DECONTAMINATION OF RADIOACTIVE ISOTOPES

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Abstract

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Removal of radioactive isotopes under controlled conditions is determined by a number of physical and chemical properties considered radiocontaminating and by the characteristics of the contaminated object. Determination of quantitative and qualitative factors for equilibrium in a contamination-decontamination system provides the basis for rational and successful decontamination. The decontamination of various “solid/liquid” systems is interesting from the scientific and technological point of view. These systems are of great importance in radiation protection (decontamination of various surfaces, liquids, drinking water, fixation or collection of radiocontaminants). Different types of decontamination systems are discussed. The dependence of rate and efficiency of the preparation conditions and on the ageing of the scavenger is described. The influence of coagulating electrolyte on radioactive isotope fixation efficiency was also determined. The fixation of fission radio-nuclide on oxide scavengers has been studied. The connection between fundamental investigations and practical decontamination of the “solid/liquid” systems is discussed.

1. INTRODUCTION

Nonconstituent ions bound in the adsorption layer or in the crystal lattice matrix can be substituted by various ions. The process of this exchange for different combinations of ions is quantitatively defined on the basis of the Mirnik concept [1]. According to this concept the process of decontamination of a nonconstituent ion from the surface should be identical for both the isotopic and nonisotopic carriers if their ionic species in the water solution are of the same kind. In order to apply these findings we examined the decontamination of polystyrene, glass powder, silicon dioxide, and titanium dioxide.

Chemical precipitation is a very effective treatment for removing most radioactive elements from wastes and can be used with high-salt-content liquids. It is well known that a simple iron (III) hydroxide precipitation will remove about 95% of the transuranic alpha emitters and 75% of most beta emitters from a typical waste and may be sufficient to decontaminate a low-level effluent.
stream for disposal. In this work the aim was to find out the best conditions for the pre-concentration of $^{106}$Ru and $^{54}$Mn prior to decontamination.

When the scavengers were left to equilibrate with the solution for sufficiently long periods of time, or if the same scavenger was precipitated at a high temperature, it was possible to show that after a critical ageing time, or at the critical precipitation temperature, the exchange of radiocontaminant ions became an order of magnitude slower. This paper represents also a search for conditions in the scavenger-$^{131}$I$^-$ systems under which the fraction exchange remains smaller than 1 for a long period of time.

The influence of coagulating ion charge and concentration on the rate of heterogeneous exchange of I$^-$ ions with coagulated silver iodide shows a complex mutual phenomenon between all the species present [2]. In the present paper the influence of Mg(NO$_3$)$_2$ concentration on the rate of heterogeneous exchange process in the stable AgI-I$^-$($^{131}$I$^-$) system is shown.

2. EXPERIMENTAL

Glass Duran 50 and polystyrene (Styron)-beads of 100—120 mesh were used throughout the experiments; both the powders were contaminated with the radioactive solution Eu($^{152,154}$Eu)(NO$_3$)$_3$ of high specific radioactivity. The adsorbed $^{152,154}$Eu was decontaminated from the polystyrene and glass powder with Eu(NO$_3$)$_3$ 0.0001N, and with Al(NO$_3$)$_3$ 0.0001 or 0.01N solutions at pH = 3.9 — 4.1. After 10 minutes the liquid phase was separated from the solid phase; 1 ml was used for the determination of radioactivity $R$. This procedure was repeated five times.

The chemicals used were analytical grade reagent; water was doubly distilled. The concentration of the FeCl$_3$ stock solution was determined by a standard gravimetric method. Radionuclides of ruthenium (c.f. $^{106}$Ru as chloro-complex in conc. hydrochloric acid) and manganese (c.f. $^{54}$MnCl$_2$ in 0.1 mol-dm$^{-3}$ hydrochloric acid) were used. Iron (III) hydroxide was precipitated with sodium hydroxide solution of an appropriate concentration. The precipitation was performed in the presence of a trace element. The total concentration of sodium chloride in the systems was 0.15 mol-dm$^{-3}$.

