Magnetic properties of the reactive sorbents based on the CeO_2/Fe_2O_3 composite powders

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Introduction

A new kind of magnetically separable composite consisting of maghemite grains and cerium oxide nano-crystalline surface layer (CeO_2/Fe_2O_3) was developed. It was successfully used as so called reactive sorbent to decompose certain dangerous organophosphorus pesticide (parathion methyl) and the chemical warfare agents (soman and VX).
The aim of the paper is investigation of changes in magnetic behavior and microstructural properties of sorbents in dependence on the annealing process because ability and efficiency of degradation process are closely related to the various calcination (annealing) temperature T_{calc} ranging from 300°C to 900°C at which sorbents are prepared [*Janoš et al. 2015*].

Experimental devices

- Magnetic behavior of sorbents was investigated by the vibrating sample magnetometer (VSM) - EV9, MicroSense, Massachusetts, USA.
- Microstructure of sorbents was analyzed by X-ray diffraction (XRD) measurements using a PANalytical XPert PRO diffractometer.

Measurement and analysis

Room temperature magnetization (hysteresis) loops were measured up to magnetic field ±1600 kA/m with the step of 1600 A/m and the basic loop parameters; H_c – coercive field, M_s – saturation magnetization and M_r – remanent magnetization; were determined.
The interparticle magnetic interactions were studied using the Henkel plots $\delta M(H)$ (determined by the isothermal remanence curve – *IRM* and DC demagnetization curve – *DCD*).

$$\delta M(H) = 2\frac{IRM(H)}{IRM(\infty)} - \frac{DCD(H)}{DCD(\infty)} - 1$$

The nucleation behavior of a system consisting of interacting particles was analyzed using the switching field distribution (SFD) and by irreversible susceptibility κ_{irr}, respectively. The peaks of the $\kappa_{irr}(H)$ curve correspond with the nucleation field H_n

$$\kappa_{irr}(H) = \frac{d(M_{irr}(H))}{d(H)},\ \ M_{irr}(H) = \left[IRM(\infty) - DCD(H)\right]/2IRM(\infty)$$

XRD measurements (in Bragg-Brentano geometry) were presented in an interval of 2q from 20° to 70°. The measured data were processed by Rietveld refinement procedure that allows estimation of crystallite lattice sizes.

Results and discussion

T_{calc}	H_c	M_s	M_r	Henkel minimum	H_n	*d* CeO_2	*d* maghemite	*d* hematite
°C	kA/m	Am^2/kg	Am^2/kg	kA/m	kA/m	nm	nm	nm
300	0.64	32.92	0.525	~ 3.3	--	1.8	9.9	--
400	0.67	34.18	0.695	~ 3.0	--	2.0	9.7	--
500	0.92	32.08	0.802	~ 2.7	--	2.8	9.9	--
600	0.53	5.43	0.089	~ 0.9	--	5.1	9.9	69.8
700	8.93	0.61	0.06	108.8	40.0	10.9	--	78.5
800	41.38	0.47	0.099	252.9	44.7	24.3	--	119.8
900	72.98	0.47	0.118	265.7	49.5	51.9	--	195.5

Table 1: Selected microstructural and magnetic properties of CeO_2/Fe_2O_3 sorbents in dependence on the calcination temperature T_{calc}. H_c – coercive field; M_s – saturation magnetization; M_r – remanent magnetization; Henkel minimum – magnetic field of the peak of Henkel plot; H_n – nucleation field; *d* – size of crystallites.

According to the obtained results (from the magnetic and microstructural measurements) samples can be divided into two groups

