Separation of fission produced $^{106}$Ru from simulated high level nuclear wastes for production of brachytherapy sources

Magdalena Blicharska · Barbara Bartoś · Seweryn Krajewski · Aleksander Bilewicz

Received: 25 March 2013 / Published online: 20 June 2013 © The Author(s) 2013. This article is published with open access at Springerlink.com

Abstract An effective and simple process for the isolation of $^{106}$Ru from high-level liquid wastes was developed. Radioactive ruthenium was oxidized by H$_5$IO$_6$ in HNO$_3$ solution and was extracted to CCl$_4$ phase in the form of RuO$_4$. In order to obtain ruthenium in the suitable form for production of brachytherapy sources, RuO$_4$ in organic phase was reduced and re-extracted to aqueous phase. The efficiency of extraction of $^{103}$Ru to organic phase was 86 %, re-extraction to aqueous solution was near 100 %, so the overall recovery of $^{106}$Ru is estimated at more than 80 %.

Keywords $^{106}$Ru · Brachytherapy · Separation techniques

Introduction

Brachytherapy is the common method for treating various tumors, and currently the ruthenium-106 and iodine-125 applicators are the most frequently used. Considering that $^{106}$Ru is a $\beta^-$ emitter with maximum energy of 3.54 MeV, it is best indicated in the treatment of small melanomas, with up to 20 mm tissue range [1]. It also replaced $^{90}$Sr/$^{90}$Y sources because of it higher energy of emitted $\beta^-$ particles [2] and possibility of simpler source preparation.

$^{106}$Ru is commercially obtained from neutron irradiated high enrichment $^{235}$U target in process of production $^{99}$Mo. After isolation of $^{99}$Mo radioisotope and decaying of $^{103}$Ru, ruthenium is separated from the wastes by multistep procedure. At present, there are only a handful of ageing reactors worldwide capable of producing the $^{99}$Mo, therefore alternative strategies for production of this key medical isotope are explored. In our work, we propose to use liquid high-level radioactive waste as a source of high activity of $^{106}$Ru.

The potential utilisation of fission-produced platinum metals (fission platinoids) as valuable products has attracted attention in the last few decades, as large amounts of spent nuclear fuel have accumulated worldwide [3]. Table 1 presents the isotopic composition of ruthenium isotopes after 5 years cooling of liquid nuclear waste [4].

Simple calculations indicate that 1 dm$^3$ of waste solution after reprocessing of nuclear fuel contains about 500 GBq of $^{106}$Ru after 4 years of cooling. This amount of activity is enough for production of about few thousands of brachytherapy sources.

During reprocessing of the spent fuel, the metallic Ru is dissolved in concentrated nitric acid and forms stable Ru-nitrosyl complexes [5]. In the high acidity the dominating ruthenium species are the $\left[\text{RuNO(NO}_2\text{)}_2(\text{NO}_3\text{)(H}_2\text{O})_2\right]^0$ and $\left[\text{RuNO(NO}_2\text{)}_2(\text{H}_2\text{O})_3\right]^+$. The concentration of different species depends mainly on the composition of the medium and also the time of ageing.

Ruthenium metal was efficiently separated from other fission products by oxidation and distillation of RuO$_4$ with absorption in NaOH solution. El-Absy et al. [7, 8] separated Ru radionuclides from a $^{131}$I-free fission product acidic solution containing KMnO$_4$, by boiling for 40 min. In other work, ruthenium was electrochemically eliminated from a 3 M HNO$_3$ solution of high-level waste, as RuO$_4$, in the presence of AgNO$_3$ at 60 °C [9]. Gandon et al. [10] coprecipitated ruthenium with copper ferrocyanide neutral solution. D. Banerjee et al. [11] used conventional ion exchangers and chemical precipitation based processes for the effective removal of the $^{106}$Ru activity from NH$_4$NO$_3$.
effluent generated during wet processing of rejected sintered depleted uranium fuel pellets.

Present communication reports results of our process development studies on the recovery of ruthenium radioisotopes from simulated solution of high level radioactive waste using oxidation-extraction method.

Experimental

Radionuclide

For reasons of availability we used in experiments the $^{103}$Ru nuclide instead of $^{106}$Ru. The latter nuclide $^{106}$Ru is separated in complicated procedure from fission products of $^{235}$U, while $^{103}$Ru is produced in a simple way by direct thermal neutron irradiation of natural ruthenium. $^{103}$Ru was obtained by neutron irradiation of ruthenium salt $(NH_4)_2[RuCl_5(H_2O)]$ at a neutron flux $7 \times 10^{13}$ n cm$^{-2}$ s$^{-1}$ for 8 h in the nuclear reactor Maria at Świerk, Poland. The irradiated target was dissolved in 1 M HNO$_3$.

