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Effect of Chemical State of Dispersed Phase on Magnetic Filtration Efficiency

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ABSTRACT

Magnetic filtration is a technology that uses magnetic forces to remove particles from a suspension of dispersed particles. The magnetic force occurs either because of the difference of magnetic susceptibility between the medium and the dispersed particles, and/or the difference of magnetic susceptibilities between particles composed of different materials. There is a small effect of the chemical state of the medium on magnetic filtration efficiency for filtrating ferromagnetic and/or strongly magnetizable paramagnetic materials, such as Fe_3O_4. In contrast, however, we showed that the chemical state affects the magnetic filtration efficiency when separating paramagnetic materials from each other, and that controlling the chemical state is important for controlling magnetic filtration processes. We demonstrated this by measuring the magnetic

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filtration efficiency for a weakly magnetizable paramagnetic Eu_2O_3 powder dispersed into solutions with varying salt concentration and pH, both of which affect the zeta potential of dispersed particles. We measured the filtration efficiency for a 0.8 Tesla magnetic field applied to a magnetic filter. Our experimental results indicate that the filtration efficiency increased for decreasing zeta potential. When zeta potentials of Eu_2O_3 powder are 30 and 0 mV, the collection efficiency was 30% and 38%, respectively. This occurs because the repulsion force decreases for decreasing zeta potential, and at low zeta potentials the electrical repulsion forces are sufficiently weak so that particles can approach each other without hindrance by the electric force. Lower zeta potential also allows particles to agglomerate and grow. Larger particles are more easily removed by the filter, thereby increasing the filtration efficiency.

Key Words: High-gradient magnetic field; Chemical state; pH; Salt concentration; Zeta potential.

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INTRODUCTION

Spent nuclear fuel materials consist of uranium oxide, plutonium oxide, fission products of existing metallic precipitates, metallic oxide precipitates, and dissolved materials in the uranium matrix.[1] Figure 1 shows the magnetic

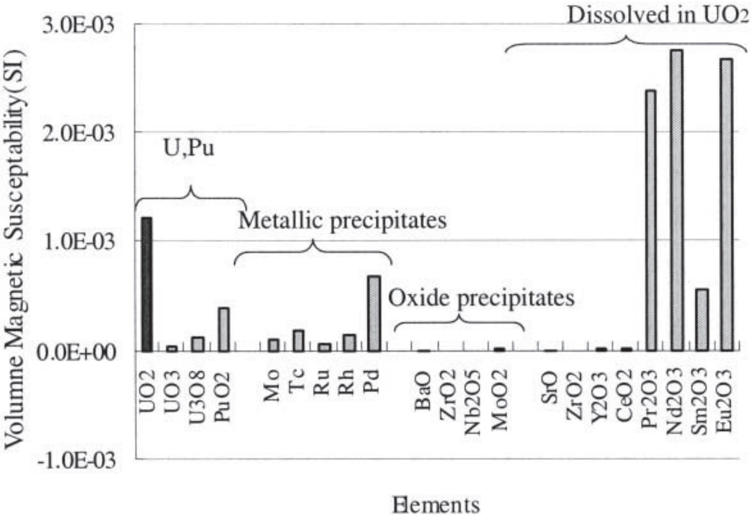

Figure 1. Volume magnetic susceptibility of major materials in the spent nuclear fuel.

susceptibility of materials in the spent nuclear fuels. It is obvious that metallic precipitates are paramagnetic,[2] and almost-oxide precipitates in spent fuels are very small. We propose applying high-gradient magnetic separation (HGMS) to separate nuclear materials from fission products, as suggested by Schake et al., who used HGMS to separate small amounts of uranium trioxide and plutonium dioxide from the radioactive contaminated soil.[3] Because the magnetic susceptibility of uranium dioxide is larger than that of plutonium oxide, a well-designed magnetic filter could trap uranium as well as plutonium.

HGMS can be used in nuclear reprocessing as a pretreatment process, because by heating spent nuclear fuel in air to above 450°C, a powder state can be obtained, and HGMS can be used to separate the powder. Reduction in hydrogen gas at 510°C leads the uranium return to the same chemical state as the spent nuclear fuel,[4] so that conventional nuclear reprocessing can be used. The advantage of this HGMS method is that this physical filtration method involves no secondary waste and decreases nuclear waste from the reprocess.

