

MIXTURES FOR THE ADSORPTION AND STORAGE OF RADIONUCLIDES CONTAINED IN NUCLEAR WASTE AND CONTAMINATED GROUNDWATER

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ABSTRACT

This paper describes the prospects for a mixture of three complementary high-capacity adsorbents which adsorb most of the important transition, rare-earth and actinide radionuclides. With these three adsorbents, used in combination, the radionuclides can be removed and immobilized from storage tank liquor or from contaminated ground water and the concentration of radionuclides can be reduced to levels which are safe. The major materials investigated are based on modifications of Brimac 216 Natural Carbon, a material used for over 100 years, on a large-scale, for the adsorption of color bodies from brown sugar in the industrial production of white sugar. Adsorption tests were carried out on Brimac 216, on Brimac 216 Powder and the magnetic Brimac 216 powder. Approximately 0.5g of the sample was mixed with 20 ml of a 2M NaNO₃ solution containing a ²⁴¹Am, ¹⁰⁹Cd, ¹³⁹Ce, ⁶⁰Co, ¹³⁷Cs, ⁵⁴Mn, ¹¹³Sn, ⁸⁵Sr, ^{99m}Tc, ⁸⁸Y and ⁶⁵Zn. The best choice of these modified Brimac 216 materials, namely the magnetic Brimac 216 powder, when used with other materials, the combination can provide an excellent adsorbent for a wide range of radionuclides and provide a matrix for the safe long-term storage of nuclear waste.

INTRODUCTION

This paper describes the uptake of important radionuclides by various adsorbents based on Brimac 216 Natural Carbon as the major material. Brimac 216 Natural Carbon is a product made by heating milled animal bones to approximately 800 C in the absence of air and consists of approximately 76% hydroxyapatite Ca₅(PO₄)₃OH, 10-15% amorphous carbon C, 7-9% calcium carbonate CaCO₃ and other minor constituents. However in other work it has been shown that a number of radionuclides are removed by apatites[1, 2]. In any adsorption process which uses large porous particles, the uptake takes place in two steps, the first step being the diffusion of the solution into the particle and the second step is the adsorption of the hydrated radionuclide ion onto a suitable site. There is an interest in using Brimac 216 Natural Carbon fine powder into order to reduce the time taken by the diffusion process in the first step. Fortunately, Brimac 216 Natural Carbon is very brittle and appreciable quantities of fines are produced during the industrial processing of the material.

Recently, Lidzey has deposited magnetite within bone char powder making the material amenable to recovery from suspension by high gradient magnetic separation. The material has a magnetic susceptibility of 4.5×10^{-4}