Others radionuclides, $^{131}$I in the form of Na$^{131}$I solutions was obtained from NCBJ-Polatom Świerk and $^{99m}$Tc in the form of $^{99m}$TcO$_4^{-}$ was milked from $^{99}$Mo/$^{99m}$Tc generator.

Radioactivity measurements

The $^{103}$Ru radioactivity was measured using an ORTEC system with a high resolution HPGe detector using photo peak at $E_γ = 497.05$ keV (88.7 %) and in NaI $γ$-scintillation counter LG-1b, ICHTJ, Poland.

Reagents

The following commercial chemicals were used without additional purification: $H_3IO_6$ was from Fluka and $(NH_4)_2[RuCl_5(H_2O)]$ from Alfa Aesar, other reagents, carbon tetrachloride from Chempur, Poland, reductants and acids were from POCh Gliwice, Poland. Desirable concentrations of reagents were obtained by dilution of stock solutions.

Solvent extraction studies

Experiments were carried out under ambient conditions by shaking equal volume (5 ml each) of organic and aqueous phase in a separatory funnel using wrist action shaker. Phase separation was done by centrifugation and suitable aliquots (1 ml) of each phase were assayed. The distribution ratio “D” of the metal was determined as the ratio of metal concentration in organic phase to that in aqueous phase. Percentage extraction of metal ion was calculated by equation:

$$\% E = \frac{D}{D + 1} \times 100 \% .$$

Results

Extraction of $^{103}$Ru to CCl$_4$ phase

In oxidizing solutions ruthenium forms tetroxide, RuO$_4$, which is easily extractable to organic phase. Formation of RuO$_4$ is indicated by color change from deep orange to golden yellow. The RuO$_4$ formed was extracted to an organic phase. Unfortunately, the RuO$_4$ is not stable in the CCl$_4$ phase and formation of black RuO$_2$ precipitate is observed after a few hours. To avoid reduction of RuO$_4$ to RuO$_2$ the organic phase was contacted with a solution generating Cl$_2$ molecules: 0.01 M HCl + 0.05 M H$\text{I}_2$O$_6$.

The Cl$_2$ molecules, formed in aqueous solution, are very soluble in CCl$_4$ and distributed among the two liquid phases keeping ruthenium in the form of RuO$_4$ in the organic phase for several month [12].

Influence of the various oxidants and acids on ruthenium oxidation-extraction process were studied to optimize the process. Table 2 presents results of $^{103}$Ru extraction from solutions containing various oxidizing agents. Concentration of used oxidants was the same taking into account the number of electrons involved in the reaction.

As show in Table 2 the obtained results indicate that the best oxidant is orthoperiodic acid (86.0 % extraction), a

Table 2 Efficiency of Ru extraction in various oxidizing solutions

| Oxidant        | Distribution coefficient | % of extraction |
|----------------|--------------------------|-----------------|
| $H_3IO_6$      | 6.17                     | 86.1            |
| KIO$_4$        | 3.02                     | 75.1            |
| KMnO$_4$       | 3.88                     | 79.6            |
| K$_2$Cr$_2$O$_7$ | 0.045                    | 4.30            |

Aqueous phase 1 M HNO$_3$, organic phase CCl$_4$
somewhat worse, but also possible to use is a potassium metaperiodate (75.1 %) and potassium permanganate (79.5 %). The obtained results well correlate with oxidation potential of reagent used.

An important parameter was the selection of a suitable amount of oxidant to obtain complete oxidation of ruthenium to RuO$_4$ and thus its extraction into the organic phase. We have studied the $^{103}$Ru extraction depending on the concentration of orthoperiodic acid. The results are presented in Fig. 1.

In concentration range from 5 to 40 g l$^{-1}$ of H$_5$IO$_6$ only insignificant increasing of $^{103}$Ru extraction is observed. Therefore, it can be assumed that that solution containing only 10 g l$^{-1}$ of H$_5$IO$_6$ should be sufficient for effective extraction of $^{103}$Ru to CCl$_4$ phase.

In the next step, influence of various acids and acid concentrations on $^{103}$Ru extraction were studied. We examined the following acids: nitric acid, sulfuric acid, hydrochloric acid and perchloric acid. The results are presented in Tables 3 and 4.

