

**RELEASE AND STABILITY OF ALUMINUM METAL NANOPARTICLES IN SURFACE WATER:  
EFFECTS OF PARTICLE LOADING**

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**РАСТВОРЕНИЕ И СТАБИЛЬНОСТЬ НАНОЧАСТИЦ АЛЮМИНИЯ В ПОВЕРХНОСТНЫХ  
ВОДАХ: ВЛИЯНИЕ НАВЕСКИ ЧАСТИЦ**

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*При определении экотоксичности наночастиц важную роль играют условия пробоподготовки суспензий. В работе с помощью фотонной кросскорреляционной и атомной абсорбционной спектроскопии показано влияние концентрации суспензии (10 и 100 мг/л) на степень растворения и агрегацию электровзрывных наночастиц алюминия в растворе, моделирующем поверхностную воду пресного водоема.*

The demand and production of nanosized powders is growing due to a rapidly emerging use of nanomaterials on the global market. From this follows an increased need for an improved understanding of characteristics and potential toxicity of nanomaterials, essential data for classification and risk assessment. Nanosized particles represent a new class of potential pollutants of the environment. As the properties of nano-powders may change significantly when exposed to test media of varying characteristics, the assessment of their toxic response is not straightforward [1-2].

Several parallel processes take place upon introduction of nano-powders into aqueous media. Metal release is the predominant process that largely depends on water chemistry and on surface oxide characteristics [2] (often different compared with micron sized particles or massive surfaces). Depending on particle reactivity, surface properties and amount of particles in solution (particle loading), nano-powder particles form aggregates of different size and stability in solution at the same time as different dissolution/metal release processes take place. The wide range of nano-powders available and limited quantitative and mechanistic understanding of these processes (often both chemically and electrochemically induced) make it very difficult to predict their behavior in solution.

The aim of this work was to evaluate the effect of particle loading on the extent of particle dispersion and release of aluminum from a metallic nano-powder in artificial surface water with time. Electroexplosive aluminum (Al) nano-powder sized 90-110 nm was supplied by LLC “Advanced Powder Technologies”, Tomsk, Russia.

All experiments were performed in standard solution of artificial surface water (OECD 203 medium, ISO 6341: CaCl<sub>2</sub>·2H<sub>2</sub>O – 29.4 mg/L; MgSO<sub>4</sub>·7H<sub>2</sub>O – 12.3 mg/L; NaHCO<sub>3</sub> – 6.48 mg/L; KCl – 0.58 mg/L; pH = 6). The solution pH was adjusted by acid-base titration with a 0.95 % solution of H<sub>2</sub>SO<sub>4</sub>.

Two particle loadings, 10 mg/L and 100 mg/L, were investigated. Triplicate samples were prepared for each time period (0.25, 0.5 and 1 h). The nano-powder was weighed in Nalgene® polymethylpentene jars using a Mettler Toledo XP26 balance with an accuracy of 0.00001±0.000002 g to which 50 mL of the OECD 203 test medium was carefully added. Prepared suspensions and corresponding blank solutions (only OECD 203 test media, no added nano-powder) were exposed for the different time periods at 21°C in closed vessels under conditions of delicate bi-linear agitation and light conditions. After the predetermined exposure times, 15 mL of the suspensions were removed using a pipette dispenser and consecutively centrifuged for 10 min (13400 rpm/min) to separate particles from solutions. The solution was, after separation, pH adjusted to a pH<2 and the total aluminum concentration in solution determined by means of atomic absorption spectroscopy-graphite furnace, AAS-GF (Perkin Elemer AAnalyst 800, USA).

Size distribution measurements of nanoparticles in solution with time were measured in parallel using photon cross-correlation spectroscopy, PCCS (Nanophox, Sympatec GmbH, Germany). The prepared suspensions were manually shaken for 1 min before transferring 1 mL of the suspension to a cuvette for the measurements, performed every 60 s for 1 h.

AAS measurements show very low amounts of released aluminum in solution up to 1 h of exposure (<0.5% of the particle mass), amounts that were slightly reduced with time (significant only between 0.5 and 1h) for both particle loadings, 10 mg/L and 100 mg/L. Generated findings are presented in Fig. 1. This effect could be explained by changes in particle size distribution and extent of particle agglomeration with time and concomitant changes in the exposed surface area to solution volume ratio, and possibly to a minor extent, be related to complexation and sedimentation of released aluminum as Al<sup>3+</sup> ions only are stable in solution at acidic conditions [3].

