

Advanced fluorescent nanotracers: a broad field of application

O. Raccurt, J. Samuel, O. Poncelet, S. Szenknect, F. Tardif

Commissariat à l'Energie Atomique, Department of Nano-Materials, Laboratory of Tracer Technologies, 38054 Grenoble, France

ABSTRACT

Optical and magnetic nanoparticles are both attractive fields of investigation which are gaining in importance due to their potential markets e.g. polymer nano-composite, colloidal dispersion, environmental monitoring or biomedical diagnostics, etc. A very large set of fluorescent particles can be bought or synthesized thanks to recent progress in nanotechnologies. Their diameter, their surface functionalization, their spectral signature can be tailored for specific applications. This article describes the interesting potentiality for tracing nanoparticles into three different applications such as the monitoring of the distribution of nanocharges in polymer composites, the characterization of colloidal stability of sols in liquids of various polarity and finally, the colloidal transport in porous media. In all the case, nanotracers may be constituted by engineered fluorescent particles chemically and structurally similar to the colloids of interest.

Keywords: nanotracers; nanoparticles; fluorescence; surface functionalization, colloidal particles as transport agents

1 INTRODUCTION

Optical and magnetic nanoparticles are both attractive fields of investigation which are gaining in importance due to their potential markets e.g. polymer nano-composite [1,2], colloidal dispersion, environmental monitoring or biomedical diagnostics [3], etc. Among all the spectroscopic mechanisms used in order to monitor tracers, fluorescence is the most attractive because of its simplicity to use and inherently low detection limits. A very large set of fluorescent particles can be bought or designed. Their diameter, their surface functionalization, their spectral signature can be tailored for specific applications. For instance, these fluorescent nanotracers with controlled size and surface properties offer an interesting potential for different application such as nanofiller homogeneity monitoring in polymer composite [4], characterization of colloidal stability in liquids and colloidal transport in porous media.

2 NANOTRACERS

First, how define what a nanotracer is? First at all, a nanotracer has to be similar in size, density, surface charges to the species which have to be traced. So it can be reasonably expected that the nanotracer particles will physically behave like the nanocharges which have to be

traced. Moreover the nanotracer must be detectable using a particular physical property for example luminescence or magnetism. In each case of application presented here, we have chosen to use fluorescent nanotracers because it is easy to detect them by classical fluorescence imaging and to set analytical apparatus around process equipment.

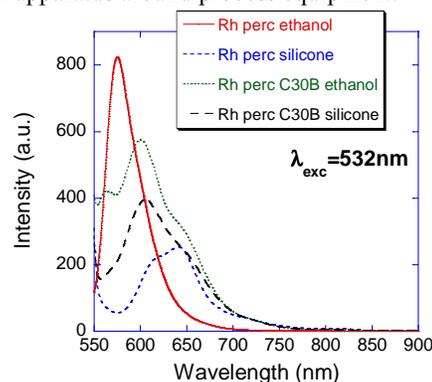


Figure 1: Fluorescent spectra of rhodamine B perchlorate and nanotracers closite 30 B nanoclay with intercalated rhodamine B perchlorate in ethanol and silicone oil. All tracers are excited at 532 nm.

Typically there are two approaches for designing a nanotracer, the first one is the direct incorporation of a fluorescent organic dye in the nanoparticle, this is a convenient way for clays wherein some ionic exchanges can be carried out. The second one is to encapsulate a fluorescent organic dye during the synthesis of nanoparticles, this can be done by using the sol-gel chemistry of silica.

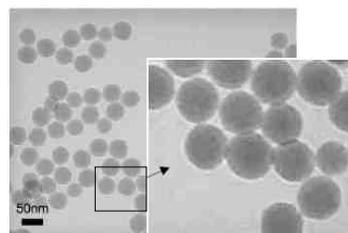


Figure 2: TEM image of silica nanotracers including organic fluorophores embedded into a silica matrix covered by a nanoshell, whose zeta potential can be tailored for each application.

