

THE PREPARATION OF MAGNETIC NANOPARTICLES BASED ON COBALT FERRITE OR MAGNETITE

PRIPRAVA MAGNETNIH NANODELCEV NA OSNOVI KOBALTOVEGA FERITA ALI MAGNETITA

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Cobalt ferrite and magnetite nanoparticles are superparamagnetic materials. Stable suspensions of superparamagnetic nanoparticles are magnetic fluids. Stable magnetic fluids are prepared by the addition of surfactants to supporting polar or nonpolar media. We have studied the preparation of magnetic nanoparticles based on cobalt ferrite or magnetite, and stabilized the obtained product in an aqueous suspension. We found the optimal co-precipitation time for cobalt ferrite at 90 °C to be 2 h. Under such conditions the product exhibited the lowest amount of amorphous phase (46.2 %), average particle diameter 10.2 nm and a relatively high proportion of agglomerated particles (≈ 30 %). The product is therefore destabilized in an aqueous solution of polyvinylpyrrolidone K. The optimal co-precipitation time for magnetite at 90 °C is 30 min. After 30 min the product has no amorphous phase, average particle diameter is 6.8 nm and the proportion of agglomerated particles is low (≈ 3 %). The product is poorly stabilized because the proportion of agglomerated particles increases when the magnetite is re-dispersed in an aqueous solution of polyvinylpyrrolidone K. Magnetite prepared with the Massart method has a small amount of amorphous phase (≈ 4 %), average particle diameter is ≈ 6 nm and a low proportion of agglomerated particles (4.5 %) and is therefore well stabilized in an aqueous solution of polyvinylpyrrolidone K.

Keywords: cobalt ferrite, magnetite, superparamagnetic nanoparticles, co-precipitation, stabilization of magnetic fluids

Nanodelci kobaltovega ferita in magnetita imajo superparamagnetne lastnosti. Stabilne suspenzije superparamagnetnih nanodelcev imenujemo magnetne tekočine. Stabilne magnetne tekočine pripravimo z dodatkom surfaktantov v nosilni polarni ali nepolarni medij. Sintetizirali smo magnetne nanodelce kobaltovega ferita in magnetita ter dobljeni produkt stabilizirali v vodnem mediju. Določen je bil optimalen čas soobarjanja kobaltovega ferita pri 90 °C, in sicer 2 h. V tem času ima produkt najnižjo vsebnost amorfnе faze (46,2 %), povprečno velikost delca 10,2 nm in delež neželenih aglomeratov pa je ≈ 30 %. Ko se delce kobaltovega ferita redispersira v vodi z dodanim surfaktantom, nastane destabilizirana suspenzija, katere vzrok je visok delež aglomeratov. Optimalen čas koprecipitacije magnetita pri 90 °C je 30 min. Takrat produkt ne vsebuje amorfnе faze, povprečna velikost delca je 6,8 nm, delež aglomeriranih delcev je ≈ 3 %. Produkt se nato redispersira v vodnem mediju z dodanim surfaktantom, kjer je magnetit slabo stabiliziran zaradi povečanja deleža aglomeratov med redispersijo. Magnetit, pridobljen z metodo po Massartu, vsebuje ≈ 4 % amorfnе faze, ima povprečno velikost delca ≈ 6 nm, delež aglomeratov 4,5 % in je zato odlično stabiliziran v vodni raztopini polivinilpirolidona K.

Ključne besede: kobaltov ferit, magnetit, superparamagnetni nanodelci, koprecipitacija, stabilizacija magnetnih tekočin

1 INTRODUCTION

Magnetic fluids are stable dispersions of magnetic nanoparticles in an organic or aqueous medium. Magnetic nanoparticles are solid-state particles that are affected by magnetic fields. The term "nano" indicates particles that are in the size range below 100 nm. Magnetic nanoparticles occur in the form of ferrites with the general formula MFe_2O_4 , where M is a divalent metal cation (nickel, cobalt, manganese, zinc or iron). Ferrites crystallize in the spinel crystal structure.¹⁻³

