



## **SESSION E:**

# **Nanoparticles in the environment.**

**HOW CAN MAGNETIC RESONANCE IMAGING (MRI) AND PARTICULATE CONTRAST AGENTS WITH FINELY TUNED INTERFACIAL PROPERTIES HELP UNDERSTANDING PARTICLE TRANSPORT IN SOIL.**

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The capability to predict the fate in the soil of colloidal particles is of paramount importance for scientists, engineers or policy makers, as such particles can often carry adsorbed pollutant towards the groundwater or be themselves pollutants. Current models often fail to predict actual transport properties, indicating the need for a better understanding of the processes controlling particle attachment, detachment and transport in the soil. Some of these processes can only be studied indirectly (e.g. particle breakthrough curve during simulated rainfalls), and soil columns can be considered as “black box” systems.

Imaging techniques (X-ray tomography, MRI) have been increasingly used to study water movement in soil cores, but they have seldom been applied to investigate the fate of colloidal particles in intact soils.

With the aim of comparing their transport properties, in both saturated sand columns and repacked soil cores, we synthesized maghemite nanoparticles (NP) and stabilized them by adsorbing onto their surface either sodium citrate (NP-Cit) or neutral hydrophilic poly(ethylene-glycol) polymer chains (NP-PEG).

The ferrimagnetic nanoparticles provided an important contrast for MRI (longitudinal relaxation better than  $35 \text{ s}^{-1} \text{ mM}^{-1}$ ). Using a double spin echo sequence (acquisition duration 1 min 09 s), we monitored the particle concentration as a function of the core depth (15 cm, resolution  $390 \mu\text{m}$ ) and time.

In this contribution we will discuss how this combination of spatial information obtained monitoring particles with finely tuned interfacial properties and its analysis with ad hoc models provides new insights into the dynamics of particle transport processes.

**TRANSPORT AND DEPOSITION OF NANOPARTICLES IN (MODEL) SOILS**

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Improved knowledge about mobility of nanoparticles (NP) is required in order to assess their environmental risk. In this study, transport experiments with functionalized <sup>14</sup>C-labeled carbon nanotubes (CNT) and surfactant-stabilized silver NP (AgNP) were carried out in columns packed with quartz sand and a sandy soil, respectively. To obtain breakthrough curves, the concentrations in the effluent were determined by LSC and ICP-MS, respectively. Then, the packing was removed and analyzed in 1 cm layers to establish deposition profiles. Breakthrough of NP was decreasing with increasing ionic strength, decreasing flow velocity, and decreasing grain size of the quartz sand. Additionally, breakthrough was significantly influenced by NP's input concentration. Retention profiles were mostly of exponential shape with highest retention close to the column inlet. In the disturbed and undisturbed soil, respectively, AgNP were highly mobile at low ionic strength while CNT were generally mobile only at very low suspension concentrations. Physical removal mechanisms such as attachment, blocking, and straining are assumed to play an important role in the deposition of nanoparticles studied and were evaluated by using e.g. a modified HYDRUS computer code.

**TRANSFER OF TiO<sub>2</sub> NANOPARTICLES IN A SANDY POROUS MEDIUM DRIVEN BY THE ADSORBING NATURAL ORGANIC MATTER**Labille J.<sup>1,2\*</sup>, Pelinovskaya N.<sup>1,2</sup>, Masion A.<sup>1,2</sup>, Bottero J.-Y.<sup>1,2</sup><sup>1</sup>CEREGE, UMR7330 CNRS Aix-Marseille Université; Europole de l'Arbois; BP 80; 13545 Aix-en-Provence Cedex 04; France<sup>2</sup>ICEINT, international Center for the Environmental Implications of NanoTechnology; CNRS-CEA; <http://www.i-ceint.org>

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The effect of tannic acid (TA) on the transfer of TiO<sub>2</sub> nanoparticles through a sandy porous medium saturated with water was studied according to the pH and the ionic strength (I) of the solution. Batch and column experiments were conducted to distinguish and quantify the preferential interactions occurring between the three components TiO<sub>2</sub> nanoparticles, SiO<sub>2</sub> sand grains, and TA molecules. Adsorption isotherms revealed that TiO<sub>2</sub> nanoparticles and sand display very different affinities for the TA molecules, with preferential adsorption of TA onto sand rather than onto TiO<sub>2</sub>, both being driven by equilibrium constants. Moreover, in the case of sand this equilibrium constant was also dependent of the pH, since hydrophobic attraction with quartz surface is favored at acidic pH when the TA molecules get protonated and less ionized. These interactions strongly modify the surface properties of the metal oxides, altering the fate of the nanoparticles in the porous medium. The nanoparticles were first let to interact with TA before their injection through the porous medium. Depending on pH and ionic strength (I), TA may favor either the breakthrough or the deposition of the nanoparticles as compared to experiments carried free of TA: (IEP<sub>TiO<sub>2</sub></sub> and CCC<sub>TiO<sub>2</sub></sub> are respectively the pH of zero zeta potential and the critical concentration of NaCl salt for coagulation of the nanoparticles.)

