*Dedicated to Professor Liviu Literat, at his 80th anniversary*

# MAGNETIC FLUIDS – MATERIALS WITH REMARKABLE APPLICATIONS

## ANDRA TĂMAŞ[a], ZENO GROPŞIAN[a], ROMULUS MINEA[a]

**ABSTRACT.** The paper presents contributions to MF preparation through magnetite chemical co-precipitation followed by stabilization with oleic acid and dispersion into a carrier liquid, or through carrier liquid exchange technique (mineral or paraffin oil). Based on the estimation and correlation of fluid specific properties (concentration, density, dynamic viscosity, the saturation magnetization) has been presented the posibility to intensify the separation of aqueous two-phase systems with oily compounds content under magnetic filed action. The device contains a separator with immersed permanent magnets for oily phase separation from waste waters. It was established the separation efficiency as a function of separator feeding specific flow.

**Keywords:** *extraction, magnetic fluids, magnetic separator, oily phase*

## INTRODUCTION

Magnetic fluids (MF) or ferrofluids (FF) are colloidal suspensions of ultrafine particles (~ 10 nm) of ferro- and ferri- magnetic materials stabilized and dispersed into a carrier liquid. MF represent macroscopic uniform two-phase systems. One phase–the liquid carrier- determines the chemical and mechanical properties of the system, the other–a ferromagnetic substance in ultradisperse state–specifies the magnetic properties of a system.

In order to maintain the aggregative stability of MF the adsorption of surfactant molecules on the particle surface may be employed. Adsorption layers (their effective width varying between 3 and 100 nm as a function of the structure and molecular weight of the solvent and stabilization agent) form the potential barrier preventing particles from approaching each other. The layer width should be sufficient to keep the particles from approaching each other to the distance when the Van der Waals and dipole interaction forces come into prominence. Besides, the adsorbed molecules should ensure the lyophilization of particles and their compatibility with the dispersion medium [1, 2].

---

[a] *Universitatea "Politehnica" din Timişoara, Facultatea de Chimie Industrială şi Ingineria Mediului, P-ţa Victoriei 2, RO-300006 Timişoara, andra.tamas@chim.upt.ro; r.minea@rdslink.ro*

MF were obtained for the first time at NASA (1960) as part of the spatial technology researches to realize a system with the function of control the fluid fuels flow in imponderability conditions.

The most used magnetic particles to MF preparation are: transition metals (Fe, Co, Ni, Zn), alloys (Fe-Co, Ni-Fe, Fe-Co-Ni), iron oxides, magnetite, ferrite ($Me_{x+y}Fe_2O_4$; Me=Co, Ni, Zn, Mn, Cu, Ba; x + y = 1), nitride ($Fe_3N$), boride (FeB), silica-coated iron particles [1-4].

The particles used are, preferably, of iron oxides because of their resistance to oxidation, rather than the transition metals, which have the benefit of higher saturation magnetization [5].

As stabilizers are used compounds with a COOH group able to fixed on the magnetic particle and a hydrocarbon chain which allows dispersion into a liquid carrier. Stabilizing effects were obtained using: fatty acids (oleic, elaidic, lauric, stearic, erucic, linoleic, linolenic) or their salts, nonylphenyl-polyethylene glycol, triethanolamine (TEA), glycol esters with dibasic fatty acids (adipic), perfluorocarboxylic acids salts (C ≥ 8).

As carrier liquids are used: petroleum, hydrocarbons (B, T, X, hexane, heptane, decane etc), fluorinated and chlorinated hydrocarbons (dichloroethane, carbon tetrachloride, trichloroethane), $C_{1-5}$ alcohols, water, ethylene glycol, oils (mineral, parafin or silicon), esters of adipic, sebacic, citric, ftalic acids [6].