There have been many HGMS studies on filtration of slurries containing ferromagnetic and/or paramagnetic particles. Many papers have reported filtration mechanisms of suspended particles by accounting for physical conditions such as flow rate, magnetic field, magnetic susceptibility, and diffusion of dispersed particles. Gerber et al., reported a generalized HGMS theory including influences of these conditions on filtration efficiency.[5,6] However, there have been few systematic studies on the chemical effect of the dispersed phase on the filtration efficiency.[7]

Uranium oxide particles should be separated based on differences of magnetic susceptibility from spent nuclear fuels including fission product materials; however, these differences would not be enough to collect the purified uranium. Therefore, it would be necessary to consider other factors that could influence separation, such as chemical conditions of dispersed phase. Europium oxide was chosen in order to make clear the influence of these conditions because it has relatively large magnetic susceptibility. In addition, Eu154, which emits gamma rays, is one of the major fission products and major isotopes to be considered as radiation protection. Therefore, it is a great advantage if it can be separated from uranium by magnetic filtration at the early stage of reprocessing.

Based on our experiments, we found that the chemical state affects the ability of HGMS to separate paramagnetic materials from each other. Filtration can be regarded as a means to bring particles close to each other. During magnetic filtration, as particles approach each other the zeta potential causes them to repel each other.[8] The salt concentration and pH in the dispersed phase affects the zeta potential of the particles, which in turn

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affects the magnetic filtration properties of paramagnetic materials. Therefore, the chemical state can be used to optimize the filtration efficiency. For collecting ferromagnetic materials, the effect of the electrical force is negligible compared with the magnetic force.

MATERIALS AND METHODS

Materials

We used reagents supplied from Wako Pure chemicals industry, Osaka, Japan. NaCl and CH_3COONH_4 were used to study the influence of salt concentration on the suspension recovery, because their degree of electric dissociation was nearly 1 at all of our experimental conditions. Acetic ions (CH_3COO^-) adsorb on the surface of the particles, whereas chloride ions do not. Therefore, these two ionic species should have different effects on the filtration efficiency. We conducted magnetic filtration experiments to compare the filtration efficiency of CH_3COONH_4 to that of NaCl.

We prepared buffer solutions from mixtures of the acid and base reagents shown in Table 1. We ground Eu_2O_3 powder with an agate mortar before adding the solutions. The average particle size was measured with a Horiba Ltd. CAPA-300 particle-size distribution analyzer, and it was 1.2×10^{-6} m.

Table 2 shows volume magnetic susceptibilities of the reagents used for adjusting the dispersing solution. The reagents were diamagnetic chemicals with magnetic susceptibilities negligibly small compared to the suspended material, Eu_2O_3. Because the strength of the magnetic force is proportional to the difference of the magnetic susceptibilities of the suspension and the solution, none of the reagents listed in Table 2 affected the measured magnetic filtration efficiency.

Table 1. Buffer solutions.

Reagents		pH
CH_3COOH	10 mM	
NaOH	6.8 mM	5
HCl	10 mM	
NH_4	6.8 mM	8
HCl	10 mM	
NH_4	1.4 mM	9
Deionized water		6.8

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Table 2. Molar susceptibility of reagents.

Materials	Molar susceptibility (m^3/mol)
Water[a]	-1.6×10^{-10}
NaCl[a]	-3.8×10^{-10}
CH_3COONH_4[b]	-5.2×10^{-10}
HCl[a]	-2.8×10^{-10}
CH_3COOH[a]	-4.0×10^{-10}
NaOH[a]	-2.0×10^{-10}
NH_4OH[a]	-4.0×10^{-10}
Eu_2O_3[a]	1.3×10^{-7}

[a] Handbook of Chemistry and Physics, CRC Press 81st edition(2000)

[b] Relaxation Paramagnetique, Volume 7, Masson (1957)

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Apparatus

Figure 2 shows a schematic diagram of the magnetic separation system. It uses a 0.8 Tesla electromagnet (ISM-70; IDX.inc, Tokyo Japan) and a magnetic filter made of SUS430 stainless steel wool (0.05 mm fiber diameter, 1 mm aperture; NEC Environment Engineering Ltd.) packed in a 6 mm I.D., 5 mm long plastic tube. The magnetic filter had a volume loading of 1.7 volume%. A peristaltic pump (Master flex L/S; Cole-Parmer Instrument company) was used to pump the solution through the filter at a flow rate of 5 mL/min (0.3 cm/sec). The total volume of the solution filtered with this system was 30 mL. The volume of the beaker used to mix the solution was 50 mL. To prevent suspended particles from adhering to the inner surface of the tubes, we used tetrafluoroethylene tubes (0.8 mm inner diameter) to connect the beaker, the magnetic filter, and the peristaltic pump.

