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## Degradation of tetraphenylphosphonium bromide at high pH and its effect on radionuclide solubility

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### Abstract

Recently, tetraphenylphosphonium bromide (TPPB) has been used to remove technetium from some radioactive waste streams. However, before TPPB could be approved for use it was necessary to show that TPPB and its degradation products would not have a significant detrimental effect on post-closure performance of a radioactive waste repository. TPPB is known to be stable at neutral pH, however, under alkaline conditions it degrades by an alkaline hydrolysis mechanism to triphenylphosphonium oxide (TPPO). Degradation can also occur by radiolysis to produce triphenylphosphine (TPP). The kinetics of the alkaline hydrolysis degradation of TPPB is described and the solubility of europium, iodine, nickel, technetium(VII) and uranium(VI) in aqueous solutions of TPPB and its degradation products is reported. These results were used to support the use of TPPB in removing technetium from some waste streams.

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Keywords: tetraphenylphosphonium bromide (TPPB), alkaline hydrolysis, degradation products, solubility.

## **Introduction**

30 During reprocessing of Magnox fuel using the PUREX process the irradiated and decanned uranium fuel rods are dissolved in nitric acid. Plutonium and uranium are separated from the resulting solution by liquid extraction using a mixture of 30% tributylphosphate (TBP) solution in odourless kerosene. One of the waste streams from this chemical separation process is an aqueous acidic  
35 medium active liquor. The liquor contains a range of radioactive species such as caesium, strontium, plutonium and other alpha and beta emitters, including technetium. The medium active liquor is then concentrated by evaporation to produce a medium active concentrate (MAC) (Reed, 2004).

40 MAC is collected and stored in tanks prior to treatment in the Enhanced Actinide Removal Plant (EARP). Sodium hydroxide and a flocculating agent are added to the MAC within the EARP and an insoluble floc is then formed which contains the main alpha and plutonium species. The ion exchange reagent is incorporated into the floc and removes additional species, mainly caesium.  
45 Therefore soluble radioactive species are made insoluble by the production of the floc. The floc is then dewatered by ultrafiltration prior to encapsulation in 500 litre steel drums with cement. The permeate which contains a small fraction of the radioactivity in the MAC is discharged to sea (Gordan, 2004).

50 Technetium-99, a low energy  $\beta$  emitter ( $E_{\max} = 0.29$  meV), is produced in relatively large quantities as a fission product. Present in some nuclear waste streams as pertechnetate,  $\text{TcO}_4^-$ , it is an important species in terms of the safety case for nuclear waste disposal because of its high yield in radioactive waste (6% of all fission products consists of  $^{99}\text{Tc}$ ) and long half-life ( $2.14 \times 10^5$   
55 yr). In the past technetium was not removed into the floc by either of the processes described above and was therefore discharged to the sea in the permeate. At the time technetium, present as  $^{99}\text{TcO}_4^-$ , was thought to disperse widely as it is carried from the Irish Sea by the Gulf Stream which flows past the British Isles to the Arctic and the Barents Sea. En route,  $^{99}\text{Tc}$  accumulates in  
60 seaweed (Brown et al., 1999; Webster et al., 2003; Mas et al., 2004) and lobsters (Olsen, 2003; Coplestone et al., 2004) along the Norwegian coastline. It was therefore preferable to remove technetium from the permeate prior to discharge to sea.

65 Although a three month trial, in which ca.  $250\text{ cm}^3$  of MAC floc was treated with TPPB, showed that TPPB successfully removed most of the technetium before being accepted for use in the plant a further investigation on TPPB and its degradation products had to be undertaken to show that they would not have a significant detrimental impact on post-closure performance of a radioactive  
70 waste repository.

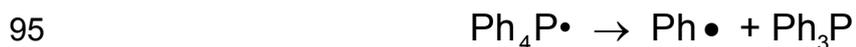
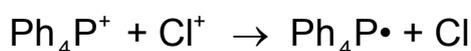
One possible option for the management of low- and intermediate-level radioactive waste (LLW and ILW) is, to store it in an underground radioactive waste repository. The repository when then be backfilled with cementitious

75 material known as Nirex Reference Vault Backfill (NRVB). Once closed, the repository will become saturated with groundwater, and then a highly alkaline pore water will develop. The initial pH of this pore water will be approximately 13.4 however, this value will decrease to 12.5 as the ground water flow dissolves and removes any sodium and potassium hydroxides present. The  
80 mineral phases in the cement will act as a buffer and maintain the pH at that level for approximately  $10^5$  years. In this highly alkaline cement pore water the radionuclides will show limited solubility.

