INFLUENCE OF ANNEALING TEMPERATURE ON DEGRADATION EFFICIENCY AND IRON OXIDE TRANSFORMATIONS IN CeO$_2$/Fe-OXIDE SORBENTS

O. Živovský,¹ J. Luňáček,¹ Y. Jirásková,² J. Buršík,² J. Ederer,³ P. Janoš,³ K. Čabanová⁴  
¹ VŠB-Technical University of Ostrava, Department of Physics, Ostrava, Czech Republic, pavel.janos@ujep.cz, jiri.lunacek@vsb.cz  
² CEITEC IPM, Institute of Physics of Materials, AS CR, Brno, Czech Republic, jirasko@ipm.cz  
³ Faculty of the Environment, University of Jan Evangelista Purkyně, Ústí nad Labem, Czech Republic, jakub.ederer@ujep.cz, pavel.janos@ujep.cz  
⁴ VŠB – Technical University of Ostrava, Centre of Advanced Innovation Technologies, Ostrava, Czech Republic, kristina.cabanova@vsb.cz

AIM: Preparation, microstructural, and physical characterization of magnetically separable CeO$_2$(5 wt.%)/Fe-oxide powder sorbents with a demonstration of degradation capabilities against selected pesticides.

**SAMPLE PREPARATION**

- Magnetically separable sorbent – composite material consisting of iron oxide serving as a magnetically separable core or carrier and cerium dioxide (CeO$_2$) serving as active constituent capable to destroy dangerous chemicals
- Magnetcite core – synthesized by the co-precipitation of the Fe$^{2+}$ (ferrous sulphate monohydrate) and Fe$^{3+}$ (ferric sulphate) salts from cheap and commercially available raw materials
- CeO$_2$/Fe-oxide reactive sorbent – ferrimagnetic core re-dispersed in the solution containing 5 wt.% of cerium (III) nitrate, and the cerium (III) carbonate prepared by precipitation with ammonium hydrogen carbonate – finally cerous carbonate/magnetcite precursor annealed (calcined) in a muffe furnace at various temperatures $T_a$ ranging from 473 to 1073 K for 2h
- Testing the effectiveness of sorbents – using the pesticides parathion methyl in an apricot environment and paraxion methyl in an aqueous environment

**EXPERIMENTAL TECHNIQUES**

- XRD (X-Ray Diffraction) – XPERT PRO diffractometer (Panalytical) equipped with Co Kα radiation (λ = 0.17906 nm), 20 range 20° - 135°, evaluation – Rietveld structure refinement method using by the HighScore Plus program and the ICSD database
- SEM (Scanning Electron Microscopy) – TESCAN LYRA 300U FESEM; accelerating voltage 20 kV equipped with an X-MaxN Oxford Instruments energy-dispersive X-ray (EDX) detector
- FTIR (Fourier Transform Infrared) spectroscopy – Nicolet 660 (Thermal Scientific), single ATR mode on diamond crystal (32 scans, 4 cm$^{-1}$ resolution), range of wavelengths 2.5 - 25 μm
- VSM (Vibrating-Sample Magnetometer) – Microsense E29, room temperature (RT) magnetization and virgin curves - maximal magnetic field 1600 kA/m, first-order reversal curves (FORC) with step 8 kA/m
- PPMS (Physical Property Measurement System) – Quantum design, Inc., field-cooled (FC) and zero-field-cooled (ZFC) curves in the temperature range 2-293 K in magnetic field of 8 kA/m
- X’PERT (X’Pert) diffractometer (Panalytical) — Pole figure of L(001) plane of samples (673 K and 1073 K).

**RESULTS**

- The results of Rietveld analysis of sorbents annealed at $T_a$ temperature; phase content (A), lattice parameters (a, b, c), microdomain size (d).
- SEM and EDX analysis indicate that the powders contain a mix of grains of different sizes, some are enriched in Ce, others are Ce depleted.
- XRD results show that transformation of magnetite and maghemite to hematite starts at 773 K and finishes at 973 K, microdomain size of CeO$_2$, and hematite gradually grows with increasing $T_a$.
- FTIR spectra – sorbents annealed at 873 K – 1073 K show two peaks at 518 cm$^{-1}$ and 436 cm$^{-1}$ characteristic for stretching vibrations of Fe-O bond in hematite, sorbents annealed below 873 K exhibit one peak moved to 540 cm$^{-1}$ reflecting magnetite (maghemite), vibrations Ce-O (about 520 cm$^{-1}$) were not conclusively confirmed by FTIR.
- Degradation efficiency – about 30% for sorbents with 5 wt.% CeO$_2$ annealed at 473 K – 773K, it could be increased by adding higher content of cerium dioxide.

**MAGNETIC PROPERTIES**

- Magnetic properties measured at different annealing $T_a$ temperatures.
- ZFC/FC curves of samples annealed at 673 K and 1073 K (inset), first-order reversal curves (FORC) of sorbents annealed at 673 K, 873 K, and 1073 K.
- RT magnetic properties obtained from hysteresis loops and Henkel plots in dependence on annealing $T_a$ temperature; magnetization at magnetic field 1600 kA/m ($M_{H_{1600}}$), remanent magnetization ($M_r$), coercive field ($H_c$), position of peak ($\Delta H$, $\Delta M$) from the Henkel plot.
- RT hysteresis loops detect predominantly strong iron oxide reactions, which are several orders of magnitude higher than that of cerium dioxide.
- Sorbents annealed at 473 K – 773 K: low $H_c$ and high $M_{H_{1600}}$ at RT, blocking and irreversible temperatures about 220 K and 256 K, increase of $H_c$ and $M$ after cooling to 2 K.
- Sorbents annealed at 873 K – 1073 K: increase of $H_c$ and decrease of $M_{H_{1600}}$ at RT due to main hematite contribution, hysteresis loops consist of ferromagnetic reversal followed by the linear increase of magnetization corresponding to antiferromagnetic order, Morin transition about 200 K.
- Henkel plots – obtained from virgin and hysteresis loops at RT, correlation curves showing negative (dipole) magnetic interactions for all samples, the strongest interactions observed at the peak position $\Delta H$, $\Delta M$ (see table), marked increase of $\Delta H$ after annealing at 873 K.
- FORC diagrams – map of the magnetic response of all particles in a sample with irreversible magnetizations in terms of the coercivity (switching field) $H_c = H_{\Delta M}$, and magnetic interaction field $H_{\Delta M}$ distribution, the maximum close to zero (sample 673 K) indicates of magnetite and maghemite, clear contours with one central peak correspond to the dominance of the hematite (samples 873 K and 1073 K), $H_c$ is very close to the $\Delta H$.