We measured the zeta potential of Eu_2O_3 particles suspended in the dispersed phase by using a System 3000 automated electro kinetics analyzer (Pen Kem Inc.).

Experimental

We poured 20 mg of Eu_2O_3 powder into 30 mL of solution and homogenized it with an ultrasonic bath. We confirmed that the light absorbancy is proportional to the concentration of the suspension. We measured the light

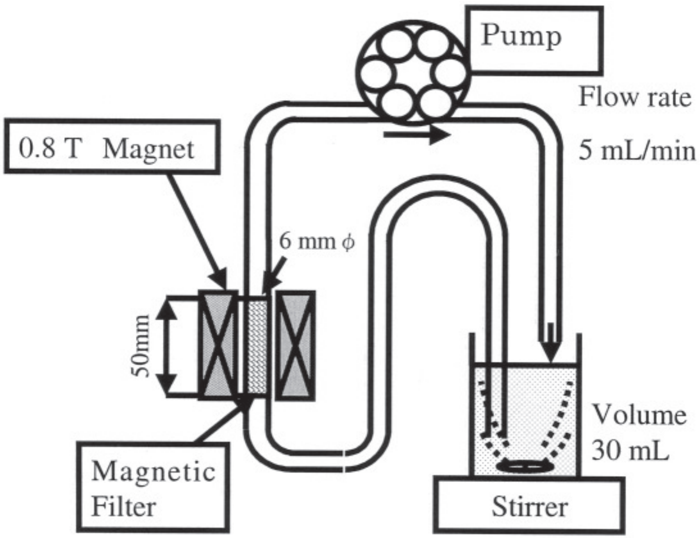

Figure 2. Magnetic filtration system.

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absorbance of 10-mm thick solution samples at intervals of 1 min. We used a calibration curve to calculate the Eu_2O_3 concentration from the measured light absorbance.

RESULTS AND DISCUSSION

Figures 3(a) and (b) show typical measured particle collection curves of the magnetic filter. We plotted the relative absorbence at passed-through volume. Figure 3(a), left graph, was the filtration results under $H = 0T$, and the right, Fig. 3(b) was $H = 0.8T$ at different NaCl concentrations. The relative absorbance is defined as the light absorbance normalized by the light absorbance at the beginning of a run. The relative absorbance is proportional to the suspension concentration of the dispersed phase. The particle collection curves in Fig. 3(b) follow the so-called exponential law. Figure 3(a) also shows the concentration of particles in the solution without any magnetic force. This means that the magnetic filter works as both a conventional and a magnetic filter for Eu_2O_3 particles. The change of the particle concentration in Fig. 3(b), C, in the filter can be expressed as

$$\frac{dC}{dl} = -(C_H + C_m)l \qquad (1)$$

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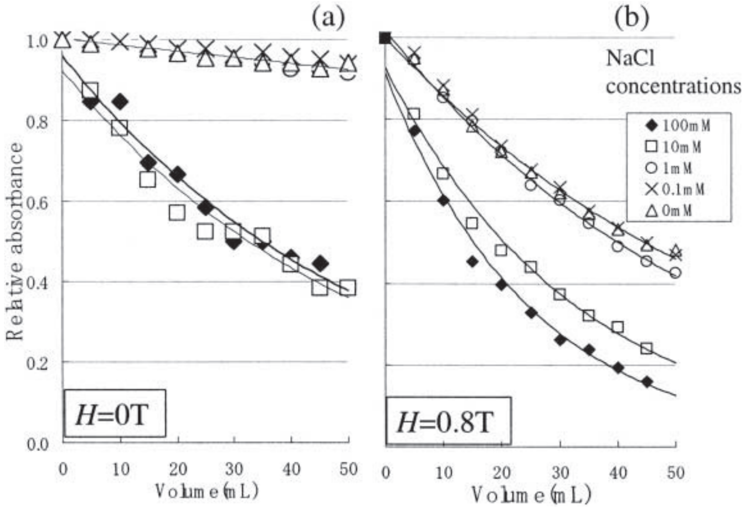