Montmorillonite nanoclay material is a good example to illustrate the first approach. We incorporated in a Montmorillonite nanoclay (South Clay Co.) by ionic exchange an organic fluorescent dye. To ensure the

exchange, the dye has to be positively charged, so we have chosen Rhodamine B perchlorate. Intercalation of fluorescent dye is characterized by ATG, RX and fluorescent measurement. Figure 1 shows the fluorescent spectral data for Rhodamine B perchlorate only and intercalated into clay (MMT Cloisite 30B from South Clay Co.) in non polar solvent. The split of the peak from one to tree is representative from the position of organic dye compared to the clay material: free in polymers, adsorbed on the external surface of nanoclay particles and intercalated between the layers of the nanoclay (see figure 1). So in this case, the fluorescence measurements will monitor both the distribution of the nanocharges but also the affinity of the particles versus the organic part of the composite.

The second approach can be illustrated by the synthesis of fluorescent silica nanoparticle by reverse micelle sol-gel route. More detail of the synthesis protocol is given in another abstract of this conference [1]. The process controlled the size actually from 40 nm to 200 nm. The surface properties were modified by addition of silane coupling agents to obtain the appropriate surface potential or hydrophobic or hydrophilic properties. Two example of application of this family of nanotracer will be discussed for the measurements of the dispersion of nanoparticles in an organic binder and for the tracing of the mobility of natural colloids into soils column laboratory experiments

3 EXAMPLES OF APPLICATIONS

3.1 Luminescent clays nanotracers in polymers¹

The quality of the mixing of nanocharge in polymer matrix is a key point to design in a reproducible way high-tech composite. For the first application, dispersion of nanoparticles such as luminescent nano-clays into polymer has been studied by measurement of the fluorescence. For nano-clays, the intercalation of the fluorescent organic dyes into natural clay is studied. These fluorescent nano-clay are used to monitoring the mixing and the exfoliation process during extrusion [3].

The objective of this experiment is to observe the dispersion of nanoclay during the mixing into the extrusion of polymers. The experimental setup is show in figure 3. A transparent tube with a standard screw extrusion is installed in closed circuit. The PDMS polymer is used for this transparence at the wavelength scale for fluorescence measurement. The viscosity of PDMS is chosen to simulate the viscosity of a real molten polymer in the screw. Nanotracers (Cloisite 30B with rhodamine B perchlorate intercalated) are first dispersed into 20 mL of PDMS at 1% in mass concentration. This “labeled” volume is introduced at the beginning of the screw with a syringe. Four cameras

with adapted long band pass filters shoot the distribution of nanotracer during extrusion (see fig 4).

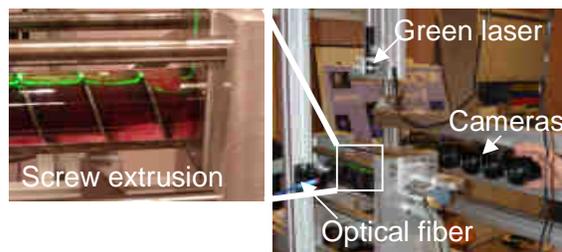


Figure 3: Experimental display for tracing luminescent nanoclay mixing into the polymer during extrusion processes, right. Zoom view of screw extrusion at the end of mixing show laser plan excitation and nanotracers into polymers (red), left.



Figure 4: Imaging the fluorescent nanotracer into the screw extrusion during mixing

A green laser (532 nm, 10 mW) with lense is used to excited nanotracers by a laser plane (see figure 3 left). An optical fiber record at a portable spectrophotometer (USB2000 from Ocean Optics) is placed at the end of the screw to measure the fluorescence in function of time during the experiment. The time acquisition is synchronized to the rotation rate of the screw. Evolution of spectral response of the nanotracer in function of time during the mixing is showing in figure 5.

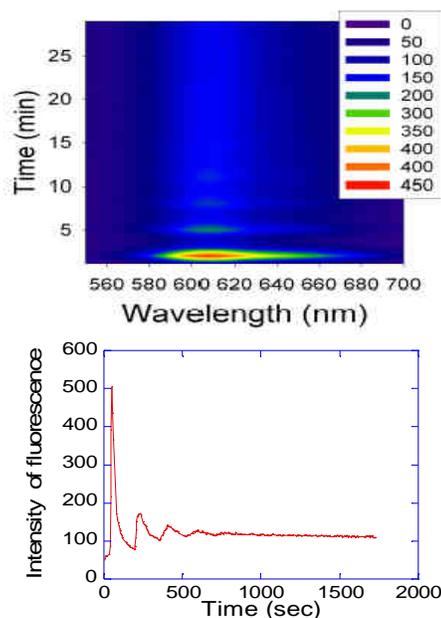


Figure 5: Evolution in function of time of the spectral fluorescence of tracer during the mixing (top complete spectral data, bottom @ 610 nm)

¹ the authors would like to thank A. Esposito, J Balcaen and J. Duchet from LMM/IMP UMR CNRS for their collaborative work on the study of mixing nanoclay

The results show an amortized oscillator function characteristic of a mixing process. First, immediately after the injection of tracer, the maximum of fluorescence become after 2.5 minutes corresponding to the time of tracers become from the detector. After that the maximum of fluorescence @ 610 nm decrease with oscillation to tend with a constant value. The mixing is completed after 5 cycles.