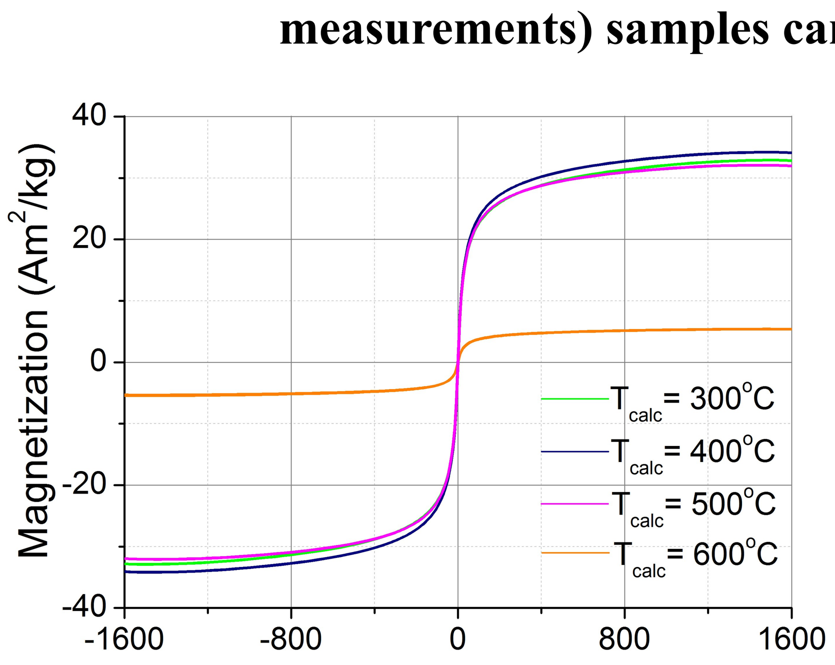

Fig. 1: Hysteresis loops of the samples annealed at temperatures from T_{calc} = 300°C to T_{calc} = 600°C.

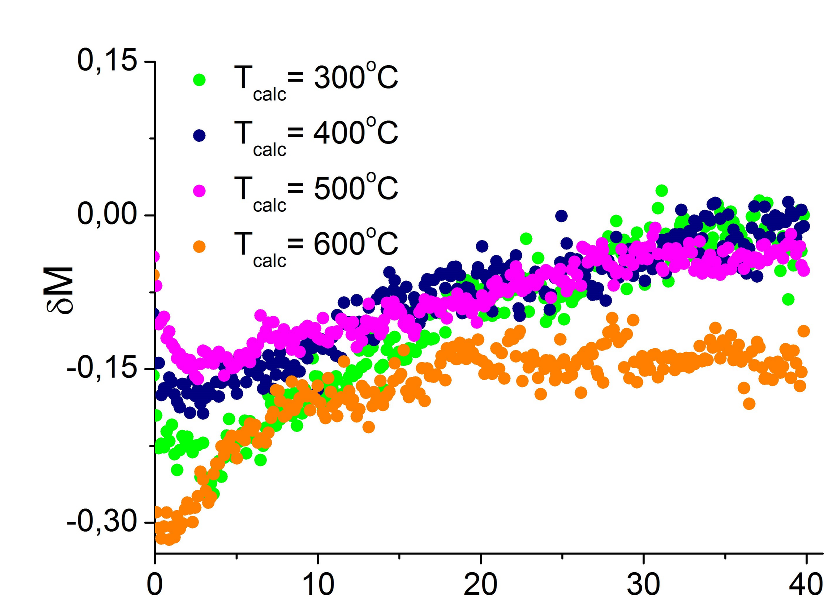

Fig. 2: Henkel plots of the samples annealed at temperatures from T_{calc} = 300°C to T_{calc} = 600°C.

The first group - the samples annealed at T_{calc} < 600°C
presence of maghemite

- low H_c, high M_s, higher M_r
- negative interparticle interactions (unclear low minima of Henkel plots)
- size of CeO_2 and maghemite crystallites is approximately constant
- SFD functions do not exhibit any extremes → H_n close to zero
- XRD patterns exhibit only peaks corresponding to maghemite and cerianite