Preparation of magnetic colloids: the size reduction by grinding of magnetic powder in the presence of a carrier solvent and a surfactant dispersing agent, for long periods of time (~ 1000 hours); by thermal decomposition of metal carbonyls ($Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$, $Co_4(CO)_{12}$, $Ni(CO)_4$) in various liquid organic media (B, T, pentane, alcohols etc), gases or in vacuum (as stabilizers are used different types of polymers which facilitates the formation of small particles, moreover, by adsorbing on the particles it furnishes the solution aggregative stability); stable ferromagnetic colloids of iron can be obtained using high-intensity ultrasound to sonochemically decompose volatile organometalic compounds [7]; the electrolytic deposition of fine Fe, Co, Ni particles or their alloys on a cathode made by a solid (Ni, Ag or steel) or liquid (Hg) metal from an electrolyte which contains the respective ions) in presence of a diluted solution of surfactant (oleic acid) in an hydrocarbon medium; by evaporation of a metal by making use of the electric discharge and subsequent condensation of a vapour in the form of hyperfine drops. MF preparation methods based on magnetite chemical co-precipitation or carrier liquid exchange are well-known [2, 8].

## RESULTS AND DISCUSSION

MF preparation by chemical co-precipitation technique consists of magnetite precipitating from $Fe^{2+}$ and $Fe^{3+}$ solutions (usually $FeSO_4$, $FeCl_3$) in alkali (usually $NH_4OH$), followed by stabilization and precipitate washing and dispersion into desired carrier liquid.

Method of carrier liquid exchange consists in flocculation of magnetic stabilized particles with polar agents (e.g. acetone), magnetic sedimentation and redispersal in a second carrier liquid. Sometimes it is necessary to use another type of stabilizer. In this manner were prepared MF with mineral oil, paraffin oil or dioctyladipate as carrier liquids.

Physico-chemical properties of MF depend on magnetic material type, its concentration, the way of stability and the dispersion medium. Also, extremely important are, chemical composition of the magnetic material. In the case of magnetic particles based on ferrite is important $Fe^{2+}$:$Fe^{3+}$ ratio, or other metals (Ni, Cr, Co) for mixed ferrites.

Magnetic component concentration has a direct effect on the liquid carrier density modification. For MF based on stabilized magnetite dispersed in petroleum, it was established the relation:

$$\rho_{MF} = \rho_P + 0.97 \cdot \theta \tag{1}$$

where: $\theta$ - magnetite concentration, [$kg \cdot m^{-3}$], $\rho_{MF}, \rho_P$ - MF and liquid carrier densities, [$kg \cdot m^{-3}$].

Magnetization $M$ has the applied field direction and its value is equal to the magnetic moments ($\overline{m}$) sum of the "$n$" particles contained in a volume unit:

$$\mu_0 \cdot M = n \cdot \overline{m} \tag{2}$$

In this manner, the magnetic attraction force ($F_m$) and pressure ($P_m$) have the next expressions:

$$F_m = \mu_0 \cdot M_S \cdot gradB \cdot V_d , \; P_m = -\mu_0 \cdot \int_0^H M \cdot dH \tag{3a, b}$$

where: $gradB$ - magnetic field gradient, $M_s$ - the saturation magnetization, $\mu_0$ - magnetic permeability and $V_d$ the drops volume with magnetic component content.

Dynamic viscosity of MF, $\eta$, depends on the liquid carrier viscosity, $\eta_0$, and the stabilized particles volumic concentration, $\Phi$, [$m^3 \cdot m^{-3}$]:

$$\eta / \eta_0 = 1 / 1 + a \cdot \Phi + b \cdot \Phi^2 \tag{4}$$

where $a$ and $b$ are specifically constants.