The sorption was characterized by comparing the radioactivity of the separated liquid electrolyte phase with the radioactivity of a homogeneously distributed suspension of the sample. The counting rates were measured with a well-type NaI(Tl) scintillation crystal in conjunction with an EKCO Electronics preset time scaler. The pH measurements were made with glass and calomel electrodes using Radiometer pH M-26 pH-meter. All experiments were carried out at 293 K. Other experimental details are described in previous papers [3, 4].
The radiometry results were calculated as the fraction exchange
\[ F = \frac{(A_0 - A_t)}{(A_0 - A_{\infty})} \] and the A values were determined as follows: a solution
of 0.0002M AgNO₃ was added to an agitated solution of 0.0004 mol·dm⁻³ NaI. After the precipitating systems were left ageing for \( t_A \) (100 and 100 000) minutes they were labelled by means of carrier-free \(^{131}\)I⁻. After a given exchange time \( t_E \) AgI was precipitated, using a Sorvall RC2/B superspeed centrifuge. The clear supernatant was counted in a well-type NaI(TlI) scintillation counter with an EKCO Electronics scaler. In this way the \( A_t \) values were determined. The \( A_0 \) values were obtained by counting the systems prepared in the same way but containing no AgI. The \( A_{\infty} \) value was determined in the same way as the \( A_t \) values, except that the radioactive \(^{131}\)I⁻ was added prior to precipitation with AgNO₃.

Stable silver iodide hydrosols were prepared by addition of 5.00 ml of
0.0200M AgNO₃ solution to an equal volume of 0.0400M NaI solution. The solution in the flask was shaken by a magnetic stirrer. The systems were aged for 3000 minutes (= \( t_A \)) at a temperature of 293 K : 15 seconds before the predetermined \( t_A \) was reached, 0.1 ml of a Mg(NO₃)₂ solution of various concentrations was added to the systems. The resulting concentrations of Mg(NO₃)₂ in the systems were from 0.000003 to 0.01 mol·dm⁻³. 3000 minutes aged systems were labelled by 0.050 ml of carrier-free \(^{131}\)I⁻. The radioactivity

FIG. 1. Schematic presentation of the fraction exchange \( F \) versus the exchange time \( t_E \) function.
FIG. 2. Fraction exchange $F$ measured as a function of the temperature $K$ of the solid scavenger, for different $t_E$ (O/150 min, $\bullet$/450 min, $\triangle$/1000 min, $\Delta$/5000 min).

$A_t$ of the clear liquid phase was determined after the exchange times $t_E$ using a scintillation counter. The fraction exchange $F$ was presented as a function of $t_E$.

3. RESULTS AND DISCUSSION

The radii as well as the crystallographic modifications of the scavenger particles taking part in the observed exchange processes are not known. It is therefore impossible to calculate the diffusion coefficients from the results obtained. Meanwhile, in the preceding papers of this series [5] the theory was...
put forward that the decontamination via heterogeneous exchange observed on the majority of the systems was generally caused by the recrystallization of the solid.

In Fig. 1 a schematic proposed exchange mechanism is shown. At the time of labelling, $t_0$, the fraction exchange, $F$, is zero. In the time interval from $t_0$ to $t_1$ large crystals L and medium M grow, incorporating radioactivity, while the smallest crystals S will be completely dissolved. Thus the fraction exchange increases and reaches its first maximum. From time $t_1$ to $t_3$ the radioactive crystal layer of crystal M will dissolve while L grows, the net results being increasing solution radioactivity and decreasing fraction exchange. After a minimum has been reached (the radioactive layer of crystal M completely dissolves), only crystal L continues to grow, incorporating radioactivity. The course of the exchange process then increases as a monotonous $F, \log E$ function up to $F = 1$. In real systems $F, \log E$ plots mostly show several minima and maxima, stemming from a wide size distribution and/or the contribution of other equilibration processes. The lower $F$ values (Fig. 2) for silver iodide precipitated at
higher temperatures are the consequences of different rates and conditions at which the primary crystallites form. The systems allowed to stand for 100 000 minutes show an adequately lower $F$ value than those aged for 100 minutes before the beginning of the exchange process. In general, radiometric data of the systems investigated suggest that the recorded behaviour of AgI scavenger is in some way connected with the properties of the crystal space.

