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Tungsten and Rhenium Sorption Study on Alumina to Prepare $^{188}W/^{188}Re$ Generators

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Abstract: Rhenium-188 is a radionuclide with favorable physical characteristics suitable for radiotherapeutic purposes ($T_{1/2}$ 16.9 h, $E_{\beta max}$ 2.12 MeV; E_{γ} 155 keV (15%)) for radiotherapeutic purposes and can be continually obtained from $^{188}W/^{188}Re$ generator systems. The preparation conditions of an alumina based $^{188}W/^{188}Re$ generator are reported. Initially, the W and Re sorption behavior on alumina in NaCl and HCl medium was performed evaluating the following parameters: medium pH, alumina size particle, sorption capacity, and kinetic. Re-188 is not adsorbed in HCl and NaCl medium whereas W-188 is strongly adsorbed in both media at $pH < 5$. The strongest sorption of W was obtained in alumina with a particle size of 0.075–0.048 mm. The weight capacity of alumina is approximately 0.337 meq/g and the sorption equilibrium in static conditions is attained after 18 hours. This data was used to construct and evaluate alumina $^{188}W/^{188}Re$-generators for a period of six months.

Keywords: Alumina, generators, rhenium, tungsten

INTRODUCTION

Rhenium-188 is an recommended radioisotope for diagnostic and therapeutic techniques because of its attractive physical and chemical properties: half-life 16.98 hours, a strong particulate emission (beta

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energy of 2.12 MeV), and an imageable gamma emission (15%, 155 keV) ideal for current gamma camera imaging of tumors (1–3). Radiopharmaceuticals labeled with ^{188}Re are currently used in clinical trials, such as: ^{188}Re-mercaptoacetylglycylglycylglycine (MAG_3) and ^{188}Re-diethylenetriamine pentaacetic acid (DTPA), renal excreting agents used for the prevention of coronary arterial restenosis; ^{188}Re-hydroxyethylidene diphosphonate (HEDP), ^{188}Re-alendronate (ABP), and ^{188}Re-ethylenediamine-N,N,N′,N′-tetrakis(methylene phosphoric) acid (EDTMP) applied for palliation of metastatic bone pain; ^{188}Re-n-hexyldiaminedithiol (HDD)-lipiodol employed for treatment of liver cancer; ^{188}Re-labeled colloids and microspheres used for treatment of diseases such as rheumatoid arthritis, peritoneal effusion, and other solid tumors, and more specific ^{188}Re-labeled radiopharmaceuticals for target lesions such as cancer-specific monoclonal antibodies and peptides (4,5).

^{188}Re can be prepared either by irradiation of enriched ^{187}Re in a nuclear reactor (6,7) or as the daughter product of ^{188}W/^{188}Re generator with a useful shelf-life of several months and can continually provide a supply of ^{188}Re to remote sites at a reasonable cost. This characteristic is especially important in developing regions which involve long distances and expensive distribution costs (2,3,8,9). Thus ^{188}W/^{188}Re generator systems have been preferably studied and developed using mostly chromatography columns charged with a matrix, where ^{188}W is adsorbed and ^{188}Re is eluted with saline solution (2). Adsorbent materials such as aluminium oxide, hydrous zirconium oxide, hydrous manganese dioxide, hydrated titanium dioxide, hydrated antimony pentoxide, hydrous tin oxide, hydrous cerium dioxide, hydroxyapatite, lead fine granular, silica-gel, charcoal activated, zirconium or titanium polymer compound adsorbents (PZC), and anion exchange resins (AG1-X12, Dowex-1, Mesoporous Organosilicas) have been investigated and proposed as matrices of ^{188}W/^{188}Re generators (2,10–14). Matrices prepared by precipitation of low specific activity ^{188}W with zirconium or titanium salts to form tungstate gels or with zinc, cobalt, nickel, manganese, and lead salts to form tungstates have been also examined to improve the capacity of this generator (15–19).

Rhenium and tungsten separations have also been performed by:

1. Organic solvents such as pyridine, isobutyl methyl ketone, methyl ethyl ketone, or acetone. In this case the organic phase is evaporated and the rhenium dissolved in NaCl or precipitated as tetraphenylarsonium perrhenate or rhenium sulphide (20,21)
2. Thermochromatographic processes where ^{188}W-tungsten metal is inserted in a vertical thermochromatographic device containing an inner quartz tube where $H^{188}ReO_4$ is adsorbed. This system functions at temperatures between 900 to 1000°C with a yield of 65% (22,23).

^{188}W/^{188}Re generator systems based on chromatographic columns are presently used in hospitals for therapy and research due to its simplicity and compact nature. Alumina is the most commonly used adsorbent material for the preparation of ^{188}W/^{188}Re generators and ^{188}Re is obtained commercially carrier free as Na^{188}ReO$_4$ from these generators. However, analytical studies of the preparation conditions of alumina based ^{188}W/^{188}Re generators have not been extensively reported. Iller et al. cite adsorption studies of tungstate solutions on two types of alumina over a wide range of pH (9.7–2.5) and temperature (0–34°) in the presence of chloride, acetate, nitrate, and phosphate ions. Nevertheless there are no results on the adsorption studies explaining the generator preparation conditions selected in their investigation (24). Mikolajczak et al. describe the preparation methodology of the alumina based ^{188}W/^{188}Re generators and present the performances obtained in these generators, however the methodology followed from W and Re adsorption data on alumina is not justified (25). Kamioki et al. reported W adsorption on alumina in 0.05 mol/L NH_4NO_3 at pH 4 and for Re in 0.05 to 0.5 mol/L NH_4Cl, 0.16 mol/L NaCl, 0.05 mol/L NH_4NO_3, and 0.014 mol/L HNO_3 as a function ^{188}W breakthrough as well as the influence of the W load in the columns on ^{188}Re yield. However, the W and Re distribution coefficients were not reported thus making this data valid only under experimental conditions described by Kamioki (26). Vučina et al. report some distribution coefficients of W and Re in HCl, HNO_3, and NaCl media, and the ^{188}W breakthrough and saturation capacities of alumina for W(VI) at three pH value under dynamic conditions (27). Dadachova et al. present a study on the surface interaction between WO_4^{2-} ions and the alumina in the alumina ^{188}W/^{188} Re generators in 0.05 mol/L NH_4NO_3 at pH 5 (28). Therefore, the aim of our study is to provide an analytical support to select preparation conditions of an alumina based ^{188}W/^{188}Re generator. A systematic study of W and Re sorption on alumina as a function of the medium concentration, medium pH, alumina particle size, and alumina weight (capacity) and an evaluation of the performances of the ^{188}W/^{188}Re generator systems constructed from the W and Re adsorption data are reported.