In nonmagnetic field, MF present a Newtonian behaviour. The temperature dependence of dynamic viscosity was expressed as Arrhenius type equations:

145

$$\eta = A \cdot e^{E_a/R \cdot T} \tag{5}$$

This fact allows to calculate the viscous flow activation energy, $E_a$, [$kJ \cdot mol^{-1}$], (Table 1):

**Table 1.** Some MF characteristics

| Liquid carrier | Density, $kg \cdot m^{-3}$ | Magnetization, $Gs$ | Arrhenius type relation | $E_a$, $kJ \cdot mol^{-1}$ |
|---|---|---|---|---|
| Petroleum | 1085 | 300 | $\eta = 2.38 \cdot 10^{-5} \cdot e^{1615/T}$ | 13.4 |
| Petroleum | 1430 | 600 | $\eta = 2.57 \cdot 10^{-5} \cdot e^{1685/T}$ | 14.0 |
| Toluene | 1150 | 300 | $\eta = 2.32 \cdot 10^{-5} \cdot e^{1385/T}$ | 11.5 |
| Mineral oil | 1235 | 350 | $\eta = 1.56 \cdot 10^{-6} \cdot e^{3100/T}$ | 25.7 |
| Paraffin oil | 1220 | 400 | $\eta = 2.33 \cdot 10^{-7} \cdot e^{4020/T}$ | 33.4 |

The interactions between MF and the external applied magnetic field (permanent magnets or electromagnets) are basic for the main applications in technical and biomedical field. The most MF applications are based on the possibility to place and control magnetic materials using a magnetic field with a suitable flux distribution: magnetodensimetric separation (based on the levitation effect of nonmagnetic or low magnetic bodies in ferrofluids under an external magnetic field action, applied to useful minerals with different densities separation); pressure transducers and magnetofluidic clinometers, magnetooptical sensors, electroacoustical transducers; pressure sealings (magnetic field placed the MF in the gap between the surfaces of mobile and stationary elements); ferrofluidic lubricating; ferrofluidic dampers (based on MF restraint in spaces subject to vibrations using magnetic field); liquid carriers for different heat-exchange devices, especially in devices for magnetocaloric energy conversion; biomedical applications (separation and purification processes, in immunoassays, as agents for the destruction of cells via magnetic fields, as contrast agents to enhance magnetic resonance imaging (MRI) and for targeted delivery of therapeutic agents, MF present good effects in the wound healing process of the skin lesions, anti-inflammatory effects and anti-radiation protection, as a magnet-controlled haemosorbent for extracorporeal detoxication of biological media); growth and organogenesis stimulation; vitroplants obtaining, intensification of two-phase systems separation (in mass transfer processes) [9-11].

MF based on oily compounds (hydrocarbons, mineral oils) can be used for oily components restraint through dissolution from waste or accidentally impurified waters. This process consists in oily component

distribution between the liquid carrier of the MF and the aqueous phase. The mass transfer process is amplified thanks to the intimate contact result from the strong phases mixing. This fact leads to some emulsions formation. It is possible to establish a correlation between the values of the separation time in gravitational ($\tau_g$) and magnetic ($\tau_m$) field, at different values of $M_s$ for the oily phase and different magnetic field values [12]:

$$\tau_g / \tau_m = 1 + K \cdot gradB^a \cdot M_S^b \qquad (6)$$

The coefficient $K$ and the exponents $a, b$ are specific to the used emulsion.

To intensify the separation of such two-phase system were tested separators based on electromagnets, rotating or immersed permanent magnets [12-15]. Through the direct setting between the magnet and the emulsion with MF content there is the possibility of a maximum attraction force development in the liquid layers in contact with the whole surface of the magnet (internal, external, frontal). Thus, the MF drops are submitted to an intense coalescence process obtained in a zone around the magnet body. The amount of MF retained on the magnet surface is much increased when the magnet is immersed in the aqueous medium due to the Archimedean force. The detailed scheme for the separator with immersed ring-shaped magnet (Dxdxh=130x60x54mm) is shown in Figure 1:
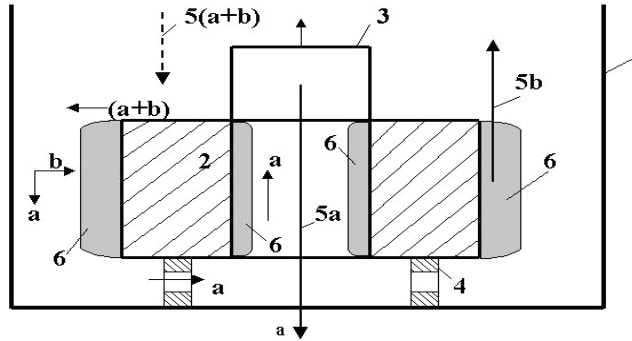