Figure 3. Eu_2O_3 concentrations vs. solution volume passed through magnetic filter, varied with disperse phase of NaCl concentrations.

where $C_H =$ collection factor based on particle capture by magnetic force; $C_m =$ collection factor based on mechanical particle capture; $C =$ concentration of suspension; and $l =$ solution volume passed through magnetic filter.

By integrating Eq. (1), we obtain the exponential law of particle concentration as

$$C = C_0 \exp(-(C_H + C_m)l) = C_0 \exp(-C_t l) \tag{2}$$

where C_0 is the initial particle concentration in the solution and C_t $(= C_H + C_m)$ is a total collection factor.

C_m can be determined by fitting measured concentration curves with Eq. (2) when $H = 0$ and $C_H = 0$. The C_H can be calculated by fitting the curve for combined magnetic and mechanical filtration to obtain the total collection factor and subtracting C_m from C_t.

Effect of Salt Concentration

Figure 4 shows the calculated collection factor, C_H vs. NaCl and CH_3COONH_4 concentrations and indicates that C_H increases with increasing salt concentration, C_{salt}. There was no significant difference in C_H between

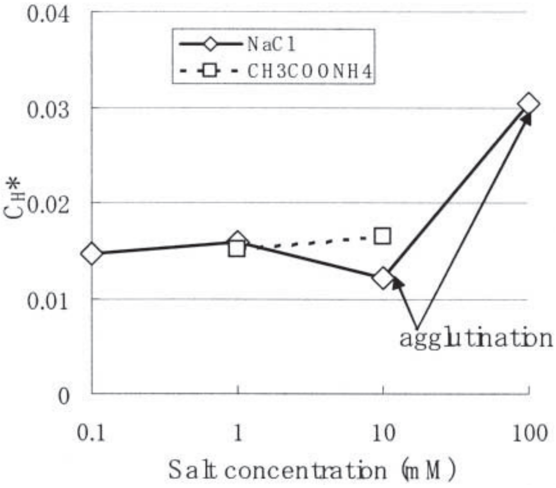

Figure 4. Collection factor vs. salt concentration.

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solutions at the same molar concentration of 1 mM with NaCl and CH_3COONH_4.

When the NaCl concentration was greater than 10 mM, suspended materials were not stable in the solutions during filtration. Suspensions were collected by the filter even at $H = 0$. White particles about 0.1 mm in diameter precipitated onto the sample powders. When the salt concentration, e.g., NaCl, becomes large, electric double-layers at the surface of particles are compressed, repulsion force between particles decreased. Then the aggregation velocity becomes evident. This phenomenon is known as the salting-out effect.

The collection of particles by a magnetic filter is governed by the competition of magnetic and drag forces. Magnetic forces attract particles to the filter wool, and drag forces remove trapped particles from the filter wool. Because the magnetic force is proportional to the volume of particles and the drag force is proportional to the cross-sectional area of the particles, aggregated particles are more easily filtered with a magnetic filtration system.

Effect of pH

Figure 5 shows the relation between C_H and pH. It indicates that C_H was maximum at the pH 9. Salt concentrations in the solutions, C_{salt} at pH 5 and 10 were both 11.4 mM, whereas C_{salt} in the water (pH 6.8) is 0. From the

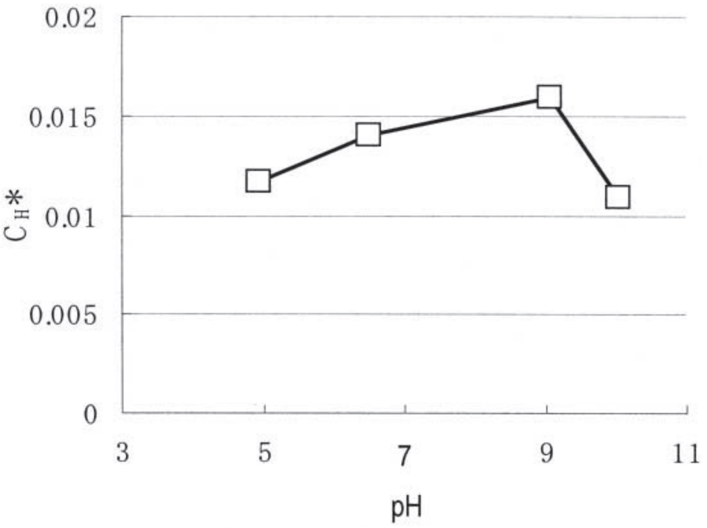

Figure 5. Collection factor vs. pH.