The most important characteristic of magnetic nanoparticles is superparamagnetism. Superparamagnetism relates to nanoparticles whose magnetic moments are oriented irregularly and do not show any magnetic properties in the absence of an applied magnetic field. However, even when these nanoparticles are exposed to a small external magnetic field, dipole moments are formed within the particles. The dipole moments are

directed in accordance with the source of the magnetic field.⁴

There are several techniques for the preparation of magnetic nanoparticles. The most common are: co-precipitation, sol-gel synthesis, hydrothermal synthesis and synthesis in microemulsions. When magnetic nanoparticles are obtained it is better if the resulting particles are crystalline, have a narrow size distribution and have the same shape.^{1,3}

The developing product must be stabilized so it does not agglomerate due to the attractive forces between the particles. The techniques of stabilization are electrostatic, steric and electrosteric. Electrostatic stabilization is the mechanism in which the attractive forces are due to the Coulomb forces between the charged colloidal particles. The repulsion between the particles is achieved with an equally charged electric double layer surrounding the particles. Steric stabilization is accomplished by the adsorption of long-chained molecules called surfac-

tants on the particle's surface. These surfactants then form a coating that creates a repulsive force and separates one particle from another particle. Electrosteric stabilization is a combination between electrostatic and steric stabilization. The repulsion between the particles is achieved by the adsorption of charged polymeric molecules on the nanoparticle's surface.^{4,5}

The applications of magnetic fluids are primarily in engineering and medicine as seals for rotating mechanical parts, as in the heat dissipation system in speakers and as a contrast agent in imaging with the nuclear magnetic resonance technique.^{6,7}

2 EXPERIMENTAL

The main goal of this study was to prepare magnetic nanoparticles based on cobalt ferrite or magnetite, and stabilize the obtained product in an aqueous suspension. The product was quantitatively and qualitatively analysed with a Rietveld analysis and morphologically described using scanning electron microscopy. The cobalt ferrite and magnetite were prepared by co-precipitation at 90 °C and pH = 13. The magnetite was also synthesized with the Massart method, where the product is instantaneously precipitated at room temperature with vigorous stirring. The product was stabilized with polyvinylpyrrolidone K in an aqueous medium.

2.1 Synthesis of cobalt ferrite and magnetite at elevated temperature

A solution of Co²⁺ and Fe³⁺ ions or a solution of Fe²⁺ and Fe³⁺ ions was mixed in a laboratory reactor with a reflux condenser using a magnetic stirrer (**Figure 1**). Then, in deionized water dissolved sodium hydroxide

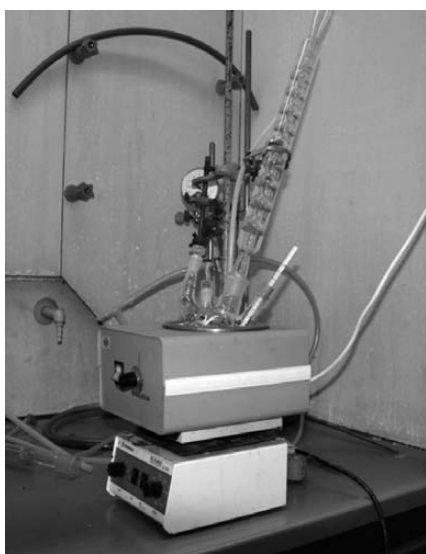
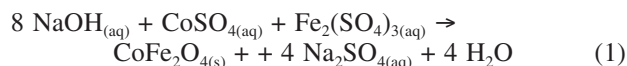


Figure 1: Laboratory reactor used for co-precipitation at elevated temperature

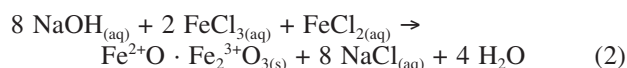
Slika 1: Laboratorijski reaktor za koprecipitacijo pri povišani temperaturi

was added, which allows the progress of the synthesis at pH = 13. The stirring was continued. Immediately after the addition of sodium hydroxide the dark precipitate was formed.

The chemical reaction for the cobalt ferrite preparation is as follows:



The chemical reaction for the magnetite preparation is as follows:



Next, the oleic acid was added to the reaction mixture and it was heated up to 90 °C. This temperature was regulated until the end of the reaction. Following the synthesis the pH of the precipitate was reduced from 13 to 5.5, after which the mixture was filtered and the obtained nanoparticles were re-dispersed and stabilized in an aqueous medium with the addition of a surfactant.

