New Applications of Heat and Mass Transfer Processes in Temperature Sensitive Magnetic Fluids

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A review of new applications of thermomagnetic and magnetic diffusion processes in temperature sensitive magnetic fluids is given. One of the most interesting applications of thermomagnetic convection in the injector-type convective cooling devices can be realized only if new magnetic fluids having low Curie temperatiires are used. Usually the Mn-Zn ferrite or the other complex ferrite chemically coprecipitated nanoparticles in ferrofluids do not indicate well defined Curie temperature Tc but the particle magnetization temperature dependente curves follow an exponentially decreasing law even when temperature is higher than Tc of bulk ferrite materials. Some experimental results of magnetogranulometry analysis of the ferrofluid particle subfractions separated in ultracentrifuge show that chemically coprecipitated nanoparticles are not only polydispersive but also chemicalIy nonhomogeneous. Such nonhomogenity may he the cause of the difference between thermomagnetic properties of colloidal particle ensembles and those of corresponding hulk materials. It is shown that tlie high-gradient niagnetic separation might be very useful in orcler to separate the ferrofluidls various subfractions having different Curie temperatures. Thermomagnetic particle separation in thermodiffusion columns are of special interest in tlie present case.

I. Introduction

The magnetocaloric energy conversion proposed more than 25 years ago[1] has not been realized yet because of the weak pyromagnetic coefficients of conventional magnetic fluids. It the last decade positive results in the preparation of new temperature-sensitive magnetic fluids have been achieved[2,3] and the problem of magnetocaloric energy conversion, particularly for the development of new thermomagnetic cooling systems, acquires the practical interest. Usually the magnetocaloric energy converters provide four stages of the thermodynamic cycle which includes the heating of the liquid in a strong magnetic field, its cooling in a zero field region as well as the heat rejection during isothermic fluid magnetization at temperature T_1 and the heat addition during the fluid demagnetination at higher temperature T_2. Such principle of thermomagnetic convective cooling devices may be used only when the heat source is located in the region of high magnetic field, for example, by the cooling of loudspeakers. In recent years another principle for thermomagnetic heat exchangers has been proposed[4]. Instead of the magnetic fluid heating through the pipe walls in a high magnetic field region, a meclianical mixing of two different temperature magnetic fluid flows is considered. The device includes cooling and heating loops as well as an injector-type mixing chamber. The advantage of mixing two flows of different temperatures as opposed to heating the fluid in the thermomagnetic pump is not only the higher heat exchange efficiency but also tlie possibility of removing both the cooler and the heater from the magnetic field region. For this reason, the injector-type magnetic energy converters seem to be very promising heat exchangers not only for the cooling of different electrotechnical devices but also for zero-

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gravity applications. In Ref. [5] it has been shown that by using the hypothetic magnetic fluid with exactly defined Curie temperature T_C, high convection velocity may be achieved in the injector-type pump with the temperature of the mixed flow higher than T_C. In the present paper, a more realistic situation of asymptotic magnetization decrease at increasing temperatures for complex ferrite containing temperature-sensitive magnetic fluids is considered. Some methods of improving the pyromagnetic properties of fluid by using high-gradient magnetic separation of nonhomogeneous ferrite particle dispersions are reviewed.

II. Efficiency of the injector-type thermomagnetic energy conversion

The efficiency of the ideal energy conversion in an injector- type thermomagnetic pump was analysed in Ref. [6]. It was assumed that the injector is located in the region of constant magnetic field H and that the length of the field region is great enough to insure the complete ejection and injection flow mixing. Thus, the relation between the inlet temperatures T_1' (for active flow) and T_2' (for the passive one) and the temperature at the end of mixing chamber T_m' can be written as follows:

$$q\int_{T_1'}^{T_m'} c(H,T)dT + (1-q)\int_{T_2'}^{T_m'} c(H,T)dT = 0 \quad (1)$$

where q is the ratio between the magnetic fluid flow rate in the cooling loop and the integral flow rate in the mixing chamber while $c(T,H)$ is the magnetic fluid specific heat capacity. Taking into consideration the relation between temperature T (in zero field) and T' (in the presence of magnetic field) during the magnetic fluid isoentropic and adiabatic magnetization in the form of

$$T' = T\exp\left(-\frac{\mu_0}{c_0}\right)\int_0^H \frac{\partial M}{\partial T}\Big|_{T'} dH, \quad (2)$$

for the thermodynamic cycle shown in Fig. 1, the following relation for ideal energy conversion efficiency in Ref. [6] was obtained:

$$\eta = \frac{Q_1 + Q_2}{Q_a} \quad (3)$$

where

$$Q_1 = q\int_0^H \mu_0(M(H,T_1') - M(H,T_m'))dH, \quad (4)$$

$$Q_2 = (1-q)\int_0^H \mu_0(M(H,T_2') - M(H,T_m'))dH, \quad (5)$$

$$Q_a = c_0(1-q)(T_2 - T_m) \ . \quad (6)$$

M is the fluid magnetization for temperatures T_1', T_2' and T_m', c_0 is the fluid specific heat capacity in zero magnetic field

