

Sedimentation of Fe₂O₃ and metallic iron nanoparticles exhibiting Brownian movement

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Abstract. Sedimentation of nanoparticles in water solutions was studied *in situ* by transmission Mössbauer spectroscopy in horizontal and vertical geometry. The studied specimens were Fe₂O₃ of a commercial pigment and metallic iron nanoparticles in slurry used in a water purification technology. The sedimentation is selective and leads to the gradual removing of the bigger particles from a solution. The iron nanoparticles in the solution are relatively chemically stable until, due to the drying, the sediment becomes exposed to the air.

Key words: Brownian movement • nanoparticles • sedimentation

Introduction

The application of Mössbauer spectroscopy for the study of the diffusion of small particles due to the Brownian movement has been recognized soon after the discovery of recoil free absorption of the nuclear radiation [1], but later nearly neglected. Recently, due to the boom for nanotechnology, this aspect of Mössbauer spectroscopy is finding new fields of applications [2–4, 6]. Similarly, the study of sedimentation is most frequently related to the geological processes, studied by the chemical and physical properties of the deposits [5, 7]. In the presented studies an attempt of the joint experimental treatment of these thermodynamically competitive processes is presented.

The random walking of iron nanoparticles may be easily and relatively precisely monitored by the broadening of the resonance absorption lines in Mössbauer spectra [6]. This is, however, restricted to the case where the mean absolute displacement of the nanoparticles during the half lifetime of ⁵⁷Fe, 141 ns, being in the range of 0.01 to 10 nm, i.e. their velocity fits to the Mössbauer velocity scale of 0.1–10 mm/s.

The ordered movements of nanoparticles like sedimentation or convection with the corresponding, but in this case macroscopic velocity, are more difficult to observe with the use of Mössbauer spectroscopy because of the long time needed for the recording of spectra, which makes difficult the diagnostic of evolution of the system.

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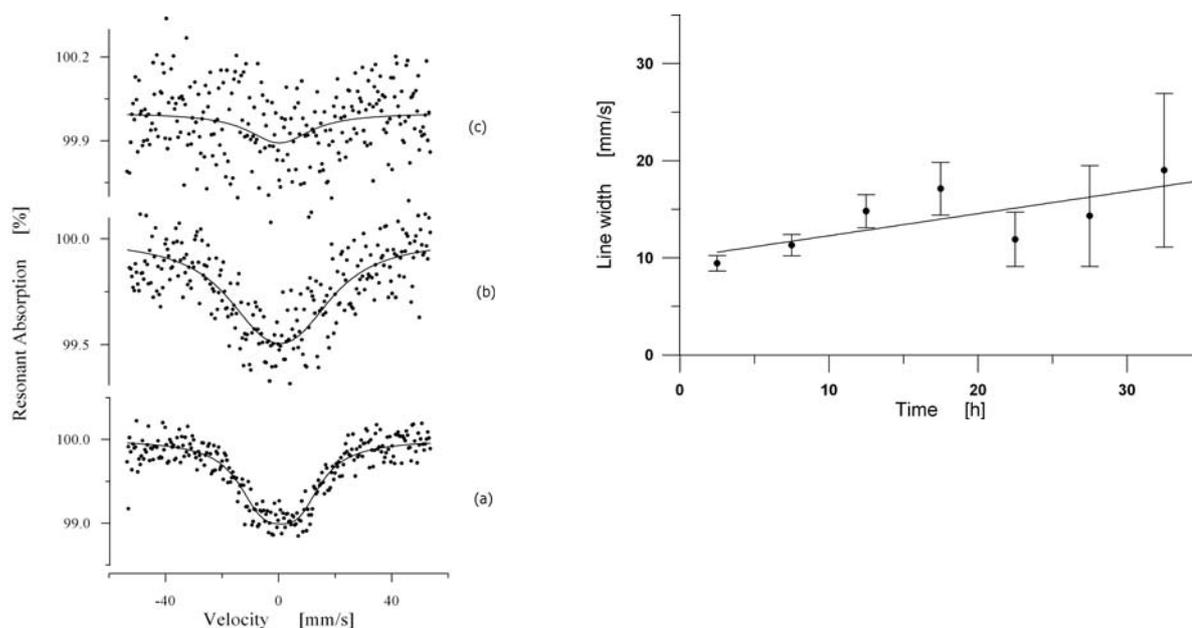


Fig. 1. Left: the selected Mössbauer spectra of hematite nanoparticles in water solution, 1 cm below the surface, measured after 5 h (a), 15 h (b) and 35 h (c). Right: the corresponding resonance absorption line width broadening.

In this work we propose a methodological idea illustrated by preliminary results concerning the sedimentation of hematite and iron nanoparticles in two commercial systems: (i) fluid pigment Mix-Bud max no. 8, containing about 100 nm Fe_2O_3 particles (90 wt.%) and, (ii) Nanofer 25S slurry of 17 wt.% metallic iron nanoparticles, about 50 nm in diameter, that can be utilized in waste water treatment.