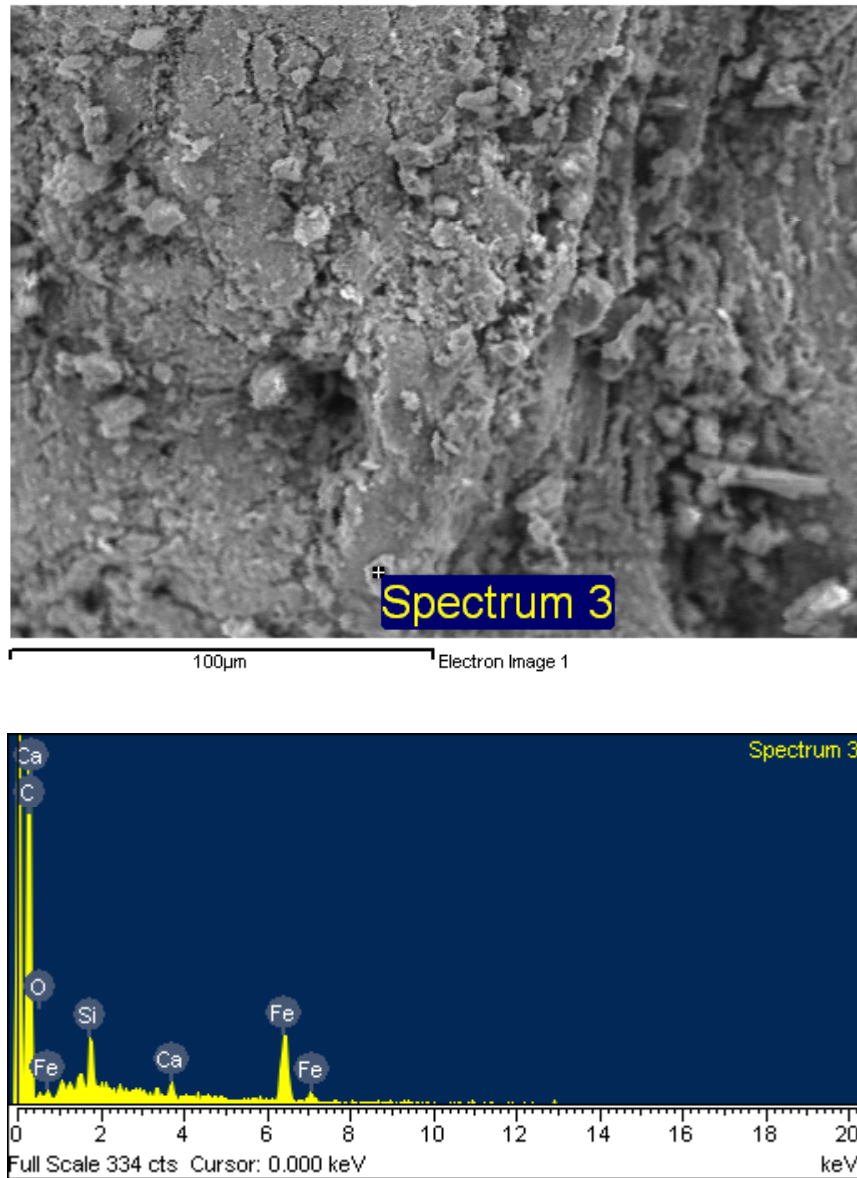


Fig. 1. A Scanning Electron Microscope (SEM) picture of the magnetic Brimac 216 Natural Carbon, produced by Lidzey, with an EDS spectrum labeled with + at the top, left hand corner of the Spectrum 3 insert. The spectrum (below) shows a strong signal of Fe together with strong O and C signals.

Methodology

Radiotracer experiments were undertaken using calibrated solutions of ^{241}Am , ^{109}Cd , ^{139}Ce , ^{57}Co , ^{60}Co , ^{137}Cs , ^{203}Hg , ^{54}Mn , ^{113}Sn , ^{85}Sr , ^{88}Y and ^{65}Zn . These solutions of radionuclides were supplied by Amersham International who certify the solution concentrations to $\pm 2\%$, however, in the experiments the concentrations were measured directly. All the above isotopes are γ ray emitters requiring a γ ray spectrometer to detect the changes in activity. Amersham International also supplied solutions of individual radionuclides of $^{99\text{m}}\text{Tc}$, as TcO_4^- . All the vials and containers used were acid washed in 2 % Spectrosol HNO_3 for 24 hours and then washed in Milli-Q high purity water prior to use. Metal uptake experiments were undertaken in 30 ml universals (Sterilin, acid washed) containing deoxygenated distilled water obtained by passing nitrogen gas through the water for 30 minutes prior to the addition of a small accurately measured volume of the radionuclides. A blank containing no adsorbent for calibration of the solution and to check for non-specific sorption or other loss mechanisms. When this was done approximately 0.5g of the of Brimac 216 Natural Carbon sample (labeled GAU689-1 in Figs 2 & 3) was mixed with 20 ml of a 2M NaNO_3 solution containing a ^{241}Am , ^{109}Cd , ^{139}Ce , ^{60}Co , ^{137}Cs , ^{54}Mn , ^{113}Sn , ^{85}Sr , $^{99\text{m}}\text{Tc}$, ^{88}Y and ^{65}Zn .

Sodium nitrate solution was chosen as a medium as this approximates to the bulk composition of aqueous wastes from spent nuclear fuel reprocessing plants but in the absence of reprocessing plants chloride can be used as the anion. The solid and solution were thoroughly mixed on a tumble wheel for one hour. The mixture was then filtered through a 0.45 μm membrane filter and the aqueous phase was measured by gamma spectrometry. The activity of each nuclide was quantified using Fitzpeaks spectral deconvolution software and the quantity of nuclide adsorbed to the solid phase was calculated.