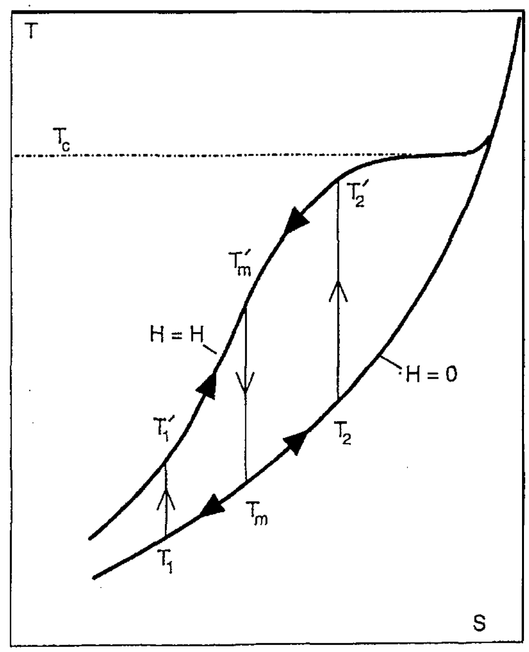

Figure 1: $T - S$ diagram of the pumping power cycle.

It is well known that the conventional single-cycle thermomagnetic pump can operate if magnetic materials having positive values of the pyromagnetic coefficient $K = -\partial M/\partial T$ are used. This condition allows all the known ferro-and ferrimagnetic materials to be employed. In the two-loop ejector-type device, the cooler loop acts as a thermomagnetic pump but the heater loop may be considered as a heat pump. The positive work in the two-loop system may be achieved if $Q_1 > -Q_2'$. This condition is valid only for magnetic fluids having positive values of the pyromagnetic coefficient temperature derivatives, $\partial^2 M/\partial T^2 > 0$. The above requirement contradicts the magnetization temperature dependence curves of conventional ferromagnetic materials for $T < T_C$. Conversely, the thermomagnetic behaviour of temperature- sensitive magnetic fluids containing, for example, the Mn-Zn ferrite nanoparticles allows us to realize the above flow mixingprinciple in thermomagnetic pump because their magnetization temperature decrease law is close to the exponential one

$$\mathrm{M} = \mathrm{Mo}\exp(-a(T - \mathrm{To})) \ . \tag{7}$$

Taking into account tlie fact that in ferrofluids usually $\mu_0 \int_0^H T\partial^2 M/\partial T^2 dH << c_0$ from Eqs. (3), (4), (5), (6) and (7) it follows:

$$\eta = A\left(\frac{1-\exp(q-1)x}{1-q} + \frac{\exp(-x)-\exp(q-1)}{q}\right)\frac{1}{x} \tag{8}$$

where $x = a(T_2 - T_1)$ and

$$A = -\frac{\mu_0}{c_0}\int_0^H \left.\frac{\partial M}{\partial T}\right|_{T_1} dH$$

is tlie one-loop thermomagnetic energy conversion efficiency for small pyromagnetic coefficient values. Calculation results of equation (8) show that for realistic x values close to x = 1, approximately only 10% of tlie one-loop device energy conversion efficiency may be achieved. The optimal flow rate ratio q is close to 0.5 [6]. Thus, when $T_m < T_C$, the efficiency of tlie two-loop thermomagnetic pump is relatively low. Only by using magnetic fluids with exactly defined Curie temperatures at $T_m > T_C$ can the maximumvalue of ■ = A be predicted.

