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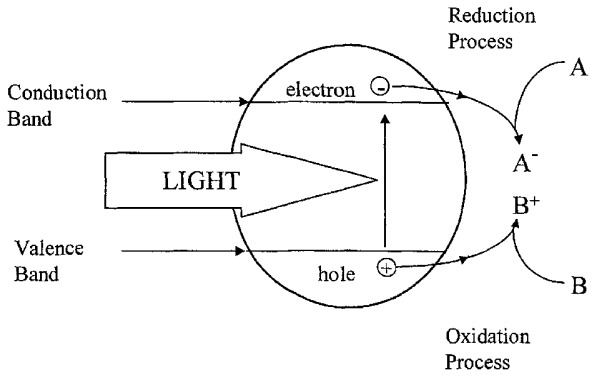
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(54) Title: PROCESS FOR CONTROLLING VALENCE STATES



The primary reactions occurring at a particulate semiconductor photocatalyst illuminated by electromagnetic radiation of sufficient energy to photoexcite the photocatalyst.

(57) Abstract: The present invention provides a process for controlling the oxidation state of a metal ion wherein the oxidation state or valency of the metal ion is changed or maintained by photocatalysis. The is preferably concerned with controlling oxidation states or valencies of metal ions in nuclear fuel reprocessing and most preferably comprises adding a particulate semiconductor photocatalyst and a soluble electron donor for the semiconductor photocatalyst to a solution containing dissolved actinide metal ions, and irradiating the semiconductor photocatalyst with electromagnetic or ionising radiation. The process typically involves a system which is further modified by the addition of a soluble stabiliser for actinide metal ion reduction, the stabiliser being capable of suppressing the action of any photogenerated substance that may promote inhibition of the desired reduction reaction. The process avoids the complex reprocessing procedures which are associated with the methods of the prior art.

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PROCESS FOR CONTROLLING VALENCE STATES

Background of the Invention

This invention relates to valence control and more specifically to valence control in nuclear fuel reprocessing. The invention is particularly concerned with the separation of uranium from plutonium and the separation of neptunium from plutonium and uranium.

Most commercial plants use the Purex process in which the spent fuel is dissolved in nitric acid and the dissolved uranium and plutonium are subsequently extracted from the nitric acid solution into a non-aqueous organic phase of tributyl phosphate (TBP) dissolved in an inert hydrocarbon such as n-decane (also known as odourless kerosene or OK). The non-aqueous organic phase is then subjected to solvent extraction techniques to partition the uranium from the plutonium.

More particularly, the non-aqueous organic phase is subjected to separation of fission products by solvent extraction and in some cases then the removal of technetium, before the so-called U/Pu split. In the U/Pu split, Pu(IV) is reduced to Pu(III) which is in-extractable into the non-aqueous organic phase and therefore follows the aqueous stream while the U, which is in the U(VI) state, remains in the organic stream. Usually, the reducing agent used in the U/Pu split is U(IV). Np(VI) in the non-aqueous solvent stream is also reduced by the U(IV) to Np(IV). Np(IV) is extractable into the non-aqueous organic solvent and so exits the contactor in the non-aqueous stream with the U(VI) product. The unit for carrying out the partitioning of the U and Pu in practice comprises a contactor having a multiplicity of stages, for example six stages might be used in a modern centrifugal contactor.

The process has two disadvantages: (i) Np is not separated from U so additional downstream processes are needed to remove Np from U; and (ii) a high excess of U(IV) reductant is required to reduce Pu(IV) to Pu(III), so reducing the value of the

recovered uranium, unless ^{235}U enrichment of the U(IV) reductant matches that of the non-aqueous feed solution.

Neptunium valency control can be a significant problem in Purex reprocessing. Np is present in the Purex process as a mixture of three different states: Np(IV), Np(V) and Np(VI). Np(IV) and Np(VI) are both extractable into the non-aqueous solvent phase whereas Np(V) is inextractable into this phase. In order to direct Np to raffinate streams, Np is normally stabilised in the (V) state. This is a complex matter, since not only is it the middle oxidation state of the three, but Np(V) also undergoes competing reactions, such as disproportionation to Np(IV) and (VI), and is oxidised to Np(VI) by nitric acid. Neptunium control is therefore difficult and efficient neptunium control is a major aim of an advanced reprocessing programme. In commercial Purex reprocessing plants, Np is typically separated from uranium during the uranium purification cycle (UP). Np(IV) may be converted to Np(V) and Np(VI) by heating in the aqueous phase in a conditioner at high temperature. The conditioned aqueous liquor is fed to an extract and scrub mixer-settler where the Np(V) is rejected to the aqueous raffinate. Any Np(VI) present in the aqueous feed may be reduced to Np(V) by a reducing agent such as hydroxylamine, which is fed to the scrub section of the contactor. In a typical process, two or three mixer-settlers are required to decontaminate the uranium product from neptunium.

The generation and storage of the U(IV) reductant can also be a significant problem in Purex reprocessing. The use of U(IV) as a reductant, which can be electrolytically generated from U(VI), was first introduced in the 1960s and has the advantage of not adding any extra salts to the process and so does not increase waste. During Purex, U(IV) is initially produced at 150 g U/l (about 0.65 M) and then undergoes a series of dilutions, first to 60 g U/l (about 0.25 M) and then to 7 g/l (about 0.03 M), at which point it is stored for a short period. During this storage period, it has been observed that U(IV) exhibits some instability and is at least partially oxidised to U(VI) by nitric and nitrous acids. One possible mechanism for this oxidation is given by the

reaction between U(IV) and nitric acid to give U(V), in the form of UO_2^+, and nitrous acid:

$$2U^{4+} + HNO_3 + 3H_2O \rightarrow 2UO_2^+ + HNO_2 + 6H^+$$

The UO_2^+ disproportionates to form U^{4+} and UO_2^{2+} while the nitrous acid oxidises further U(IV), although with a higher rate than nitric acid.

It would therefore be desirable to provide a process for controlling the oxidation states of actinides in the reprocessing of nuclear fuel and which avoided or mitigated the difficulties of the prior art processes. More generally, it would be desirable to devise a technique to obtain the controlled conversion of oxidation states, for example for the purpose of altering the solubilities of one or more metal ions in order to separate different metals.

Colloidal semiconductor particles are known to act as photocatalysts for a range of useful reactions. The primary step in all of these reactions is the absorption of ultra-band gap energy photons by the particles, which generates conduction band electron-valence band hole (e^-, h^+) pairs within the semiconductor lattice. The valence band holes can oxidise oxidisable species in solution or particle surface/lattices sites, while conduction band electrons can reduce reducible species in solution or particle surface/lattice sites, as illustrated in Figure 1.

Statements of Invention

The present inventors have surprisingly found that it is possible to utilise the photocatalytic properties of colloidal semiconductor particles in order to control the oxidation states of actinides in the reprocessing of nuclear fuel. Accordingly, the present invention provides a process for controlling the oxidation state of a metal ion wherein the oxidation state is deliberately changed or maintained by photocatalysis.

More specifically, the invention involves the use of photocatalysis to control oxidation states or valencies, of metal ions in nuclear fuel reprocessing.

The process involves the addition of a particulate semiconductor photocatalyst and a soluble electron donor for the semiconductor photocatalyst to a solution containing dissolved actinide metal ions, and irradiating the semiconductor photocatalyst with electromagnetic or ionising radiation. The radiation should have sufficient energy to excite the semiconductor photocatalyst.

The semiconductor photocatalyst may be utilised in the process of the invention in a dispersed form. However, it is generally desired that, following completion of the desired photocatalysed actinide ion reduction process, the particulate semiconductor photocatalyst should be removed from the solution containing the actinide metal ions. This is particularly important when the described photocatalysed processes are employed as part of a nuclear reprocessing cycle, since the solid catalyst obtained after such a solid/liquid separation adds to the overall waste requirement of the reprocessing cycle. In such cases, difficulties in the removal of the photocatalyst may be experienced when it is in a dispersed form, and means of facilitating easier removal are desirable. This may be achieved by immobilisation of the photocatalyst, and the preferred techniques involves the use of a macroscopic solid support that can be easily inserted into and removed from a reprocessing stream, and on which the photocatalyst becomes immobilised.

