VI) and Pb(II) Aqueous Solutions Using Supported, Nanoscale Zero-valent Iron. Environmental Science & Technology 2000, 34(12):2564–2569.
- [25] Varanasi P, Fullana A, Sidhu S: Remediation of PCB contaminated soils using iron nano-particles. *Chemosphere* 2007, 66(6):1031–1038.
- [26] Nutt MO, Hughes JB, Michael SW: Designing Pd-on-Au bimetallic nanoparticle catalysts for trichloroethene hydrodechlorination. Environmental science & technology 2005, 39(5):1346–1353.
- [27] Cao J, Elliott D, Zhang Wx: Perchlorate Reduction by Nanoscale Iron Particles. Journal of Nanoparticle Research 2005, 7(4-5):499–506.
- [28] Liu Y, Majetich SA, Tilton RD, Sholl DS, Lowry GV: TCE Dechlorination Rates, Pathways, and Efficiency of Nanoscale Iron Particles with Different Properties. Environmental Science & Technology 2005, 39(5):1338–1345.
- [29] Sueyoshi T, Naono H, Kawanami M, Amemiya M, Hayama H: Morphology of iron fine particles. *IEEE Transactions on Magnetics* 1984, 20:42 – 44.
- [30] Wang CB, Zhang WX: Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. Environmental Science and Technology 1997, 31(7):2154–2156.
- [31] Crane R, Dickinson M, Popescu I, Scott T: Magnetite and zero-valent iron nanoparticles for the remediation of uranium contaminated environmental water. Water Research 2011, 45(9):2931–2942.
- [32] www.nanoiron.cz/en/nanofer-star.
- [33] Hoch L, Mack E, Hydutsky B, Hershman J, Skluzacek J, Mallouk T: Carbothermal synthesis of carbon-supported nanoscale zero-valent iron particles for the remediation of hexavalent chromium. *Environmental Science and Technology* 2008, 42(7):2600–2605.
- [34] Hoag G, Collins J, Holcomb J, Hoag J, Nadagouda M, Varma R: Degradation of bromothymol blue by "greener" nano-scale zero-valent iron synthesized using tea polyphenols. *Journal of Materials Chemistry* 2009, 19(45):8671–8677.
- [35] Scott T, Dickinson M, Crane R, Riba O, Hughes G, Allen G: The effects of vacuum annealing on the structure and surface chemistry of iron nanoparticles. Journal of Nanoparticle Research 2010, 12(5):1765–1775.

- [36] Crane R, Scott T: Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology. Journal of Hazardous Materials 2012, 211-212(0):112-125.
- [37] www.nanoiron.cz/en/nanofer-25.
- [38] Schrick B, Hydutsky BW, Blough JL, Mallouk TE: Delivery Vehicles for Zerovalent Metal Nanoparticles in Soil and Groundwater. Chemistry of Materials 2004, 16(11):2187–2193.
- [39] Phenrat T, Saleh N, Sirk K, Kim HJ, Tilton RD, Lowry GV: Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation. Journal of Nanoparticle Research 2008, 10(5):795–814.
- [40] Johnson RL, Johnson GO, Nurmi JT, Tratnyek PG: Natural organic matter enhanced mobility of nano zerovalent iron. Environmental Science & Technology 2009, 43(14):5455–5460.
- [41] Tiraferri A, Chen KL, Sethi R, Elimelech M: Reduced aggregation and sedimentation of zero-valent iron nanoparticles in the presence of guar gum. *Journal of Colloid and Interface Science* 2008, 324(12):71–79.
- [42] Sun YP, Li XQ, Zhang WX, Wang HP: A method for the preparation of stable dispersion of zero-valent iron nanoparticles. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2007, 308(13):60–66.
- [43] Kanel SR, Nepal D, Manning B, Choi H: Transport of surface-modified iron nanoparticle in porous media and application to arsenic(III) remediation. Journal of Nanoparticle Research 2007, 9(5):725–735.
- [44] Raychoudhury T, Naja G, Ghoshal S: Assessment of transport of two polyelectrolyte-stabilized zero-valent iron nanoparticles in porous media. Journal of Contaminant Hydrology 2010, 118(34):143–151.
- [45] Saleh N, Kim HJ, Phenrat T, Matyjaszewski K, Tilton RD, Lowry GV: Ionic strength and composition affect the mobility of surface-modified Fe0 nanoparticles in water-saturated sand columns. Environmental Science & Technology 2008, 42(9):3349–3355.
- [46] Fatisson J, Ghoshal S, Tufenkji N: Deposition of carboxymethylcellulosecoated zero-valent iron nanoparticles onto silica: roles of solution chemistry and organic molecules. Langmuir: the ACS journal of surfaces and colloids 2010, 26(15):12832–12840.