In the solutions of HNO$_3$, H$_2$SO$_4$, and HClO$_4$ extraction of $^{103}$Ru was comparable. Only in HCl solution extraction was significantly lower. Additionally, the use of HCl solution is not desirable due to the formation of Cl$_2$ gas by reaction of orthoperiodic acid with hydrochloric acid. For further experiments HNO$_3$ solution was selected. This choice was dictated by the fact that the high-level radioactive waste are generally in the form of a HNO$_3$ solution.

As shown in the Table 4 only very small increasing of $^{103}$Ru extraction was observed when HNO$_3$ concentration increased from 1 to 5 M. Summarizing results on optimization of $^{103}$Ru extraction process, we can conclude that 86 % of extraction could be obtained for using H$_5$IO$_6$—10 g l$^{-1}$ as oxidant and 1 M HNO$_3$ solution. Using of higher H$_5$IO$_6$ and HNO$_3$ concentrations gave only insignificant increasing of the process efficiency.

The PUREX raffinate contains also other long-lived fission products like $^{135,137}$Cs, $^{90}$Sr, $^{241}$Am, $^{99}$Tc, $^{129}$I, $^{97}$Zr, among which $^{99}$Tc and $^{129}$I could be potentially co-extract with $^{106}$Ru. In oxidizing solution technetium could be extracted as HTcO$_4$ and iodine in I$_2$ or interhalogen form. The $^{135,137}$Cs, $^{90}$Sr, $^{241}$Am and other metallic radionuclides in HNO$_3$ solution, not containing complexing agents, are present in either cationic form or nonextractable species.

For co-extraction studies of $^{99m}$Tc and $^{131}$I we used short-lived isotopes $^{99m}$Tc and $^{131}$I. The extraction of both radionuclides were performed in solution of concentration of 10 g l$^{-1}$ H$_5$IO$_6$ in 1 M HNO$_3$. We did not observe extraction of radionuclide studied, radioactivity of the $^{99m}$Tc and $^{131}$I in the organic phase was below the background level.

Since the $^{106}$Ru sources for brachytherapy are usually obtained by electrochemical deposition from aqueous solutions [13], we investigated the possibility of ruthenium transfer from the organic to aqueous phase. Because RuO$_4$ is the only form of ruthenium, which is stable in CCl$_4$ phase, for re-extraction of $^{103}$Ru we decided to reduce RuO$_4$ to Ru(III) and Ru(II) oxidation state. The following compounds were selected as reductants: sodium sulfite, hydroxylamine, hydrazine and sodium borohydride. Results of $^{103}$Ru extraction from the organic into aqueous phase are shown in Table 5.

| Table 3 | Efficiency of Ru extraction in various acid solutions |
| --- | --- |
| Acid (1 M) | Distribution coefficient |
| HNO$_3$ | 6.17 |
| H$_2$SO$_4$ | 6.25 |
| HClO$_4$ | 6.34 |
| HCl | 4.21 |
| H$_5$IO$_6$—10 g l$^{-1}$ |

| Table 4 | Extraction of $^{103}$Ru in various HNO$_3$ concentrations, concentration of H$_5$IO$_6$—10 g l$^{-1}$ |
| --- | --- |
| HNO$_3$ (M) | Distribution coefficient |
| 1 | 6.17 |
| 2 | 6.26 |
| 5 | 6.71 |

Fig. 1 Extraction of $^{103}$Ru from 1 M HNO$_3$ solution containing various concentration of H$_5$IO$_6$. 
As shown in Table 5, the best results were obtained for 0.1 M aqueous solutions of hydrazine and for hydroxylamine hydrochloride. These reductants are most sufficient, because of their relatively high solubility in the organic phase, where reduction of RuO$_4$ to the Ru(III) and Ru(II) took place. Reduced forms of ruthenium are insoluble in CCl$_4$ phase and passed immediately to the aqueous phase.

Kinetic studies were carried out in the system 103RuO$_4$ in CCl$_4$ (organic phase) and Na$_2$SO$_3$ 0.1 M HCl (aqueous phase). The results presented in Fig. 2 indicate that the process is relatively fast and after 40 min equilibrium state is achieved.