2.2 Synthesis of magnetite using the Massart method

Aqueous solutions of Fe²⁺ and Fe³⁺ ions were mixed in a beaker. During vigorous stirring ammonia was added. This leads to the formation of a black, magnetic precipitate. After the reaction, when all the ingredients are well mixed, the mixture was filtered and the nanoparticles were re-dispersed and then stabilized in an aqueous medium with the addition of a surfactant.

The chemical reaction of the magnetite prepared with the Massart method can be described by Eqs. (3) and (4):



2.3 Stabilization of the magnetic fluids

The first level of stabilization was achieved with the addition of oleic acid during the development of the synthesis. Oleic acid is an unsaturated fatty acid (between the carbons atoms there is at least one double bond) with the molecular formula C₁₈H₃₄O₂. The oleic acid surrounds the nanoparticles and prevents their further growth and agglomeration during the synthesis.

The second level of stabilization was realized after the purification of the product. The resulting cake of particles was necessary to re-disperse and stabilize in an aqueous medium. Steric stabilization with polyvinylpyrrolidone [(C₆H₉NO)_n] label K was used. Its molecular weight is 30000 g/mol. Polyvinylpyrrolidone is freely soluble in polar solvents, where it creates films that can serve as a coating for the particles.

2.4 X-ray powder diffraction and Rietveld analysis

X-ray diffraction shows whether the desired product (cobalt ferrite or magnetite) is formed. A subsequent Rietveld analysis determines the amount of amorphous phase in a sample.

X-ray powder analysis provides information about the chemical composition, the degree of crystallinity and the size or symmetry of the crystal unit cell. With this method an X-ray beam is irradiated at the sample's surface at an angle Θ . During the operation the sample is synchronously rotated by half the speed of the detector so that the angle between the source of radiation and the sample is always equal to the angle between the sample and the detector. At every Θ the X-rays are apparently deduced from the samples surface. If the phase shift between the various parallel X-rays is equivalent to a multiple of the wavelength (peak of one wave coexists with the top of the second wave) then the X-rays are strengthened, otherwise they override.^{8,9}

The samples were recorded on X-ray diffractometer PANalytical X'Pert PRO using Cu-K α 1 radiation with a wavelength of 1.5406×10^{-10} m.

Using the Rietveld method the sample was quantitatively analysed. The relative proportions of the individual crystal phases within the sample are determined. Measured and calculated powder patterns are compared using the Rietveld analysis. Also, the contribution of the individual phases in multiphase samples can be detected, including amorphous components or an unknown phase (with the addition of a crystalline or amorphous standard with a known mass fraction).¹⁰

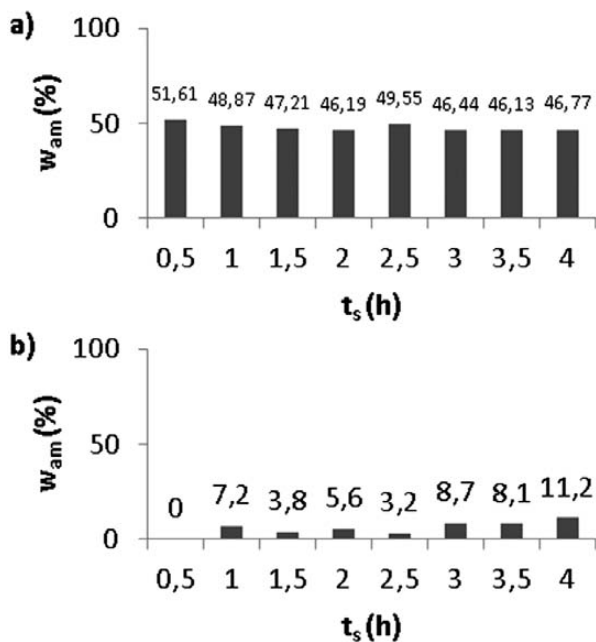


Figure 2: Dependence of the proportion of amorphous phase vs. time for the synthesis of: a) cobalt ferrite and b) magnetite