**Figure 1.** Separator for emulsions with magnetic fluid content.

The magnet **(2)** is placed into the cylindrical body of the separator **(1)** and the ring- shaped portion is continued, to the upper side, with a bell **(3)**. The role of this one is to direct the emulsion submitted to separation to the ring-shaped area between magnet and the separator body where it circulates descending, through the inferior frontal portion **(4)**, and after that the separated aqueous phase is collected in the inner part of the bell. The ferrofluid is collected as a continuous layer **(6)** on the magnet surface and is aspirated periodically. The separated water crosses the magnet inferior frontal portion and goes into the bell (route **5a**), in direct contact with the magnet inner surface, to remove all the unseparated MF drops.

147

Magnetic field distribution in the inner (a) and outer (b) position of a ring-shaped magnet is presented in Figure 2.

To establish the separation effect of the ring-shaped magnet, water with oil content (0.5÷2%) was used in which was added the proper amount of magnetic fluid so that the MF/water ratio was 1÷ 5 ml MF/1000ml water. After a strong combined mixing (mixer and recirculating pump) the emulsion was led through the separator, with various flow values. The magnetic fluid is retained around the magnet and the water with a high epuration degree is collected and analyzed.
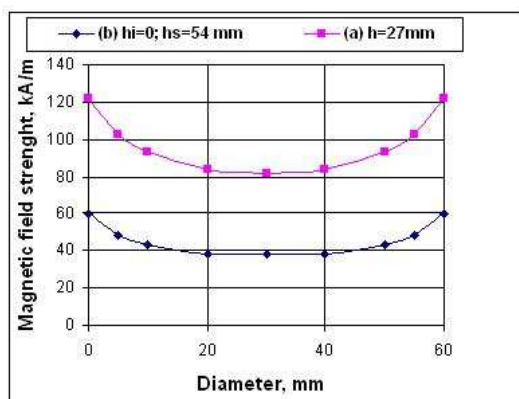


**Figure 2.** Magnetic field distribution.

The equipment that containe the magnetic separator is shown in Figure 3:



**Figure 3.** Pilot-equipment with magnetic separator (1-separator; 2- vessel with stirring; 3-stirrer; 4-recirculation pump; 5- tank for MF; 6- collecting vessel).

From the photoresistive experimental values the oily phase concentrations in the preepurated water samples were established. Based on these results we calculated the remove efficiencies (the ratio between the separated oil fraction and the one existent initially in water) of the organic magnetic phase after the wastewater passed through the separator (Table 2).

**Table 2.** The final concentrations of organic phase and the separation efficiencies

| Specific flow, $m^3 \cdot m^{-2} \cdot h^{-1}$ | $\Delta R/R$ | Organic phase concentration $ml\ oil/1000ml\ water$ | | Separation efficiency, % |
|---|---|---|---|---|
| | | initial | final | |
| 3.47 | 0.316 | | 0.67 | 96.6 |
| 6.53 | 0.485 | 20 | 1.30 | 93.5 |
| 9.92 | 0.583 | | 1.75 | 91.2 |

It was found that the specific flow increasing leads to a less efficient separation of the organic component from the system. This conclusion is proved both by the photoresistance value increasing due to the less emulsion transparency (MF presence) and the remove efficiency decreasing.

## CONCLUSIONS

Using chemical co-precipitation technique and carrier liquid exchange were prepared MF with estimated concentrations/magnetizations and good stability.