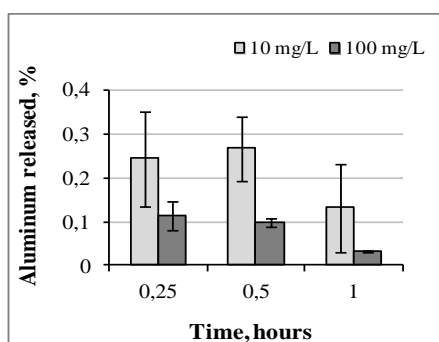


Fig.1 Amount of released aluminum with time compared with the loaded particle mass for aluminum nanoparticles exposed in OECD 203 surface water medium of pH 6.0

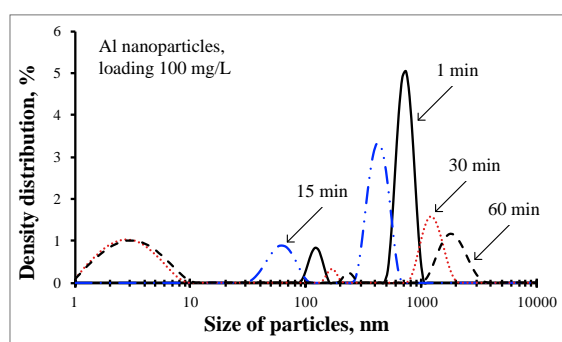


Fig.2. Changes in particle size distribution with time illustrated for the higher loading (100 mg/L).

The total amount of released aluminum measured in solution from the particle suspensions was 24 and 115 µg/L after 15 min of exposure and particle separation of the 10 and the 100 mg/L suspensions, respectively.

However, although the total concentration of released aluminum in solution was higher for the highest particle loading, was the released fraction compared with the total particle mass lower when compared with the suspension of lower loading, illustrated in Fig. 1. These effects are mainly believed to be attributed to differences in exposed surface area and extent of particle agglomeration. The probability for particle collision and aggregation increases with particle loading.

Time resolved measurements, illustrated for the highest loading (100 mg/L), clearly show (Fig. 2) the formation of agglomerates of increased size up to 1 h of exposure, i.e. reduced surface area, Fig. 2 and Fig. 3b. Relatively similar scattered light intensities with time indicate that most particles remained suspended during the investigated time frame (Fig. 3b).

Observed scattered light intensities for the lower loading (10 mg/L) were too low to generate any measurable particle size distribution (Fig. 3a), effects related to detection limitations and/or possibly to particle sedimentation after 3 min of exposure. However, even the suspension of lower particle loading resulted in measurable amounts of released aluminum (Fig. 1) that may induce toxic effects.

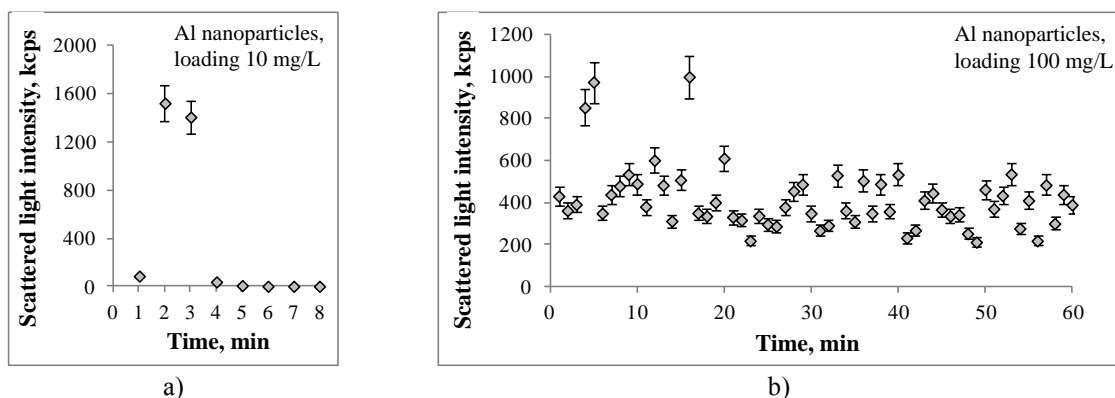


Fig. 3. Changes in scattered light intensity, measured by means of PCCS, of aluminum metal nanoparticle suspensions exposed up to 1h in OECD surface water at two different loadings, 10 mg/L (a) and 100 mg/L (b).

In all, the particle loading influences the total amount of released aluminum in solution and the extent of agglomeration with time. Observed findings underline the importance for an improved understanding of how standard experimental conditions of e.g. ecotoxicity testing influence the transformation and agglomeration of metal nanoparticles.

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