The experiment was repeated at pH 1 and pH 4.6 A blank test was also conducted at each pH whereby the charcoal was replaced with an inert polyacrylamide resin This test gives an estimate of the proportion of the radionuclide removed. Finally, this procedure was repeated with Brimac 216 Natural Carbon fine powder (labeled GAU689-2 in Figs 2 & 3), Brimac 216 Natural Carbon fine powder (labeled GAU689-3 in Figs 2 & 3) and an inert polyacrylamide resin (Labeled BLANK in Figures 2 and 3).

Test 1 - pH 1

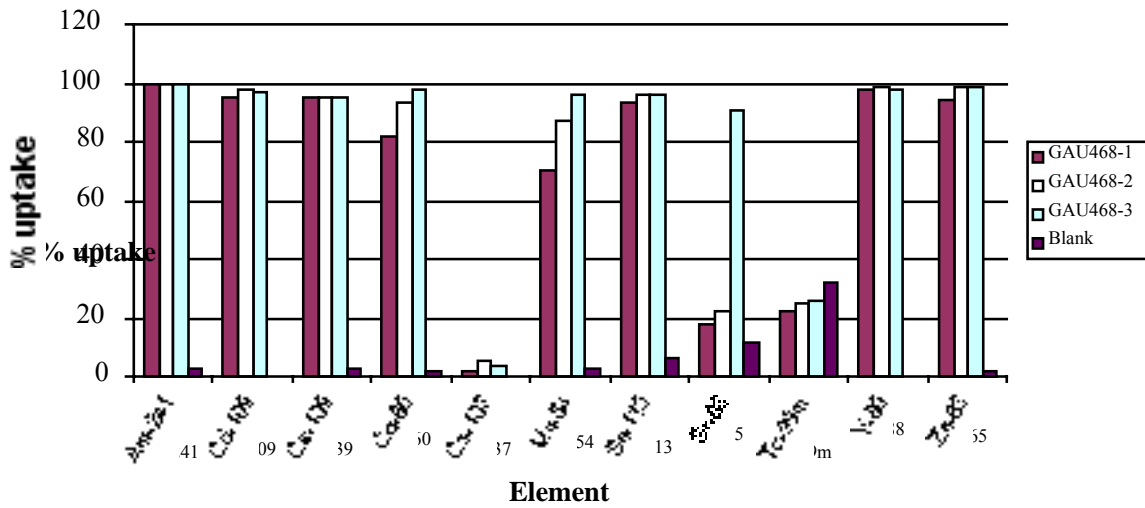


Fig. 2. The percentage uptake for the radionuclides from the Amersham solution at pH=1 by the various adsorbents and the blank test.

Test 2 - pH 4.6

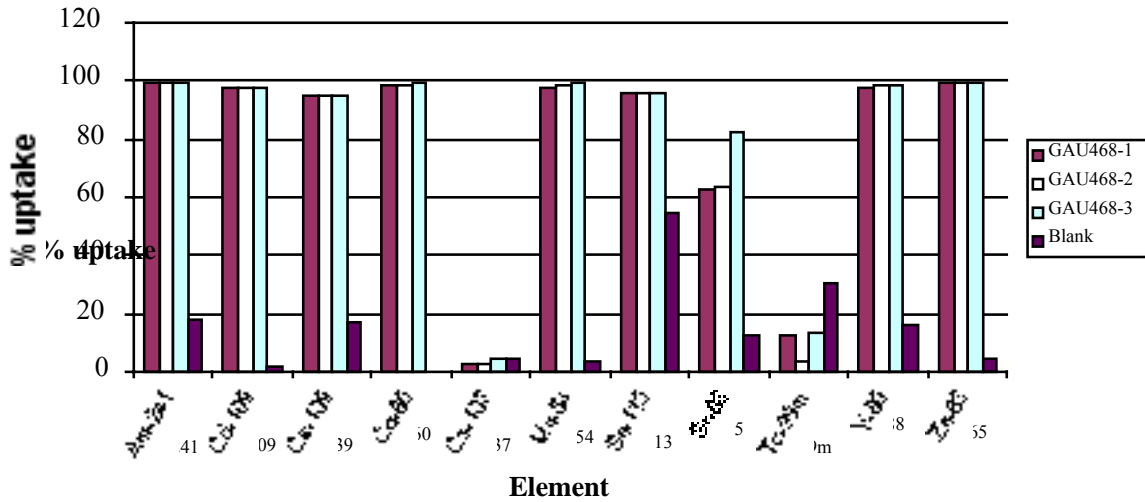


Fig. 3. The percentage uptake for the radionuclides from the Amersham solution at pH=4.6 by the various adsorbents and the blank test.

