



## ZETA POTENTIAL AS A TRACER FOR IRON ORE TAILING INPUT

*Caroline Fiório Grilo<sup>1</sup>; Valéria da Silva Quaresma<sup>2</sup>; Claire Chassagne<sup>3</sup>; Paul van Kan<sup>4</sup>; Alex Cardoso Bastos<sup>5</sup>*

**Palavras-Chave** – Rio Doce, rejeito de minério, floculação

In November 2015, a mining dam failure dumped approximately 32 million m<sup>3</sup> of very fine iron-rich tailing material into the Doce River watershed and the adjacent continental shelf, Southeast Brazil. Previous settling column experiments demonstrated different properties and behavior of flocs between natural sediment samples and those contaminated by the iron ore tailing, in which the presence of smaller and more porous flocs in the last was explained by a very fine fraction of clay and or a metallic coating (Grilo et al., 2018). As nanoparticles possess unique physical and chemical properties due to their high specific area and nanoscale size, their transport, persistence and bioavailability in the environment are essential aspects to be considered in risk assessment and management (Wiesner et al., 2009). Nanoparticles such as iron oxyhydroxide hold high reactivity with different ions (Antelo et al., 2005), where adsorption may increase or decrease the charge on the surface of nanoparticles and affect their stability (Breeuwsma and Lyklema, 1973).

After entering the aquatic environment, the composition of fluid fine mineral tailings will evolve with respect to the water chemistry and presence of other suspended particles. The stability of the suspension is described by the DLVO theory (Verwey, 1947; Derjaguin and Landau, 1941), when colloidal particles are in presence of electrolyte solution. While the attractive force of van der Waals allows the particles to adsorb, the electrostatic forces can act as repulsive. The resultant of the forces will determine the stability of the suspension (i.e. if particles will aggregate or not) and can be inferred by zeta potential analysis. Zeta potential measurements were carried out in order to verify such inhibition of suspensions with sediment samples contaminated with the iron ore tailing sludge that reached the continental shelf after the Fundão dam breach (Minas Gerais – Brazil). Data acquired indicates the suspension stability dependence on varying pH and different electrolyte solution (monovalent and divalent salts) in a way to confirm resistance to aggregation (and consequently increase of residence time in the water column) due to the presence of goethite when in marine environment. Zeta potential analysis was also carried out for synthetic goethite (bought) and pure goethite (made) suspensions as an iron oxide reference due to its great abundance in the iron ore tailing sludge (Quast, 2012; Santos and Brandão, 2003; Pires et al., 2003). Samples from the mining dam, inside the river, and continental shelf were collected to describe different scenarios and properties of the sediment before and after the iron ore mining dam collapse. A sample from the continental shelf prior to the mining dam failure was used for comparison purposes.

Synthetic goethite was bought from Sigma-Aldrich (Fe 30-63% with varying amounts of MgO<sub>2</sub>, SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>). Pure goethite was acquired from precipitation of Iron (III) Nitrate Nonahydrate ((Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) by KOH addition. The electrophoretic mobility of the suspensions was measured using a Zetasizer Nano ZS (Malvern Panalytical) device, at the Physical Chemical Laboratory of Deltares (The Netherlands). The zeta potential values were acquired in suspensions with different pH (2 to 10) adjusted by adding acid (HCl) or base (NaOH) and with monovalent (NaCl, KCl and NaNO<sub>3</sub>) and divalent (MgCl<sub>2</sub> and CaCl<sub>2</sub>) salts. Electrolyte solutions were made with demi-water (conductivity < 10 microS/cm). Apparent Zeta

1) Universidade Federal do Espírito Santo, Av. Fernando Ferrari 514 - Goiabeiras, Vitória – ES. Brasil, carolinegrilo@gmail.com

2) Universidade Federal do Espírito Santo, Av. Fernando Ferrari 514 - Goiabeiras, Vitória – ES. Brasil, vdsquaresma@gmail.com

3) Universidade Tecnológica de Delft, Mekelweg 5, 2628 CD Delft. The Netherlands, C.Chassagne@tudelft.nl

4) Van Kan Scientific, Korenbloemstraat 6, 6542NJ, Nijmegen. The Netherlands, pjmvkan@xs4all.nl

5) Universidade Federal do Espírito Santo, Av. Fernando Ferrari 514 - Goiabeiras, Vitória – ES. Brasil, alexcardosobastos@gmail.com



Potential (AZP) dependence on pH and monovalent (KCl, NaCl and NaNO<sub>3</sub>) and divalent (MgCl<sub>2</sub> and CaCl<sub>2</sub>) salts were carried out.

The AZP analysis allowed to infer about flocculation behavior of sediments and goethite under influence of varying pH (2 to 10) and ionic strength of monovalent (NaCl, KCl and NaNO<sub>3</sub>) and divalent (MgCl<sub>2</sub> and CaCl<sub>2</sub>) salts. Although dissolved salts were not an effective flocculant, pH was the determinant factor for goethite flocculation. When sediments were also submitted to pH variation, goethite signal could be clearly tracked in other environmental matrices containing the tailing sludge input, such as sediment samples from the Mining Dam, River and Continental Shelf after the mining dam breach. While sediment for continental shelf before the input of iron ore tailing material presented the classical behavior of sediments containing clay minerals, sediments contaminated with the iron ore tailing had a clear influence of goethite on their pattern. This is of great implication to the transport and deposition of this new sediment (mixture of clay minerals and iron ore tailing sludge) on the continental shelf, as it is more prone to be dispersed in marine environments due to a charge reversal of goethite at basic pH. Some chemisorption of nitrate ion on the surface of synthetic goethite particles was observed but it was not present in pure goethite neither in the sediment samples. The chemisorption may be as a result of impurities (MgO<sub>2</sub>, SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>) in synthetic goethite composition. Although sediment samples may also contain such impurities, interaction with clay particles and isomorphic substitution of iron for aluminum in the goethite from the tailing sludge may be inhibiting the chemisorption.

The present study was conducted on hydrochemical conditions (pH and dissolved salts) very common in natural environments, turning the results very useful for predicting the transport and deposition of goethite nanoparticles as well sediments contaminated by iron ore tailing sludge. The zeta potential behavior of sediments could also be used as tracer for iron ore mining tailings input into fluvial and marine environments and it could support prediction of sediment transport and deposition.

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