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Theoretical consideration for oxygen enrichment from air using high-T_C superconducting membrane

***Abstract**. In the present study a new route of paramagnetic and diamagnetic gas separation is suggested using the magnetic properties of membranes. The application of a porous High Temperature Superconducting (HTS) membrane as a gas filter is described in this paper. Porous superconductors can be used to separate a mixture of paramagnetic and diamagnetic gases. The separation occurs when the magnetic field is applied and is based on the Meissner effect.*

Streszczenie.** W artykule rozważana jest możliwość separacji gazów przy wykorzystaniu właściwości membran. W proponowanym rozwiązaniu membraną jest porowaty nadprzewodnik wysokotemperaturowy (HTS) umieszczony w polu magnetycznym. Warunkiem skutecznej separacji mieszaniny gazów różniących się właściwościami magnetycznymi (para- i diamagnetyczne) jest silna niejednorodność pola magnetycznego. Wykorzystuje się w tym celu efekt Meissnera występujący w nadprzewodniku. **Rozważania teoretyczne dotyczące wzbogacania tlenu z powietrza z wykorzystaniem wysokotemperaturowej membrany nadprzewodnikowej.

Keywords: superconductivity, Meissner effect, magnetic separation, oxygen enrichment,
Słowa kluczowe: nadprzewodnictwo, efekt Meissnera, separacja magnetyczna, wzbogacanie tlenu.

Introduction

When fine particles are dispersed in air, water, sea water, oil, organic solvents, etc., their separation or filtration by using a magnetic force is called magnetic separation. Magnetic separation of paramagnetic or ferromagnetic materials from diamagnetic ones has been widely studied in the context of various technologies. Principles of the separation of the particles mixture with different magnetic properties are shown in Fig. 1. [1].

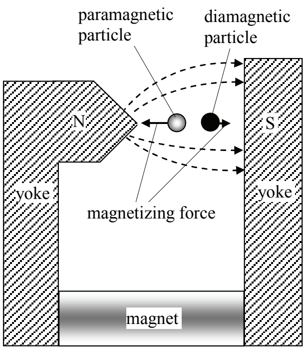

Fig. 1. Magnetizing force under magnetic field

High-gradient magnetic separation (HGMS) is a term that has been applied for many years to the separation of solid particles (dust, pyritic impurities in ground coal, tiny steel filings in the blast furnace effluent, and magnetic impurities in kaolin) from other materials in a gaseous or liquid stream. Open-gradient magnetic separation (OGMS) is a continuous process that achieves a spatial separation in the open, unobstructed magnet bore (Fig. 2).

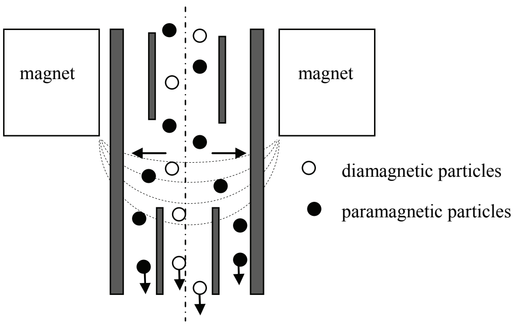

Fig.2. Principle of the Open Gradient Magnetic Separation (OGMS)

In OGMS systems, paramagnetic species are drawn toward the bore wall while diamagnetic species are repulsed from the field toward the center of the bore. The desired separation is achieved by physically splitting the process stream at the exit of the magnet bore.

In the present study, a new route to paramagnetic and diamagnetic gas separation is suggested using the magnetic properties of membranes. The separation is carried out in OGMS system.

Magnetic susceptibilities for several common gases are presented in Table 1 [2]. The data indicate that the gas species O_2 and NO are strongly paramagnetic; this is in contrast to most other gases, which are weakly diamagnetic, and to a few ones that are weakly paramagnetic. Hence, O_2 and NO might be economically separated from gas mixtures, such as air or flue gases, by passing the mixture through a magnetic field having a strong gradient. The paramagnetic component is drawn in the direction of the field gradient (or toward the magnet) and diffuses through the remainder of the gas, which is weakly repelled from the magnet (see Fig. 2).