Results

The radionuclides used and their initial activities shown Bq.ml⁻¹ in brackets are as follows: ²⁴¹Am(6.24), ¹⁰⁹Cd(17.5), ¹³⁹Ce(0.194), ⁶⁰Co(3.26), ¹³⁷Cs(5.28), ⁵⁴Mn(2.17), ¹¹³Sn(0.723), ⁸⁵Sr(0.212), ^{99m}Tc(15.51), ⁸⁸Y(0.778) and ⁶⁵Zn(4.1).

It was found that magnetic Brimac 216 powder (GAU689-3) performed consistently better than the other two materials used in the tests. For the tests at pH=1, none of the three materials performed well with ¹³⁷Cs or ^{99m}Tc. However, for the remainder of the radionuclides, the magnetic Brimac powder removed greater than 95% of the radionuclides with the exception of ⁸⁵Sr removing 91%. The average uptake for the magnetic Brimac 216 powder (excluding Cs and Tc) was >97%.

The tests at pH=4.6 showed the same overall characteristics as the pH=1 test but the uptake ⁹⁹Sr fell to 82% but the average removal for the radionuclides (excluding Cs and Tc) was again greater than 97%.

DISCUSSION AND SUGGESTIONS

There are deficiencies in the uptake results for the Brimac materials described above, namely, the uptakes of ¹³⁷Cs and of ⁹⁹Tc are very poor. However by using combinations of different materials with the best Brimac 216 material perhaps these deficiencies can be overcome.

A microbially-produced iron sulfide which is strongly-magnetic consisting of mackinawite Fe_{1+x}S and greigite Fe₃S₄ has been produced by sulfate-reducing bacteria in a novel bioreactor at University of Southampton, UK. The uptake of a wide variety of radionuclides is rapid and the loading of the adsorbent is high due in part to the high surface area of the adsorbent and the fact that many of the ions are chemisorbed [3]. The surface area is of the order of 400-500m²g⁻¹ as determined by the adsorption of heavy metals, the magnetic properties, neutron scattering and transmission electron microscopy. The adsorption of the radioisotopes ¹³⁷Cs, ⁵⁹Fe, ⁶⁰Co, ¹⁰⁶Ru, ^{110m}Ag, ⁵¹Cr, ⁵⁴Mn, ²⁰³Hg, ¹⁰⁹Cd, ⁹⁰Sr, ²³⁹Pu and ²⁴¹Am. has been examined [3] allowing the adsorption process to be studied at considerably lower concentration than in previous work. More recent experimental work has revealed that the pertechnetate ion, TcO₄⁻, is chemically reduced on the adsorbent surface from Tc(VII) to Tc(IV) where it remains chemisorbed. It has been suggested that this bacterially-generated iron sulfide may provide a suitable matrix for the long-term safe storage of spent nuclear fuels [4]. The suggestion, we make here, is to include the biologically produced iron sulfide together with magnetic Brimac 216 powder so that all the Tc is adsorbed together with the remaining radionuclides except the ¹³⁷Cs.

In order to remove the ¹³⁷Cs we should include the formation of NaNiFe(CN)₆ in the liquid waste. This is usually done by adding sodium ferrocyanide and nickel sulfate to the liquid waste which precipitates sodium nickel ferrocyanide, which is strongly paramagnetic with a magnetic susceptibility $\chi = 4 \times 10^{-4}$. Much of the sodium in the precipitate of sodium nickel ferrocyanide is replaced by cesium. As the precipitate is paramagnetic the material can be removed along with the other components by magnetic separation. This process has been used with great success by the Hanford plant and in the EARP process by BNFL, Sellafield, UK [4].

These three materials, namely, magnetic Brimac 216 powder, microbially-produced iron sulfide and sodium nickel ferrocyanide, we envisage will be used to treat a variety of nuclear waste or spent nuclear fuel by methods which are the topic of next section.