The obtained contamination-decontamination results are shown in Fig. 3. The full lines correspond to the results obtained for decontamination of Duran glass powder ($D$) and the dashed ones for Styron ($S$). The results show that the decontamination by the isotopic carrier is more efficient than by the non-isotopic carrier of the same concentration, although the differences are not great. In fact the efficiency of the nonisotopic carrier is quite adequate.
For instance, a hundred times larger concentration of aluminium ions compared to europium gave a much better decontamination. This is of importance in practice because of the cheapness of the nonisotopic carrier, and owing to the possibility of using a single nonisotopic carrier for different contaminating ions. Quite the same results were recorded for the contaminated SiO₂ and TiO₂ (Fig. 4): decontamination factor D₁ is quite adequate for the nonisotopic carrier (Al). The results obtained are in good agreement with the Mirnik concept [1]. Figure 5 represents the dependence of the sorption of ¹⁰⁶Ru and ⁵⁴Mn on solution acidity pH. A marked increase in sorption of ¹⁰⁶Ru is observed with increasing pH between 3.5 and 4.5. The maximum of sorption of manganese is shifted to higher pH values. The sorption of ¹⁰⁶Ru and ⁵⁴Mn on iron(III) hydroxide can be explained as follows. At low pH values, where little sorption occurs, there is no attraction between the sorbate and the positively charged surface of the iron(III) hydroxide precipitate. "Amorphous" iron (III) hydroxide precipitate has an isoelectric point of solid (IEP(s)) of 7.2, which means that below pH 7.2 the surface is positively charged, whereas above pH 7.2 it is negatively charged [6]. As the pH increases, the metal ions become able to replace hydrogen ions on or near the surface, giving rise to a specific sorption reaction and a measured increase in sorption. The observation that the sorption maxima for ¹⁰⁶Ru and ⁵⁴Mn cations occur at different pH values suggests that cation hydrolysis has a greater influence on sorption than variation of surface charge of sorbent with pH and information about hydrolysis of ruthenium(III, IV) [7] and manganese(II) [8] tends to support this.
FIG. 6. The sorption of ruthenium-106 and manganese-54 with different amounts of sorbents.

FIG. 7. The sorption of ruthenium-106 and manganese-54 on iron(III) hydroxide as a function of log($t_{sorp}$).
FIG. 8. Fraction of exchange $F$ plotted versus the exchange time $t_E$ (log scale) for systems containing various concentrations of $\text{Mg(NO}_3\text{)}_2$.

Figure 6 shows the variation of the sorption of $^{106}\text{Ru}$ and $^{54}\text{Mn}$ as a function of the amount of sorbent. The sorption of $^{54}\text{Mn}$ on iron(III) hydroxide precipitate is 100% with $1.0 \times 10^{-2}$ mol·dm$^{-3}$ FeCl$_3$ and at pH 7.5. $^{106}\text{Ru}$ is 100% sorbed with $5.0 \times 10^{-2}$ mol·dm$^{-3}$ FeCl$_3$ and at pH 4.7. The results indicate that an iron(III) hydroxide precipitate can be used for the purification of radioactive waste waters contaminated with $^{106}\text{Ru}$ and $^{54}\text{Mn}$.

The results shown in Fig. 7 indicate that sorption does depend on duration of the contact between the sorbate and the sorbent ($t_{\text{sorp}}$). With manganese, peaks are obtained at $\log(t_{\text{sorp}}) 3.5$. The changes in sorption yields with time probably result from structural and surface transformations of the iron(III) hydroxide precipitate and from the hydrolysis reactions of $^{106}\text{Ru}$ and $^{54}\text{Mn}$ cations.