Table 1. Physical properties of selected gas molecules [2]

Gas molecules	Magnetic property at boiling temperature χ_m [$(10^{-6}cm^3/mol)$]	Boiling temperature [K]	Kinetic diameter [Å]
Oxygen (O_2)	Paramagnetic (+3402) (+7667 liq)	90.1	3.46
Nitrogen (N_2)	Diamagnetic (-12.05)	77.4	3.64
Argon (Ar)	Diamagnetic (-6.99)	87.3	3.35
Nitric acid (NO)	Paramagnetic (+1461)	121.4	~3.8
Carbon dioxide (CO_2)	Diamagnetic (-20)	194.7	~4.0

The discovery of high temperature superconductors working at liquid nitrogen temperature is considered to be very important in terms of industrial applications due to its economic availability compared to conventional low temperature superconductors. One of the important applications is thought to be membrane gas separation based on the Meissner effect, since the oxygen molecules are paramagnetic while the nitrogen or argon gases are diamagnetic. Therefore, a superconducting membrane could be used to separate such gases using the difference of magnetic properties. For example, the nitrogen molecules can pass through the diamagnetic superconducting membrane while the paramagnetic oxygen molecules would be expelled depending on the directions of gas flow and magnetic flux.

Magnetic Force

A magnetic force, $\vec{F}$, acting on a material in a magnetic field is given by [3]:

$$\vec{F} = \vec{M}\frac{d\vec{H}}{dx} = \frac{\vec{M}}{\mu_0}\frac{d\vec{B}}{dx} \tag{1}$$

where $\vec{H}$ is the applied field intensity, $\vec{B}$ is the induced magnetic field intensity, $d\vec{B}/dx$ is the magnetic field gradient, μ_0 is the magnetic permeability of a vacuum and $\vec{M}$ is the magnetization. Magnetization $\vec{M}$ is given by:

$$\vec{M} = \chi_m \vec{H} = \frac{\chi_m}{\mu_0}\vec{B} \tag{2}$$

where χ_m is the magnetic susceptibility.

The magnetic susceptibility of paramagnetic materials (such as oxygen O_2 or nitric acid NO) is positive and that of diamagnetic materials (such as argon Ar, nitrogen N_2) is negative (see Table 1) . Equations (1) and (2) can be rearranged to give:

$$\vec{F} = \frac{\chi_m}{\mu_0^2}\vec{B}\frac{d\vec{B}}{dx} \tag{3}$$

Two types of materials interact with the magnetic field and the field gradient inversely and the interaction force is proportional to $\vec{B}$, ($d\vec{B}/dx$), and χ_m. According to Eq. (3), if a magnetic field is applied to an oxygen/nitrogen mixture, the force acting on the oxygen molecules is opposite to the force acting on the nitrogen atoms. In other words, a mixture of oxygen and nitrogen can be separated in a magnetic field. It is, however, difficult to obtain a high magnetic gradient ($d\vec{B}/dx$) using a standard permanent magnet or a coil, and therefore a porous superconducting material can be used to overcome this problem.

Meissner effect in a superconductor

The Meissner effect is the expulsion of a magnetic field from a superconductor during its transition to the superconducting state (Fig.3) [4]. Walther Meissner and Robert Ochsenfeld discovered the phenomenon in 1933 by measuring the magnetic field distribution outside superconducting tin and lead samples (Fig. 4) [4]. The samples, in the presence of an applied magnetic field, were cooled below what is called their superconducting transition temperature. Below the transition temperature the samples cancelled nearly all magnetic fields inside. They detected this effect only indirectly; because the magnetic flux is conserved by a superconductor, when the interior field decreased the exterior field increased. The experiment demonstrated for the first time that superconductors were more than just perfect conductors and provided a uniquely defining property of the superconducting state.