Slika 2: Odvisnost deleža amorfne faze od časa sinteze za: a) kobaltno ferit in b) magnetit

2.5 Scanning electron microscopy (SEM)

The microstructure of the samples was characterized with scanning electron microscopy (SEM). The microstructure of the materials is related to their properties (mechanical, electrical, optical and magnetic) and thus their usefulness and purpose. SEM is used to observe the surface of non-volatile solid samples. This technique allows the interaction of electrons with the surface atoms and gives information about the shape, size, grain size distribution, elemental composition and the proportion of each element in the sample.^{9,11}

For a nanostructure analysis a Zeiss Ultra Plus (FE-SEM) scanning electron microscope equipped with an EDS detector SDD Oxford was used. From SE images the morphological characteristics of the prepared products, especially the particle size, were defined.

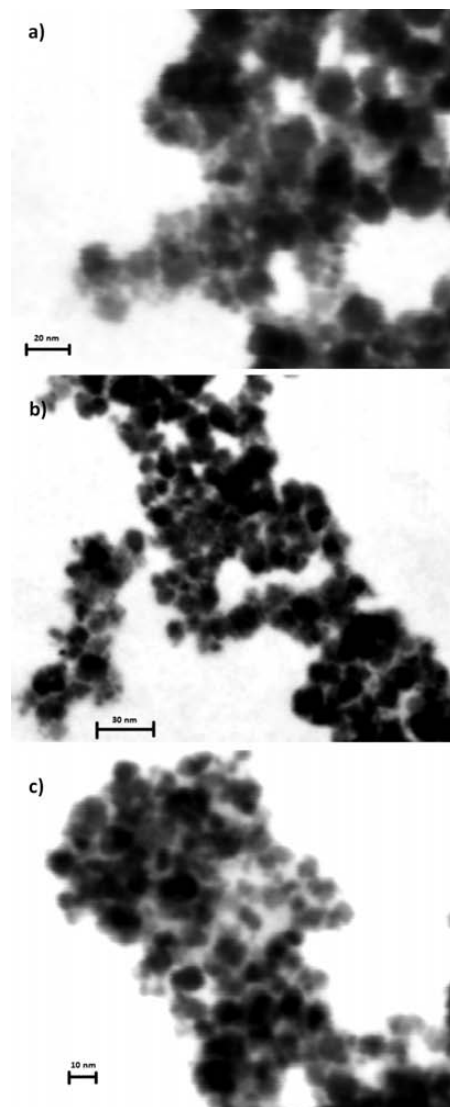


Figure 3: SE images of cobalt ferrite after: a) 0.5 h, b) 2 h and c) 4 h of co-precipitation

Slika 3: SE-posnetki kobaltnovega ferita po: a) 0,5 h, b) 2 h in c) 4 h koprecipitacije

3 RESULTS AND DISCUSSION

When preparing cobalt ferrite and magnetite at elevated temperature, we were interested in the proportion of amorphous phase in the sample during the synthesis in order to determine the optimal synthesis time. For this purpose we used the Rietveld method.

Figure 2a shows that the proportion of amorphous phase in the cobalt ferrite is in a high range of about 50 % for all 4 h of synthesis. The reason for such a high proportion may be an incomplete reaction, old reactants or very fast precipitation. If the degree of supersaturation is high, then the precipitation is finished extremely quickly. Therefore, the particles do not have sufficient time to organize into a proper structure, which leads to the formation of an amorphous phase. This mechanism is quite possible as the average particle size varies very little after 30 min during the reaction. This means that