SORTION BEHAVIOUR OF W AND Re ON ALUMINA

Determination of Distribution Coefficients

Distribution coefficients (Kd) of rhenium and tungsten in alumina were determined by a radiotracer technique using ^{187}W and ^{188}Re under static conditions. The ^{187}W was produced by irradiation of 100 mg tungstic acid

(H_2WO_4), in the TRIGA MARK III Reactor of the National Institute of the Nuclear Research (ININ) in Mexico, to a neutron fluence rate of 1.6×10^{12} n $cm^{-2}s^{-1}$ for 1.5 min. The irradiated material was dissolved in 5 mol/L NaOH and the pH of this solution adjusted at 5 with 12 mol/L HCl, obtaining a W concentration of 5.9 mg/mL and a specific activity of 0.74 MBq/mL (12). The ^{188}Re were provided by ININ Material Radioactive Department as solutions of sodium ^{188}Re-perrhenate ($Na^{188}ReO_4$) obtained from the elution of a $^{188}W/^{188}Re$ generator made in ORNL (30 MBq/ mL).

Acidic aluminum oxide (pH 4.5) for chromatography (0.05–0.15 mm) from Fluka was used in these experiments. The alumina was sieved and four particle sizes were separated: >0.075, 0.075–0.048, 0.048–0.038, and <0.038 mm.

The technique for Kd determination consisted of contacting a weighted mass of alumina (m_{alu}) with 30 mL of the medium (V_{sol}) HCl or 0.9% NaCl (see Table 1). Solid and aqueous solutions were brought to equilibrium by shaking the mixture for 3 days, followed by addition of 100 μL of radioactive solutions containing the $^{187}WO_4{}^{2-}$ or $^{188}ReO_4$ and shaken again for 3 hours. The alumina and liquid phase were then separated by centrifugation. Alumina adsorption characteristics were determined by comparing the ^{187}W (685.74 KeV) or ^{188}Re (155 KeV) activities of 4 mL aliquots (A_{sol}) with a 4 mL aliquot of reference solutions (A_{sta}). The reference solutions were prepared with the same amount of the tracer solutions in 30 mL of the medium. Radioactivity measurements were performed with a coaxial gamma detector HPGe (Canberra 7229P) connected to a PC–multichannel analyzer (ACUSSPECT-A,

Table 1. Sorption experimental conditions of W and Re on alumina

Series	Metal	Concentration medium	Medium pH	Alumina (mg)	Alumina size particle (mm)	Equilibrium time (d)
A	W	10^{-6} –3 mol/L HCl	0–6	150	0.048–0.038	3
B	Re	10^{-6} –3 mol/L HCl	0–6	150	0.048–0.038	3
D	W	0.9% NaCl	1–12	150	0.048–0.038	3
F	Re	0.9% NaCl	1–12	150	0.048–0.038	3
E	W	0.9% NaCl	5.6	150	>0.075 0.075–0.048 0.048–0.038 <0.038	3
C	W	0.9% NaCl	5.6	150–1000	0.048–0.038	3
G	W	0.9% NaCl	5.6	150	0.075–0.048	5 min–4 d

Canberra). Gamma-ray spectra were analyzed using the gamma software for "Genie 2000" Canberra Acquisition and Analysis with fixed geometry and varied counting time between 300 and 500 seconds (12). The corresponding photopeaks used to calculate the Kd values were 685.74 KeV for ^{187}W and 155 KeV for ^{188}Re.

The distribution coefficients Kd were calculated using the classical relation:

$$K_d = \left\{\frac{A_{init} - A_{sol}}{A_{sol}}\right\}\left\{\frac{V_{sol}}{m_{alu}}\right\}$$

The ratio (V_{sol}/m_{alu}) was fixed at 200 (30 mL of solution and 150 mg of alumina) and the following five parameters were evaluated: HCl concentration, pH of the 0.9% NaCl solutions, alumina particle size, capacity of the alumina, and equilibrium time alumina-metal in 0.9% NaCl. (see Table 1).

The Kd value was used to determine the feasibility of separating the $^{187}WO_4{}^{2-}$ or $^{188}ReO_4{}^{-}$ ions calculating the separation factors ($\alpha_{W,Re}$). This can be defined as the ratio of the distribution coefficients of two adsorbed solutes measured under the same conditions ratio of Kd values of W and Re (12).

Results

Sorption Behavior of W and Re on Alumina in HCl Medium

Figure 1 shows the W and Re sorption behavior on alumina as a function of the HCl concentration. In the case of tungsten, the Kd value decreases with an increase in HCl concentration. This behavior can be expressed mathematically by the equation (1). The distribution coefficients are more than 1000 cm^3/g at [HCl] less than 0.1 mol/L.

$$\log \mathrm{Kd} = 2.64 - 0.45 \log[\mathrm{HCl}] \tag{1}$$

Approximately 99% of the W is adsorbed on alumina between 1×10^{-5} and 0.1 mol/L HCl. This percentage decreases radically at [HCl] more than 0.1 mol/L.

Rhenium presents Kd value and sorption % unchanging between 1×10^{-6} and 1×10^{-3} mol/L HCl, after this concentration and until 0.1 mol/L, both parameters show a drastic decrease. At [HCl] >0.1 mol/L

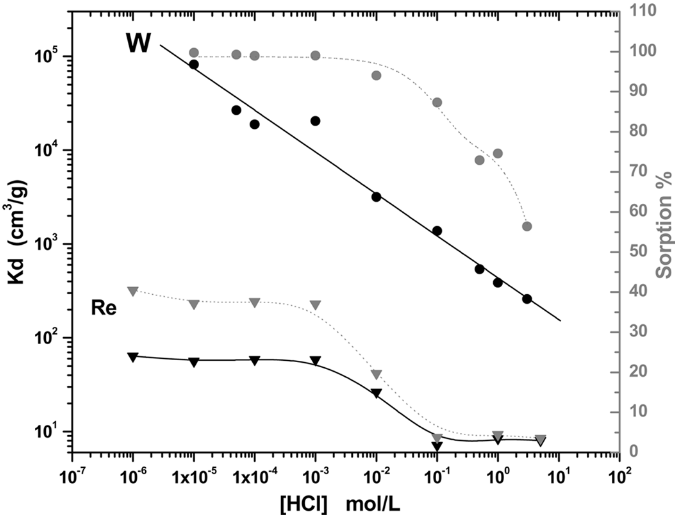


Figure 1. W and Re sorption behaviour on alumina as a funtion of the HCl concentration.

Kd and sorption % are practically constant. It is important to note that the maximum Kd value and sorption% for Re are 63 cm^3/g and 40% respectively. At $HCl > 0.1$ mol/L, the rhenium practically is not adsorbed on alumina.