Treatment and Storage of Radioactive Waste

The flow chart for this proposed treatment method is shown in Fig. 4. It is supposed that the feed contains ^{241}Am , ^{109}Cd , ^{139}Ce , ^{60}Co , ^{137}Cs , ^{54}Mn , ^{113}Sn , ^{85}Sr , $^{99\text{m}}\text{Tc}$, ^{88}Y and ^{65}Zn and has been adjusted to pH=7. The first material to be removed is ^{137}Cs together with other isotopes of Cs. This done by the addition sodium ferrocyanide and nickel sulfate to produce sodium nickel ferrocyanide precipitate which will exchange sodium for Cs. It is proposed to add enough sodium nickel ferrocyanide to remove almost all of the Cs. It is proposed that sufficient residence time is allowed for this by using channel flow. After this process is completed mackinawite and magnetic Brimac 216 char is added to the turbulent flowing suspension the flow in the tube should take sufficient time so that the pertechnetate ions are reduced from $^{99}\text{Tc(VII)}$ to $^{99}\text{Tc(IV)}$ [3] the insoluble material and magnetic Brimac 216 char will have captured the remaining ions with the help of the mackinawite [4]. As all the suspended solids are magnetic they can be removed by high gradient magnetic separation (HGMS) described more fully in the Appendix. HGMS divides the suspension into radioactive solids and a decontaminated liquid which is safe for disposal. The solids are washed out at about 30-35% solids and can be dried to about 50% solids for medium term storage. This moisture is required for safety; if the solids are dry and if the temperature exceeds 207-270 C then the ferrocyanide can explode. Radiolysis can destroy the ferrocyanide and produce chemical which are much more stable. When this radiolysis has been completed, the waste can be dried and held for long term storage. A reducing atmosphere is maintained by the presence of mackinawite and presence of magnetic Brimac 216 powder raises the pH which further increases the stability.