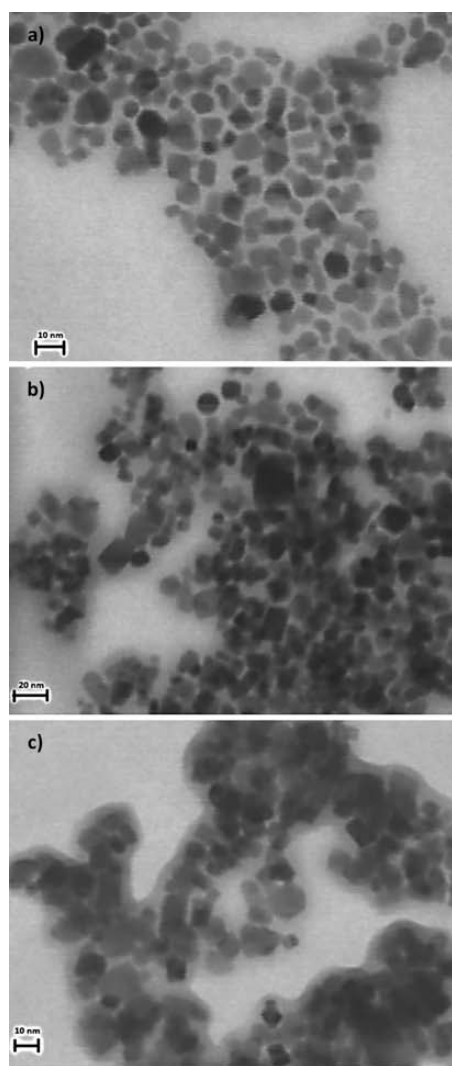


Figure 4: SE images of magnetite after: a) 0.5 h, b) 2 h and c) 4 h of co-precipitation

Slika 4: SE-posnetki magnetita po: a) 0,5 h, b) 2 h in c) 4 h koprecipitacije

the majority of the precipitation has come to an end much before 30 min. After 30 min of reaction the amount of amorphous phase is 51.61 % and then it is slightly decreasing for another hour and a half, when it reaches a value of 46.19 %. After 2 hours of synthesis the amount of amorphous phase varies. The minimum value is reached after 3.5 h, i.e., 46.13 %, but due to possible method errors, very small values deviation and economic reasons (long-term progress of the synthesis results in higher costs) it is enough to conduct the synthesis of the cobalt ferrite for 2 h or at least one hour. Because cobalt ferrite has a relatively high content of amorphous phase, the material has poor superparamagnetic properties as the particles react quite slowly on the magnet.

Figure 2b reveals a slight increase in the proportion of amorphous phase with the time of synthesis for the magnetite. Since after 30 min of reaction there is no amorphous phase in the magnetite, we have further operated with synthesis for just as long. Due to the lower levels of amorphous phase the superparamagnetic properties of the material are much better.

A Rietveld analysis was also performed for the magnetite synthesized using the Massart method. The proportion of amorphous phase was 4.3 %.

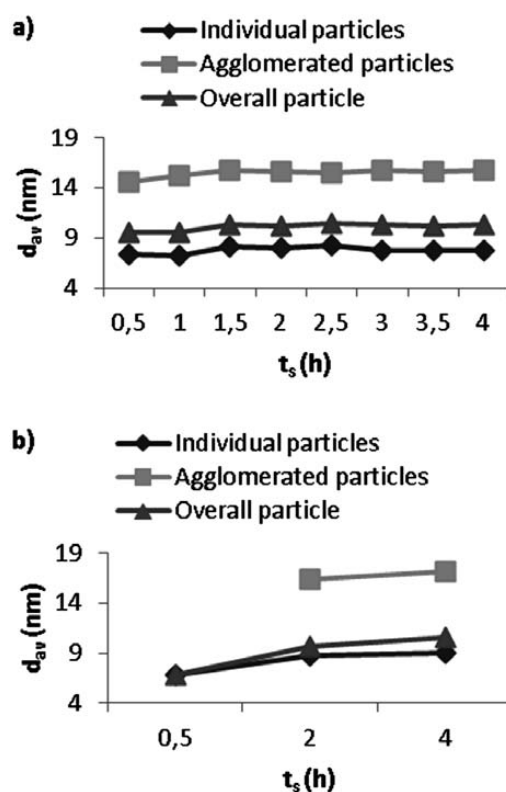


Figure 5: Average diameter changes of individual particles, agglomerated particles and overall particle for the synthesis of: a) cobalt ferrite and b) magnetite

Slika 5: Spreminjanje nadomestnega povprečnega premera posameznih delcev, aglomeriranih delcev in vseh delcev s časom sinteze za: a) kobaltov ferit in b) magnetit

SE images (**Figures 3 and 4**) were used to determine the morphological characteristics of the prepared products. The developing cobalt ferrite particles have predominantly a spherical shape, while the magnetite particles have a cubic shape.