Rhenium presents Kd value and sorption% unchanging between 1×10^{-6} and 1×10^{-3} mol/L HCl, 63 cm^3/g and 40% respectively, after this concentration and until 0.1 mol/L, both parameters have a drastic decrease. At $[HCl] > 0.1$ mol/L, rhenium practically is not adsorbed on alumina, and Kd value ($\sim$10 cm^3/g) and sorption% (5%) are constant.

Sorption Behavior of W and Re on Alumina in 0.9% NaCl Medium

The Kd value and the sorption% of W on alumina are about 7 cm^3/g and 1% respectively, at pH more than 7 (see Fig. 2) which implies that tungsten is not sorbed on alumina in basic 0.9% NaCl solutions. In acid medium ($pH < 5.3$), the tungsten shows the Kd value and the sorption percentages of more than 700 cm^3/g and 90% respectively. Tungsten is strongly sorbed on alumina at 0.9% NaCl solutions with pH less than 5.5. In the case of the Re, our results show the Kd value of the Re are slight, around 2 and 3 cm^3/g, between pH 1 and 12. Consequently the

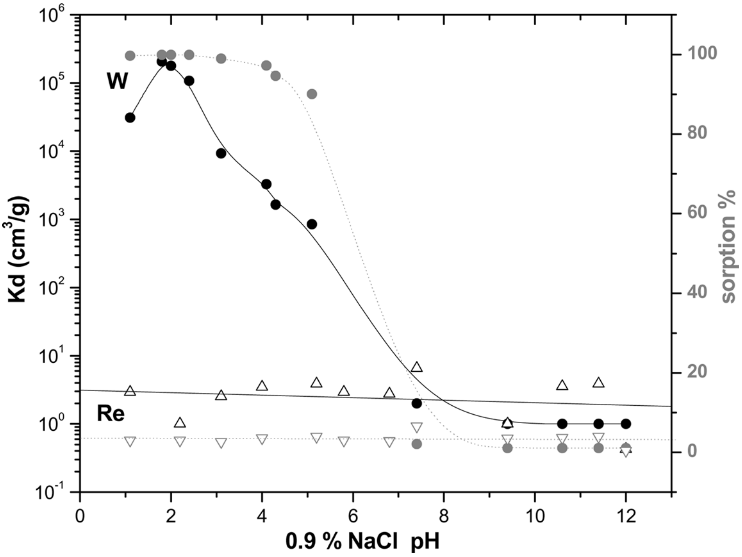


Figure 2. W and Re sorption behavior on alumina as a function of the pH values in 0.9% NaCl.

sorption percentages are also low, about 2 and 4%. That means Re is not sorbed on alumina in saline medium between pH 1 and 12.

Figure 3 shows the effect of the alumina particle size on the adsorption of the W in 0.9% NaCl solutions. The distribution coefficients and the sorption% demonstrate a Gaussian behavior with maximum value occurring at particle sizes of 0.075–0.048 mm. The lowest value of Kd and sorption% were obtained using alumina particle sizes more than 0.075 mm or less than 0.038 mm.

The alumina capacity in 0.9% NaCl solutions was determined under static conditions by means of the weight variation of alumina and tungsten in the W sorption experiments. Figure 4 shows the Kd value and the sorption% of W on alumina as a function of the weight alumina and the ratio of the tungsten and alumina weight. Mathematically both parameters can be expressed by the equation 2 and 3 respectively:

$$\log \mathrm{Kd} = 4.09 + 0.67 \log[g] + 0.25 \log[g]^2 \tag{2}$$

$$\mathrm{S\%} = 100.18 - 0.199[\mathrm{R}] \tag{3}$$

Where “g” is the alumina weight and “R” is the mg W/g alumina ratio.

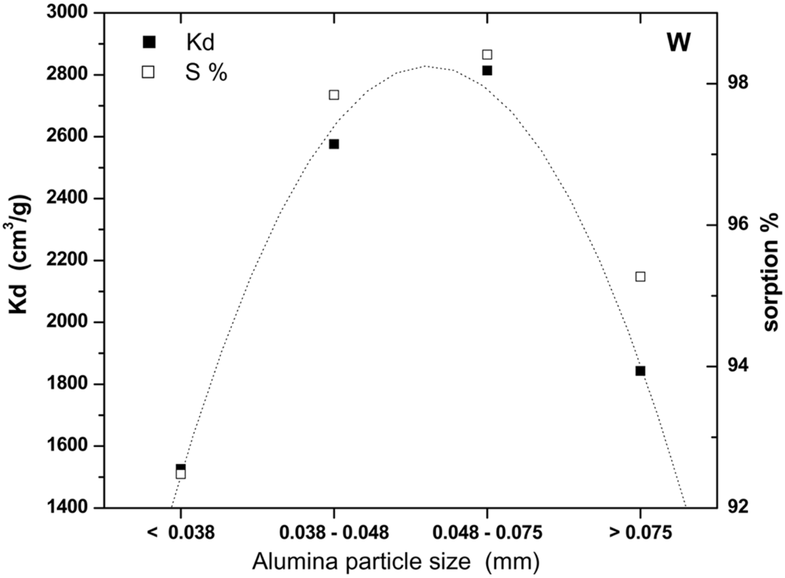


Figure 3. Effect of the alumina particle size on the W sorption behavior in 0.9% NaCl.

From weight ratio was determined the capacity of alumina: 0.346 meq/g alumina which equals to 10.5 mg W/g alumina. At this ratio, the tungsten is sorbed about 99.9% and at a ratio of 20 mg W/g alumina the sorption% is about 96%.

The W adsorption rate on alumina as a function of contact time between alumina and W is shown in Fig. 5. The W distribution coefficients increase gradually with the contact time alumina-tungsten. Kd value are practically constant for 20 hours, reaching a maximum value of 40000 cm^3/g, for which 80% of this value is attained at 6 hours of contact time. Data was fitted to the following quadratic equation (4):

$$\log \mathrm{Kd} = 2.15 + 1.42 \log[t] - 0.20 \log[t]^2 \qquad (4)$$

where t is the contact time between alumina and tungsten.