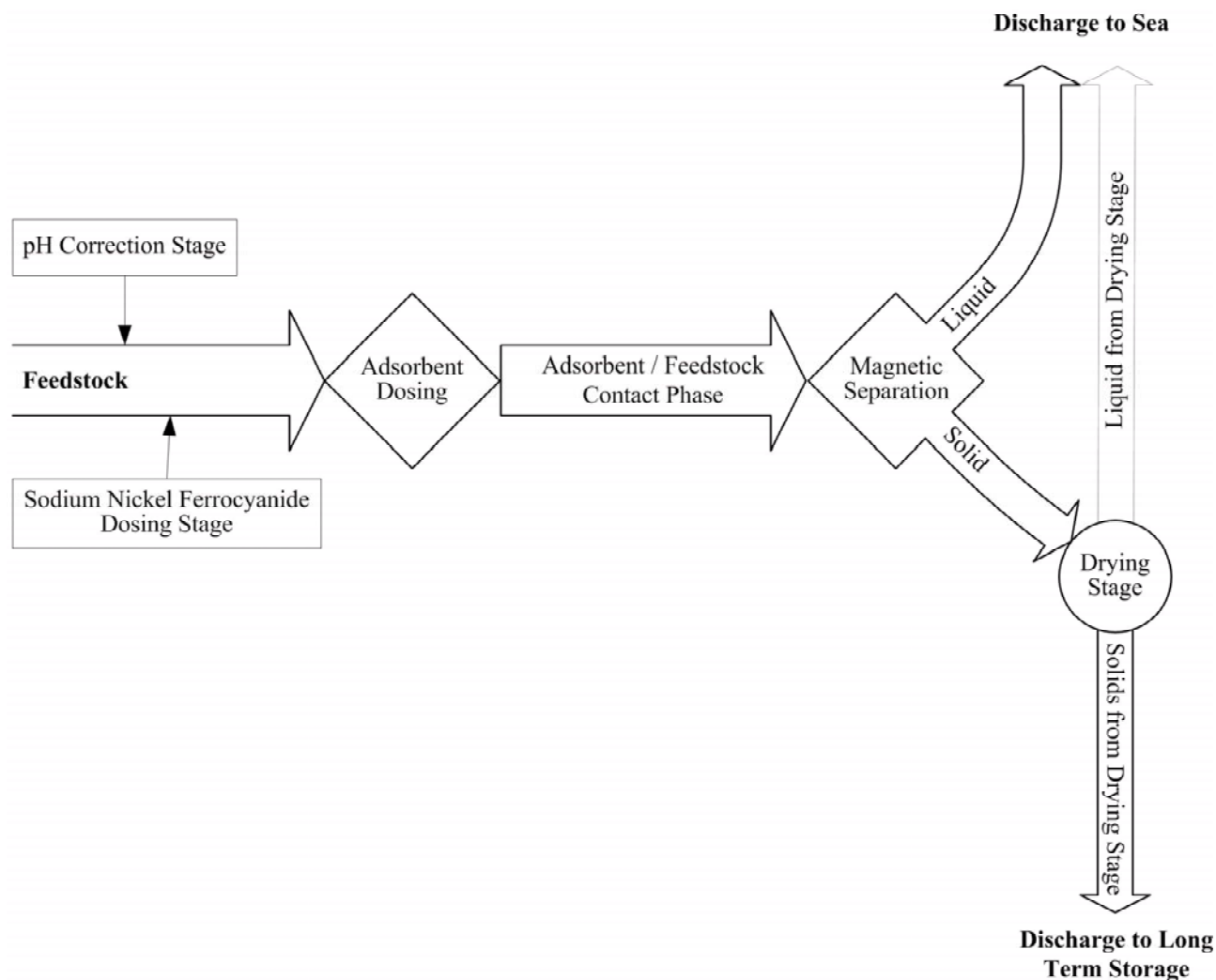


Fig. 4. Shows the flow chart for the proposed method of water treatment.

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APPENDIX

High Gradient Magnetic Separation Systems

In HGMS the slurry, containing paramagnetic particles to be extracted, is passed through a matrix of fine ferromagnetic wire which is magnetised by an externally applied magnetic field. The paramagnetic particles are attracted and held onto the wires by magnetic forces. Eventually the efficiency of the trapping process becomes impaired by the accumulation of the captured particles. These trapped particles can be released, and the efficiency of the matrix restored, by switching off the applied magnetic field and washing the particles from the matrix or by withdrawing the matrix from the magnetic field and then washing the particles from the matrix. Thus HGMS is a cyclical process with a collection phase and a washing phase. Machines of this type, the so-called reciprocating canister machines, have been developed in the UK and are in use throughout the world on a large-scale.

A theoretical analysis of the capture of paramagnetic particles has been developed based on the interaction between a paramagnetic particle carried by a fluid past a ferromagnetic wire magnetized by a uniform applied magnetic field H_0 [1-4]. In the analysis it was assumed that the wires composing the matrix were perpendicular to the applied field; those portions of the matrix parallel to the field create no field gradient. It was found that if a quantity V_m , called the magnetic velocity, was introduced, the equations of motion simplified. This simplification revealed that the particle capture cross-section/unit length of matrix wire, and the overall extraction efficiency of a filter composed of these wires, depended on the ratio V_m/V_0 , where V_0 is the background velocity of the fluid. V_m , the magnetic velocity, is given by [1] :

$$V_m = (2/9)(\chi b^2 M_s H_0) / \eta a \quad (1)$$

Here χ is the volume susceptibility of the particles of radius b , M_s is the saturation magnetisation (Tesla) of the ferromagnetic wire matrix with strand radius a (m), η (Pa-s) is the viscosity of the fluid and H_0 is the applied magnetic field (amp/meter). When $V_m \gg V_0$ the capture of the particles is very strong and the separator behaves like a filter [5]. The output $R(L, nT)$ at time nT for an initial concentration R_0 is given by the equation (2)

$$R(L, nT)/R_0 = -L/L_0 + R_0 V_0 nT / N_T L_0 \quad (2)$$

Where L is the length of the separator, $L_0 = 3\pi a / (4(1-\epsilon_0)R_{co}\beta)$ where $(1-\epsilon_0)$ is the fractional volume of the matrix wire in the separator, usually around 0.05, R_{co} is the capture radius [1] so that $2R_{co}a$ is the particle capture cross-section per unit length of matrix wire, V_0 is the fluid velocity, $T = \epsilon_0 L / V_0$ is the time taken for the fluid to pass through the separator. A canister

volume is $\varepsilon_0 LA$ where n is the number of canister volumes of fluid which pass through the separator in time nT , β is a particle packing fraction and is usually taken as 0.67 and finally N_T is the total number of particles which can be captured per unit volume of the separator.

References for the Appendix

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