Petroleum, mineral or paraffin oil based MF present Newtonian behaviour, the temperature influence been represented by Arrhenius type equations.

For biphasic systems with MF, the external magnetic field action has an intensifying effect to phase separation.

It was built and tested a pilot-equipment for oily components recovery from waste waters using MF and a separator with immersed permanent magnet. The separation degree as a function of the waste waters specific flow was established.

## EXPERIMENTAL SECTION

For stabilized magnetite preparation, aqueous solutions of $FeSO_4$ (0.35M) and $FeCl_3$ (0.7M), heated to 65°C were treated, under strong stirring, with a $NH_4OH$ solution (25%), 20% excess. Afterwards, oleic acid diluted in petroleum is added (1:1). The heating is continued (t ~ 102°C) until the magnetic precipitate is separated in comparison with the aqueous solution which contained dissolved salts $NH_4Cl$ and $(NH_4)_2SO_4$. Clarifying and recurrent washing of the stabilized magnetic precipitate are followed by its

dispersion into the carrier liquid (petroleum), under heating and stirring. Through filtration (that can be intensified using magnetic field), is obtained MF whose concentration depends on the added amount of the carrier liquid.

MF characterization required density, dynamic viscosity, saturation magnetization and Fe(II): Fe(III) ratio determination.

From petroleum based MF were obtained mineral or paraffin oil based MF (MF-MO, MF-PO) through the carrier liquid exchange technique.

# REFERENCES

1. E. Blums, A. Cebers, M.M. Maiorov, "Magnetic Fluids", Walter de Gruyter Berlin, New York, **1997**.
2. R.E. Rosensweig, "Ferrohydrodynamics", Dover Publications, Inc. Mineola, New York, **1997**.
3. S. Taketomi, Y. Ozaki, K. Kawasaki, S. Yuasa, H. Miyajima, *J.Magn. Magn. Mater.*, **1993,** *122*, 6.
4. L.N. Donselaar, "Silica-magnetite colloids and magnetic fluids: Synthesis and particle interactions", PhD Thesis, Utrecht University, **1998**.
5. S.W. Charles, *Romanian Reports in Physics*, **1995**, *47* (3-5), 249.
6. D. Bica, R. Minea, Patent RO 93109, **1987**.
7. I. Bica, *Romanian Reports in Physics*, **1995**, *47* (3-5), 273.
8. E. Luca, Gh. Călugăru, R. Bădescu, C. Cotae, V. Bădescu, "Ferofluidele şi aplicaţiile lor în industrie"*,* Ed. Tehnică, Bucureşti, **1978**.
9. I. Anton, I. De Sabata, L. Vekas, Conf. Maşini hidraulice şi hidrodinamică, IP Timisoara, **1985**, 141.
10. M. Şincai, D. Argherie, D. Gângă, D. Bica, L. Vekas, Proceedings of ISACB Congress, Gainesville, USA, **2002**.
11. R. Minea, A. Tămaş, M. Corneanu, G. Corneanu, *Annals of West Univ. of Timisoara, Series Chemistry*, **2003**, *12(3)*, 1561.
12. A. Tămaş, "Contribuţii la obţinerea şi caracterizarea fluidelor magnetice – Emulsii cu conţinut de fluide magnetice", Teză de doctorat, Univ. "Politehnica" Timisoara, **2004**.
13. Z. Gropşian, R. Minea, E. Brînzei, A. Tămaş, *Rev. Chim.(Bucuresti)*, **2004**, *55(8)*, 577.
14. A. Tămaş, R. Minea, *Romanian Reports in Physics*, **2006**, *58(3)*, 351.
15. R. Minea, A. Tămaş, E. Brînzei, M. Şuta, "The behaviour of emulsions with ferrofluid content in magnetic field", 4th European Congress of Chemical Engineering, Granada, Spain, **2003**.