In summary, alumina is an excellent sorbent for tungsten in HCl solutions diluted ($HCl < 0.1$ mol/L) and at $pH < 5.5$ in 0.9% NaCl solutions while Re is not adsorbed at this conditions. These results agree with the separation factors (α) for W and Re, given by expressions 5 and 6 for HCl and saline media respectively which indicate the possibility to

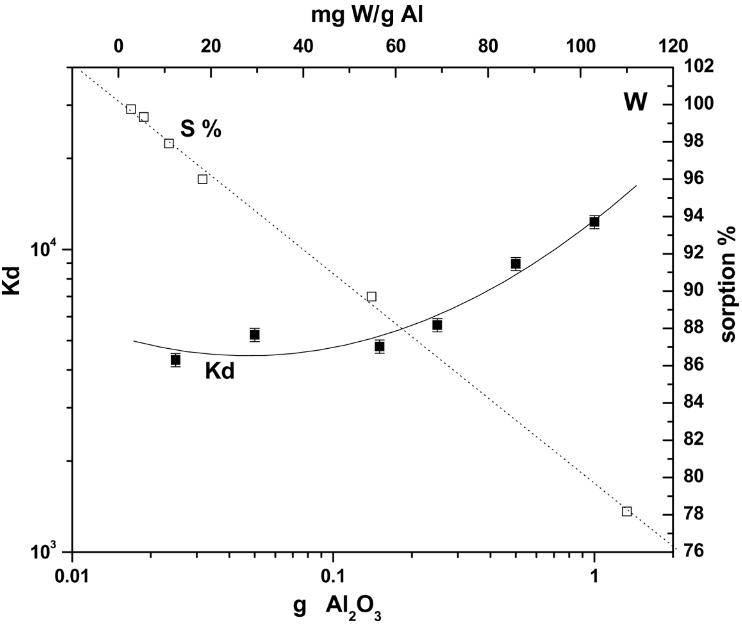


Figure 4. Effect of the W weight on the W sorption behavior on alumina in 0.9% NaCl.

efficiently separate W and Re in HCl solutions diluted (HCl < 0.1 mol/L) and at pH < 5.5 in 0.9% NaCl solutions.

$$\log[\alpha] = -1.76 + 0.25 \log[\mathrm{HCl}] \tag{5}$$

$$\log[\alpha] = -5.40 + 0.809\ \mathrm{pH} - 0.025\ \mathrm{pH}^2 \tag{6}$$

In accordance with the previous results, it is possible to prepare alumina ^{188}W/^{188}Re based generators from HCl solutions (<0.1 mol/L) or 0.9% NaCl solutions (pH < 5.5) which can be used as to fix the ^{188}W as to elute the ^{188}Re. The alumina particle size and the ratio mg W/g alumina recommendable to prepare these generators are 0.048 to 0.075 mm and 10.5 mg W/g alumina respectively.

The 10.5 mg W/g alumina ratio chosen to prepare ^{188}W/^{188}Re generator could be increased because 95% of the tungsten is still sorbed on alumina at a 25 mg W/g alumina ratio, i.e, an increase of about 58% in the W weight on alumina and consequently a decrease in the chromatographic column size and in the elution volumes of ^{188}Re.

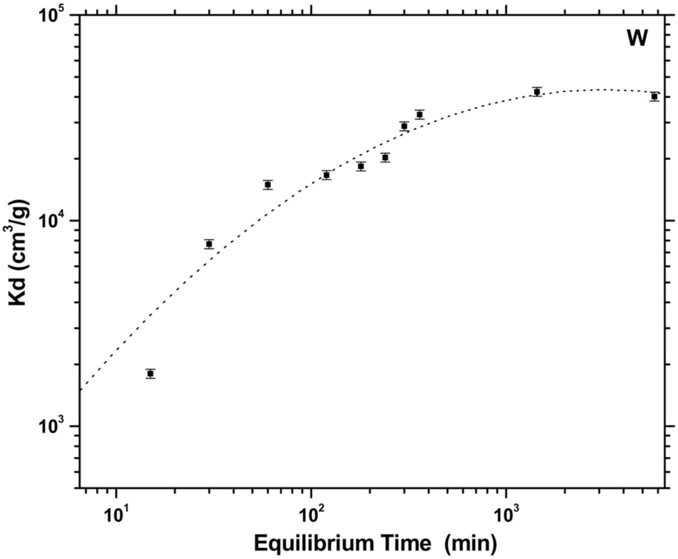


Figure 5. Effect of the equilibrium time on the W sorption behavior on alumina in 0.9% NaCl.

ALUMINA BASED ^{188}W/^{188}Re GENERATOR

From the results of the adsorption data obtained in the previous section for tungsten and rhenium, four alumina-based ^{188}W/^{188}Re generators were constructed. The effect of the medium and the tungsten mass on the ^{188}W/^{188}Re generator performance were evaluated.

Preparation of Generator Systems

Sodium^{188}W-tungstate solutions ($Na_2{}^{188}WO_4$) with ^{188}W specific activities of 197.2 GBq/g (9.7 GBq/mL) from NIIAR (State Scientific Centre of Russia-Research Institute of Atomic Reactors) were provided by IAEA (International Atomic Energy Agency) and their pH adjusted at 4 with HCl. Alumina (pH 4.5) from Fluka with a 0.075–0.048 mm particle size was mixed in the selected medium (see Table 2) and packed in glass chromatographic columns (12 × 70 mm). ^{188}W (49.1 g/L, 0.2 GBq) were then fixed in the column and the latter washed with 20 mL of the medium studied. Four alumina based ^{188}W/^{188}Re generators were prepared to the conditions shown in Table 2. The generators were eluted over a period of six months.

Table 2. Preparation conditions of alumina based $^{188}W/^{188}Re$ generators

Generator	^{188}W Fixation medium	Elution medium	Medium'pH	Alumina (mg)	Alumina size particle (mm)	mgW/g Al_2O_3
G1	0.01 mol/L HCl	0.9% NaCl	5.6	2200	0.075–0.048	10
G2	0.01 mol/L HCl	0.01 mol/L HCl	2	720	0.075–0.048	10
G3	0.9% NaCl	0.9% NaCl	5.6	720	0.075–0.048	10
G4	0.9% NaCl	0.9% NaCl	5.6	352.7	0.075–0.048	20

Eluate Analysis of Generators

Eluted ^{188}Re was measured in a CRC-10 R Capitec dose calibrator and the elution efficiency calculated. The ^{188}Re elution profile was obtained by collecting 500 µL volume fractions. The ^{188}W breakthrough (%) and ^{188}Re activities were determined in a HPGe detector (Caberra 7229P) at a constant geometry with low deadtime (<5%). The activity of ^{188}W and ^{188}Re were determined by quantification of the photopeaks: 290 keV and 155 KeV respectively. The ^{188}W activity in the eluates was counted after three weeks of the elution (12).

The radiochemical purity of the ^{188}Re eluate was determined by paper chromatography using 3 CHR (Whatman®) paper as solid phase and acetone as mobile phase. The $^{188}ReO_4^-$ R_f was 1. Aluminum concentration in ^{188}Re eluates was determined by the aluminon method at 535 nm, using an aluminum standard solution of 100 mg/L (NIST, USA) (29).