### Table 5

| Reducing solution | % of re-extraction |
|-------------------|--------------------|
| 0.1 M Na$_2$SO$_3$ + 0.01 M HCl | 83.6 |
| 0.1 M Na$_2$SO$_3$ + 0.1 M HCl | 89.3 |
| 0.1 M Na$_2$SO$_3$ + 1 M HCl | 94.9 |
| 1 M Na$_2$SO$_3$ + 1 M HCl | 96.1 |
| 0.1 M NH$_2$OH | 95.0 |
| 0.1 M NH$_2$OH + 0.1 M HCl | 100 |
| 0.1 M N$_2$H$_4$ | 100 |
| 0.1 M N$_2$H$_4$ + 0.1 HCl | 92.6 |
| 0.1 M NaBH$_4$ | 87.0 |

Fig. 2: Kinetic of 103Ru re-extraction from CCl$_4$ to aqueous phase (0.1 M hydrazine)

As shown in Table 5, the best results were obtained for 0.1 M aqueous solutions of hydrazine and for hydroxylamine hydrochloride. These reductants are most sufficient, because of their relatively high solubility in the organic phase, where reduction of RuO$_4$ to the Ru(III) and Ru(II) took place. Reduced forms of ruthenium are insoluble in CCl$_4$ phase and passed immediately to the aqueous phase.

Kinetic studies were carried out in the system 103RuO$_4$ in CCl$_4$ (organic phase) and Na$_2$SO$_3$ 0.1 M HCl (aqueous phase). The results presented in Fig. 2 indicate that the process is relatively fast and after 40 min equilibrium state is achieved.

### Conclusion

A highly effective and flexible process for the separation of 106Ru from simulated high-level liquid waste was elaborated. It was found that the optimal way for extraction of 103Ru to CCl$_4$ organic phase is oxidation of ruthenium nitrozyl complexes to RuO$_4$ by 10 g l$^{-1}$ H$_3$IO$_6$ in 1 M HNO$_3$ solution. It was found that in re-extraction process to aqueous phase the most efficient compounds for reduction of RuO$_4$ in CCl$_4$ phase are hydrazine and hydroxylamine hydrochloride. The overall recovery of 106Ru is estimated at more than 80%.

Production batches of hundreds GBq of 106Ru radioisotope separated from 1 l of PUREX raffinate can be achieved using the above-mentioned separation technique. For verification of the obtained results further experiments with real wastes solutions is necessary.

### Acknowledgments

This work was carried out as part of the Strategic Project “Safe Nuclear Power Engineering Development Technologies” supported by The National Centre for Research and Development, Poland.

### Open Access

This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

### References

1. Podgorsak EB (2005) Radiation oncology physics: a handbook for teachers and students. International Atomic Energy Agency, Vienna, p 466
2. Lee C, Love G (2011) In: Hoskins P, Coyle C (eds) Radiotherapy in practice—brachytherapy. Oxford University Press, New York, p 11
3. Kolarik Z, Renard EV (2003) Potential applications of fission platinoids in industry. Platinum Met Rev 47:79–90
4. Bush RP (1991) Recovery of platinum group metals from high level radioactive waste potential, possibilities of separation and use re-evaluated. Platinum Met Rev 35:202–208
5. Emel’yanov VA, Fedotov MA (2006) The state of ruthenium in nitrite–nitric acid solutions as probed by NMR. Russ J Inorg Chem 51:1811–1819
6. Greenwood NN, Earnshaw A (eds) (1998) Chemistry of the elements. Butterworth Heinemann, Oxford
7. El-Absy MA, Aly HM, Mousa M, Mostafa M (2004) Sequential distillation of fission-produced radioiodine and radioruthenium from sulfuric acid solutions. J Radioanal Nucl Chem 261:163–172
8. El-Absy MA, El-Amir MA, Mostafa M, Abdel Fattah AA, Aly HM (2005) Separation of fission produced 106Ru and 137Cs from aged uranium targets by sequential distillation and precipitation in nitrate media. J Radioanal Nucl Chem 266:295–305
9. Adonet JM. and Madic C (1989) New strategy for minor actinides partitioning: preliminary results on the electrovolatilization of ruthenium and on the stabilization of Am(IV) in nitric with phosphotungstate ligand. In: Proceedings of the workshop on partitioning and transmutation of minor actinides, Karlsruhe
10. Gandon R, Boust D, Bedue O (1993) Ruthenium complexes originating from the PUREX process—coprecipitation with copper ferrocyanides via ruthenocyanide formation. Radiochim Acta 61:41–45
11. Banerjee D, Rao MA, Chinnaesakki S, Wattal PK (2011) Removal of 106Ru traces from NH$_4$NO$_3$ effluent generated during recycling of sintered depleted uranium fuel pellets. J Radioanal Nucl Chem 290:375–380
12. Bartos B, Kowalska E, Bilewicz A, Skarnemark G (2009) 103Ru/103mRh generator. J Radioanal Nucl Chem 279:655–657
13. Molenda E, Mielcarski M (1998) Electrodeposition of 106Ru and 241Am and derived information on preparing sealed radiation sources. J Radioanal Nucl Chem 238:159–162