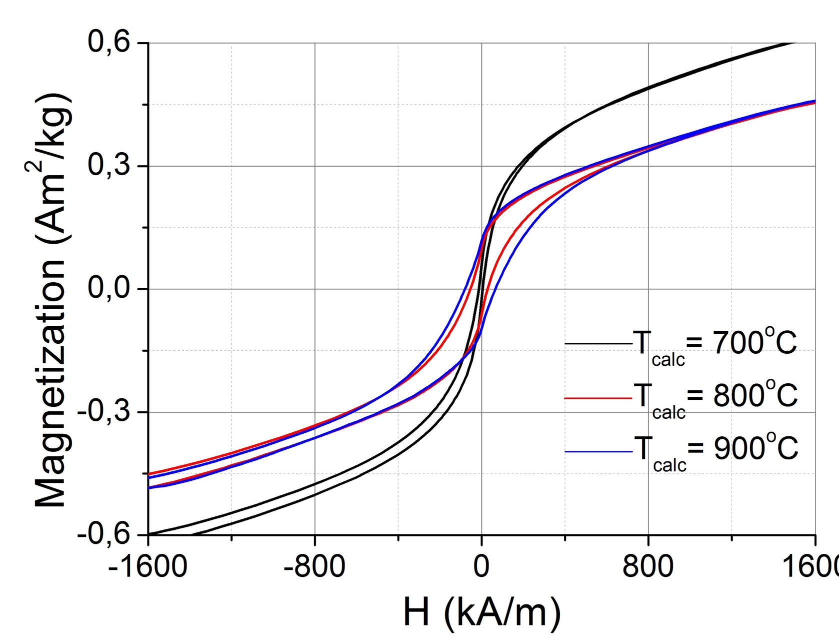

Fig. 3: Hysteresis loops of the samples annealed at temperatures from T_{calc} = 700°C to T_{calc} = 800°C.

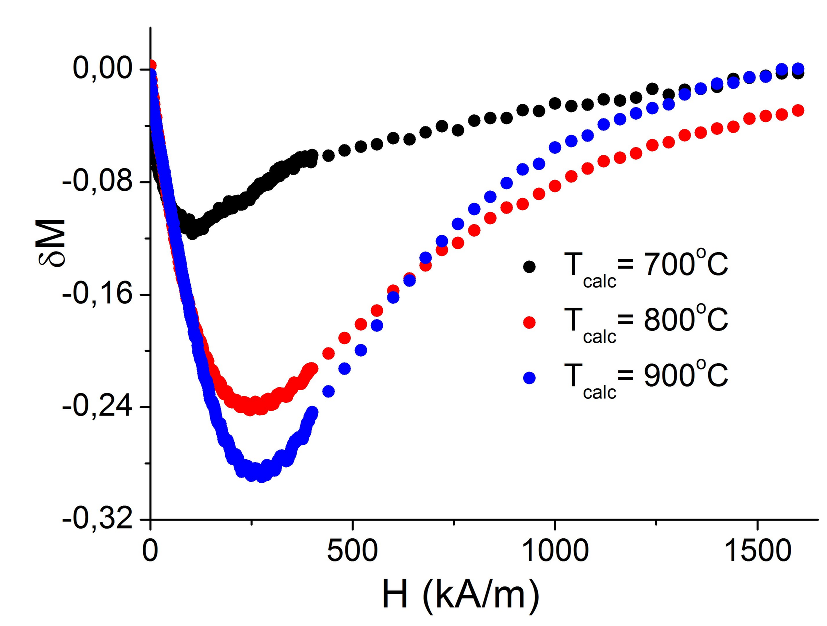

Fig. 4: Henkel plots of the samples annealed at temperatures from T_{calc} = 700°C to T_{calc} = 800°C.

The second group - samples annealed at T_{calc} > 600°C
presence of hematite

- high H_c, H_c linearly increases with T_{calc}, low M_s (loops not fully saturated), lower M_r
- negative interparticle interactions (clear minima of Henkel plots)
- size of CeO_2 and hematite crystallites significantly increases
- SFD functions exhibit extremes → H_n linearly increases with T_{calc}
- XRD patterns exhibit only peaks corresponding to hematite and cerianite

The unique sample with "dual" properties - annealed directly at T_{calc} = 600°C
combination of maghemite and hematite properties

- low H_c, lower M_s (loop fully saturated), lower M_r
- negative interparticle interactions (unclear minimum of Henkel plot)
- size of CeO_2 crystallites increases
- SFD functions do not exhibit extreme → H_n close to zero
- XRD patterns exhibit combination of peaks of both magnetic oxides (maghemite and hematite) as well as cerianite