Results

Performance of Alumina-Based $^{188}W/^{188}Re$ Generators

Table 3 summarizes the performances of the alumina-based $^{188}W/^{188}Re$ generators prepared under the experimental conditions as previously described. The value reported in Table 3 are the average data of the elutions obtained during six months.

Elution Profiles. Figure 6 shows the elution profiles of the alumina-based $^{188}W/^{188}Re$ generators prepared under the experimental conditions

Table 3. Alumina based ^{188}W/^{188}Re generators performances

Generator	Eluate volume (mL)	pH eluates	Average% ^{188}Re elution yield	$^{188}ReO_4^-$ radiochemical purity (%)	Average ^{188}W breakthrough (%).	Aluminum µg/cm^3
G1	8.3	5.5	83 ± 3.3	92 ± 3	$6.4\times10^{-4} \pm 2.8\times10^{-4}$	<10
G2	40	2–5	84 ± 3.6	93 ± 5	$3.09 \times 10^{-2} \pm 1.87 \times 10^{-2}$	<10
G3	3.8	6–7	73 ± 15	97 ± 4	3.83 ± 3.13	<10
G4	3.6	6–7	58 ± 25	94 ± 3	7.39 ± 4.07	<10

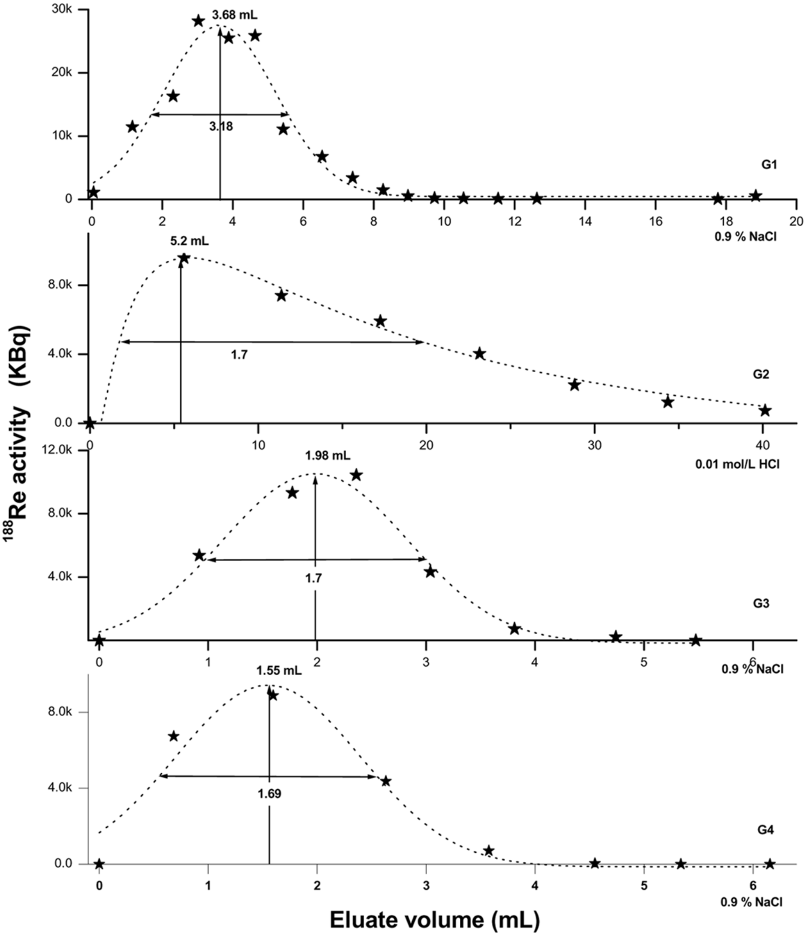


Figure 6. Elution profiles of alumina based -^{188}W/^{188}Re generators.

displayed in Table 2. The elution profile data of the generators eluted with 0.9% NaCl (G1, G3 and G4) were fitted with an exponentially modified Gaussian function presenting similar shapes but different elution volumes (30). The G3 and G4 generators require about 3.8 mL of 0.9% NaCl to recover the 99% of ^{188}Re while the G1 generator needs 8.3 mL. These differences are caused by the variations of the alumina weight used in the chromatographic columns of the generators (see Table 2) which modified the bed alumina length and consequently the width of the chromatographic peak. The G2 generator, eluted with 0.01 mol/L HCl, consumes about 40 mL of acid to elute the 99% of ^{188}Re and presents an asymmetrical elution profile. The chromatographic peak is in this case wider to those of generators eluted with 0.9% NaCl. Data was fitted to a lognormal function.

It is known that the shape of chromatographic peaks is modified by the solid-phase adsorption kinetics, factors such as migration rates determined by the distribution coefficients, or the adsorption rate are involved, and by the experimental operation conditions as the column size, the alumina particle size, the flow rate, the concentration of the eluate, etc. (31,32). The asymmetrical elution peak of the G2 generator can be explained therefore from the value of the distribution coefficients of Re in alumina at 0.01 mol/L HCl which has a higher Kd value ($\sim$30 cm^3/g) compared with those in 0.9% NaCl medium ($\sim$2 cm^3/g) (see Figs. 1 and 2) and thus Re moves at the lower rates in HCl medium that in 0.9% NaCl medium. A low adsorption rate of Re in the alumina could also be affected by the boundary sharpness. Unfortunately this hypothesis was not verified because the low value of Kd presented by Re in HCl and NaCl media complicates the performance of the kinetic studies.

^{188}Re Yield. Figure 7 shows the ^{188}Re elution yields of the generators as a function of the elution number. The G1, G3 and G4 generators result in ^{188}Re elution yields of more than 90% during the first four elutions, after which the yields decrease. The ^{188}Re elution yields of the G1 generator stayed between 80 and 85% during 196 days consuming 407 mL of 0.9% NaCl, whereas the yields of the G3 and G4 generators decrease continuously from 95% to 20 and 10% respectively in 168 days consuming 220 mL of 0.9% NaCl. This diminution is more evident from day 66 (120 mL of 0.9% NaCl) especially in the G4 generator. Consequently the ^{188}Re elution yield average of this generator is about 58%, the lower elution yield of the generators studied while the G1 and G2 generators showed the higher yields.