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experimental results of Fig. 4, C_H was predicted to be higher for pH 5 and 10 than for pH 6.8. However, Fig. 5 indicates that C_H at pH 6.8 is bigger than pH 5 and pH 10. It is found that pH, which is concentration of proton, is affected by correction factor. Since the proton adsorbs and/or desorbs on the surface of the oxide particles, zeta potential of the particles depend on the pH of the solution. To account for these pH effects, we consider the effect of a zeta potential at the surface of the particle to the magnetic filtration efficiency.

Zeta Potential

The zeta potential is normally used to evaluate the agglutination reaction. We measured the zeta potential of Eu_2O_3 as a function of pH. Figure 6 shows the zeta potential vs. pH for Eu_2O_3. For pH < 8 the zeta potential is positive, and for pH > 8 it is negative. The isoelectric point (point at which the zeta potential vanishes) should exist between a pH of 6 and 8.[9] Therefore, solutions nearly pH 8 have a low absolute value of zeta potential, whereas C_H is the highest.

Table 3 lists zeta potentials and C_H for Eu_2O_3 powder for various salt concentrations and pH. Figure 7 shows the collection factor vs. zeta potential. As the zeta potential approaches zero, C_H becomes a maximum. At low zeta potential the mutual electrical repulsion between particles is also lower than

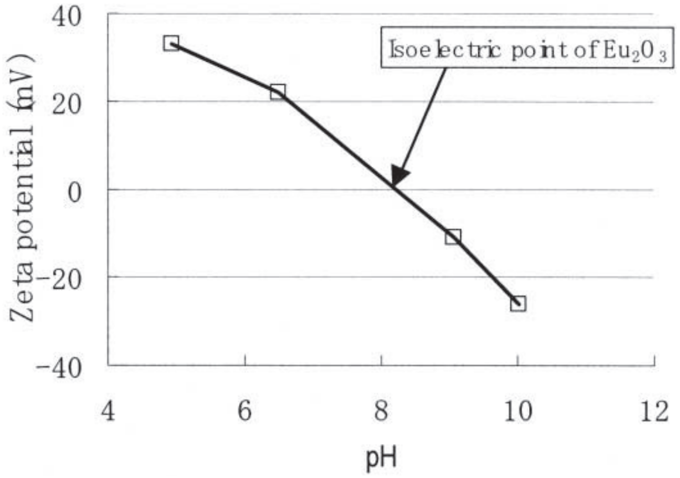

Figure 6. Zeta potential vs. pH, showing isoelectric point of Eu_2O_3 (point at which zeta potential is 0).

at higher zeta potential. This occurs because particles can approach each other without any repulsion force by the potential at the filtration and also agglutination occurs at low zeta potentials. For low zeta potential, particles are easily trapped by the filter and grow in the dispers phase. These particles are strongly attracted by magnetic forces and are trapped by the filter through magnetic forces. Therefore, higher filtration efficiency was obtained at low zeta potential.

Table 3. Effect of chemical state on zeta potential and collection factor for Eu_2O_3 powder

Reagents	Chemical condition: Salt concentration (mM)	Chemical condition: pH	Zeta potential (mV)	Collection factor (C_H)
Pure water	0	6.8	22	0.0140
NaCl	1	—	8.2	0.0159
CH_3COONH_4	10	—	5.4	0.0164
$CH_3COOH + NaOH$	16	4.9	33	0.0117
$NH_4OH + HCl$	16	9.1	−11	0.0159
	11	10.0	−26	0.0109