The average size of the cobalt ferrite's individual particles after the first hour is approximately 7.3 nm, which then increases to about 8 nm. The same trend is also visible for the overall particle (individual and agglomerated), where the average size is in the range 9.46 nm to 10.37 nm (**Figure 5a**). The proportion of cobalt ferrite agglomerated particles is about 30 % for all 4 h of synthesis. A slight increase in the size of the individual particles is due to the co-precipitation mechanism, which in this case is not so definite. After 0.5 h the proportion of smallest particles (less than 4 nm) is about 20 % and after 1 h it dropped to 10 %. The conclusion from the morphological analysis of the cobalt ferrite particles is that in a time interval of 0.5 h to 1 h the formation of a new crystal nucleus is significantly reduced, but the particles are still growing. After 1 h of synthesis there

are no noticeable changes so the crystal growth must have decelerated. The same trend was also observed for the agglomerated particles.

The size of the individual, agglomerated and overall particles of magnetite is slowly increasing with the synthesis time. The average individual particle grows from 6.84 nm to 8.97 nm and the overall average particle (individual + agglomerated) grows from 6.84 nm to 10.49 nm (**Figure 5b**). The overall average particle size increases much more than the individual particle because the proportion of agglomerated particles increases considerably with the synthesis time (from 2.86 % to 21.36 %). When the magnetite was precipitated, typical mechanisms of co-precipitation were observed. After 30 min there are no agglomerated particles in the system. With the extension in the synthesis time the amount of the smallest particles decreases, which implies a decline in the formation of the crystallization nucleus. However, the particles are growing more noticeably and consequently agglomerating with an increase of the synthesis time. The observed behaviour of the Fe_3O_4 system during the synthesis where the magnetite particles are growing slowly, while slowly increasing the proportion of amorphous phase with synthesis time, indirectly indicates the mechanism of formation of the solid phase magnetite in two stages. The first stage is relatively fast and results in magnetite nanoparticles with a number of defects higher than equilibrium. The second stage is substantially slower. On the initially precipitated Fe_3O_4 surface new, smaller magnetite grains with an equilibrium number of defects should re-precipitate.

The magnetite synthesized by the Massart method has a low proportion of agglomerated particles (4.6 %) so the possibility of their stabilization is extensive. The average individual particle size is 6.1 nm, and the overall particle size is 6.4 nm.

The last stage of the research was to stabilize the magnetic fluid with PVP K. The addition of a surfactant should take care of the steric stabilization in an aqueous medium.

A range of the mass fractions $w = 0.001 \%$ to 1% PVP K was added in the polar aqueous medium and 1% in decane. **Figure 6a** shows that cobalt ferrite is not stabilized in an aqueous medium with PVP K, irrespective of the quantity of added PVP K. Poorly stabilized, whereas the precipitate is settling, is the cobalt ferrite in a non-polar decane on the far right of **Figure 6a**. Despite everything, the settling of the particles was noticeably slower in the suspensions with a higher mass fraction of PVP K and faster in those with a lower mass fraction of PVP K.

In **Figure 6b** the suspensions of magnetite are shown. The stability of the suspensions is evidently improved compared to the cobalt ferrite, but the suspensions are still far from ideal. Again, 0.001% to 1% of PVP K was added and once again we observed an improved stability for a larger addition of PVP K.