- At pH  $\approx$  IEP<sub>TiO<sub>2</sub></sub> or I > CCC<sub>TiO<sub>2</sub></sub>, bare TiO<sub>2</sub> nanoparticles free of TA underwent homo-aggregation and exhibited decreased breakthrough, while the TA-coated nanoparticles displayed a lower IEP, i.e. anionic surface charge, and remained well dispersed in water and more mobile in the porous medium.
- At pH > IEP<sub>TiO<sub>2</sub></sub> and I < CCC<sub>TiO<sub>2</sub></sub>, while the bare nanoparticles negatively charged were well dispersed and mobile in the porous medium due to electrostatic repulsions with both neighbor nanoparticles and sand grains, the TA-coated nanoparticles underwent new attractive interactions with the sand via TA bridging and deposited more heavily.
- At pH < IEP<sub>TiO<sub>2</sub></sub> and I < CCC<sub>TiO<sub>2</sub></sub>, the bare nanoparticles were oppositely charged to the sand surface and underwent total deposition through the porous medium. In the presence of TA, being preferentially adsorbed to the sand, the molecules were certainly first partly desorbed from the nanoparticles, due to the equilibrium constant, allowing a limited breakthrough.

## References:

- Labille J., Solovitch N., et al. Fate of manufactured nanoparticles in the environment: Effects and persistence of the surface functionalisation in a lifecycle perspective. Case study for TiO<sub>2</sub>. In Encyclopedia of Nanotechnology. Springer, 2012
- Solovitch-Vella N., Labille J., et al. Concurrent aggregation and deposition of TiO<sub>2</sub> nanoparticles in a sandy porous media ES&T 2010, 44 (13) 4897

## Introduction



## NANOSCALE TiO<sub>2</sub> PARTICLES: RELATIONSHIP BETWEEN SURFACE PROPERTIES AND TOXICITY MEASUREMENTS

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Titanium oxides nanoparticles have been widely used in industrial applications such as cosmetics, food industries, environment, paints and surface coatings... Face to their growing use in various domains and the difficulties to separate them from the aqueous phase during wastewaters treatment due to their nanometric size, one can expect that the final host for these particles should be environmental compartments (soil, air and water).

Nanometric-sized particles are known to cause pulmonary damages and to be toxic for mammals (mice, rats). Nevertheless, few studies dealt with the toxic impact of nanoparticles with ecosystems. Previous studies have shown that the toxic effect was dependent (i) on the size of the particles and (ii) on the allotropic form of TiO<sub>2</sub> (anatase or rutile). But a lack of information remains concerning the relationship between the surface properties of TiO<sub>2</sub> nanoparticles (surface site density, surface charge) and the observed toxicity.

In this study we were interested in anatase (15 nm, 32 nm, 44 µm) and rutile (1 µm) commercial particles. Their toxic effect (acute or chronic) versus microcrustaceans, algae and plants was measured and compared to the particles size. Surface properties of each TiO<sub>2</sub> particles were determined by acid-base titration, and electrokinetics measurements, in order to complete data concerning the relationship between nanoparticles toxicity, size and allotropic form.



### MULTIBIOMARKER ASSESSMENT OF CERIUM AND TITANIUM DIOXIDE NANOPARTICLES (nCeO<sub>2</sub> AND nTiO<sub>2</sub>) SUBLETHAL EFFECTS ON FRESHWATER INVERTEBRATES

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Cerium and titanium dioxide nanoparticles are among the most widely used in everyday products. As a result, the release of nCeO<sub>2</sub> and nTiO<sub>2</sub> and the subsequent environmental exposure are predicted to be consequent, while the risks incurred are still unknown. Most of the aquatic ecotoxicological studies published from now have focused on the acute toxicity of those nanoparticles, often at environmentally irrelevant concentrations, and have shown their relative innocuousness. However, with environmental concentrations in surface waters predicted to be in the low µg/L range, it is unlikely that we could extrapolate real impacts of those nanoparticles on aquatic ecosystems from the results of those studies, especially given that the physico-chemical properties of nanoparticles at these concentrations are expected to be quite different. Moreover, few studies have used multi-biomarker approaches to evaluate impacts of those nanoparticles on aquatic ecosystems.

