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 temperatures are used. Usually the Mn-Zn ferrite or the other complex ferrite chemically coprecipitated nanoparticles in ferrofluids do not indicate well defined Curie temperature $T_c$ but the particle magnetization temperature dependente curves follow an exponentially decreasing law even when temperature is higher than $T_c$ 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 chemically nonhomogeneous. Such nonhomogenity may be the cause of the difference between thermomagnetic properties of colloidal particle ensembles and those of corresponding hulk materials. It is shown that the high-gradient magnetic separation might be very useful in order to separate the ferrofluids various subfractions having different Curie temperatures. Thermomagnetic particle separation in thermodiffusion columns are of special interest in the present case.

I. Introduction

The magnetocaloric energy conversion proposed more than 25 years ago 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 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 demagnetization 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. Instead of the magnetic fluid heating through the pipe walls in a high magnetic field region, a mechanical 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 the 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 $T_i$ (for the passive one) and the temperature at the end of mixing chamber $T_m$ can be written as follows:

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

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

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

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

$$Q_1 = q \int_0^H \mu_0(M(H,T'_1) - M(H,T_m)) dH, \quad (4)$$

and

$$Q_a = c_0(1-q)(T_2 - T_m). \quad (5)$$

$M$ 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.](image)
in thermomagnetic pump because their magnetization
temperature decrease law is close to the exponential one

\[ M = M_0 \exp(-a(T - T_0)) \]  

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

\[ \eta = A \left( \frac{1 - \exp(q - 1) \alpha}{1 - q} \frac{\exp(-\alpha) - \exp(q - 1)}{\alpha} \right) \frac{1}{x} \]  

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

\[ A = -\frac{\mu_0}{c_0} \int_0^H \frac{\partial M}{\partial T} \left| \frac{dH}{\partial T} \right| dH \]

is the 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 the 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 the two-loop thermomagnetic pump is relatively low. Only by using magnetic fluids with exactly defined Curie temperatures at \( T_m > T_C \) can the maximum value of \( \eta = A \) 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[8]. 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], the 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[6]. 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 with the exponential law (7) and give parameters \( a \) with values between 0.0031 and 0.0060. The maximum 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 such disagreement is caused not only by the uncertain value of \( y \) but also by the chemical nonhomogeneity of particles or even by some fundamental changes of thermomagnetic behaviour in ultrafine particles[10].

Figure 2: Thermomagnetic properties of magnetic fluid samples. \( \text{Mn}_y \text{Zn}_{1-y} \text{Fe}_2 \text{O}_4 \) 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 the 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 physical and chemical nonhomogeneity 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 the light (m₁) and the heavy (mₕ) fractions: m₁ = 10²μₜ, mₕ ≈ 2.4 · 10⁴μₜ. The X-ray diffraction spectra analysis gives the following values of the mean particle sizes of both fractions: d₁ = 3 nm and dₕ = 13 nm. The corresponding particle mean volume ratio value of 81 is approximately 3 times smaller than the value of magnetic moment ratio, mₕ/m₁ = 240. The saturation magnetization calculations made with respect to the relation m = M · V give different values for the magnetic moment per molecule of both fractions: n₁ = 0.5μₜ and nₕ = 1.65μₜ. Both of them are essentially smaller than n = 6.93μₜ 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 pyromagnetic coefficient for the light fraction if compared to that of the heavy one [9] (see Fig. 3). We suspect that this is caused by the difference of Langevin parameters for both fractions. Nevertheless, the effect of chemical nonhomogeneity of both fractions or even the dependence of pyromagnetic properties on the 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.

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

Our previous studies 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 the 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 when convection through the filter is free. From the filtration process analysis performed on the basis of the quasi-monodisperse approximation it follows [12] that separation of 10 nm sized particles in magnetic filters employing free convection occurs approximately 10³ times faster than that of 2 nm sized particles. HGMS performed by variations of temperatures makes it possible to separate nanoparticles of different pyromagnetic coefficients or even of different Curie temperatures.

In HGMS of temperature-sensitive magnetic fluids there is a new physical phenomenon - the 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 been shown that in non-isothermic fluids when \( \text{grad} T \) is directed parallel to the direction of the homogeneous magnetic field, the particle’s thermophoretic velocity considered in Stokes’ approximation is the following:

\[
\mathbf{u}_t = -\frac{r^2 \mu_0 H^2}{\rho \nu} \frac{\partial \mu_f}{\partial T} \left( \frac{8K_\mu}{15} - \frac{K^2 \mu}{20} \right) \text{grad} T. \tag{9}
\]

The coefficient \( K_\mu \) for spheres is the following: \( K_\mu = (\mu_p - \mu_f)/(\mu_p + 2\mu_f) \) where \( \mu_p \) and \( \mu_f \) are the magnetic permeability of the sphere and of the surrounding liquid. In the more simple approximation this effect may be interpreted as a magnetophoretic particle transport in a nonhomogeneous magnetic field when \( \text{grad} \mathbf{H} \) is caused by nonhomogeneity of magnetic fluid magnetization. From \( \text{div} \mathbf{B} = 0 \) it follows that \( \text{div} \mathbf{H} = -\text{div} \mathbf{M} \). In such approximation the magnetophoretic velocity of particles is the following:

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Figure 3: Thermomagnetic behaviour of the light (curve 1) and the 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.
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 colloidal 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 thermodiffusion column gives the following mass transfer equation:

\[
\frac{\partial c}{\partial t} = D' \frac{\partial^2 c}{\partial z^2} - \beta \frac{\partial c}{\partial z} \tag{11}
\]

where

\[
D' = D \left(1 + \frac{1}{9} S_c^2 (Gr_T - k Gr_c)^2 \right), \tag{12}
\]

\[
\beta = \frac{\nu T}{6} S_c (Gr_T - k Gr_c). \tag{13}
\]

\[S_c = \nu / D\] is the Schmidt number but the thermal 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 \(l\):

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

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

The stationary convection velocity profiles in the column for various particle transport parameter values \(k = u_d l / D\), 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.

For the typical column width of \(l = 10^3\) 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 \(\Delta c = \beta l / D' \) (L is the column height) may be achieved. Duration of the nonstationary mass transfer processes characterizes the Fourier number \(D' l^2 / L^2\). Steady regime is reached when \(Fo\) 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 greater than \( 10^3 \) ) the critical Grashof number \( Gr' \) values decrease in the following way: 
\[
Gr' = \frac{3500}{Pr^{1/2}} \frac{1}{17}.
\]
Moreover, the thermomagnetic force \( \mu_0 M \text{ grad}H \) 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.

References