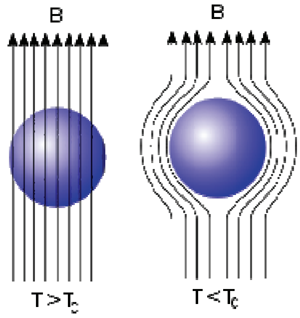

Fig. 3. Idea of Meissner's effect [4]

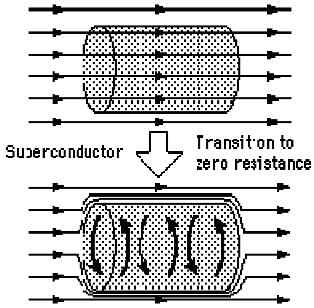

Fig.4. Illustration of the Meisnner effect in the superconductor [4]

Meissner effect (an excellent diamagnetism of the superconductor) is to be easily stated while observing the phenomenon of magnetic levitation. (Fig.5).

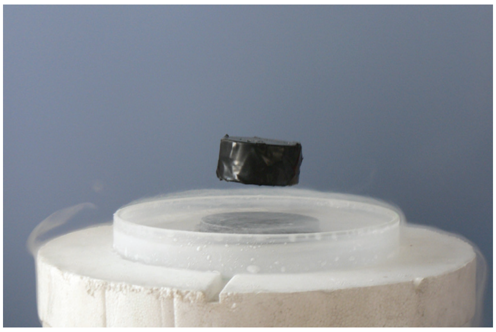

Fig. 5. A magnet levitating above a superconductor cooled by liquid nitrogen

In 1986 Bednorz and Muller discovered superconductivity for the first time in a layered perovskite, $La_{2-x}Ba_xCuO_4$ which has a T_c > 30 K, and later, various superconducting oxides were discovered as shown in Table 2 [2].

Table 2. Various physical properties of high temperature superconductors [2]

Super-conductor	H_{c1} (mT)	H_{c1} (mT)	H_{c2} (mT)	T_c (K)
Bi2201				20
Bi2212	85		~89000	85
Bi(Pb)2223		650	~184000	110
YBCO	~25	~90	~120000	90
T12223			~750000	125

If the superconductor is cooled down to below T_c in the presence of a magnetic field, the magnetic flux is expelled by a diamagnetic superconductor membrane as shown in Figure 6b, which means that the field gradient is formed as the concentration of the magnetic flux. Such a field gradient may force the paramagnetic or ferromagnetic materials to move in the concentrated magnetic field direction, and *vice versa* for diamagnetic materials. That is, the paramagnetic oxygen can be accumulated in front of the pore entrance while the diamagnetic nitrogen can pass through the superconducting body, where the magnetic field is most dilute. Thus, the oxygen molecules collected preferentially at the pore may pass through the membrane by the pressure difference across it. Molecule behavior of oxygen and nitrogen can be seen in Fig. 7.

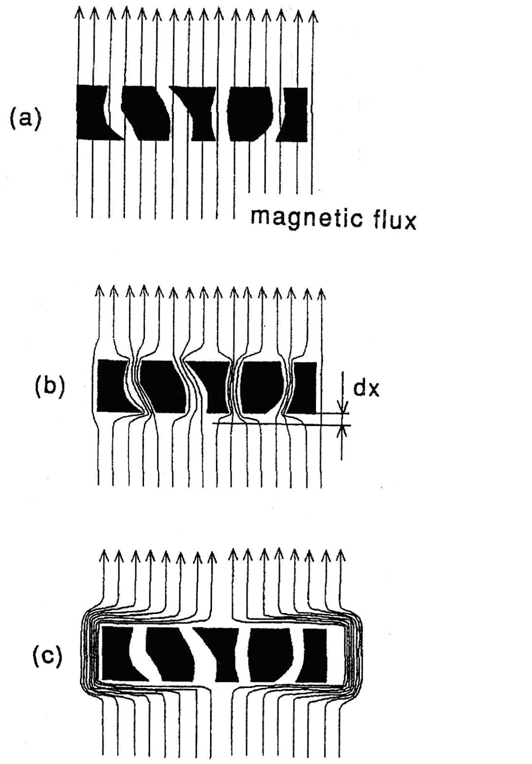

Fig. 6. Magnetic flux around the porous superconducting filter. (a) magnetic flux before cooling down the superconducting filter, (b) magnetic flux after cooled to a temperature lower than the critical temperature from the state (a), and (c) magnetic flux applied after cooling down the filter. Note that the magnetic flux is concentrated in pores in (b), and the gradient of magnetic flux becomes higher at the surface of pores of the superconducting filter. Pore diameter should be larger than the London penetration depth, λ. [3]