In this work, we filled those knowledge gaps by investigating sublethal effects of nCeO<sub>2</sub> and nTiO<sub>2</sub> on two aquatic invertebrates, the freshwater mussel *Dreissena polymorpha* and the freshwater amphipod *Gammarus roeseli*, at concentrations close to predicted environmental concentrations (10 and 100 µg/L and 20 and 1000 µg/L for nCeO<sub>2</sub> and nTiO<sub>2</sub> respectively) for 96 hours. A broad set of biochemical and histological biomarkers were used to evaluate nCeO<sub>2</sub> exposure effects on 1) antioxidant and antitoxic defences (catalase, GPx, GPx-Se and GST activities, metallothionein concentration), 2) cellular damages (lipoperoxydation), 3- iono/osmoregulation (Na<sup>+</sup>/K<sup>+</sup>-ATPase activity and haemolymph osmolality), 4) lysosomal system and 5) behavioural responses (locomotion and ventilation for *Gammarus* only). The first results showed an absence of significant adverse effects of nCeO<sub>2</sub> on all tested biomarkers. On the contrary, nCeO<sub>2</sub> seems to exhibit antioxidant properties, decreasing lipid peroxydation and catalase activity, and this protective activity will need to be more thoroughly investigated. The result analysis for nTiO<sub>2</sub> is still in progress.

Keywords: cerium dioxide nanoparticles (nCeO<sub>2</sub>) - titanium dioxide (nTiO<sub>2</sub>) – biomarkers – *Gammarus roeseli* – *Dreissena polymorpha*



## INTERACTIONS BETWEEN MICROORGANISMS AND TiO<sub>2</sub> NANOPARTICLES IN NATURAL WATER

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The physicochemical interactions between manufactured TiO<sub>2</sub> nanoparticles and the cyanobacteria *Synechocystis* were studied in natural water (Seine River, Paris). SEM (Scanning Electron Microscopy) and cryo-TEM (Transmission Electron Microscopy) techniques were combined to toxicity assessment experiments (colony forming unit) and Reactive Oxygen Species (ROS) quantification in order to define the impact of the sorption extent to the cell mortality. It has been found that the aggregation state of the nanoparticles in the natural water controls their sorption capacities [1]. Moreover, a strong correlation exists between the extent of nanoparticles sorption and the cell wall structure, particularly the presence of exopolysaccharides (EPS), controlling directly the toxicity of nanoparticles toward the microorganisms. Indeed, EPS depleted mutants of *Synechocystis* are by far more sensitive to TiO<sub>2</sub> nanoparticles under photocatalysis than the endowed wild type.

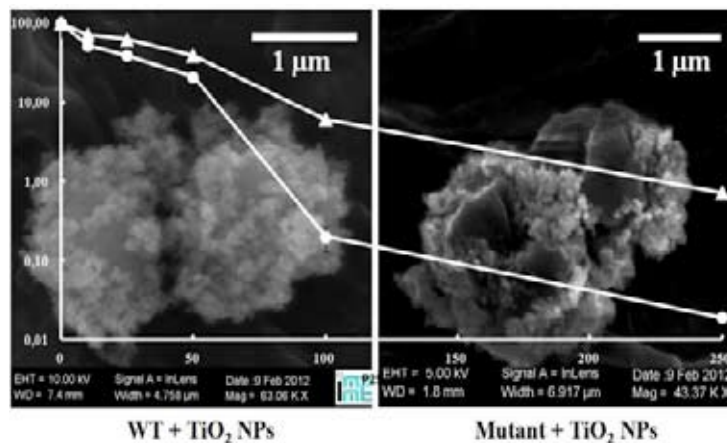


Figure 1: TiO<sub>2</sub> NPs adsorption and toxicity on *Synechocystis* Wild type and Mutant

[1] M. Planchon, R. Ferrari, F. Guyot, A. Gélabert, N. Menguy, C. Chanéac, A. Thill, M. F. Benedetti, O. Spalla *Env. Sci. Technol.* 2012 (submitted)