The G2 generator eluted with 0.01 mol/L HCl, yielded about 80 to 85% in the first 100 days of elution after which the yields fall drastically

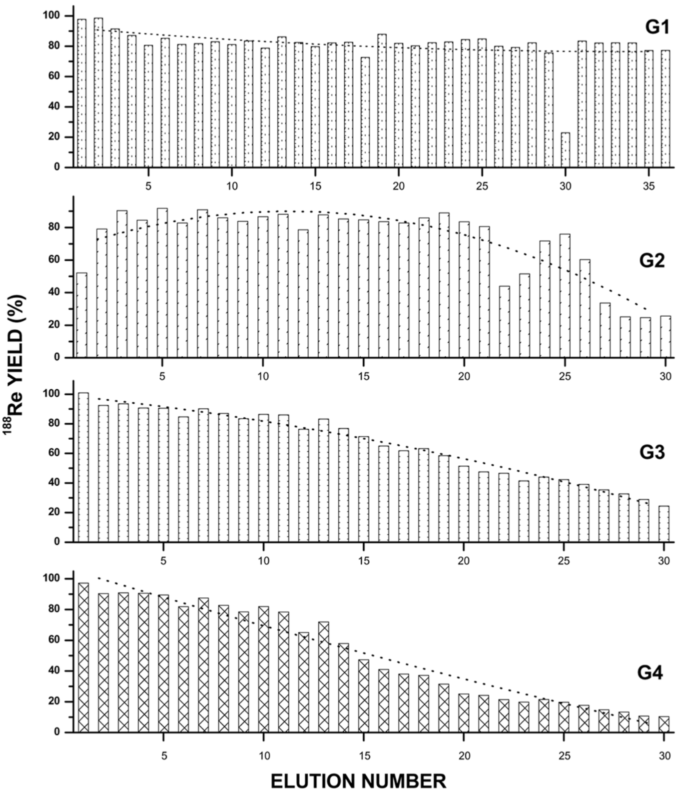


Figure 7. Elution yield of alumina based -$^{188}W/^{188}Re$ generators.

to about 60% because the obstruction of the chromatographic column during the twenty second elution.

^{188}W Breakthrough. The only radioactive contaminant detected in the eluates was the ^{188}W. The G1 generator presented the lower ^{188}W breakthrough percentages ($\sim 6.4 \times 10^{-4}$%) whereas the higher percentages (~7.39%) was obtained in the eluates of the G4 generator (see Fig. 8). The percentages of ^{188}W breakthrough decreased slowly in the G1 generator and increased gradually in the G3 and G4 generators over elution studied. In the case of the G2 generator the ^{188}W breakthrough reduced in the first 10 days and until the 100th days remained practically constant at about 0.001%, after the percentages rose because of column blockage.

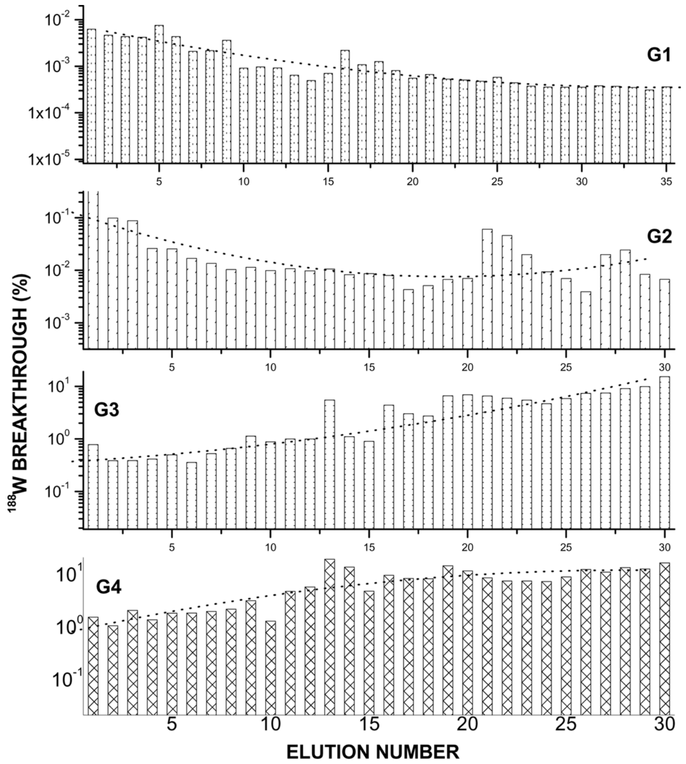


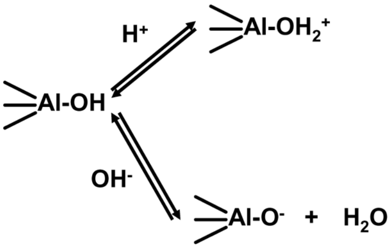
Figure 8. ^{188}W breakthrough percentage of the alumina based ^{188}W/^{188}Re generators.

The radiochemical purity and the aluminum content of the ^{188}Re eluates were more than 90% and less than 10 μg/cm^3 respectively in all generators. With regard to the pH value of the ^{188}Re eluates, the G1 generator presented a pH value of 5.5 in all the elution study, the G3 and G4 generators oscillated between 6 and 7, and the G2 generator increased from 2 to 5 in the last 30 days of the elution cycle studied (see Table 3).

DISCUSSION

To understand the tungsten and rhenium adsorption behavior in alumina (Figs. 1 and 2) and the generator performances prepared in this work (Table 3), it is necessary to analyze the effect of the pH value and the concentration medium in alumina and tungstate solutions.

Alumina is an ion exchange with amphotheric properties whose dissociation may be schematically represented as follows:



The upper reaction, producing anion-exchange properties, is favored by acid conditions, whereas the lower reaction, which is favored by high pH, result in cation-exchange characteristics (33–35). The isoelectric point of the alumina varies from 5.6 to 9 depending on the type and concentration of electrolyte present (34,35). Thus the most important mechanism of adsorption between W and Re and alumina is the ion exchange.