- [47] Reardon EJ, Fagan R, Vogan JL, Przepiora A: Anaerobic Corrosion Reaction Kinetics of Nanosized Iron. Environmental Science & Technology 2008, 42(7):2420-2425.
- [48] Kanel SR, Manning B, Charlet L, Choi H: Removal of Arsenic(III) from Groundwater by Nanoscale Zero-Valent Iron. Environmental Science & Technology 2005, 39(5):1291–1298.
- [49] Ramos MAV, Yan W, Li Xq, Koel BE, Zhang Wx: Simultaneous Oxidation and Reduction of Arsenic by Zero-Valent Iron Nanoparticles: Understanding the Significance of the CoreShell Structure. The Journal of Physical Chemistry C 2009, 113(33):14591–14594.
- [50] www.malvern.com[http://www.malvern.com/labeng/products/zetasizer/ zetasizer\_nano/zetasizer\_nano\_zs.htm].
- [51] Jiang J, Oberdrster G, Biswas P: Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. J Nanopart Res 2009, 11:7789.
- [52] Garrick S, Zachariah M, Lehtinen K: Modeling and simulation of nanoparticle coagulation in high reynolds number incompressible flows. In Proceeding of the National Conference of the Combustion Institute 2001:2527.
- [53] Beneš P, Rodrigo María de M, Mašín P, Kubal M: Nanoirons activity measurement technique and soil enrichment possibilities. In Nanocon 2009, Ronov pod Radhotm: TANGER 2009.
- [54] Einstein A: On the movement of small particles suspended in stationary liquids required by the molecular-kinetic theory of heat. Annalen der Physik 1905, 17:549–560.
- [55] Johnson PR, Elimelech M: Dynamics of Colloid Deposition in Porous Media: Blocking Based on Random Sequential Adsorption. Langmuir 1995, 11(3):801-812.
- [56] Wentworth CK: A Scale of Grade and Class Terms for Clastic Sediments. The Journal of Geology 1922, 30(5):377–392.
- [57] Rosická D, Šembera J, Maryška J: Theoretical study of electrical charge influence on aggregation rate of zero valent iron. In Book of Abstracts of ICCE-18, Anchorage, Alaska, USA 2010:641–642.
- [58] Derjaguin B, Landau L: Theory of the Stability of Strongly Charged Lyophobic Sols and of the Adhesion of Strongly Charged Particles in Solutions of Electrolytes. Acta Phys. Chim. URSS 1941, 14:633–662.

- [59] Verwey EJW: Theory of the Stability of Lyophobic Colloids. The Journal of Physical and Colloid Chemistry 1947, 51(3):631–636.
- [60] Kopeliovich D: www.substech.com 2013, [http://www.substech.com/ dokuwiki/doku.php?id=stabilization\_of\_colloids].
- [61] Zhang Wx, Elliott DW: Applications of iron nanoparticles for groundwater remediation. Remediation Journal 2006, 16(2):721.
- [62] Stumm W, Morgan JJ: Aquatic chemistry: chemical equilibria and rates in natural waters. Wiley 1996.
- [63] Rosicka D, Sembera J: Assessment of Influence of Magnetic Forces on Aggregation of Zero-valent Iron Nanoparticles. Nanoscale Research Letters 2010, 6:10.
- [64] McCurrie RA: Ferromagnetic materials: structure and properties. London: Academic Press 1994.
- [65] Dunlop DJ: Hysteresis properties of magnetite and their dependence on particle size: A test of pseudo-single-domain remanence models. Journal of Geophysical Research: Solid Earth 1986, 91(B9):9569–9584.
- [66] Butler RF, Banerjee SK: Theoretical single-domain grain size range in magnetite and titanomagnetite. Journal of Geophysical Research 1975, 80(29):4049–4058.
- [67] Votruba V, Muzikar C: Teorie elektromagnetického pole. Akademia Praha 1958.
- [68] Sembera J, Rosicka D: Computational Methods for Assessment of Magnetic Forces Between Iron Nanoparticles and Their Influence on Aggregation. Advanced Science, Engineering and Medicine 2011, 3(1-2):149-154.
- [69] Rosicka D, Sembera J: Influence of structure of iron nanoparticles in aggregates on their magnetic properties. Nanoscale Research Letters 2011, 6:527.
- [70] Sedlak B, Stoll I, Man O: Elektřina a magnetismus. Praha: Academia Karolinum 1993.
- [71] Rosicka D, Sembera J: Inclusion of electrostatic forces to assessment of rate of magnetic forces impact to iron nanoparticle aggregation. In Nanocon 2011, Brno: TANGER 2011.
- [72] Rosicka D, Sembera J: Changes in the nanoparticle aggregation rate due to the additional effect of electrostatic and magnetic forces on mass transport coefficients. Nanoscale Research Letters 2013, 8:20.

- [73] Vilks P, Miller N, Vorauer A: Laboratory bentonite colloid migration experiments to support the sp Colloid Project. Physics and Chemistry of the Earth, Parts A/B/C 2008, 33(1416):1035–1041.
- [74] Baik MH, Lee SY: Colloidal stability of bentonite clay considering surface charge properties as a function of pH and ionic strength. Journal of Industrial and Engineering Chemistry 2010, 16(5):837–841.
- [75] Hokr M: Transport model implementation by double porosity model. Technical report, Technical University of Liberec, Liberec, Czech Republic 2001.
- [76] Šembera J: Development and implementation of tools additively modulating process of bioremediation of soil and water. Annual research report of the project FR-TI1/456, Technical University of Liberec, Liberec, Czech Republic 2011.
- [77] Říha J: Simulation of iron nanoparticle injection. Diploma thesis, Technical University of Liberec, Liberec, Czech Republic 2010.