## RELEVANCE OF INTERFACIAL PHENOMENA FOR THE FATE AND BEHAVIOUR OF SYNTHETIC ZNO NANOPARTICLES IN AQUEOUS ENVIRONMENTS

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The toxicological and environmental impact of engineered nanoparticles (NPs) in aqueous environments depends on a number of physicochemical phenomena that take place at the particle-water interface, which are particularly relevant due to the high specific surface area of these materials. These phenomena determine the behaviour of the NPs (solubility, aggregation, transport, etc.) at the pH, salinity and organic matter content of natural waters. In the particular case of ZnO NPs, parameters such as particle size and solute adsorption may influence the release of free Zn<sup>2+</sup> ions, which, in turn, play an important role in the toxic effects of these NPs [1]. Moreover, these NPs show a strong tendency to associate with dissolved organic matter (DOM), which alters their surface charge, and, consequently, their stability and transport in natural waters. All these effects remain largely unknown to date.

In this work, the new technique AGNES (*Absence of Gradients and Nernstian Equilibrium Stripping*) [2] was used to obtain *in situ* information on the equilibrium and dynamic release of Zn<sup>2+</sup> ions in aqueous dispersions of ZnO NPs without the requirement of solid-liquid separation (as in conventional solubility techniques). The results show that particle size effects on the equilibrium solubility appear below 20 nm of primary particle diameter, whereas the kinetics of ion release seems to be controlled by aggregation processes [3]. The adsorption of DOM on the NPs does not affect the equilibrium concentration of Zn<sup>2+</sup> in the dispersion.

The interaction of DOM (humic acid) with the NPs was further characterized through UV-vis and Laser Doppler Electrophoresis, to conclude that DOM adsorbs readily on the NPs, and inhibits further aggregation at humic concentrations above 1.5 mg/L, by stabilizing the NP agglomerates through electrostatic repulsion. Finally, the aggregation, diffusion and settling dynamics of the NP agglomerates were studied through UV-vis absorption and Dynamic Light Scattering. The results were successfully compared with numerical solutions of a transport model based on Brownian diffusion and Stokes sedimentation of fractal, polydisperse NP clusters [4].

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 229244 (ENNSATOX).

**AGGREGATION OF CERIUM OXIDE NANOPARTICLES IN AQUEOUS SOLUTION**

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To characterize the environmental transport and quantify the risk of nanoparticles (NPs), it is important to fundamentally understand the aggregation of NPs and to describe this process quantitatively. In this work, with CeO<sub>2</sub> chosen as a model NP owing to its broad industrial applications, we systematically investigated the aggregation kinetics of NPs through assessment of the effect of solution chemistries (e.g., ionic strength and natural organic matter) and modeling approaches. Using time-resolved dynamic light scattering, we studied the aggregation kinetics of CeO<sub>2</sub> NPs under different concentrations of electrolytes (K<sub>+</sub> and Ca<sub>2+</sub>) and humic acid [1-2]. The experimental observations were further evaluated by theoretical models developed on the basis of von Smoluchowski's population balance equation and Extended Derjaguin–Landau–Verwey–Overbeek (EDLVO) theory. The model predictions are in close agreement with experimental observations. Moreover, a new theoretical approach was proposed for evaluating the attachment efficiency of CeO<sub>2</sub> NP aggregation on the basis of Maxwell-Boltzmann distribution combined with the DLVO theory [3]. The new approach successfully interpreted the effect of ionic strength, humic acid, and temperature on the aggregation kinetics of CeO<sub>2</sub> NPs, indicating the balanced consideration of interfacial energy and Brownian motion in evaluating the aggregation kinetics of NPs. Overall, this work provides insights into the NP aggregation with experimental and modeling approaches, and allows us to better understand and predict environmental transport and risk of NPs.

**ADSORPTION OF ORGANIC ACIDS ON MAGNETITE NANOPARTICLES, PH-DEPENDENT COLLOIDAL STABILITY AND SALT TOLERANCE**Tombácz E.<sup>1\*</sup>, Tóth I. Y.<sup>1</sup>, Nesztor D.<sup>1</sup>, Illés E.<sup>1</sup>, Hajdú A.<sup>1</sup>, Szekeres M.<sup>1</sup>, Vékás L.<sup>2</sup><sup>1</sup>Department of Physical Chemistry and Material Science, University of Szeged, Hungary<sup>2</sup>Center of Fundamental and Advanced Technical Research, RA-TD, Timisoara, Romania

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In aqueous medium, the colloidal stability of dispersed magnetite nanoparticles as an example of environmentally relevant metal oxides depends sensitively on not only the pH, but also the amount of organic acids occurring mainly in surface waters. These organic compounds can modify the surface charge properties of magnetite entirely or partially depending on their chemistry and amounts adsorbed.