#### **Degradation of Tetraphenylphosphonium Bromide**

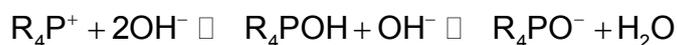
85 Although tetraphenylphosphonium ion is known to be stable at neutral pH, it is prone to degradation by alkaline hydrolysis at high pH. The tetraphenylphosphonium ion is also prone to radiolytic degradation in a repository environment.

90 The mechanism for radiolytic degradation of tetraphenylphosphonium chloride is thought to be as shown below (Horii et al., 1976; Horii et al., 1979; Horii et al., 1982).



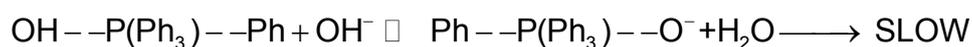
The products are generally phenylphosphine compounds.

100 The mechanism for the alkaline hydrolysis of quaternary phosphonium salts has been suggested to be as follows (Khalil, 1973; Khalil, 1974):



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Or in detail for TPPB:



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The alkaline hydrolysis of TPPB is thus thought to produce triphenylphosphine oxide.

## 115 **Experimental**

Deionised water produced by a Barnstead NANOpure ultrapure water purification system, and AR reagents, were used throughout. TPPB, TPPO and TPP were purchased from Aldrich and  $^{63}\text{Ni}$ ,  $^{152}\text{Eu}$ ,  $^{125}\text{I}$  and  $^{99}\text{Tc}$  were purchased from Amersham.  $^{233}\text{U}$  was purchased from [www.isotopes.com](http://www.isotopes.com). pH was measured using a glass electrode and an Orion 720A pH meter. The electrode was calibrated using a volumetric standard sodium hydroxide solution purchased from Aldrich.  $^{63}\text{Ni}$ ,  $^{99}\text{Tc}$  and  $^{233}\text{U}$  were measured by liquid scintillation counting in a Packard Tri Carb 2750 TR/LL counter using Ecoscint

cocktail.  $^{152}\text{Eu}$ ,  $^{125}\text{I}$  were counted in a Packard Cobra II Auto Gamma counter.

125 UV/Vis absorption was measured in a Varian 50 Bio UV/Vis spectrophotometer using a 1 cm square cell.

### ***Kinetic Studies***

Aqueous solutions of TPPB ( $0.02 \text{ mol dm}^{-3}$ ,  $250 \text{ cm}^3$ ) and sodium hydroxide ( $0.6$   
130  $\text{mol dm}^{-3}$ ,  $250 \text{ cm}^3$ ) were prepared. The temperatures of the individual solutions were then adjusted to 293 K using a water bath before mixing them together and holding them at 293 K.

Samples were taken at certain time intervals, and placed immediately into 10  
135  $\text{cm}^3$  of hydrochloric acid ( $5 \text{ mol dm}^{-3}$ ) to prevent the alkaline hydrolysis reaction continuing during measurement. The samples were then filtered through a  $0.22 \mu\text{m}$  syringe filter before measuring their absorbance at 268 nm. The concentration of TPPB remaining in solution was determined from a calibration graph of absorbance at 268 nm against TPPB concentration.

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This procedure was then repeated at 313, 333 or 353 K.

The investigations were then repeated for sodium hydroxide concentrations of 0.1, 0.3 or  $1 \text{ mol dm}^{-3}$ .

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### ***Solubility Studies***

TPPB, TPPO, and TPP were weighed into separate polythene vials in quantities determined to produce  $0.001 \text{ mol dm}^{-3}$  solutions in  $20 \text{ cm}^3$  of  $0.30 \text{ mol dm}^{-3}$

sodium hydroxide. The elements under investigation were then added in non-  
150 active form, again in suitable quantities so as to produce  $0.001 \text{ mol dm}^{-3}$   
solutions. Small quantities of the appropriate radionuclide were then added.  
However, as there are no inactive technetium isotopes, technetium experiments  
were conducted using an initial technetium concentration of  
*ca.*  $4 \times 10^{-7} \text{ mol dm}^{-3}$ . After two weeks, samples were filtered through a  $0.22 \mu\text{m}$   
155 syringe filter and the radioactivity in each solution was measured. All samples  
were counted for 10000 counts, therefore the error due to counting statistics  
alone is  $\pm 1\%$ . The measurements were repeated after 4 and 8 weeks.