In a preferred process, irradiation is carried out using monochromated electromagnetic radiation, the radiation having sufficient energy to excite the semiconductor photocatalyst, and having a wavelength outside the absorption wavelength region of both the actinide and the soluble electron donor, and of a precursor substance capable of producing a derivative which promotes inhibition of the desired actinide reduction reaction.

More preferably, the solution content of the system is further modified by the addition of a soluble stabiliser for actinide metal ion reduction, the stabiliser being capable of suppressing the action of any photogenerated substance that may promote inhibition of the desired reduction reaction. In a particularly preferred embodiment of the invention, the electron donor for the semiconductor photocatalyst and the stabiliser for actinide metal ion reduction are one and the same component.

Detailed Description of the Invention

In choosing suitable particulate semiconductor photocatalysts for use in the present invention, it is necessary that certain performance criteria should be provided. Thus, suitable materials are required to have the following properties:

(i) the ability to absorb a specific band of electromagnetic radiation to excite the electrons in the valence band in order to generate negative electrons in the conduction band and positive holes in the valence band at the same time, i.e. the capability of undergoing photoexcitation;

(ii) chemical resistance to all chemical and radiolytic environments encountered in the reprocessing of nuclear fuels and most especially the non-aqueous environments provided by mixtures of tributyl phosphate and n-decane in various proportions, and aqueous environments of high acidity ($pH < 2$);

(iii) conduction band thermodynamics that have been either identified or tailored through deliberate synthesis as being appropriate to perform the target reduction; and

(iv) particle size in the range 1 nm to 10 μm.

An extensive range of semiconducting materials is available from which a choice may be made as to which is the most suitable for photosensitising the targeted actinide reduction process. In addition to the above criteria, these materials should be photostable (i.e. not liable to photoanodic or photocathodic corrosion) and, preferably, cheap. In order for a semiconductor to be photochemically active as a

sensitiser for the reaction of interest, the redox potential(s) of the photogenerated valence/conduction band holes/electrons must be sufficiently positive/negative to perform the desired oxidation/reduction. Different semiconductors exhibit different band edge energetics; thus, matching the semiconductor energetics to the thermodynamics of the desired reaction – in this case the targeted reduction of one or several actinide ions – is crucial for overall process efficiency.

Control of the particle valence/conduction band oxidation/reduction potential is not only achieved through a judicious choice of particle component material; band edge redox thermodynamics of a single material are also affected by solution pH, semiconductor doping level and particle size. The relevant properties of the metal ion probe are its range of available valence states and, for aqueous systems, the pH dependence of the thermodynamics of inter-valence conversion. Consequently, any study of semiconductor particle induced valence control would have to be conducted in close consultation with the thermodynamic potential-pH speciation diagrams of both the chosen metal ion system and semiconductor material. This information is freely available in the electrochemical literature and can be used to identify candidate particle materials whose thermodynamics in aqueous solution are compatible with those of a range of actinide metal ions

By following such a procedure, SnO_2 can be identified as a candidate semiconductor for valence control applications in nuclear fuel reprocessing systems. This can be achieved by study of the potential-pH diagram for the Sn-H_2O system overlaid with SnO_2 conduction band edge, as shown in Figure 2. Inspection of this diagram indicates that SnO_2 is thermodynamically stable over the pH range –2 to 16 and is not prone to any photocathodic decomposition reaction. Investigation of relative positions of the tin oxide band edges with respect to areas of stability on the U-H_2O system, Np-H_2O system and Pu-H_2O system potential-pH diagrams provides an indication of the suitability of SnO_2 as a photocatalyst for actinide metal ion reduction. This process then allows identification of a pH range where illuminated

colloidal SnO_2 facilitate the aqueous phase separation of Np from Pu species during the Purex process. Similar conclusions are possible for TiO_2 and ZrO_2 systems.

Inspection of the potential-pH diagrams for the U-H_2O system (Figure 3), Np-H_2O system (Figure 4) and Pu-H_2O system (Figure 5) indicates that the conduction band energy of SnO_2 is such that the conduction band electrons of SnO_2 are sufficiently energetic to reduce U(VI) to U(IV), reduce Np(VI) and Np(V) to Np(IV) and reduce Pu(VI), Pu(V) and Pu(IV) to Pu(III). Consequently, tin oxide is a particularly preferred material for use in the process of the present invention.

Further inspection of the potential-pH diagrams for the U-H_2O, Np-H_2O and Pu-H_2O systems indicates that a semiconductor photocatalyst with a conduction band edge lying in the potential range 1.24 to 1.44 V at 1> pH > -1 would be possessed of electrons sufficiently energetic to stablise the U(VI) state, reduce Np(VI) to Np(V), so stabilising that state, and reduce Pu(VI) and Pu(V) to Pu(IV), so stabilising that state. Whilst the conduction band edge of SnO_2 is inappropriate for this particular embodiment, such a catalyst may be realised from a modified SnO_2, providing a material which is used in a further preferred embodiment of the invention. The means for providing such a catalyst will now be described.

Butler and Ginley (*J. Electrochem. Soc.*, **125**, 228, 1978) have demonstrated that a correlation exists between the flat-band potential of a semiconductor (which may be identified with the conduction band edge in highly doped n-type materials) and its electron affinity. They calculate the position of the conduction band edge from the following formula:

$$E_{cs}^{0} = E^{e} - EA \qquad (1)$$

where EA is the electron affinity, E^e is the energy of free electrons on the hydrogen scale and E_{cs}^{0} is the energy of conduction band electrons at the point of zero zeta potential (pzzp). The electron affinity of the material is estimated based on its

electronegativity. The electronegativity, X, of a semiconductor is assumed to be identical with the mid band gap energy, $\frac{1}{2}(E_c + E_v)$. Specifically, EA is given by

$$EA = X - \frac{1}{2}E_g \quad (2)$$

The conduction band edge at the pzzp is therefore given by:

$$E_{cs}^0 = E^e - X + \frac{1}{2}E_g \quad (3)$$

According to the Butler and Ginley analysis, X for the semiconductor is given by the geometric mean of the electronegativities of the composite atoms, e.g. for SnO_2, the conduction band edge at the pzzp is given by:

$$E_{cs}^0 = E^e - \{X(Sn)\, X^2(O)\}^{1/3} + \frac{1}{2}E_g \quad (3)$$

Bin-Daar, Dare Edwards, Goodenough and Hamnett (*J. Chem. Soc., Faraday Trans. 1*, **79**, 1199, 1983) have shown that the effect of dopants on the energy of the conduction band edge may be predicted from equation (3) by inclusion of the dopant electronegativity within the term for the geometric mean of the electronegativities of the composite atoms.

Thus, the conduction band edge of SnO_2 may be rendered more oxidising - such that it lies in the potential range 1.24 to 1.44 V vs SHE at $1 > pH > -1$ and is thus thermodynamically capable of the simultaneous generation of NpO_2^+ from NpO_2^{2+}, and stabilisation of PuO_2^{2+} – by the addition to the material lattice of an appropriate dopant. Equation (3) allows calculation of the energy of the conduction band edge at the pzzp, which for SnO_2 based materials is at about pH 4.3. The value of the energy of the conduction band edge decreases by 0.059 eV per pH unit, implying that the potential of the conduction band edge of doped SnO_2 should have a value of about 1.1 V vs SHE at pzzp, if that material is to photocatalytically drive the desired actinide valence control at $1 > pH > -1$. As the potential of the conduction band edge

of SnO_2 at pH 4.3 is about 0.45 vs SHE, this requires that tin oxide be doped with a metal that is

(i) more electronegative than Sn; and

(ii) capable of forming a solid solution with SnO_2.