In the present work, the adsorption of different organic acids and their influence on the pH-dependent charging, salt tolerance and so the colloidal stability of magnetite nanoparticles are compared.

The synthetic magnetite nanoparticles (MNPs) can bind different carboxylic acids to their <sup>o</sup>Fe-OH surface sites [1, 2]. A series of organic acids was chosen systematically, such as small molecular complexant (citric acid - CA), synthetic (poly(acrylic acid) - PAA) and natural (humic acid - HA) macromolecules and a small aromatic acid (gallic acid - GA) polymerizing *in situ* on the surface. Adsorption isotherms were measured and bond formation on <sup>o</sup>Fe-OH sites was detected by ATR-FTIR measurements. The pH-dependent charge state of MNPs was characterized by electrophoretic mobility and their aggregation by dynamic light scattering (DLS). The electrolyte tolerance was tested in coagulation kinetic measurements.

Although the feature of adsorption, the adsorption capacities, the type of bonding (either H-bonds or metal ion-carboxylate complexes can form between the <sup>o</sup>Fe-OH sites and the adsorbed carboxylate groups) and so the bond strengths are significantly different; nevertheless the following trends can be found in general.

A smaller amount of organic acids only neutralizes the positive charges of magnetite at pH lower than its pH PZC ~8, and so it promotes the aggregation between the particles having both positive sites and negative acid covered patches on the surface. These conditions, promoting sedimentation of oxide nanoparticles, are relevant in natural waters, where fine oxide particles are dispersed in water at neutral or slightly acidic pH and have only trace amount of organic acids dissolved in it. In the presence of greater amounts of organic acid, above the adsorption saturation, the surface coverage of magnetite becomes completed causing a sign reversal of particle charge and overcharging of oxide nanoparticles. The thicker layer of macromolecular acids (PAA, HA, *in situ* PGA) provides better electrosteric stability than CA and GA coatings. It has been proved that the pH sensitivity of amphoteric magnetite can be completely eliminated by organic acids studied here, but only the polyanionic coverage provides a significant increase in salt tolerance.

Acknowledgement: This work was supported by OTKA (NK 84014) foundation.

[1] E. Tombácz, et al. *Langmuir* 2009, 25, 13007.

[2] A. Hajdú, E. Illés, E. Tombácz, I. Borbáth *Coll. Surf. A* 2009, 347, 104.



## CHARACTERISING NANOPARTICLES IN SUB-OXIC ENVIRONMENTS

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Characterising nanoparticles in sub-oxic environments is important for understanding pollution transport and attenuation within a range of situations, e.g. in waste water treatment plants, hyporheic zones and within groundwater. It has been shown that multi-method approaches are essential in an environmental context for adequate characterisation [1]. In the last decade there has been a focus on the use of manufactured nanoparticles for contaminant attenuation and remediation of groundwater e.g. Elliot and Zhang [2], Reinsch et al. [3]. Obtaining a representative sample and maintaining the environmental redox status throughout the field and laboratory work is a real challenge when working in these environments. To date, very few studies have successfully sampled and characterised nanoparticles in sub-oxic environments, e.g. anaerobic groundwaters, using a range of state-of-the-art techniques.

The focus of our research was to develop a robust methodology to sample and characterise nanoparticles in sub-oxic environments using a range of techniques. To test and develop this method a shallow sub-oxic alluvial groundwater system within the floodplain of the River Thames, locally impacted by a landfill plume, was selected as the field site. Iron-rich and organic nanoparticles were sampled and characterised in sub-oxic four groundwater samples, under oxygen-free conditions, by atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy with energy-dispersive X-ray diffraction (SEM-EDX) and field-flow fractionation (FFF) with UV absorbance detection. Figure 1 shows an example of AFM images and particle size ranges obtained from groundwater before and after aeration. Dramatic changes in nanoparticle sizes and morphology were observed following mild aeration under controlled laboratory conditions.

This study has shown that detailed characterisation of environmental nanoparticles in sub-oxic environmental waters is possible using a range of complimentary techniques. This has important implications for field and laboratory based studies focused on understanding the fate, transport and toxicity of trace elements and engineered nanoscale materials such as zerovalent iron and silver oxide in the environment.