3.2 Luminescent silica nanotracers to measure the dispersion of nanocharges into polymers

The second application concerns the characterization of the dispersion and the colloidal stability in different solvents. In this part we will show the impact of the surface properties on the dispersion of fluorescent silica nanoparticle into polymeric material. Fluorescent silica nanoparticles synthesized by sol-gel micro-emulsion process showing in [5]. The hydrophobic or hydrophilic surface properties are tuned by the covalent bounding of silane coupling agents.

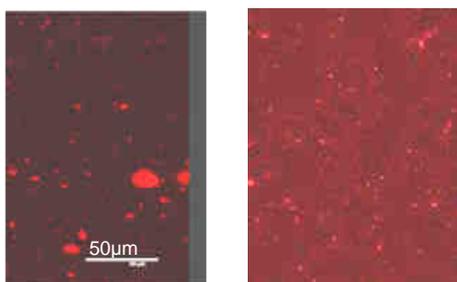


Figure 6: Confocal microscopy image of silica nanotracer with fluoro/hydrophobic (left) and amino/hydrophilic (right) surface function into PVA polymer

The fluorescent silica nanoparticles (diameter: 40nm) are easy to disperse in water or in acetone (Fig. 2). By modifying the protocol, other sizes can be easily obtained [6,7]. Two chemical functions have been successfully covalently linked to the nanoparticles' surface: a hydrophilic amino based molecule and a hydrophobic/oleophobic one containing a fluoro carbon moiety. These molecules have an effect of the physical behavior of the nanoparticles' surface, illustrated by the zeta potential value in aqueous medium (Fig. 9). Confocal microscopy imaging (Fig. 6) shows the distribution of the luminescent silica nanoparticles in PVA films. Unambiguously, the surface treatments of the silica particles greatly impact the distribution of particle in PVA.

3.3 Luminescent silica nanotracers for tracing colloidal transport in soil

The silica fluorescent nanoparticle are using for tracing the colloidal transport into the soil. Recent field and laboratory experiments have identified colloid-facilitated transport of

contaminants as an important mechanism of contaminant migration through groundwater. Groundwater is an important receiving environment for bulk chemicals of daily use and is therefore expected to be a sink for nanoparticles as well. Indeed, the mobility of a particle in a porous medium is strongly limited by its tendency to deposit on the surface of the grains, the so-called "filtration-effect". The process of nanoparticle deposition during flow through porous media is commonly assumed to take place in two rate-limiting steps [8]: first transport to the surface of the collector by Brownian diffusion, interception, or sedimentation (for the larger ones), then, attachment to the surface. The kinetics of the transport step depends primarily on physical factors such as size, shape, density of the nanoparticles, flow velocity and pore geometry. The kinetics of the attachment step is controlled by interparticle forces: van der Waals, electrostatic, steric repulsion and hydrophobic forces between nanoparticles and grain surfaces. Due to the large number of factors influencing nanoparticles mobility in porous media, we propose here to use versatile model colloidal tracers, called "nanotracers" to gain insight into the impact of the mechanisms that drive the transport and the deposition of nanoparticles in a natural porous medium.

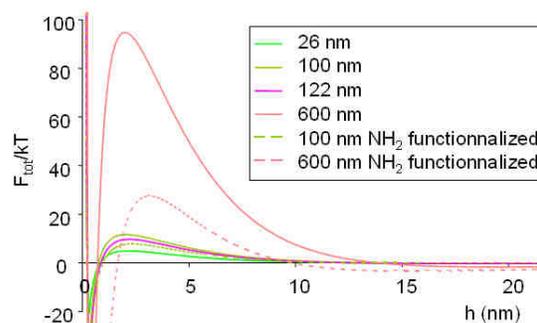


Figure 7: Comparison of total energy potential of particles (DLVO theory) as a function of interaction distance with collector surface between nanotracers (100 and 600 nm) and natural colloids (26 and 122 nm).