III. Thermomagnetic properties of Mn-Zn ferrite colloids

In Ref. [7] an attempt was made to investigate the thermo- magnetic properties of Mn-Zn ferrite ultrafine particles in hydrocarbon based ferrofluids. The samples were prepared by using the chemical coprecipitation method[3]. Molar ratios of divalent Mn and Zn as well as trivalent ferric ions during the precipitation were as follows: (y; 1 − y; 2) where y values were varied in the interval of 0.3 - 0.7 in which, according to Ref.[8], tlie maximum value of composite saturation magnetization and Curie temperatures in the interval between 70 C and 210 C are predicted. The particle saturation magnetization M_s, determined from sample magnetization measurements performed in the strong field B = $2T$, only qualitatively agree with the M_s values of the bulk ferrite materials. Such disagreement may be explained by the uncertainty of particle composition. Investigations made on the basis of particle neutron-activation analysis show that relatively large differences exist between stoichiometrically predicted and experimentally detected particle composition[7]. Thermomagnetic properties of various ferrofluid samples are presented in Fig. 2 (measurements correspond to a magnetizing field B = 2T). Measurement results in the temperature interval between 200 K and 400 K agree very well witli the exponential law (7) and give parameters a with values between 0.0031 and 0.0060. The inaximum value reached, a = 0.0060, corresponds to y = 0.3. This result as well as the exponential trend of $M(T)$ curves for samples for which the Curie temperature is expected to be near 400 K, do not agree with the results obtained for the bulk materials[8]. We suppose that sucli disagreement is caused not only by the uncertain value of y but also by the chemical nonhomogenity of particles or even by some fundamental changes of therrnomagnetic behaviour in ultrafine particles[10].

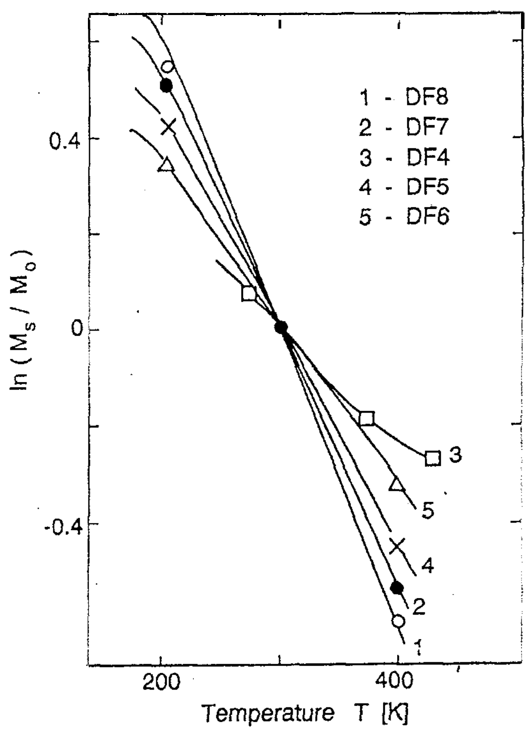

Figure 2: Thermomagnetic properties of magnetic fluid samples. $Mn_yZn_{1-y}Fe_2O_4$ particles at various y: 1 - 0.3, 2 - 0.4, 3 - 0.5, 4 - 0.6, 5 - 0.7. M_0 is the magnetization at 300 K.

In order to obtain more detailed information on tlie properties of ferrofluid nanoparticles, one of the samples, DF4 (y = 0.5), which exhibits unusual thermomagnetic behaviour, was analysed separately. The particle lattice constant value determined from the X-ray diffraction spectra measurements indicate a spinel structure of coprecipitated nanoparticles. We suppose that the unusual thermomagnetic properties may be interpreted as a result of the pliysical and chemical nonhomogenity of particles in polydisperse colloids. This conclusion is based on the results of magnetogranulometry analysis of different particle subfractions separated in ultracentrifuge showing a significant difference between mean magnetic moments of tlie light (m_l) and the lieavy (m_h) fractions: $m_l = 10^2\mu_B$, $m_h \simeq 2.4 \cdot 10^4\mu_B$. The X-ray diffraction spectra analysis gives the following values of the mean particle sizes of both fractions: d_l = 3 nm and d_h = 13nm. The corresponding particle mean volume ratio value of 81 is aproximately **3** times smaller than the value of magnetic moment ratio, $m_h/m_l = 240$. The saturation magnetization calculations made with respect to the relation $m = M_s V$ give different values for the magnetic moment per molecule of both fractions: $n_l = 0.5\mu_B$ and $n_h = 1.65\mu_B$. Both of them are essentially smaller than $n = 6.93\mu_B$ which corresponds to the bulk Mn-Zn ferrite material when $y = 0.5$ [8].