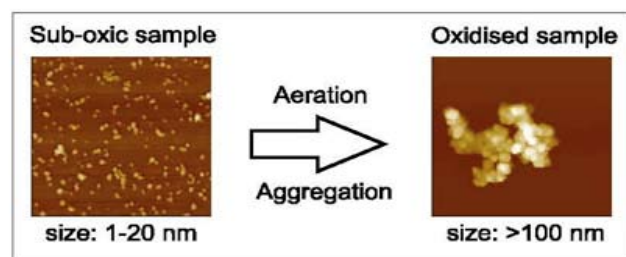


Figure 1. AFM images (2x2 m) for sub-oxic and aerated groundwater

[1] R.F. Domingos, A. Baalousha, Y. Ju-Nam, M.M. Ried, N. Tufenkji, J.R. Lead, G.G. Leppard, K.J. Wilkinson, *Environ. Sci. Technol.* 2009, 43, 7277

[2] D.W. Elliott, W. Zhang, *Environ. Sci. Technol.* 2001, 35, 4922

[3] B.C. Reinsch, B. Forsberg, R.L. Penn, G.V. Lowry, *Environ. Sci. Technol.* 2010, 44, 3455

**AGGREGATION OF TiO<sub>2</sub> NANOPARTICLES IN AQUEOUS SOLUTION: MODELLING AND COMPARISON WITH EXPERIMENTAL DATA.**Sameut Bouhaik I.<sup>1,2\*</sup>, Leroy<sup>1</sup> P., Ollivier P.<sup>1</sup>, Azaroua M.<sup>1</sup>, Mercury L.<sup>2</sup><sup>1</sup> BRGM, 3 av. Claude Guillemin, 45060 Orléans Cedex 2, France.<sup>2</sup> Institut des Sciences de la Terre d'Orléans, UMR7327, 1A rue de la Férollerie, 45071 Orléans Cedex, France.

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Extensive use of TiO<sub>2</sub> engineered nanoparticles (NPs) in consumer products in recent years raises the question about their potential effect on environment. Consequently, the relationships between physical and chemical properties of these NPs and their reactivity and mobility in natural environments need to be studied extensively. This is the focus of the present study where the stability and aggregation behavior of TiO<sub>2</sub> NPs are predicted as a function salinity (NaCl) and pH using an electrostatic surface complexation model coupled to a model based on the DLVO theory. In an aqueous solution, agglomeration of NPs is intimately related to “microscopic” forces occurring at the solid/water interface [1]. Traditionally and according to the DLVO theory [2], there are the repulsive electrostatic forces due to the diffuse layer surrounding the particles and the attractive London-van der Waals forces due to the spontaneous electric and magnetic polarization of atoms. The former is due to the imperfections of the crystal lattice and to the presence of hydroxyls surface sites. The amplitude of the electrostatic potential in the diffuse layer increases when the salinity decreases or when the difference between the pH of the bulk water and the pIIEP increases. The strength of the resulting electrostatic force is directly related to the amplitude of the electrostatic potential. A strong and repulsive electrostatic force leads to dispersed and stable NPs occupying a low volume and which can be mobile in the porous medium, as opposed to large and agglomerated NPs [1]. The description of electrostatic interaction occurring between two NPs requires the determination of electrical potential at the slipping plane called “Zeta potential” or “Electrokinetic potential”. However, this electrical potential is still poorly known because of the complexity of the interpretation of the electrophoretic mobilities. Indeed, for dilute aqueous solutions, the surface conductivity of electrically charged NPs slows down their mobility under the applied electrical field and, therefore, the apparent zeta potential inferred from electrophoresis is under-evaluated. This leads in turn to the prediction of a weaker repulsive electrostatic force. However, the electrical potential at the head-end of the diffuse layer, which can be assimilated to the zeta potential [4], can be also estimated using a CD-MUSIC coupled with a Triple Plane or an Extended Stern Model (TPM, ESM) [3]. This permits the calculation of the electrostatic force and then the prediction of the stability ratio and critical coagulation concentration (ccc) of TiO<sub>2</sub> NPs [5] as a function of salinity and pH without the need of electrophoretic measurements.

[1] K. A. D. Guzman, M. P. Finnegan, J. F. Banfield *Environ. Sci. Technol.* 2006, 40, 7688.[2] E. J. W. Verwey, J. T. G. Overbeek *Amsterdam: Elsevier* 1948, 218p.[3] P. Leroy, C. Tournassat, Bizi M. J. *Colloid Interf. Sci.* 2011, 442.[4] R. J. Hunter *Academic Press, New York* 1981, 386p.[5] A. M. Puertas, F. J. de las Nieves J. *Colloid Interf. Sci.* 1999, 216, 221.