## Results

### 160 ***Kinetic study of the degradation of tetraphenylphosphonium bromide***

In a previous study of the degradation of the tetraphenylphosphonium ion by  
alkaline hydrolysis, the chloride quaternary salt was used (Khalil, 1973; Khalil,  
1974). The rate of reaction was found to follow third order kinetics and the rate  
of reaction is given as:

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$$\text{rate} = k[\text{TPPB}][\text{OH}^-]^2$$

By following the degradation at pH 11.2 the following Arrhenius expression was  
determined:

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$$k = 2.45 \times 10^{21} e^{\left(\frac{-140.8 (\text{kJ mol}^{-1})}{RT}\right)} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

Figure 1 shows the degradation of tetraphenylphosphonium bromide at different sodium hydroxide concentrations and different temperatures. From figure 1 it can be seen that, at all temperatures, the rate of degradation is dependent on the sodium hydroxide concentration. This is because the rate of reaction is 2<sup>nd</sup> order with respect to the hydroxide ion concentration. Graphs of ln [TPPB] versus time are straight lines demonstrating that the degradation follows first order kinetics with respect to TPPB concentration.

The rate constants for the alkaline hydrolysis of TPPB at different temperatures can be obtained by measuring the degradation with respect to time (Table 1). In addition, by plotting the reciprocal of the temperature against the natural log of the rate constant (figure 2), an Arrhenius expression can be obtained for the degradation of tetraphenylphosphonium.

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From data shown in Table 2 the mean activation energy is  $105.20 \pm 3.21$  kJ mol<sup>-1</sup> and the mean pre-exponential term, ln A, is  $30.64 \pm 1.14$ . Therefore, the Arrhenius expression can be expressed as:

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$$k = 2.03 \times 10^{13} e^{\left( \frac{-105.2 (\text{kJ mol}^{-1})}{RT} \right)} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

Comparison of this Arrhenius equation with the literature (Khalil, 1973; Khalil, 1974) shows that the activation energy for the degradation of TPPB is lower than that for TPPCl and therefore the degradation of the bromide phosphonium salt is kinetically faster than that of the chloride salt.

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### ***Solubility of $^{99}\text{TcO}_4^-$ in solutions of TPPB and its degradation products***

The results for the solubility experiments of  $\text{TcO}_4^-$  in solutions containing either TPPO, TPPB or TPP are shown in figure 3. In the solutions containing TPPO and TPP it can be seen that the concentration of technetium(VII) is the same as in the solution containing only  $\text{TcO}_4^-$ . However for the solution containing TPPB the solubility of  $\text{TcO}_4^-$  is much lower as it is precipitated by the phosphonium ion. After 4 weeks it can be seen that the  $\text{TcO}_4^-$  solubility increases until, after 8 weeks the solubility of  $\text{TcO}_4^-$  reaches the inventory concentration of technetium.

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The increase in solution phase technetium is most likely because TPPB degrades by alkaline hydrolysis and  $\text{TcO}_4^-$  is released into solution. Using the rate equation above and data from this study it is possible to compare the degradation of TPPB with the release of technetium from the  $\text{TcO}_4\text{TPP}$  solid at high pH (figure 4).

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From figure 4 it can be seen that the release rate of technetium is similar to the rate of degradation of tetraphenylphosphonium bromide. The increase in the solubility of technetium with time is therefore due to the release of technetium as the tetraphenylphosphonium bromide molecule degrades via alkaline hydrolysis.

215

### ***Solubility of $^{152}\text{Eu}$ in solutions of TPPB and its degradation products***

The results for the solubility experiments of  $^{152}\text{Eu}$  in solutions containing either tetraphenylphosphonium bromide, triphenylphosphonium oxide or triphenylphosphine are shown in figure 5. At acidic pHs, europium is soluble

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and a  $0.001 \text{ mol dm}^{-3}$   $\text{EuCl}_3$  solution spiked with  $^{152}\text{Eu}$  gave a specific activity of  $3630 \text{ dpm cm}^{-3}$ . However, at pH 13.3, europium precipitated and the specific activity was reduced to  $2.4 \text{ dpm cm}^{-3}$ . Measurements showed that in all solutions the solubility of europium was the same as that in the solution containing only  $^{152}\text{Eu}$ .