In the case of the tungstate ions, they exist as monontungstate species (WO_4^{2-}) in strongly basic solutions and the acidification of these solutions produces the tungstate polymerization if the concentration of WO_4^{2-} which is more than 5×10^{-5} mol/L. The W concentration fixed in the columns was of 0.2 mol/L in the G1 generator and 0.08 mol/L in the rest of generators. Different polytungstates species, built up from WO_6 octahedra, are formed in acid medium depending on the solution pH value, the equilibrium time and the ionic strength. For this reason the formulas of some polytungstates are not well established and only qualitative schemes of aqueous tungstate polymerization have been reported to date (36–38). Two polytungstates species are represented mainly in the schemes published by Pope and Tytko and Glemser: the paratungstates and the metatungstates (see Fig. 9). The vertical arrows represent equilibria that are established rapidly (minutes or seconds) as opposed to the other processes which are slow (hours to weeks) (37,38). Thus, upon acidification of WO_4^{2-}, "paratungstate A," $[W_7O_{24}]^{6-}$, is formed rapidly but salts which normally crystallize from such solutions contain a dodecameric anion, "paratungstate B", $[W_{12}O_{42}H_2]^{10-}$. From more acidic solutions, pseudometatungstate (Ψ) is formed rapidly, but is metastable in solution and slowly transformed first into "tungstate X" and finally into true metatungstate, α-$[(H_2)W_{12}O_{40}]^{6-}$, the thermodynamically stable product (36–38). If a paratungstate A or a monotungstate solution is rapidly acidified, a further species is formed, the so-called "tungstate Y," $[W_{10}O_{32}]^{4-}$, which is accompanied by the

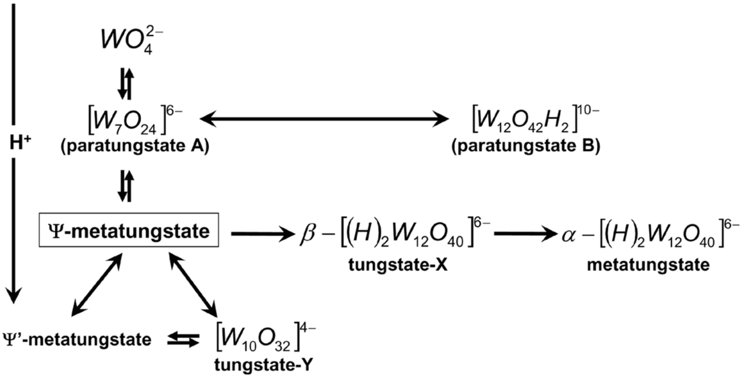


Figure 9. Scheme for aqueous tungstate polymerization (36).

Ψ-metatungstate (37,38). From this scheme, it is possible to explain the titration curves of the tungstate ion with acid solutions which present two inflection points (see Fig. 10) (19). The first end point occurs in the pH region 6 to 4.5. The buffer region preceding the inflection point corresponds to the formation of the paratungstate. The second inflection point is found in the pH region 4 to 2.45. Its preceding buffer region is attributed to the formation of the Ψ-metatungstate ion (39). It is important to note the W sorption behavior on alumina in NaCl 0.9% medium, shown in

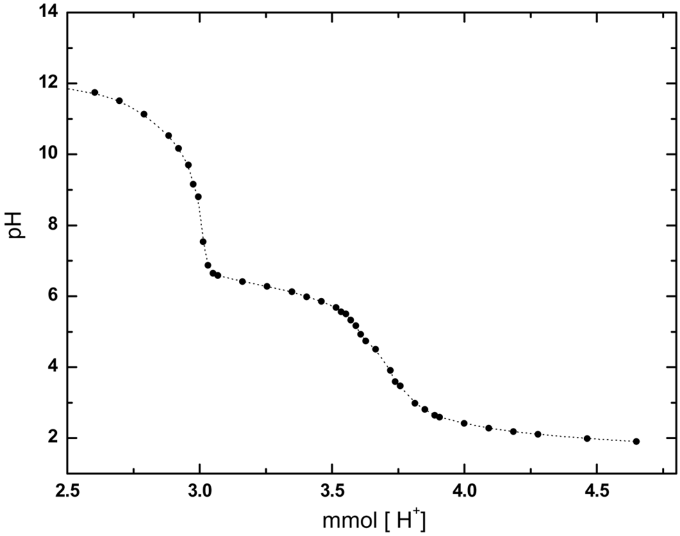


Figure 10. Titration curve of 0.01 mol/L [Na_2WO_4] with 0.1 mol/L HCl (12).

Fig. 2, which has a similar profile to the tungstate titration curve (Fig. 10). Therefore the variation of the distribution coefficients with the pH value in NaCl 0.9% medium (Fig. 2) can be explained by the presence of different tungstate species in the solution and the cation or anion-exchanger characteristics of the alumina. Figure 11, constructed by the junction of the tungstate titulation data with the acid-basic tungstates and alumina characteristics reported in the literature (19,35,37–40), allows us to propose that (see Fig. 2):

1. In the pH region 8 to 12, alumina acts as a cation exchanger and monotungstate ions (WO_4^{2-}) are present in solution. It means tungsten is not adsorbed in the alumina and so the Kd value obtained are lowest ($\sim 1\ cm^3/g$),
2. Between 6.6 and 8 pH value, a mixture of WO_4^{2-} and paratunstates $[W_7O_{24}]^{6-}$ are in solution (40), alumina is as a neutral species which cannot adsorb the anionic ions of tungsten and thus the Kd value are low,
3. From 6.6 to 4.5 pH value, paratungstates A $[W_7O_{24}]^{6-}$ and B $[W_{12}O_{42}H_2]^{10-}$ are the predominant species and alumina acts as an anionic exchanger at pH less than 6.6. The anionic tungsten species are strongly sorbed in alumina and the gradual increase of the distribution coefficients in this region can be explained by a change in the ratio of the paratungstate A and B in solution. It is known that an ion exchanger prefers the counter ion of higher valence (31) and therefore it is possible that a paratungstate B rise causes the Kd value augmentation,
4. In the pH region from 2 to 4.5, metatunsgtate $[(H_2)W_{12}O_{40}]^{6-}$ ions are in solution and strongly sorbed in the alumina and
5. At pH less than 2, tungstates Y $[W_{10}O_{32}]^{4-}$ are present in solution which are also strongly sorbed in the alumina; however, the Kd value decrease in this pH region probably because of the tungstates Y valence reduction.

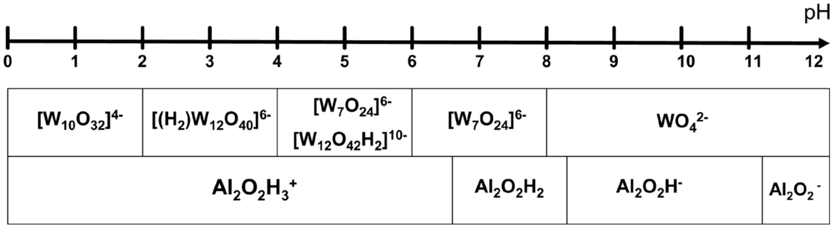


Figure 11. Scheme of species distribution of tungstates and alumina as a function of pH.