Metals that fulfil both criteria include Fe, Hg, Cr, Cd, U, Ta and W. The skilled person would also expect many of the third period of transition metals to be suitable. In order to help prevent leeching of the dopant from the particle matrix, the doped particle may be enclosed in a sheath of undoped SnO_2.

The electron donor suitable for use in the present invention is one capable of irreversibly undergoing oxidation – either by virtue of the valence holes formed by the photo-excitation of the semiconductor photocatalyst or by means of the hydroxide radicals generated by the oxidation of water by the same valence band holes – to supply electrons. Suitable materials include organic acids such as formic acid, acetic acid and the like; alcohols, for example methanol and ethanol; aldehydes, including formaldehyde and acetaldehyde; amino acids; and hydrazine and its oxidation products, for examples, hydroxylamine, dihydroxylamine and the like.

The stabiliser for actinide metal ion reduction suitable for use in the present invention is one capable of irreversibly undergoing oxidation by a derivative that may promote inhibition of the desired reduction reaction, this derivative having been generated by the action of electromagnetic or ionising radiation on a precursor substance. Commonly, the precursor substance is nitric acid and the photogenerated substance that may promote inhibition of the desired reduction reaction is nitrous acid; in such cases, suitable stabilisers include hydrazine and its oxidation products, including hydroxylamine and dihydroxylamine.

The present invention also provides a process for reprocessing nuclear fuel to form a fissile material, optionally in the form of a fuel pellet, a fuel pin or a fuel assembly,

the process involving the use of the method of the invention. From the above considerations, it is clear that the use of unmodified SnO_2 in such applications would be particularly suitable, and this is confirmed by a consideration of its photochemistry in such systems.

Examination of the E_h (electrode potential versus the standard hydrogen electrode)-pH diagrams for the U/H_2O (Figure 3), Np/H_2O (Figure 4) and Pu/H_2O (Figure 5) systems, with conduction energy levels of SnO_2 overlaid, indicates the potential availability of a photocatalytically driven process that may afford complete separation of Np from the dissolved fuel stream after the first solvent extraction step (fission products separation in a conventional Purex process) and simultaneous with the second solvent extraction step (the U/Pu split).

This photocatalytic process exploits the direct photolysis of HNO_3 and may be described as follows. The primary step may be considered to be the photonic generation of electrons and holes, which is denoted as proceeding with a rate g:

$$SnO_2 \xrightarrow{h\nu,g} SnO_2(e^-_{CB}, h^+_{VB})$$

If colloidal SnO_2 is irradiated in nitric acid environments typical of reprocessing liquors, the following photolysis of HNO_3 may occur concurrently with the generation of conduction band electrons and valence band holes:

$$HNO_3 \xrightarrow{h\nu} NO_2 + OH^{\bullet}$$

$$NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

Neptunium species in the reprocessing liquor may then react as follows:

$$NpO_2^+ \xrightarrow{h^+/OH^{\bullet}} NpO_2^{2+}$$

where the oxidation is driven by either direct valence band hole transfer (if the reorganisation energy, λ, of NpO_2^+ permits), or by OH• radicals generated by either the photolysis of HNO_3 or valence band hole driven oxidation of H_2O. The NpO_2^{2+} species may then react with HNO_2 (generated as a result of the photolysis of HNO_3) as follows:

$$2NpO_2^{2+} + HNO_2 + H_2O \rightarrow 2NpO_2^{+} + HNO_3 + 2H^+$$

so regenerating NpO_2^+ from NpO_2^{2+}. This essentially "short circuits" the scheme shown above but for the action of the conduction band electrons, which may reduce NpO_2^+ at pH > -1 to generate insoluble NpO_2:

$$NpO_2^+ \xrightarrow{e_{CB}^-} NpO_2 .$$

Examination of the potential-pH diagram for the plutonium-water system indicates that the products of Pu photolysis reactions (analogous to those described above for Np) are the solution species PuO_2^{2+} and Pu^{3+} in the pH range -1 to 2. Examination of the uranium-water potential-pH diagram indicates that the product of analogous U photolysis under the same solution conditions is U^{4+}, also a solution species:

$$UO_2^{2+} + 4H^+ \xrightarrow{e_{CB}^-} U^{4+} + 2H_2O$$

Thus, at pHs -1 to 0 (typical of those values found in reprocessing liquors), semiconductor particle driven photolysis of U, Pu and Np species results in the generation of solution phase U and Pu species, and the precipitation of Np species. Therefore, a tin oxide photocolloid driven pre-treatment of the dissolved fuel stream after the first solvent extraction step (fission products separation in a conventional Purex process) and simultaneous with the second solvent extraction step (the U/Pu split) would afford complete separation of Np from the dissolved fuel, so obviating the need for Np/Pu split steps further into the reprocessing cycle.

It is also evident from earlier considerations that modified SnO_2 would be suitable for application as a catalyst in nuclear fuel reprocessing systems, as is again confirmed by a consideration of its photochemistry in such systems.

Examination of the E_h (electrode potential versus the standard hydrogen electrode)-pH diagrams for the U/H_2O (Figure 3), Np/H_2O (Figure 4), and Pu/H_2O (Figure 5) systems indicates that a semiconductor photocatalyst with a conduction band edge lying in the potential range 1.24 to 1.44 V at $1 > pH > -1$ and derived, for example, by the modification through doping of SnO_2, hereinafter referred to as m-SnO_2, offers the potential availability of a photocatalytically driven process that may afford complete separation of Np from the dissolved fuel stream before the primary solvent extraction step of the Highly Active (HA) cycle of the Purex process.

This photocatalytic process exploits the direct reduction of Np and Pu ions using photogenerated conduction band electrons and may be described as follows. The primary step may be considered to be the photonic generation of electrons and holes, which is denoted as proceeding with a rate g:

$$m-SnO_2 \xrightarrow{h\nu,g} m-SnO_2(e^-_{CB},h^+_{VB})$$

This is followed immediately by intraparticle conduction band electron-valence band hole recombination:

$$m-SnO_2(e^-_{CB},h^+_{VB}) \rightarrow m-SnO_2$$

If the photocatalyst is irradiated in a process liquor environment, neptunium species in the liquor may then react as follows:

$$NpO_2^{2+} \xrightarrow{e^-} NpO_2^+$$

the resultant Np(V) species being inextractable into the organic non-aqueous solvent phase and so remaining in the aqueous phase. U(VI) species in the reprocessing liquor are unaffected while plutonium species may react as follows:

$$PuO_2^{2+} \xrightarrow{e^-} PuO_2^{+}$$

followed by either a further direct reduction of the Pu(V) species by conduction band electrons:

$$PuO_2^{+} + 4H^{+} \xrightarrow{e^-} Pu^{4+} + 2H_2O$$

or the disproportionation of the Pu(V) species to form Pu(VI) and Pu(IV) species:

$$2PuO_2^{+} + 4H^{+} \longrightarrow PuO_2^{2+} + Pu^{4+} + 2H_2O$$

after which the Pu(VI) species may undergo further direct reduction by conduction band electrons to form Pu(V) species which may further disproportionate to form Pu(VI) and Pu(IV) species, the Pu(V) species undergoing still further disproportionation until the stage is reached wherein all Pu(VI) and Pu(V) species have been reduced to Pu(IV). Both U(VI) and Pu(IV) are extractable into the organic non-aqueous phase and may, therefore, be separated from neptunium. Therefore, a photocatalytically driven pre-treatment of the dissolved fuel stream before the primary solvent extraction step of the Highly Active (HA) cycle of the Purex process would afford complete separation of Np as Np(V) from the U/Pu solvent stream, so obviating the need for Np/Pu separation steps further into the reprocessing cycle.