Experimental

The Mössbauer spectra of the studied specimen were taken in transmission in two geometries, namely horizontal and vertical. In the first case, the evolution of 10 wt.% water solution of Mix-Bud, 1 cm below the surface, selected by the collimation slit, was observed. In vertical geometry, the spectra of 20 wt.% water of Mix-bud solution and Nanofer 25S were studied. In this case the nanoparticles and their sediments were recorded simultaneously. The spectra were automatically saved every 5 hours.

Because the spectra of the nanoparticles in the solution exhibit dramatic line broadening, their intensity becomes rather small. Nevertheless, in spite of the miserable statistical quality, limited by the time window for the observation of the processes, they carry some reliable information because the spectra may be fitted with only three free parameters, namely the line width, the intensity and the background; the hyperfine parameters are known from the spectra of the dry samples.

Results and discussion

Horizontal Brownian movement of hematite nanoparticles in supernatant liquid

Some examples of the hematite nanoparticles in solution, 1 cm below the surface and the corresponding

evolution of the line width, are shown in Fig. 1. The gradual disappearing of the spectra with time is due to a decrease of the total area of the spectra and also to the increase of the line width. Both are the result of the selective sedimentations which is faster for the bigger particles which are less moveable due to the Brownian movement. This rather obvious result shows, at the microscopic level, that the segregation of submicron particles due to the distinguished speed of falling in water solutions, is possible. Secondly, taking into account that the shade of the paint strongly depends on the pigment particle size, such selective sedimentation leads to the enrichment of the painted surface layer in small particles and modify the final color.

Vertical Brownian movement of hematite nanoparticles

An example of the spectra is shown in Fig. 2. In this case, the entire area of the spectra is constant, but the spectra consist of two fractions. One, with the narrow-line width which is constant with time is assigned to hematite in sediment. The subspectra with the broad lines arise from the small particles in supernatant. As in the case (a) the line width of this fraction increases with time showing that the bigger particles earlier land in the sediment.

Sedimentation of Fe nanoparticles in Nanofer 25S

The selected Mössbauer spectra of iron nanoparticles in Nanofer 25S measured in the vertical geometry are shown in Fig. 3. Again, they consist of the narrow-line subspectrum from the sediment and broad line contribution related to the moveable nanoparticles. The line width of this fraction is much less than for the hematite particles although the diameter of Fe_2O_3 particles is bigger, at least nominally. Again, with time in the solution remain mainly small particles, as seen from

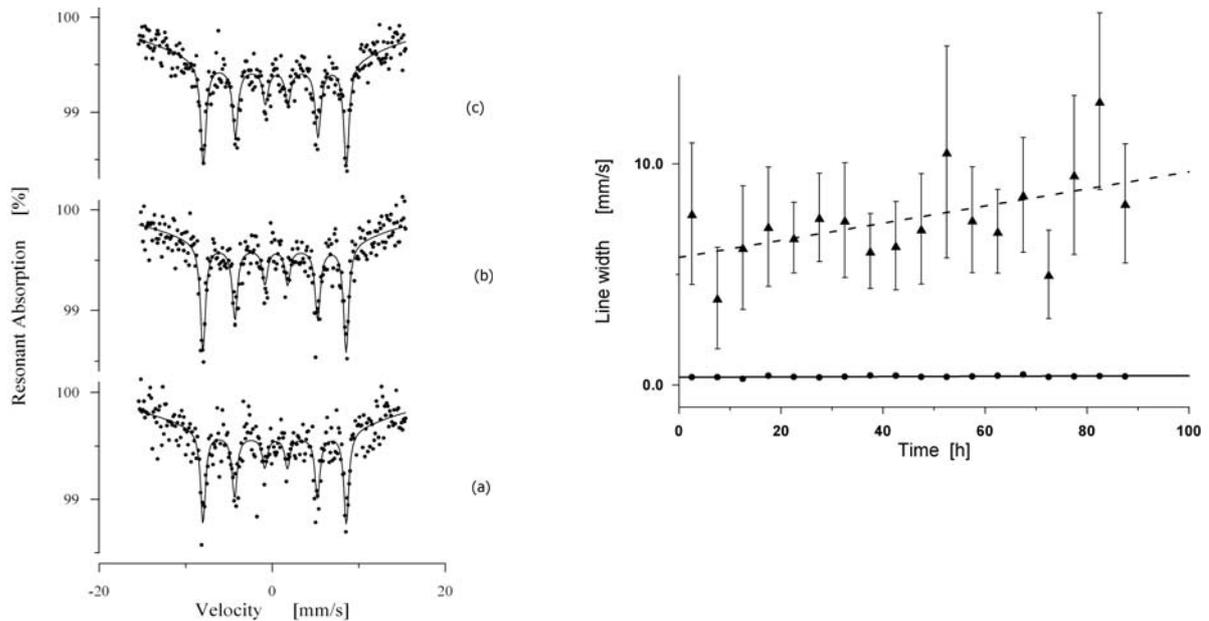


Fig. 2. Left: the selected Mössbauer spectra of hematite nanoparticles in water solution measured in vertical geometry together with their sediment, measured after 5 h (a), 50 h (b) and 90 h (c). Narrow lines in hematite spectrum correspond to nanoparticles in sediment. Right: the time evolution of the resonance absorption line widths: \blacktriangle – nanoparticles in solution, \bullet – hematite in sediment.