To demonstrate the existence of colloid-facilitated transport, three criteria must be fulfilled: (1) soil colloidal particles must be mobilized; (2) pollutants must associate with the colloids and (3) colloids must be transported through the porous media. Our aim is to determine the physicochemical conditions that lead to soil colloid generation and transport in a heterogeneous porous media and compare them with the classical mobilization theory. As this theory hardly fits to natural heterogeneous porous media, we are used new colloidal tracers to simulate the transport of natural particles. Monodispersed silica fluorescent nanoparticles were obtained from a modified Stöber synthesis [9,1]. The use of nanotracers with controlled properties allows quantification of the impact of size and the zeta potential on the mobility of the particles individually. Therefore, after production of functionalized nanotracers using amino silane

coupling agents [10,1], and characterization by Dynamic Light Scattering technique (Fig. 8 and 9), leaching experiments were performed in repacked columns under conditions representative of groundwater flow. The soil used is a calcareous alluvial deposit from a fluvial shallow aquifer. The produced nanotracer suspensions have been injected into columns of 25-30 cm in length and fluorescence followed in the outflow to determine the breakthrough curves.

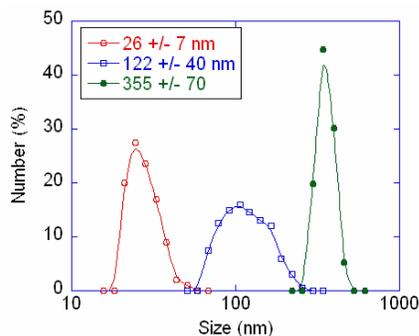


Figure 8: Size distribution of three different silica fluorescent nanotracers measured by Dynamic Light Scattering (Malvern Nanosizer)

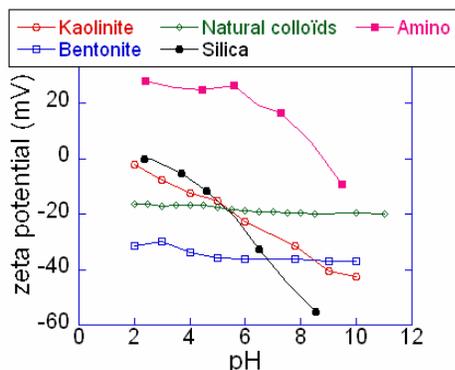


Figure 9: Zeta potential of natural colloids (Kaolinite, bentonite and unknown natural colloids) and nanotracer with and without amino functionalization

These results have been described using the classical convection-dispersion equation, with a first-order irreversible process for particle deposition. Correlations between transport and deposition parameters using size and zeta potential of the nanotracers have been established under environmentally relevant conditions. The deposition rates have also been compared with predictions made using the DLVO theory and the classical filtration theory [11], that it is known to be hardly applicable for particles transport through natural porous media. Experimental measurement of the irreversible deposition rate (K_{irr}) of colloids is performing into a column of soil. The measurement of the fluorescence of tracers before and after the soil column give an information of the colloid mobility and the quantity of nanoparticle fixing into the soil. Figure 10 show the irreversible deposition rate of nanoparticles in

function of size and the flow rate of water through the column. The results obtained indicate that the use of designed colloidal tracers is a promising tool for the estimation of nanoparticles transport parameters.

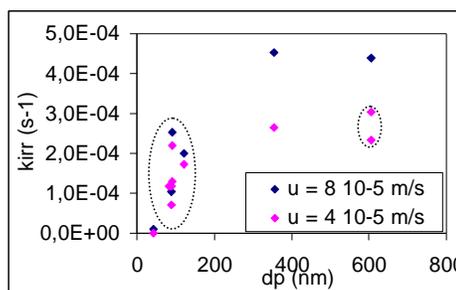


Figure 10: K_{irr} irreversible deposition rate [s^{-1}] in function of particle size measured in a laboratory column experiment

4 CONCLUSION

Through four applications we demonstrated the interest of nanotracers in the measurement of nanoparticles dispersion or movement into a media. The fluorescence techniques offer a good sensibility in the case of the media is transparent (like polymers) for in-situ observation. Fluorescent nanotracers offer a very interesting panel of possibility to observe and measure the comportement of nanoparticles into a media with a wide range of application.

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