The tungsten adsorption behavior on alumina in HCl medium (see Fig. 1) can be also explained from tungstate and alumina species distribution shown in Fig. 11 and considering that ion exchangers prefer the counter ion of higher valence, and this preference increases with dilution of the solution (31). In this medium, alumina functions as an anionic exchanger in all the HCl concentrations studies and, metatunsgtates and tungstates Y $[W_{10}O_{32}]^{4-}$ are mainly present at HCl concentrations less and more than 10^{-2} mol/L (pH >2) respectively. The reduction of the Kd value with a increase of the HCl concentration in both regions ($10^{-2} <$ [HCl] $> 10^{-2}$ mol/L) is caused mainly by the dilution of the medium and by the valence reduction of tungstates ions, from $[(H_2)W_{12}O_{40}]^{6-}$ to $[W_{10}O_{32}]^{4-}$ at [HCl] $>10^{-2}$ mol/L.

In line with this analysis, the generator performances are therefore related to the chemical form of the tungstate ion in the alumina. Considering the eluate pH value in the generators and the Kd value obtained in the previous sorption studies, we deduce that alumina acts as an anionic exchanger in all the generators, and metatunsgtates are present during the fixation of tungsten in the alumina in G1 and G2 generators whereas as paratungstates in the G3 and G4 generators. In the elution, paratungstates are sorbed in G1 generators, possibly type B $[W_{12}O_{42}H_2]^{10-}$ considering the life-time of the generator (6 months). In the case of the G3 and G4 generators, at first the paratungstates are fixed in the column, then a mixture of $WO_4{}^{2-}$ and paratunstates, alumina also presents a mixture of anionic and neutral functional groups at pH nearby to 7; in consequence the ^{188}W breakthrough in these generators rises continually as a result of the change in the ratios of the monotunstates/paratunstates states and the anionic/neutral alumina groups in the column (see Fig. 8).

With reference to the rhenium sorption behavior in NaCl medium (Fig. 2), it is evident Re forms only one chemical species in all the range of pH studied (from 1 to 12), since Kd value are practically constant at these pH value. In accordance with the radiochemical purity data of the generators eluted with NaCl 0.9%: G1, G3, and G4 (see Table 3), the ^{188}Re eluated of these generators is as perrhenate ion $[ReO_4]^-$. In HCl medium (Fig. 1), the variations of the rhenium distribution coefficients can be explained by changes in the ratio of $[Cl^-]/[ReO_4{}^-]$, fixed for HCl concentration in the medium and by the affinity of the alumina for the chlorures and perrhenate ions. In the alumina based ^{99}Mo/^{99m}Tc Tc generators, the elution of $[^{99m}TcO_4]^-$ with saline solution has been explained by the higher affinity of alumina for the Cl^- ions than for the $[^{99m}TcO_4{}^-]$ ions (35). Considering Tc and Re have similar chemical properties, it is coherent to assume the same mechanism in the case of the alumina ^{188}W/^{188}Re generators: a higher affinity of alumina for chlorure ions than for perrhenate ions $[ReO_4{}^-]$ at HCl solutions more than

10^{-3} mol/L. In analogy with the previous rationing, it is also possible to clarify the reduction of the ^{188}Re elution yields of the alumina ^{188}W/^{188}Re generators from Steigman, Stammose, and Molinski's works on the alumina based ^{99}Mo/^{99m}Tc generators (35,41,42) which propose that the loss of elution efficiency is due to the reduction of pertechnetate, possibly to technetium (IV). The latter is strongly held by the column. Two interpretations are then proposed from these works:

1. The beta particles, emitted during the disintegration of the ^{188}W, reduce to the W(VII) to W(V) which decays to Re(VI) as [ReO_4^{2-}] ion. Re(VI) is then fixed on alumina and transforms to Re(IV) by dismutation due its instability (35) and
2. Owing to the presence of high activity of ^{188}W/^{188}Re at the inter phase between alumina and aqueous solution, a radiation-induced chemical reaction is likely to occurs. Such a reaction leads to the generation of extremely reactive species such as $H^\bullet$, $HO^\bullet$, H_2O_2, H_2, solvated electrons, and so forth.

These radicals and molecules can cause oxidation and reduction reactions with the elements in the system. If a $^{188}ReO_4^-$ close to or on the alumina surface encounters a solvated electron or a hydrogen atom, it will be reduced. Owing to the reduction of some of the $^{188}ReO_4^-$ from oxidation state 7 to some lower state, such as 4 or 5, it forms either an insoluble form of ReO_2 or a more negatively charged species. These reduced species are strongly bonded to the alumina surface and elution becomes difficult (41).

^{188}Re elution yields of 83% obtained in this work could then be justified by the Re(IV) fixation on alumina and the reduction of ^{188}Re elution yields with time (see Fig. 7) could attach to the increase of the W(V) amount adsorbed in the alumina during the shelf-life of the generator and consequently to the increase of the Re(IV) amount fixed in the generator.

CONCLUSIONS

The analytical studies of the W and Re sorption on alumina in HCl and 0.9% NaCl media have shown that Re-188 is not adsorbed in HCl and NaCl medium whereas W-188 is strongly adsorbed in both media at $pH < 5.5$. The most important mechanism of adsorption between W and Re and alumina is the ion exchange (33–35). The variation of the W and Re affinity on alumina with the HCl concentration and the pH values in 0.9% NaCl medium can be explained from the acid-basic properties of the alumina and tungstate ions in solution. The W fixation on alumina is favored in acid media because at these conditions, alumina works as an anionic exchanger and tungsten forms anionic species with a strong affinity for the alumina, whereas rhenium is not adsorbed because alumina presents a higher affinity by the chlorure ions that for the perrhenate ion $[ReO_4]^-$. In accordance with the W and Re adsorption results, alumina $^{188}W/^{188}Re$ generators can be prepared and eluted with HCl (<0.1 mol/L) and 0.9% NaCl solutions (pH < 5.5), using alumina with a particle size of 0.075–0.048 mm and a ratio of 10.5 mg W/g alumina, at this ratio the W is sorbed about 99.9% on alumina and the Re around 3%. Alumina based $^{188}W/^{188}Re$ generators eluted with HCl or 0.9% NaCl solutions and with ratios of 10 or 20 mg W/g alumina were prepared and evaluated for six months. Optimum performances were obtained in the generator eluted with 0.9% NaCl solutions, a ration of 10 mg W/g alumina and ^{188}W fixed with 0.01 mol/L HCl: ^{188}Re elution yields of 83%, a ^{188}W breakthrough of 4.5×10^{-4}%, a radiochemical purity of 92%, an eluate volume and pH of 8.3 mL and 5.5 respectively and an aluminum content of less than 10 μg/cm^3.

The reduction of ^{188}Re elution yields of alumina based $^{188}W/^{188}Re$ generators can be attributed to the reduction of the Re(VII) to Re(IV), which is adsorbed by the hydroxyl groups of the alumina, induced by the beta particles emitted during the disintegration of the ^{188}W that reduce the W(VII) to W(V) (35,40,41).

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