Measurements of thermomagnetic properties of both fractions show a higher value of the pyiomagnetic coefficient for the light fraction if compared to that of the heavy one[9] (see Fig. **3).** We suspect that this is causecl by tlie difference of Langevin parameters for botli fractions. Nevertheless, the effect of chemical nonhomogenity of hotli fractions or even tlie depenclence of pyromagnetic properties on tlie nanoparticle size may not be excluded. The last prediction must be specially investigated because it is not only of great physical interest[10] but may also lead to important conclusions on practical applications of thermomagnetic processes in ultrafine particle dispersions.

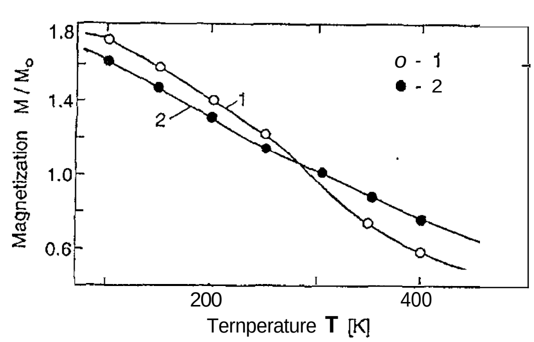

Figure 3: Thermoagnetic behaviour of the light (curve 1) and tlie heavy (curve 2) fractions of sample DF4 (y = 0.5). B = 2T, M_0 is the magnetization at 300 K. Separation in ultracentrifuge at 5000 g for 3 hours.

IV. High-gradient magnetic separation of temperature- sensitive magnetic fluids

Our previoiis stuclles show that high-gradient magnetic separation (HGMS) of particles in polydisperse colloids is more sensitive to the particle size than the separation in ultra-centrifuge[11]. Separation of small amounts of the biggest particles significantly increases tlie long-term stability of magnetic fluids and reduces both the magnetorheological effect and its relaxation time. Special increases of selectivity regarding particle sizes or magnetic moments may be achieved in HGMS devices containing electrical current carrying filtration elements wlien convection through tlie filter is free. From the filtration process analysis performed on tlie basis of the quasi-monoclisperse approximation it follows[12] that separation of 10 nm sized particles in magnetic filters employing free convection occurs approximately 10^3 times faster than that of 2 nm sized particles. HGMS performed by variations of temperatnres makes it possible to separate nanoparticles of different pyromagnetic coefficients or even of clifferent Curie temperatures.

In HGMS of temperature-sensitive magnetic fluids there is a. netv physical phenomenon - tlie thermomagnetophoretic nanoparticle transport - which may be employed. In Ref. [13] the hydrodynamics of magnetizable particles in nonisothermic liquids having paramagnetic properties was investigated. It has heen shown that in non-isothermic fluids when grad$T$ is clirected parallel to the clirection of tlie homogeneous magnetic field, tlie particle's thermoplioretic velocity considered in Stokes' approximation is the following[14]

$$u_t = -\frac{r^2\mu_0 H^2}{\rho\nu}\frac{\partial\mu_f}{\partial T}\left(\frac{8K_\mu}{15} - \frac{K^2\mu}{20}\right) gradT \,. \qquad (9)$$

The coefficient K_μ for splieres is tlie following: Ir',, = $(\mu_p - \mu_f)/(\mu_p + 2\mu_f)$ wliere μ_p and μ_f are the magnetic permeability of the sphere and of tlie surrounding liquid. In the more simple approximation this effect may be interpreted as a magnetophoretic particle transport in a nonhomogeneous magnetic field when grad$H$ is caused by nonhomogenity of magnetic fluicl magnetization. From div$\vec{B} = 0$ it follows that div$\vec{H}$ = -div$\vec{M}$. In such approximations the magnetophoretic velocity of particles is the following:

$$u_m = \frac{2\mu_0 r^2 H_0}{9\rho\nu}(\mu_p - \mu_f) gradH$$
$$= -\frac{2\mu_0 r^2}{9\rho\nu\mu_f}(\mu_p - \mu_f)H^2 \frac{\partial \mu_f}{\partial T} gradT \ , \quad (10)$$

This relation agrees well with the result of exact analysis (10).