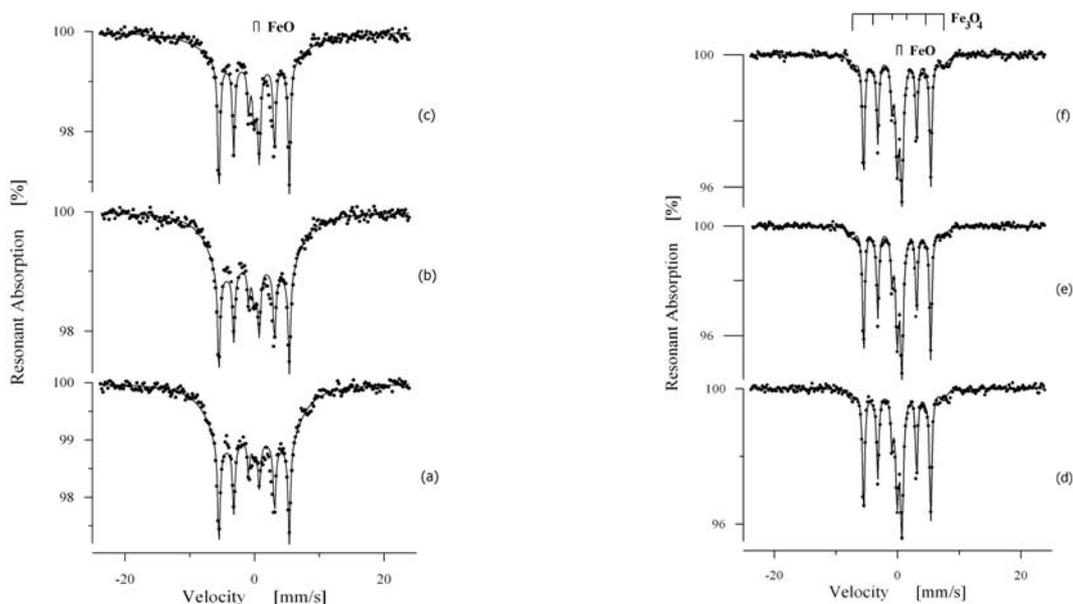


Fig. 3. The example of Mössbauer spectra of iron nanoparticles in Nanofer 25S measured in vertical geometry after 10 h (a), 25 h (b), 40 h (c), 100 h (d), 160 h (e) and 210 h (f). Narrow lines in iron spectrum correspond to nanoparticles in sediment.

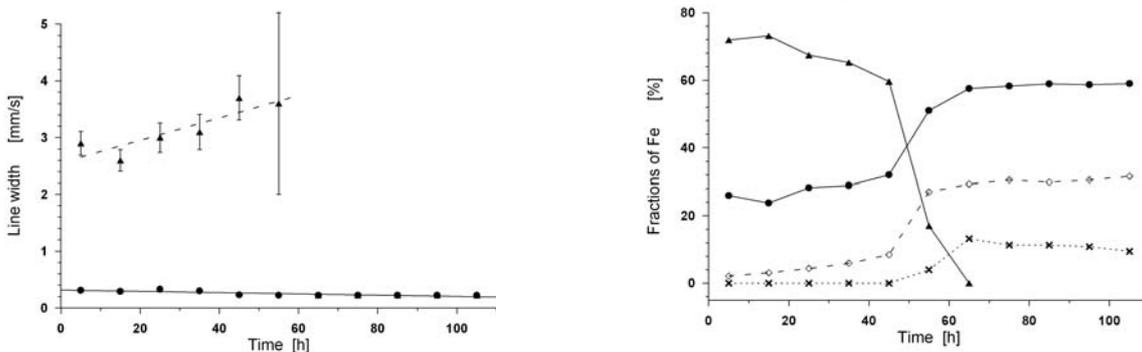


Fig. 4. Left: the time evolution of the resonance absorption line widths of iron nanoparticles in Nanofer 25S: \blacktriangle – iron nanoparticles in solution (after 65 h this fraction disappears due to the complete evaporation of the solvent), \bullet – iron nanoparticles in sediment. Right: the corresponding time evolution of the resonance absorption area: iron nanoparticles in solution (\blacktriangle), iron nanoparticles in sediment (\bullet), FeO (\diamond) and Fe_3O_4 (\times).

the increase of the width of the related absorption lines, cf. Fig. 4. The peculiarity of this measurement was that the sample container was open, thus the sedimentation was bounded with evaporation. The exposure to air caused a partial oxidation of the nanoparticles in the solution to FeO, seen as paramagnetic doublet, with the intensity increasing with time. After total evaporation after 65 h, the subspectrum of the moving particles disappeared and the oxidation lead to the formation of non-stoichiometric, poorly crystallized magnetite.

Conclusions

Mössbauer spectroscopy, traditionally applied for the investigation of the solid state problems, may be extended to the studies of dynamics of nanoparticles in suspensions. In particular, the competition between the Brownian movement and gravitational sedimentation may be observed.

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