As previously observed, titanium dioxide has also been identified as a potentially promising semiconductor for valence control applications. A consideration of the photochemistry of TiO_2 in nuclear reprocessing liquor shows that the band edge positions of this material are such that the conduction band has a potential of +0.15 V

vs SHE, and the valence band has a potential of +3.35 V vs SHE. Thermodynamic calculations indicate that when TiO_2 is subjected to ultra-band gap illumination, the photogenerated conduction band electrons are energetic enough to reduce TiO_2 to Ti^{3+} at pH < 0, while the concomitantly produced valence band holes may oxidise TiO_2 to TiO_2^{2+} at pH < 1. Consequently, illuminated TiO_2 may be expected to undergo photoanodic dissolution at pH < 1 and both photoanodic and photocathodic dissolution at pH < 0. The energetics of its conduction band, in particular, do render TiO_2 attractive for photocatalytic valence control purposes at solution pH > 1.5. Ultra-band gap illumination of TiO_2 in the presence of Np, Pu and U ions at pH 1.5 will result in the conduction band electron-driven generation of Pu^{3+}, U^{4+} and insoluble NpO_2, presenting a possible extraction route for Np.

As previously disclosed, the process of the present invention is preferably performed in the presence of a stabiliser for actinide metal ion reduction, and the role of this stabiliser will now be considered. If the semiconductor photocatalyst is irradiated in nitric acid environments typical of reprocessing liquors, the following photolysis of HNO_3 may occur concurrently with the generation of conduction band electrons and valence band holes:

$$HNO_3 \xrightarrow{h\nu} NO_2 + OH^{\bullet}$$

$$NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

The nitrous acid, HNO_2, is capable of oxidising U(IV) to U(VI):

$$U^{4+} + 2HNO_2 \rightarrow UO_2^{2+} + 2NO + 2H^{+}$$

and, similarly, capable of oxidising Pu(III) and Pu(IV) to Pu(VI). Such oxidation reactions prevent the efficient separation of Pu and U. However, these nitrous acid driven oxidation reactions can be obviated by the addition of a stabiliser such as

hydrazine to the reprocessing liquor, the stabiliser destroying the nitrous acid which oxidises the plutonium and uranium:

$$N_2H_5^+ + HNO_2 \rightarrow HN_3 + 2H_2O + H^+$$

$$N_2H_5^+ + 2HNO_2 \rightarrow N_2 + N_2O + 3H_2O + H^+$$

Thus, the addition of hydrazine to the reprocessing liquor results in photogenerated U(IV) and Pu(III) being stabilised against reoxidation, so rendering the uranium and plutonium separable by solvent extraction. A particularly preferred embodiment of this system is achieved when the electron donor for the semiconductor photocatalyst and stabiliser for actinide metal ion reduction are one and the same material, i.e. hydrazine is employed as both the stabiliser and the electron donor for the semiconductor photocatalyst.

Description of the Drawings

Embodiments of the present invention will now be described, with reference to the accompanying drawings, in which

Figure 1 shows the primary reactions occurring at a particulate semiconductor photocatalyst illuminated by electromagnetic radiation of sufficient energy to photoexcite the photocatalyst;

Figure 2 is a potential-pH diagram for the tin-water system at 298 K with SnO_2 conduction band edge overlaid. Dissolved tin activity = 0.001, $P(SnH_4)$ = 1 atm, 298 K;

Figure 3 is a potential-pH diagram of the uranium-water system at 298 K with SnO_2 conduction band edge overlaid. Dissolved uranium activity = 0.01;

Figure 4 is a potential-pH diagram of the neptunium-water system at 298 K with SnO_2 conduction band edge overlaid. Dissolved neptunium activity = 0.01;

Figure 5 is a potential-pH diagram of the plutonium-water system at 298K with SnO_2 conduction band edge overlaid. Dissolved plutonium activity = 0.01;

Figure 6 is a potential-pH diagram of the cerium-water system at 298K with SnO_2 conduction band edge overlaid. Dissolved cerium activity = 0.01;

Figure 7 shows the concentration of Ce(III) as a function of illumination time. The Ce^{3+} is generated by photocatalysed reduction of Ce^{4+}, achieved through illuminating with light of wavelength 312 nm a solution containing 0.12 mol Ce^{4+} m^{-3}, 55 mol ethanol m^{-3} and 100 g SnO_2 m^{-3}. Illumination is removed at 920 s;

Figure 8 shows the concentration of U(IV) as a function of illumination time. The U^{4+} is generated by photocatalysed reduction of UO_2^{2+}, achieved through illuminating, with light of wavelength 312 nm, a solution containing 10 mol UO_2^{2+} m^{-3}, 55 mol ethanol m^{-3} and 100 g SnO_2 m^{-3};

Figure 9 shows the concentration of photogenerated U(IV) as a function of time for the solution of Figure 8 after the source of illumination has been removed;

Figure 10 shows the concentration of U(IV) as a function of illumination time. The U^{4+} is generated by photocatalysed reduction of UO_2^{2+}, achieved through illuminating, with light of wavelength 350 nm, a solution containing 10 mol UO_2^{2+} m^{-3}, 100 g SnO_2 m^{-3} and either 550 mol ethanol m^{-3} (Series 1), or 550 mol hydrazine m^{-3} (Series 2);

Figure 11 shows the concentration of photogenerated U(IV) as a function of time for the solution of Figure 10, Series 1, after the source of illumination has been removed;

Figure 12 shows the concentration of photogenerated U(IV) as a function of time for the solution of Figure 10, Series 2, after the source of illumination has been removed;

Figure 13 shows the following two scenarios:

Series 1: Concentration of U(IV) as a function of illumination time. The U^{4+} is generated by photocatalysed reduction of UO_2^{2+}, achieved through illuminating, with light of wavelength 350 nm, a one solvent phase, aqueous solution containing 10 mol UO_2^{2+} m^{-3}, 100 g SnO_2 m^{-3} and 550 mol hydrazine m^{-3};

Series 2: Concentration of U(IV) in tributyl phospahate as a function of illumination time. The U^{4+} is generated by photocatalysed reduction of UO_2^{2+}, achieved through illuminating, with light of wavelength 350 nm, a two solvent phase system – one solvent phase being an aqueous solution initially containing 10 mol UO_2^{2+} m^{-3}, 100 g SnO_2 m^{-3} and 550 mol hydrazine m^{-3}, the other solvent phase initially containing only tributyl phosphate;

Figure 14 shows the concentration of photogenerated U(IV) as a function of time for the non-aqueous solvent phase of Figure 3, Series 2, after the source of illumination has been removed; and

Figure 15 shows the concentration of U(IV) as a function of illumination time. The U^{4+} is generated by photocatalysed reduction of UO_2^{2+}, achieved through illuminating, with light of wavelength 350 nm, an aqueous solution containing 10 mol UO_2^{2+} m^{-3}, 0.05 mol Ce^{4+} m^{-3}, 100 g SnO_2 m^{-3} and 550 mol hydrazine m^{-3}.

The roles of valence band holes and conductance band electrons in the process of the present invention, as illustrated in Figure 1, have previously been recorded. Furthermore, the importance of the potential-pH diagrams of Figures 2 to 5 in determining the suitability of specified materials for use in the process of the present invention has already been discussed. Consequently, the present discussion will focus on the remaining diagrams.

The present inventors have experimentally found that the efficiency of metal ion reduction by the irradiated photocatalyst, and the longevity of the reduced state, is influenced by the presence of an electron donor for the semiconductor photocatalyst, the presence of a precursor substance capable of producing a net reduction inhibiting substance and the presence of a stabiliser for actinide metal ion reduction. The present invention has been established by combining these factors to improve efficiency. Experimental observation of photocatalysed metal ion reduction, and the elucidation of the effect of these influences on the efficiency of that reduction will now be described.

Comparison of the Pu-H_2O and Ce-H_2O potential-pH diagrams (Figures 5 and 6) indicates that the two systems exhibit similar thermodynamics. Thus, in order to minimise waste management concerns, preliminary experiments on photocatalysed metal ion reduction were conducted using the Ce-H_2O system as a non-radioactive analogue of the Pu-H_2O system.