The influence of coagulating electrolyte on the rate of heterogeneous exchange of $\text{I}^-$ ions was previously investigated in coagulated AgI/I$^-$ systems prepared in statu nascendi [9, 10]. The results of these investigations showed a marked influence of charge and concentration of coagulating electrolyte on the rate of heterogeneous exchange process. In the present paper the influence of concentration of $\text{Mg(NO}_3\text{)}_2$ solution on the rate of heterogeneous exchange process in stable AgI/I$^-$ is shown. In order to prevent the influence of coagulating ions on the formation of sols, the coagulating electrolyte was added into the
systems 3000 minutes after precipitation. The results are represented in Fig. 8 as a set of $F$ versus log $t_E$ curves. The solid curves correspond to the results obtained in the systems with concentrations of Mg$^{2+}$ ions below the critical coagulation concentration, and the dashed curve corresponds to the results obtained in a system with concentration of Mg$^{2+}$ ions above critical coagulation concentration. The results shown in Fig. 8 show that the rate of heterogeneous exchange of I$^-$ ions increases with increasing concentration of Mg$^{2+}$ ions contained in the system. The particles of stable silver iodide hydrosols are composed of two kinds of silver iodide: metaphasic silver iodide or metaphase and crystalline silver iodide surrounded by the metaphase [11, 12]. The self-diffusion coefficient of I$^-$ ions in metaphase is considerably higher than the self-diffusion coefficient of I$^-$ ions in crystalline silver iodide, and thus the rate of heterogeneous exchange is higher in metaphase than in crystalline silver iodide [12]. Since the particles are negatively charged there is a potential barrier between particles preventing their fast aggregation. On the other hand, the potential barrier prevents not only the fast aggregation of particles, but also a contact of exchangeable ions from the liquid phase with the suspended particles. In this way, only those exchangeable ions possessing the kinetic energy needed to penetrate the particles’ potential barrier (electrostatic part of activation energy for self-diffusion-governed exchange process $E_s$) can diffuse through the interface layer. The presence of coagulating electrolyte in concentration below the critical coagulation concentration reduces the potential barrier. In this case the exchange process proceeds faster if the concentration of coagulating electrolyte in the system is higher (see Fig. 8). On the other hand, the diminishing of the potential barrier caused by adding coagulating electrolyte to the system causes acceleration of the aggregation process and thus increase of particle size [13]. Hence, the presence of coagulating electrolyte causes two opposite effects: acceleration of the heterogeneous exchange rate by decreasing the electrostatic repulsion between I$^-$ ions and negatively charged particles, and deceleration of the heterogeneous exchange rate caused by particle growth. Since the exchange rate increases with increasing concentration of Mg$^{2+}$ ions, as shown in Fig. 8, it is evident that the lowering of the repulsive force between I$^-$ ions and AgI particles caused by the action of coagulating electrolyte is more considerable for the exchange effect than the increase of particle size. If the concentration of coagulating electrolyte in the system is lower than the critical coagulation concentration, the exchange rate of I$^-$ ions between the liquid phase and the metaphasic silver iodide is relatively slow. In this case the exchange share reached by the exchange process of I$^-$ ions between metaphase and crystalline silver iodide has a marked influence on a total exchange share. When the concentration of coagulating electrolyte is equal to or higher than the critical coagulation concentration, the potential barrier is reduced to zero and the exchange rate of I$^-$ ions between liquid phase and the metaphase becomes very fast. Due to the high value of the self-diffusion
coefficient of I⁻ ions, the ¹³¹I⁻ is homogeneously distributed through the whole mass of metaphasic silver iodide for a short time. Thus, the fraction of exchange attained for a shorter exchange time is proportional to the fraction of metaphase present in the system. Since the coagulating ions in high concentration also cause the fast aggregation of particles, and thus the fast transformation of metaphasic silver iodide into the crystalline one [12], the further course of heterogeneous exchange process is determined by self-diffusion of I⁻ ions in crystalline silver iodide. After a long exchange interval (τₑ = 30 000 min) the specific radioactivity of crystalline AgI is equal to the specific radioactivity of liquid phase and F tends to 1.

REFERENCES