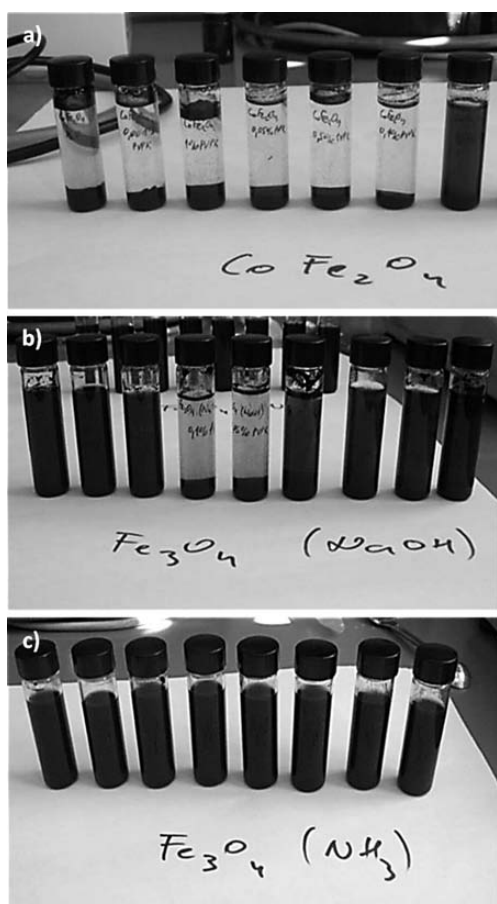


Figure 6: Magnetic suspensions with different mass fractions ($w/\%$) addition of PVP K for: a) cobalt ferrite, b) magnetite obtained at an elevated temperature and c) magnetite synthesized with the Massart method

Slika 6: Magnetne suspenzije z različnimi masnimi deleži ($w/\%$) PVP K-ja: a) kobaltov ferit, b) magnetit, pridobljen pri povišani temperaturi in c) magnetit, sintetiziran z Massartovo metodo

In the case of the magnetite synthesized using the Massart method stable suspensions were prepared. In stable suspensions the particles do not settle and are distributed throughout the volume (**Figure 6c**). All the reconstituted suspensions are stable, regardless of the amount of added PVP K.

The stability of the suspensions can be related to the particle size and the proportion of agglomerated particles. Cobalt ferrite has an average particle size of 7.45 nm, but it also has 26 % of agglomerated particles. A high proportion of agglomerated particles implies a larger number of particles with greater mass that settle smaller particles below and thus destabilize the suspension. Magnetite has an average particle size of 8.17 nm, but only about 17 % of agglomerated particles. The number of magnetite particles with higher mass is much lower, so the particles settle slowly, but eventually they all settle. Magnetite synthesized with the Massart method has a particle size of 6.37 nm and only 4.5 % of agglomerated particles. These suspensions are very stable due to the particles' small size and because the contact between the particles was prevented by the addition of the surfactant.

4 CONCLUSIONS

The synthesis of cobalt ferrite operating for 4 h at 90 °C ensures a relatively constant average size of overall particles equal to about 10 nm during the synthesis. The proportion of amorphous phase in the samples was approximately constant throughout synthesis, i.e., high $\approx 50\%$. The proportion of agglomerated particles within the suspension was around 30 %. An optimal synthesis time of 2 h was determined. After 2 h of synthesis the average particle size was 10.22 nm, the sample has 46.19 % of amorphous phase and the proportion of agglomerated particles was 30.44 %.

The synthesis of magnetite, which lasted for 4 h at 90 °C, exhibited a growth of the average particle size, an increase in the amount of amorphous phase and the proportion of agglomerated particles during the synthesis. The optimal time for the magnetite synthesis was 30 min when the particle size is 6.84 nm, the amount of the amorphous phase is 0 % and the proportion of agglomerated particles is 3 %.

Magnetic suspensions are stable when the particles are not agglomerated, dispersed all over the liquid vo-

lume and do not settle. For the stabilization of the magnetic fluids the surfactant polyvinylpyrrolidone K ($M \approx 30000$ g/mol) was used. PVP K is freely soluble in water. When the nanoparticles are re-dispersed in liquid + PVP K the magnetite particles synthesized using the Massart method are more stable than the magnetite particles synthesized at 90 °C, which are more stable than the cobalt ferrite particles. Cobalt ferrite has an average particle size of 7.45 nm, but has 26 % of agglomerated particles. A high proportion of agglomerated particles implies a larger number of particles with greater mass that settle smaller particles below and thus destabilize the suspension. Magnetite has an average particle size of 8.17 nm, but only about 17 % of agglomerated particles. Because the number of particles with a higher mass is much smaller, the particles settle moderately, but eventually they all settle. Magnetite synthesized with the Massart method has a particle size of 6.37 nm and only 4.5 % of agglomerated particles. These suspensions are very stable due to the particles' small size and because the contact between the particles has been prevented by the addition of surfactant.

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