From Figure 7, it is possible to see the effect of illuminating Ce(IV) with light of wavelength 312 nm (which has an energy high enough to photoexcite the semiconductor photocatalyst SnO_2) in the presence of colloidal SnO_2, sulphuric acid (pH 0) and ethanol as an electron scavenger for the semiconductor photocatalyst. As can be seen, upon illumination, the concentration of Ce(III), which was initially zero, increases with illumination time as a result of photocatalysed reduction of Ce^{4+}. The concentration of Ce^{3+} continues to increase until it is equal to the original concentration of Ce(IV). Upon the removal of the illumination, the cerium remains in the Ce^{3+} state, indicating that none of the constituents of the illuminated solution acts as a precursor for a net reduction inhibiting substance when illuminated with light of wavelength 312 nm.

In Figure 8, there is illustrated the effect of illuminating U(VI) with light of wavelength 312 nm (having an energy high enough to photoexcite the semiconductor photocatalyst, SnO_2) in the presence of colloidal SnO_2, sulphuric acid (pH 0) and

ethanol as an electron scavenger for the semiconductor photocatalyst. As can be seen from this diagram, upon illumination, the concentration of U(IV), which was initially zero, increases with illumination time as a result of photocatalysed reduction of UO_2^{2+}. The concentration of U^{4+} continues to increase until it is equal to the original concentration of U(VI).

The concentration of photogenerated U(IV) as a function of time elapsed after the removal of illumination is illustrated in Figure 9. When the reaction vessel is open to the air, U(IV) is oxidised back to U(VI). However, when the reaction vessel is stoppered, and oxygen is consequently excluded, the oxidation of U(IV) to U(VI) is arrested. Unstoppering the reaction vessel allows oxygen to re-enter and the oxidation to U(VI) recommences.

From Figure 10 can be seen the effect of illuminating U(VI) with light of wavelength 350 nm (having an energy high enough to photoexcite the semiconductor photocatalyst SnO_2) in the presence of colloidal SnO_2, nitric acid (pH 0) and ethanol as an electron scavenger for the semiconductor photocatalyst. Nitric acid was chosen since it is the acid that is most often used in nuclear reprocessing cycles. The diagram shows that, upon illumination, the concentration of U(IV), which was initially zero, increases with illumination time as a result of photocatalysed reduction of UO_2^{2+}. The concentration of U^{4+} continues to increase until it is equal to the original concentration of U(VI). Irradiation of the photocatalyst is conducted at 350 nm as light of this wavelength has energy high enough to excite the semiconductor photocatalyst and is outside the absorption wavelength region of nitric acid, so avoiding the photogeneration of nitrous acid. Nitrous acid is capable of reoxidising the photocatalytically generated U(IV) back to U(VI) (vide supra).

Turning to Figure 11, there is shown the concentration of photogenerated U(IV) as a function of time elapsed after the removal of illumination from the solution generated as a result of the experiment conducted in the presence of ethanol shown in Figure 10. Results are broadly similar to those presented in Figure 9. However, a

comparison of Figure 11 with Figure 9 indicates that the rate of reoxidation when the reaction vessel is stoppered (and oxygen is consequently excluded) in the presence of nitric acid is twice that recorded in the presence of sulphuric acid under similar conditions. As nitric acid is capable of undergoing photolytic reduction to nitrous acid, which in turn is capable of oxidising U(IV) to U(VI), the experiments of Figures 10 and 11 were repeated in the presence of hydrazine, which is capable of acting as both an electron donor for the semiconductor photocatalyst and as a stabiliser for actinide metal ion reduction.

Thus, it is also possible to see from Figure 10 the effect of illuminating U(VI) with light of wavelength 350 nm (having an energy high enough to photoexcite the semiconductor photocatalyst, SnO_2) in the presence of colloidal SnO_2, nitric acid (pH 0) and hydrazine as an electron scavenger for the semiconductor photocatalyst and as a stabiliser for actinide metal ion reduction. The results are broadly similar to those recorded in the presence of ethanol, the sole difference being that the reduction of U(VI) to U(IV) is slightly slower in the presence of hydrazine than in the presence of ethanol. This difference may be attributed to differences in the efficiencies of ethanol and hydrazine as electron donors for the semiconducting photocatalyst SnO_2.

In Figure 12 there is seen the concentration of photogenerated U(IV) as a function of time elapsed after the removal of illumination from the solution generated as a result of the experiment conducted in the presence of hydrazine shown in Figure 10. There is no evidence of back oxidation of U(IV) to U(VI), indicating that hydrazine is fulfilling its role as a stabiliser for actinide metal reduction and that, as in the case of photocatalysed reduction Ce(IV) to Ce(III) (the non-radioactive thermodynamic analogue of Pu(IV) reduction to Pu(III)), the photocatalysed reduction of U(VI) to U(IV) can be rendered permanent on timescales appropriate for nuclear reprocessing. An even more important observation is that, in the presence of hydrazine, U(IV) is also stable in the presence of oxygen, meaning that measures will not have to be taken to exclude oxygen when the proposed photocatalysed actinide metal ion reduction process is adopted on-line.

When deployed on-line, the photocatalysed reduction of actinide metal ions by photoexcited semiconductor particles will be employed in tandem with solvent extraction in order to achieve actinide separation. The invention therefore also envisages processes wherein semiconductor photocatalysed reduction of metal ions occurs in one of two solvent phases – one aqueous and one non-aqueous – in contact, and wherein, as a result of that reduction, the reduced metal ion is selectively retained by one of the solvent phases – either the phase it originated in, or as a result of a phase transfer reaction.

Thus, an experiment was conducted to assess both the efficacy of photocatalysed actinide metal ion reduction in a two solvent phase system, and the efficacy of simultaneous selective product retention in one of those two phases. In Figure 13, there is seen the effect of illuminating a two solvent phase system with light of wavelength 350 nm (having an energy high enough to photoexcite the semiconductor photocatalyst SnO_2), the two solvent phases being an aqueous phase containing U(VI) in the presence of colloidal SnO_2, nitric acid (pH 0) and hydrazine as an electron scavenger for the semiconductor photocatalyst and a stabiliser for actinide metal ion reduction, and a non aqueous phase of tributyl phosphate. As U(IV), the product of the photocatalysed reduction of U(VI), is extractable into the non-aqueous organic phase, the time dependence of the concentration of U(IV) in the tributyl phosphate is shown in the diagram.

Figure 13 also shows that, upon illumination, the concentration of U(IV) in the tributyl phosphate phase, which was initially zero, increases with illumination time as a result of photocatalysed reduction of UO_2^{2+} originating from the aqueous phase. The concentration of U^{4+} in the tributyl phosphate phase continues to increase until it is equal to the original concentration of U(VI) in the aqueous phase. At the end of the period of illumination, spectroscopic measurements indicate that the concentration of both U(IV) and U(VI) in the aqueous phase is virtually zero, indicating that 100% of the U(VI) has been reduced to U(IV) and transferred from the aqueous phase to the non-aqueous phase. Figure 13 also compares this two phase

data with the comparable one phase data of Figure 10 and it can be seen that the rates of U(IV) evolution are virtually identical, suggesting that the semiconductor photocatalysed reduction of U(VI) to U(IV) occurs almost exclusively in the aqueous phase, and that it is then followed by a fast phase transfer of U(IV) to the non-aqueous phase.

In Figure 14 is shown the concentration of photogenerated U(IV) as a function of time elapsed after the removal of illumination from the non-aqueous component of the two solvent phase system generated as a result of the experiment conducted in the presence of hydrazine shown in Figure 13. As in the aqueous results of Figure 12, there is no evidence of back oxidation of U(IV) to U(VI), indicating that, as in the aqueous phase photocatalysed reduction Ce(IV) to Ce(III) (the non-radioactive thermodynamic analogue of Pu(IV) reduction to Pu(III)), and U(VI) to U(IV), the photocatalysed reduction of U(VI) to U(IV) in the non-aqueous tributyl phosphate phase can be rendered permanent on timescales appropriate for nuclear reprocessing. When deployed on-line, the semiconductor photocatalyst may be required to photoreduce more than one type of actinide metal ion simultaneously. For example, SnO_2 may be used to simultaneously reduce Pu(IV) to Pu(III) and U(VI) to U(IV).

