FROM FERRIHYDRITE TO MAGNETITE AND *VICE VERSA*

M. Gotić*, T. Jurkin, and S. Musić

Division of Materials Chemistry, Ruđer Bošković Institute, P. O. Box 180, HR-10002 Zagreb, Croatia

The syntheses of nanosize magnetite particles by wet chemical oxidation of Fe^{2+} have been extensively investigated. In the present investigation the nanosize magnetite particles were synthesised without using the Fe(II) precursor. This was achieved by γ-irradiation of water-in-oil microemulsion containing only the Fe(III) precursor. The corresponding phase transformations were monitored. Microemulsions (pH~12.5) were γ-irradiated at a relatively high dose rate of ~22 kGy/h. Upon 1 h of γ-irradiation the XRD pattern of the precipitate showed goethite and unidentified low-intensity peaks. Upon 6 h of γ-irradiation, reductive conditions were achieved and substoichiometric magnetite (~ $Fe_{2.71}O_4$) particles with insignificant amount of goethite particles found in the precipitate. Hydrated electrons (e^-_{aq}), organic radicals and hydrogen gas as radiolytic products were responsible for the reductive dissolution of iron oxide in the microemulsion and the reduction $Fe^{3+} \rightarrow Fe^{2+}$. Upon 18 h of γ-irradiation the precipitate exhibited dual behaviour, it was a more oxidised product than the precipitate obtained after 6 h of γ-irradiation, but it contained magnetite particles in a more reduced form (~ $Fe_{2.93}O_4$). It was presumed that the reduction and oxidation processes existed as concurrent competitive processes in the microemulsion. After 18 h of γ-irradiation the pH of the medium shifted from the alkaline to the acidic range. The high γ-dose rate of ~22 kGy/h was directly responsible for this shift to the acidic range. At a slightly acidic pH a further reduction of $Fe^{3+} \rightarrow Fe^{2+}$ resulted in the formation of more stoichiometric magnetite particles, whereas the oxidation conditions in the acidic medium permitted the oxidation $Fe^{2+} \rightarrow Fe^{3+}$. The Fe^{3+} was much less soluble in the acidic medium and it hydrolysed and recrystallised as goethite. The γ-irradiation of the microemulsion for 25 h at a lower dose rate of 16 kGy/h produced pure substoichiometric nanosize magnetite particles of about 25 nm and with the stoichiometry of $Fe_{2.83}O_4$. The phase composition of precipitates obtained by γ-irradiation of ferrihydrite precipitate dispersed in aqueous or organic medium was also investigated. The present investigation has demonstrated the possibility of applying γ-irradiation in the synthesis of nanosize magnetite particles starting only from Fe(III) precursor. By controlling the γ-dose and γ-dose rate one can control the phase composition, stoichiometry and size of magnetite particles.