Some indirect measurements of nanoparticle thermophoretic mobility were performed in Ref. [15]. The investigations were based on nonstationary concentration measurements in a thermodiffusion column. Interpretation of results obtained was made by using a simple thermodiffusion column theory[16] which for coloidal dispersion experiments is not very accurate because the free convection in the column during the nanoparticle transport is caused not only by the thermal buoyancy force but also by the concentrational one. A more exact analysis of the convection processes in a tlzermodiffusion column gives the following mass transfer equation:

$$\frac{\partial c}{\partial t} = D' \frac{\partial^2 c}{\partial z^2} - \beta \frac{\partial c}{\partial z} \quad (11)$$

where

$$D' = D\left(1 + \frac{1}{9!}Sc^2(Gr_T - kGr_c)^2\right) \ , \quad (12)$$

$$\beta = \frac{u_T}{6!}Sc(Gr_T - kGr_c) \ . \quad (13)$$

$S_c = \nu/D$ is the Schmidt number but the therrnal and the concentration Grashof numbers include the coefficients $\beta_T = -\rho^{-1}\partial\rho/\partial T$ and $\beta_c = c_0^{-1}\partial\rho/\partial c$ and the thermodiffusion column width 1:

$$Gr_T = g\beta_T(T_1 - T_2)l^3/\nu^2 \ ,$$

$$Gr_c = g\beta_c c_0 l^3/\nu^2 \ .$$

The stationary convection velocity profiles in the column for various particle transport parameter values k $= u_t l/D$, are presented in Fig. 4. As one can see, the concentration effect on convection in the column is very significant. When k > 1 even the change of the convection direction must be observed.

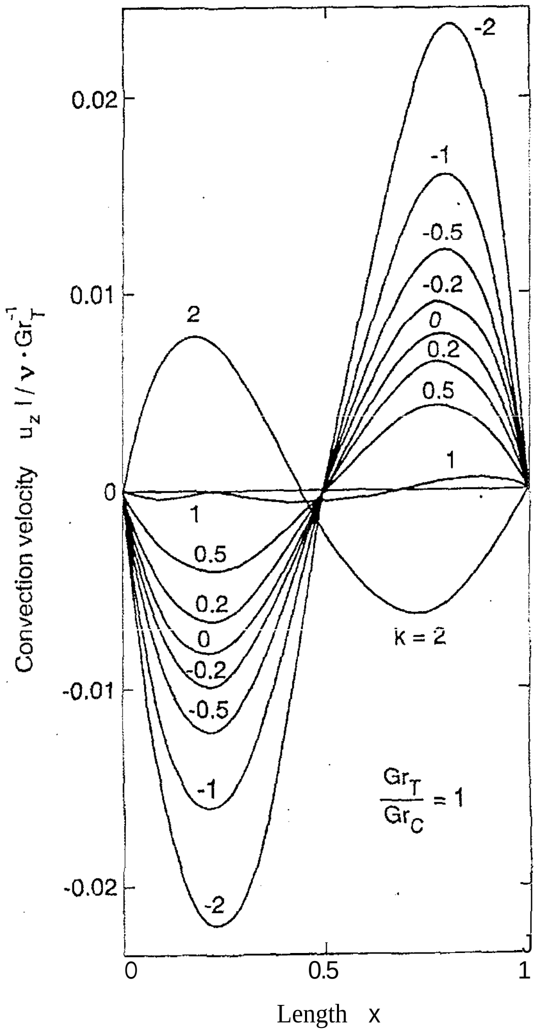

Figure 4: The convection velocity profiles in a thermodiffusion colunm at various values of k.

For the typical column width of 1 = 10^3 m the values of both the thermal as well as the concentrational Grashof numbers are of the order $10^3 - 10^4$. Therefore, a significant multiplication effect of particle separation takes place. In separation devices in which the volumes of the upper and lower containers are equal to the volume of the diffusion column, the separation effect Ac $= \beta L/D'$ (L is the column height) may be achieved. Duration of the nonstationary mass transfer processes characterizes the Fourier number $D't/L^2$. Steady regime is reached when F o values are close to 1 which corresponds to the time interval less than 1 hour.

V. Conclusions

Many of theoretical ideas discussed here have not been experimentally investigated yet. Further research of two-loop thermomagnetic pumps must clarify the following problems: i) the critical conditions of convection under the action of both the heat rejection and its addition in the zero magnetic field region, ii) the injector pump efficiency for low Reynolds number values and in the presence of conductive heat transfer through the nozzle construction elements. In the particle thermophoretic mobility studies and in the HGMS experiments in thermodiffusion columns, it is very important to control the Grashof number values because a convective instability may develop. As known, for liquids having $Pr > 30$ (this region of Pr includes concentration convection because the Schmidt number Sc values are usually greather than 10^3) the critical Grashof number Gr' values decrease in the following way: $Gr' = 3500/Pr^{1/2}$ [17]. Moreover, the thermomagnetic force $\mu_0 M$ grad$H$ directed across the column may raise a specific thermomagnetic instability, which in the presence of magnetophoretic stratification of particles is very complicated and must be investigated specially.

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