Hence, the invention also envisages processes wherein semiconductor photocatalysed reduction of two or more types of metal ion occurs simultaneously. Thus, an experiment was conducted to assess the effect of the presence of more than one type of reducible metal ion on process efficiency.

Finally, in Figure 15 there is seen the effect of illuminating U(VI) with light of wavelength 350 nm (having an energy high enough to photoexcite the semiconductor photocatalyst, SnO_2) in the presence of colloidal SnO_2, nitric acid (pH 0) and ethanol as an electron scavenger for the semiconductor photocatalyst and Ce(IV) as a non-radioactive, thermodynamic analogue for Pu(IV). Comparison of the data of Figure 15 with the data recorded under similar conditions as shown in Figure 10 indicates that the presence of Ce(IV) has no effect on the rate of photocatalysed reduction of

U(VI) to U(IV). Furthermore, spectroscopic analysis indicates that virtually all of the Ce(IV) has been reduced to Ce(III) over the same timescale, suggesting that the simultaneous semiconductor photocatalysed reduction of two or more different types of metal ion can be accomplished with no loss of yield for either reaction.

Preferred Embodiments of the Invention

A first preferred embodiment of the present invention envisages a photocatalytic process which comprises a spent fuel reprocessing method in which an aqueous liquor containing U(VI) and Pu(IV) is combined with a photocatalyst and illuminated to reduce Pu(IV) to Pu(III) and U(VI) to U(IV). A suitable photocatalyst comprises any metal oxide, doped metal oxide or mixed metal oxide that is demonstrably thermodynamically or kinetically stable under some or all of the chemical and radiolytic conditions employed during nuclear reprocessing, and is preferably selected from SnO_2, TiO_2, Nb_2O_5, Ta_2O_5, WO_3, ZrO_2, $BaTiO_3$ or $SrTiO_3$.

The Pu(III) is inextractable into organic solvent and may therefore be separated from the U which is extractable. Thus, after the photcatalysed reduction of Pu(IV) to Pu(III), this liquor may be subjected to solvent extraction using an organic solvent, to extract the U into the organic solvent phase and leave the Pu(III) in the aqueous phase.

In a second preferred embodiment of the invention, there is provided a photocatalytic process comprising a spent fuel reprocessing method wherein an aqueous liquor containing Np(VI) is combined with a photocatalyst and illuminated to reduce Np(VI) and Np(V) to Np(IV). Suitable photocatalysts comprise any metal oxide, doped metal oxide or mixed metal oxide that is demonstrably thermodynamically or kinetically stable under some or all of the chemical and radiolytic conditions employed during nuclear reprocessing, and are preferably selected from SnO_2, TiO_2, Nb_2O_5, Ta_2O_5, WO_3, ZrO_2, $BaTiO_3$ or $SrTiO_3$.

Thermodynamic calculations indicate that Np(IV) is insoluble in aqueous solution at pH values greater than –0.5, solution acidities of pH less than 0 being typical of those acidities encountered in nuclear reprocessing. Thus, at pH greater than –0.5, Np(IV) is insoluble in the aqueous phase and will precipitate and may therefore be separated from uranium and plutonium which are soluble. The aqueous liquor typically contains U(VI) and Pu(IV), both of which are extractable into the organic solvent. In accordance with the first preferred embodiment, the Pu(IV) undergoes photocatalysed reduction to Pu(III), which is inextractable into organic solvent, whilst the U(VI) is reduced to U(IV), which is extractable; after the photocatalysed reduction of Np(VI) to Np(IV), and its subsequent separation by precipitation, and the photocatalysed reduction of Pu(IV) to Pu(III), this liquor may be subjected to solvent extraction, using an organic solvent, to extract the U into the non-aqueous solvent phase and leave the Pu(III) in the aqueous phase.

A third preferred embodiment of the present invention concerns a photocatalytic process comprising a spent fuel reprocessing method in which an aqueous liquor containing Np(VI) is combined with a photocatalyst and illuminated to reduce Np(VI) to Np(V). The photocatalyst comprises any metal oxide, doped metal oxide or mixed metal oxide that is demonstrably thermodynamically or kinetically stable under some or all of the chemical and radiolytic conditions employed during nuclear reprocessing, and is preferably selected from SnO_2, TiO_2, Nb_2O_5, Ta_2O_5, WO_3, ZrO_2, $BaTiO_3$ or $SrTiO_3$. The Np(V) is inextractable into organic solvent and may therefore be separated from uranium, which is extractable. The liquor typically contains U(VI) and Pu(IV), which are extractable into organic solvent and, by judicious choice of a photocatalyst with the appropriate conduction band edge energetics, are unchanged by the photocatalysis procedure, as well as Np(VI); after the photocatalysed reduction of Np(VI), this liquor may be subjected to solvent extraction using an organic solvent, to extract the U(VI) and Pu(IV) into the solvent phase and leave the Np(V) in the aqueous phase.

A variation of the third preferred embodiment envisages a process comprising a further treatment with a second type of photocatalyst, said treatment being conducted in accordance with the first preferred embodiment, so achieving sequential removal of Np(V) to the highly active waste stream by a photocatalysed process, followed by separation of Pu(III) from U by a second photocatalysed process.

As previously indicated, a particularly preferred photocatalyst for reducing Np(VI) and Np(V) to Np(IV), and reducing Pu(IV) to Pu(III) and reducing U(VI) to U(IV) is SnO_2; another preferred catalyst for this reduction is TiO_2, provided that the pH of the aqueous liquor does not fall below 1.5. ZrO_2 is also a preferred material, since it shows adequate chemical stable at pH 0 and is suitable for reducing species, its conduction band having a potential of about –1 V versus the standard hydrogen electrode at pH 0.

A fourth preferred embodiment of the invention is concerned with the use of the photocatalyst to effect the reduction of U(VI) to U(IV) ions in an aqueous liquor, particularly nitric acid solution, wherein the U(IV) ions will subsequently be used as process reagents. The photocatalyst comprises any metal oxide, doped metal oxide, or mixed metal oxide that is demonstrably thermodynamically or kinetically stable under some or all of the chemical and radiolytic conditions employed during U(IV) generation, and is preferably selected from SnO_2, TiO_2, Nb_2O_5, Ta_2O_5, WO_3, ZrO_2, $BaTiO_3$ or $SrTiO_3$. In particular, the preferred photocatalyst is SnO2, which has been demonstrated to be particularly suitable for this purpose. This embodiment of the invention also envisages the photocatalytic stabilisation of the U(IV) ions, which may or may not have been actually generated photocatalytically during subsequent dilution and storage, before use within a nuclear reprocessing plant.

CLAIMS

1. A process for controlling the oxidation state of a metal ion wherein the oxidation state or valency of the metal ion is changed or maintained by photocatalysis.

2. A process as claimed in claim 1 which comprises controlling oxidation states or valencies of metal ions in nuclear fuel reprocessing.

3. A process as claimed in claim 2 which comprises adding a particulate semiconductor photocatalyst and a soluble electron donor for the semiconductor photocatalyst to a solution containing dissolved actinide metal ions, and irradiating the semiconductor photocatalyst with electromagnetic or ionising radiation.

4. A process as claimed in claim 3 wherein the particulate semiconductor photocatalyst is removed from the solution containing the actinide metal ions.

5. A process as claimed in claim 3 or 4 wherein the semiconductor photocatalyst is in a dispersed form.

6. A process as claimed in claim 4 or 5 wherein the semiconductor photocatalyst is immobilised.

7. A process as claimed in claim 6 which additionally comprises a macroscopic solid support on which the photocatalyst becomes immobilised.