Idea of gas separation

Therefore, it can be concluded that a porous superconductor can be used to separate e.g. oxygen and nitrogen. Having reached the superconducting state, the superconductor turns into an excellent diamagnetic (Meissner effect) and there is a concentration of magnetic fields force lines to be observed on its surface and in the pores. A magnetic field gradient of a significant value is obtained. The condition of efficient separation determined by the equation N^o 3 is met. The behavior of oxygen – nitrogen mixture of molecules in the area of strong heterogeneous field has been described above and shown in Fig. 7. It is obvious that the gradient value depends on the size pores (Fig. 9).

As for efficient gas separation what cannot be ignored is the mutual position of the directions of vectors of magnetic field and of gas flow velocity. If the vectors are placed in the way shown in Fig. 8, then a gas separation effect reverse to the above described one is obtained.

Figure 9 show schematic section views of magnetic flux and porous superconducting filter. Magnetic gradient from Fig. 9a is higher than of 9b because pore of Fig. 9a is smaller than of Fig. 9b.

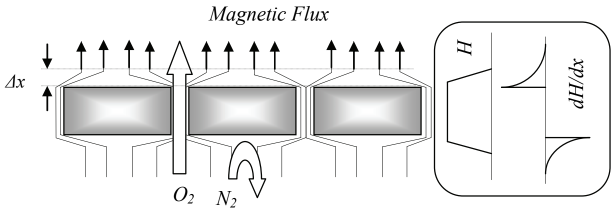

Fig. 7. Gas separation using the magnetic property where the direction of the magnetic flux is parallel to the direction of the pressure gradient

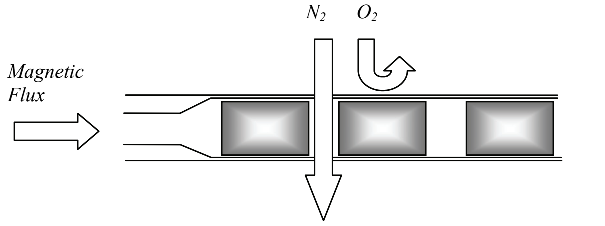

Fig. 8. Gas separation using the magnetic property where the direction of the magnetic flux is perpendicular to the direction of the pressure gradient

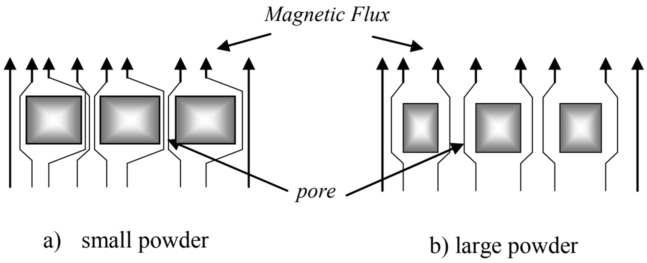

Fig. 9. Schematic section views of magnetic flux and porous superconducting filters a) a small pore filter and b) a large pore filter. *(Magnetic gradient of (a) is higher than that of (b))*

To obtain a high magnetic gradient ($d\vec{B}/dx$), the effective length *(Δx)* in Fig. 7 should be small enough to create a high value of $\vec{B}d\vec{B}/dx$.

A porous superconducting material is capable of generating such a high magnetic gradient. The magnetic flux density passing through the penetrating pore B_{por} is always higher than that of the external flux density, B_{out}. Then B_{por} is given by:

(4) $$B_{pore} = KB_{out} \quad (K > 1)$$

where K – pore configuration factor.

Calculation of the pore configuration factor K from the open porosity is as follows. It is assumed that the filter is thin enough so that the cross sectional area of a penetration pore is almost constant through the pore. The shape of a penetrating pore is assumed to be straight. The configuration factor, K is given by [3]:

(5) $$K = \frac{A_{tot}}{\sum A_{pore}}$$

where A_{tot} is a projection area of the filter and A_{pore} is a cross sectional area of a penetrating pore as shown in Fig. 10.