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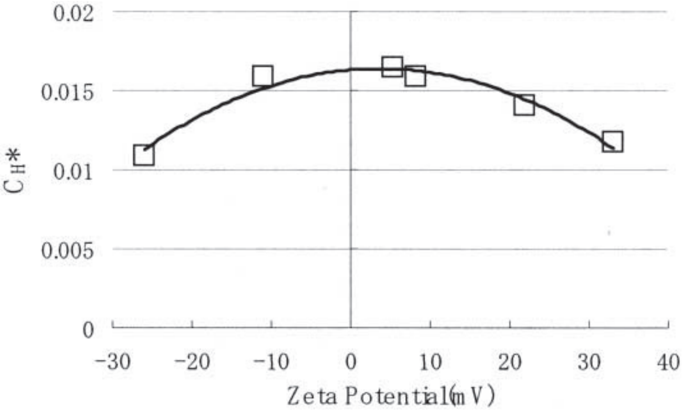

Figure 7. Collection factor vs. zeta potential.

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Filtration efficiency, E_f, is the ratio of particle amounts trapped with the filter (M_f) to that in the initial solution (M_0).

$$E_f = \frac{M_f}{M_0}$$

We used 30 mL of solution in our experiment, therefore, initial concentration, C_0, times 30 mL gives M_0.

$$M_0 = C_0 \times 30\,\text{mL}$$

M_f is calculated by subtracting the particle amount that comes out from the filter, M, from M_0. C times 30 mL gives M as the same manner as M_0 calculation.

$$M = C \times 30\,\text{mL}$$

C is calculated by equation (2) with $l = 30\,\text{mL}$

Figure 7 indicates that for $C_H = 0.012$ and 0.016, the zeta potentials are 30 and 0 mV and concentrations after filtration are 0.70 and 0.62, respectively.

The corresponding filtration efficiencies are, therefore, 30% and 38%, respectively.

SUMMARY

We demonstrated that there is a significant effect of the chemical state of a dispersed phase on the collection efficiency for a magnetic filtration system. The effect of the chemical state on the filtration efficiency can be quantified in terms of the zeta potential of the dispersed phase. As the absolute value of the zeta potential decreases to 0, the filtration efficiency increases. It is important to adjust the chemical state of the dispersed phase to obtain high filtration efficiency. Isoelectric point of the material is inherent. This fact would be favorable to obtain higher separation factors for magnetic separations of materials, whose magnetic susceptibilities are close.

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REFERENCES

1. Kleykamp, H. The chemical state of fission products in oxide fuels. J. Nucl. Mater. **1985**, *131*, 221–246.
2. Mortimer, M.J. Magnetic susceptibility measurements on fission product insolubles. IEEE Trans. Magn. **1981**, MAG-17, 2819–2821.
3. Schake, A.R.; Avens, L.R.; Padilla, D.D.; Romero, D.A.; Worl, L.A.; Prenger, C.F.; Hill, D.D.; Tolt, T.L. Magnetic separation for environmental remediation. In *Separation of f-Elements*; Nash, K.L., Choppin, G.R., Eds.; Plenum Press: New York, 1995; 257–269.
4. Uchiyama, G.; Kitamura, M.; Yamazaki, K.; Torikai, S.; Sugikawa, S.; Maeda, M.; Tsujino, T. Study on voloxidation process for tritium control in reprocess. Radioactive Waste Nucl. Fuel Cycle **1992**, *17* (1), 63–79.
5. Gerber, R.; Takayasu, M.; Friedlaender, F.J. Generalization of HGMS theory—the capture of ultra-fine particles. IEEE Trans. Mag. **1983**, *19* (5), 2115–2117.
6. Gerber, R.; Lawson, P. The HGMS filter performance exponential law. IEEE Trans. Mag. **1989**, *25* (5), 3806–3808.
7. Glew, J.P.; Parker, M.R. The influence of interparticle forces in the magnetic separation of submicron particles. IEEE Trans. Mag. **1984**, *20* (5), 1165–1167.
8. Kitahara, A.; Furusawa, K.; Ozaki, M.; Ohshima, H. *Zeta Potential*. Scientists Co. Ltd: Tokyo, Japan, 1997; (in Japanese).
9. Yoon, R.H.; Salman, T.; Donnay, G. Predicting points of zero charge of oxides and hydroxides. J. Colloid Interf. Sci. **1979**, *70*, 483–493.