8. A process as claimed in any one of claims 2 to 7 wherein irradiation is carried out using monochromated electromagnetic radiation having sufficient energy to excite the semiconductor photocatalyst and a wavelength outside the absorption wavelength region of both the actinide and the soluble electron

donor, and of a precursor substance capable of producing a derivative which promotes inhibition of the desired actinide reduction reaction.

9. A process as claimed in any one of claims 2 to 8 wherein the system is further modified by the addition of a soluble stabiliser for actinide metal ion reduction, the stabiliser being capable of suppressing the action of any photogenerated substance that may promote inhibition of the desired reduction reaction.

10. A process as claimed in claim 9 wherein the electron donor for the semiconductor photocatalyst and the stabiliser for actinide metal ion reduction are one and the same component.

11. A process as claimed in any one of claims 3 to 10 wherein the particulate semiconductor photocatalyst is capable of undergoing photoexcitation.

12. A process as claimed in any one of claims 3 to 11 wherein the particulate semiconductor photocatalyst has chemical resistance to all chemical and radiolytic environments encountered in the reprocessing of nuclear fuels.

13. A process as claimed in any one of claims 3 to 12 wherein the particulate semiconductor photocatalyst has conduction band thermodynamics appropriate to effect the target reduction.

14. A process as claimed in claim 13 wherein the energy of the conduction band of the particulate semiconductor photocatalyst is appropriate to effect the target reduction of actinide metal ions in solution in the presence of the said semiconductor photocatalyst and a soluble electron donor for said semiconductor photocatalyst.

15. A process as claimed in claim 13 wherein the particulate semiconductor photocatalyst is modified by the addition of a dopant in order that the energy of the conduction band of the particulate semiconductor photocatalyst is appropriate to effect the target reduction of actinide metal ions in solution in the presence of the said semiconductor photocatalyst and a soluble electron donor for said semiconductor photocatalyst.

16. A process as claimed in any one of claims 3 to 15 wherein the particulate semiconductor photocatalyst has particle size in the range 1 nm to 10 μm.

17. A process as claimed in any one of claims 3 to 16 wherein the particulate semiconductor photocatalyst is photostable.

18. A process as claimed in any one of claims 3 to 17 wherein the particulate semiconductor photocatalyst comprises at least one metal oxide, doped metal oxide or mixed metal oxide that is thermodynamically or kinetically stable under the chemical and radiolytic conditions employed during nuclear reprocessing.

19. A process as claimed in claim 18 wherein the metal oxide comprises SnO_2, TiO_2, Nb_2O_5, Ta_2O_5, WO_3, ZrO_2, $BaTiO_3$ or $SrTiO_3$.

20. A process as claimed in claim 18 wherein the doped metal oxide comprises doped SnO_2, doped TiO_2, doped Nb_2O_5, doped Ta_2O_5, doped WO_3, doped ZrO_2, doped $BaTiO_3$ or doped $SrTiO_3$.

21. A process as claimed in claim 20 wherein the SnO_2, TiO_2, Nb_2O_5, Ta_2O_5, WO_3, ZrO_2, $BaTiO_3$ or $SrTiO_3$ is doped with at least one metal that is more electronegative than Sn and capable of forming a solid solution with SnO_2.

22. A process as claimed in claim 21 wherein the metal comprises at least one of Fe, Hg, Cr, Cd, U, Ta and W.

23. A process as claimed in any one of claims 3 to 22 wherein the electron donor comprises at least one material capable of irreversibly undergoing oxidation to supply electrons.

24. A process as claimed in claim 23 wherein the electron donor comprises at least one organic acid, alcohol, aldehyde, amino acid, hydrazine derivative or oxidation product of hydrazine.

25. A process as claimed in claim 24 wherein the organic acid comprises formic acid or acetic acid.

26. A process as claimed in claim 24 wherein the alcohol comprises methanol or ethanol

27. A process as claimed in claim 24 wherein the aldehyde comprises formaldehyde or acetaldehyde

28. A process as claimed in claim 24 wherein the oxidation product of hydrazine comprises hydroxylamine or dihydroxylamine.

29. A process as claimed in any one of claims 9 to 28 wherein the stabiliser for actinide metal ion reduction is capable of irreversibly undergoing oxidation by a derivative that may promote inhibition of the desired reduction reaction, the said derivative having been generated by the action of electromagnetic or ionising radiation on a precursor substance.

30. A process as claimed in claim 29 wherein the precursor substance is nitric acid.

31. A process as claimed in claim 29 or 30 wherein the photogenerated derivative that may promote inhibition of the desired reduction reaction is nitrous acid.

32. A process as claimed in any one of claims 10 or 29 to 31 wherein the stabiliser comprises hydrazine or its oxidation products.

33. A process as claimed in claim 32 wherein the oxidation product of hydrazine comprises hydroxylamine or dihydroxylamine.

34. A process as claimed in any one of claims 2 to 33 which facilitates the reprocessing of nuclear fuel to form a fissile material.

35. A process as claimed in claim 34 wherein said fissile material is in the form of a fuel pellet, a fuel pin or a fuel assembly.

36. A process as claimed in claim 34 or 35 which comprises the addition of a particulate semiconductor photocatalyst which comprises unmodified SnO_2.

37. A process as claimed in any preceding claim which comprises a spent fuel reprocessing method wherein an aqueous liquor containing U(VI) and Pu(IV) is combined with a photocatalyst and illuminated to reduce Pu(IV) to Pu(III) and U(VI) to U(IV).

38. A process as claimed in claim 37 wherein, following the photcatalysed reduction of Pu(IV) to Pu(III), the reacted liquor is solvent extracted with an organic solvent, thereby extracting the U(IV) into the organic solvent phase and leaving the Pu(III) in the aqueous phase.

39. A process as claimed in claim 37 which comprises a spent fuel reprocessing method wherein an aqueous liquor additionally containing Np(VI) is

combined with a photocatalyst and illuminated to reduce Np(VI) and Np(V) to Np(IV).

40. A process as claimed in claim 39 wherein, following the photocatalysed reduction of Np(VI) to Np(IV), the Np (IV) is subsequently separated by precipitation.

41. A process as claimed in claim 39 or 40 wherein, following the photocatalysed reduction of Pu(IV) to Pu(III), the reacted liquor is solvent extracted with an organic solvent, thereby extracting the U(IV) into the organic solvent phase and leaving the Pu(III) in the aqueous phase.

42. A process as claimed in any one of claims 2 to 36 which comprises a spent fuel reprocessing method wherein an aqueous liquor comprising U(VI), Pu(IV) and Np(VI) is combined with a photocatalyst and illuminated to reduce Np(VI) to Np(V), whilst leaving the U(VI) and Pu(IV) unchanged.

43. A process as claimed in claim 42 wherein, following the photocatalysed reduction of Np(VI) to Np(V), the reacted liquor is solvent extracted using an organic solvent, thereby extracting the U(VI) and Pu(IV) into the solvent phase and leaving the Np(V) in the aqueous phase.

44. A process as claimed in any one of claims 2 to 36 which comprises a spent fuel reprocessing method wherein an aqueous liquor containing U(VI) is combined with a photocatalyst and illuminated to reduce U(VI) to U(IV), and wherein the U(IV) ions will subsequently be used as process reagents.

45. A process as claimed in claim 44 wherein the photocatalyst is SnO_2.

46. A process as claimed in claim 44 or 45 wherein the U(IV) ions are photocatalytically stabilised before use within a nuclear reprocessing plant.

47. A process as claimed in any one of claims 38, 41 or 43 wherein the organic solvent comprises a mixture comprising tributyl phosphate and n-decane.