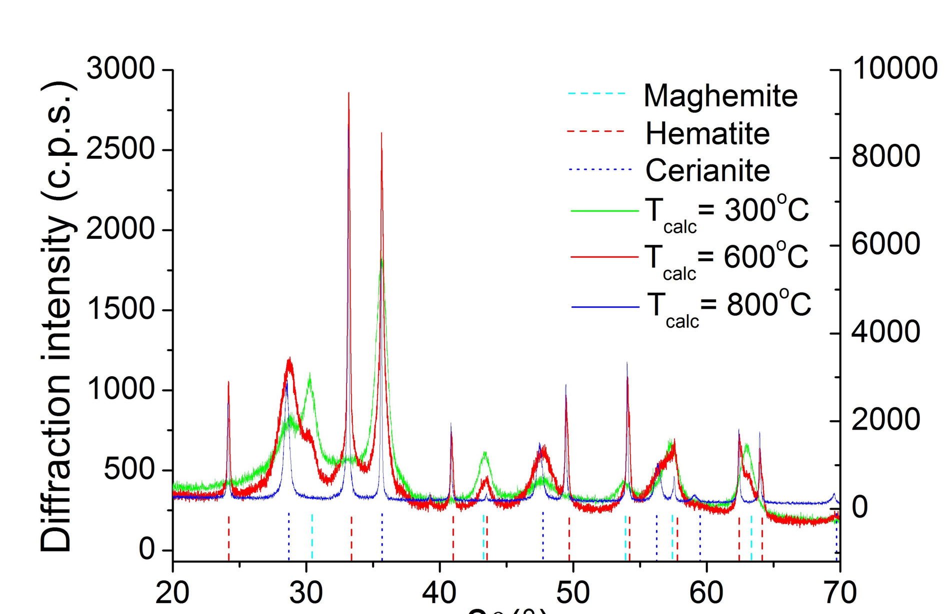

Fig. 5: XRD patterns of reactive sorbents annealed at 300°C, 600°C, and 800°C. Y -scales of 300°C and 600°C are placed on the left side, while of 800°C on the right side, respectively.

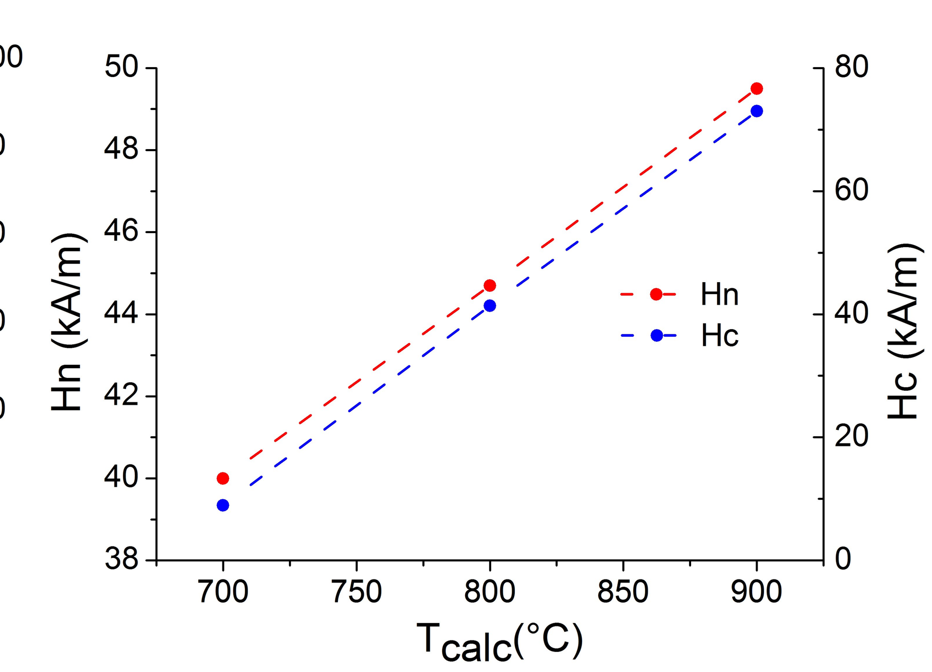

Fig. 6: Linear dependence of the coercive field H_c and the nucleation field H_n on the calcination temperature in the range from 700°C to 900°C.

Acknowledgements

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