The open porosity of the porous material is given by:

(6) $$P_0 = \frac{V_0}{V}$$

where V_0 is the total volume of the open pore and V is the volume of the porous material. The volume of the penetrating pores, V_p, is given by $V_p = \gamma V_0$, where γ has value between 0.3 and 0.8 [3], and K can be calculated as:

(7) $$K=\frac{A_{tot}}{\sum A_{pore}}\approx\frac{V}{V_p}=\frac{1}{\gamma P_0}$$

Assuming that the open porosity is 0.3, this value is calculated to be between 4-10. Since the real pores are not straight, the true value for porous materials probably exceeds 10.

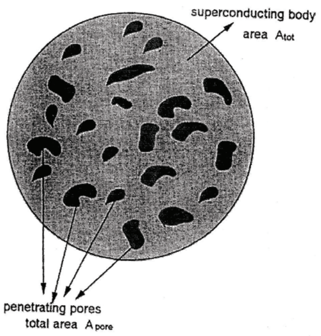

Fig. 10. Schematic illustration of distribution of penetrating pores in the superconducting body. A_{pore} is the total area of penetrating pores and A_{tot} is the total projection area of the filter. Magnetic flux passes trough penetrating pores and not through the superconducting body, thus the magnetic flux density in pores is concentrated by the factor $\left(A_{tot}/A_{pore}\right)$ [3]

Project experimental system

Figure 11 shows a schematic representation of the experimental system that makes it possible to investigate factors influencing the efficiency of oxygen enrichment. In Figure 12 it can be seen that a porous high temperature superconductor, used as a membrane with Meissner effect, has been inserted in the electromagnet inducing the outer magnetic field.

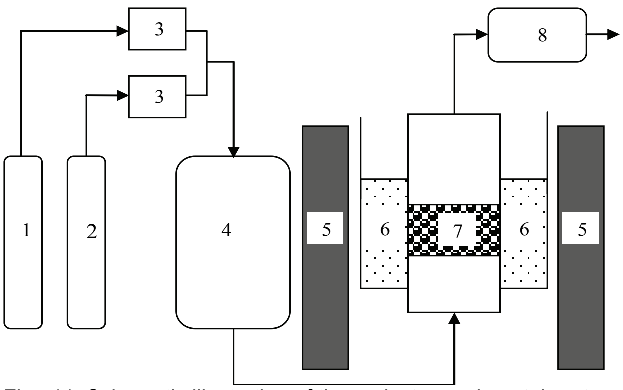

Fig. 11. Schematic illustration of the project experimental system
1 – gas_1 (N_2), 2 – gas_2 (O_2), 3 – MLF(Mass Flow Meter), 4 – buffer, 5 – superconducting coil (Low Temperature Superconductor –LTS), 6 – liquid N_2, 7 – High Temperature Superconductor – HTS (membrane with Meissner effect), 8 – gas analyzer

Conclusions

Theoretical consideration of the application of Meissner effect to a porous high temperature superconductor, used as a magnetic separator membrane, has been presented in the paper. The separation efficiency and gases' enrichment can be influenced by many factors , such as : the value of applied magnetic field, the field gradient (dependent on the size of pores in a superconductor) and the mutual position of the field intensity vector and the vector of gas flow velocity. Further researches are to be carried out with the application of the above described experimental system.

It was therefore decided therefore decided to consider the parameters required to influence the efficiency in separating nitrogen and oxygen as follows: (1) the minimum pressure, (2) the pore size limit of the membrane.

Fig. 12. View of LTS electromagnet as a source of magnetic field for experimental system

The author is going to use the system shown in Fig. 11 to do research on oxygen enrichment from air taking account of the above factors.

Pressure condition. This is necessary to reduce the pressure difference between P_i (inlet pressure) and P_o (outlet pressure)to enhance the selectivity. If the pressure difference is small, the force induced is comparable to that of magnetic field gradient. Therefore, a pressure difference of ~10^{-4} atm is needed to achieve the gas separation.

Pore size. A smaller pore size is essential to induce a larger field gradient, since it leads to a strong interaction between the magnetic field and paramagnetic oxygen. However, the size should by over 250 nm, which is the penetration depth of the superconductor. If the pore size is smaller than the penetration depth, the magnetic flux concentrated in the pore of membrane would penetrate the superconducting body. Therefore, the field gradient would not be formed effectively.

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