#### ***Solubility of $^{125}\text{I}$ in solutions of TPPB and its degradation products***

The results for the solubility experiments of  $^{125}\text{I}$  in solutions containing either TPPO, TPPB or TPP are shown in figure 5. Iodine is soluble at pH 13.3. However, iodine will be present as an anion and it might be expected to be removed in the same way as  $\text{TcO}_4^-$ . However, in all solutions the solubility of iodine is the same as that in the solution containing only  $^{125}\text{I}$ . Iodine is a less electronegative element compared to bromine, it is therefore believed that the substitution of the bromide ion for the iodide ion is not favourable.

#### ***Solubility of $^{63}\text{Ni}$ in solutions of TPPB and its degradation products***

The results for the solubility experiments of  $^{63}\text{Ni}$  in solutions containing either TPPO, TPPB or TPP are shown in figure 5. At acidic pHs, nickel is soluble and a  $0.001 \text{ mol dm}^{-3}$   $\text{NiCl}_2$  solution spiked with  $^{63}\text{Ni}$  gave a specific activity of  $11425 \text{ dpm cm}^{-3}$ . However, at pH 13.3, nickel precipitated and the specific activity was reduced to  $6.8 \text{ dpm cm}^{-3}$ . In all solutions the solubility of nickel is the same as that in the solution containing only  $^{63}\text{Ni}$ .

#### ***Solubility of $^{233}\text{U}$ in solutions of TPPB and its degradation products***

The results for the solubility experiments of  $^{233}\text{U}$  in solutions containing either TPPO, TPPB or TPP are shown in figure. 5. At acidic pHs, uranium is soluble and a  $0.001 \text{ mol dm}^{-3} \text{ UO}_2(\text{NO})_3$  solution spiked with  $^{233}\text{U}$  gave a specific activity of  $22000 \text{ dpm cm}^{-3}$ . However, at pH 13.3, uranium precipitated and the specific activity was reduced to  $625 \text{ dpm cm}^{-3}$ . In all solutions the solubility of uranium is the same as that in the solution containing only  $^{233}\text{U}$ .

### **Conclusions**

The kinetics of the degradation of TPPB by alkaline hydrolysis were first order with respect to TPPB concentration and were similar to those suggested in the literature (Khalil, 1973; Khalil, 1974). The results of the kinetic experiments were used to calculate an activation energy and develop an Arrhenius expression for the degradation of TPPB.

TPPB and its degradation products appeared to have no significant effect on the solubility of europium, iodine, nickel and uranium(VI). This was also the case for the solubility of technetium(VII) in the presence of TPP or TPPO.

Technetium showed a gradual increase in solubility over time in the presence of tetraphenylphosphonium bromide. The increase in solubility was because  $\text{TcO}_4^-$  was being released as the TPPB degraded.

As a direct result of this work it was shown that TPPB and its degradation products would not have a significant detrimental effect on post-closure

270 performance of an underground radioactive waste repository. TPPB is now used to remove technetium from some radioactive waste streams.

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### Figure Captions:

Figure 1: Degradation of tetraphenylphosphonium bromide at different sodium hydroxide concentrations ( $\diamond$   $[\text{NaOH}] = 1 \text{ mol dm}^{-3}$ ;  $\square$   $[\text{NaOH}] = 0.3 \text{ mol dm}^{-3}$ ;  $\triangle$   $[\text{NaOH}] = 0.1 \text{ mol dm}^{-3}$ ) and different temperatures (A. 293 K; B. 313 K; C. 333 K)

Figure 2: log of the rate constants (k) for the alkaline hydrolysis of TPPB against the reciprocal of the temperature at different hydroxide concentrations.

Figure 3: log of the concentration of technetium in solutions of TPPB and its degradation products against time.

Figure 4: Release rate of  $\text{TcO}_4^-$  and the degradation of TPPB against time.

Figure 5: log of the concentration ( $\text{mol dm}^{-3}$ ) of various metals in solutions of TPPB and its degradation products against time. (A. Europium; B. Iodine; C. Nickel; D. Uranium).