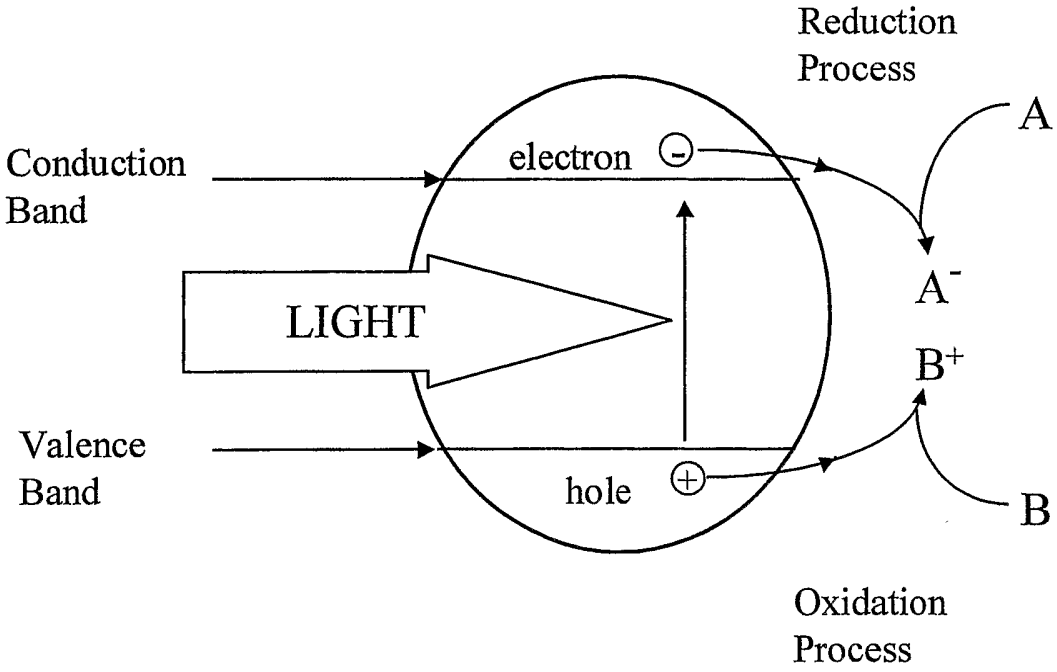


FIGURE 1

The primary reactions occurring at a particulate semiconductor photocatalyst illuminated by electromagnetic radiation of sufficient energy to photoexcite the photocatalyst.

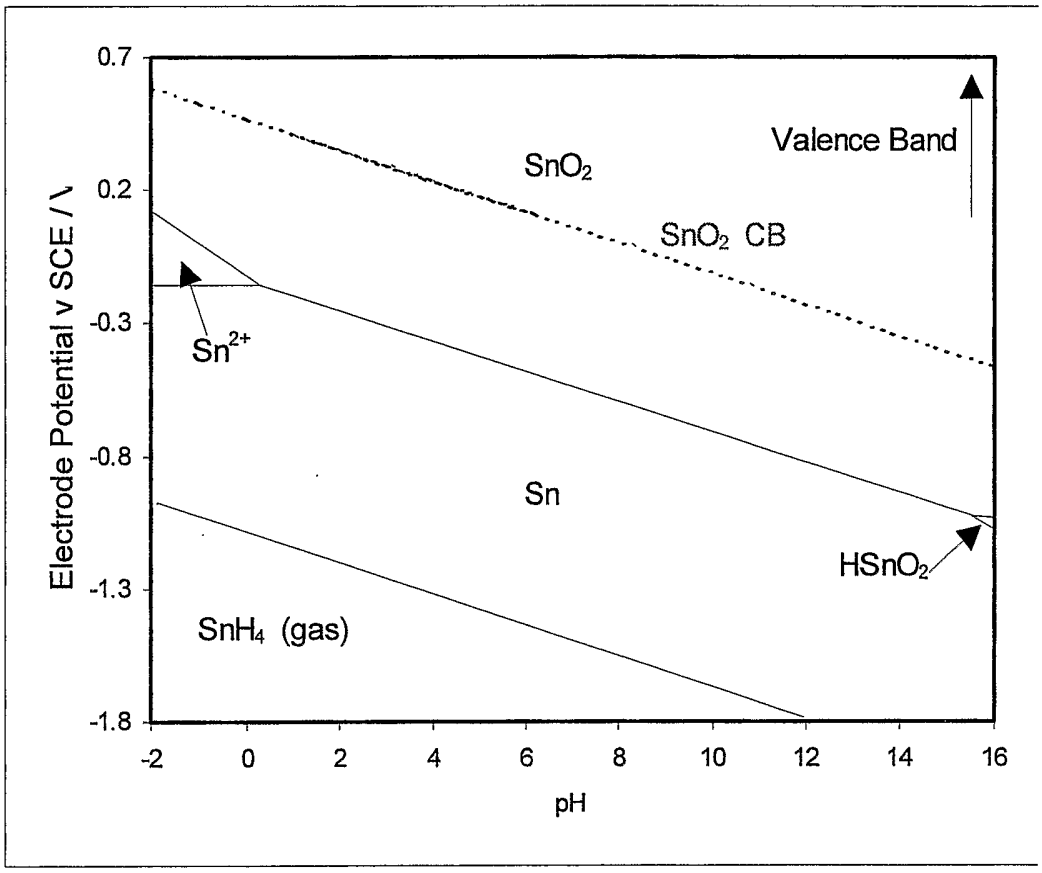


FIGURE 2

Potential-pH diagram for the tin-water system at 298 K with SnO_2 conduction band edge overlaid. Dissolved tin activity = 0.001, $P(SnH_4)$ = 1 atm, 298 K

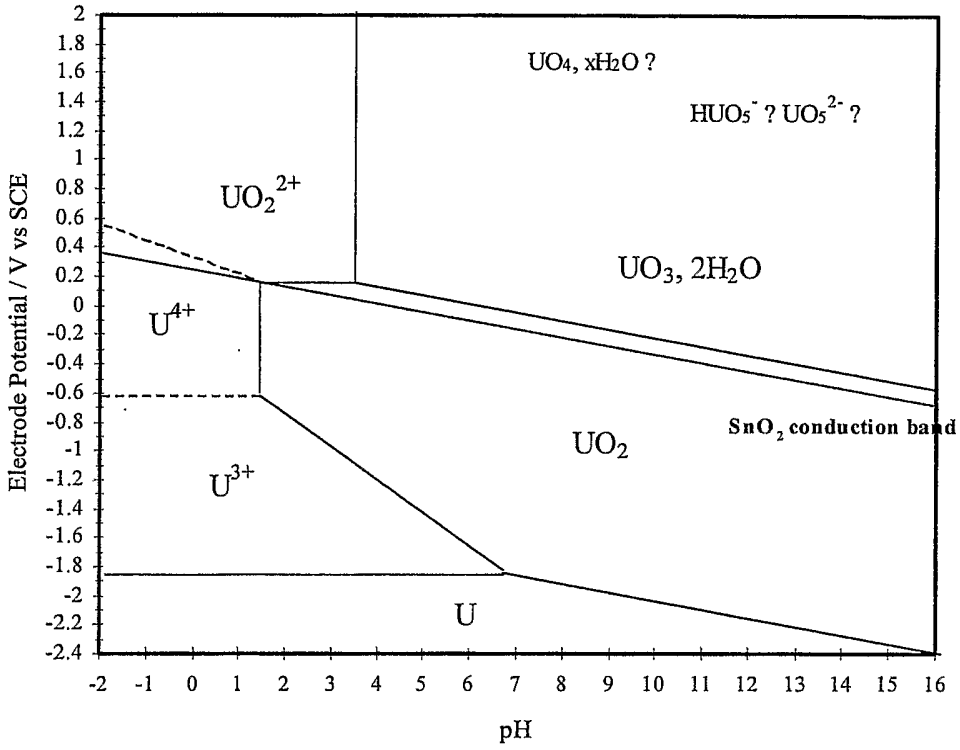


FIGURE 3

Potential-pH diagram of the uranium-water system at 298K with SnO_2 conduction band edge overlaid. Dissolved uranium activity = 0.01.

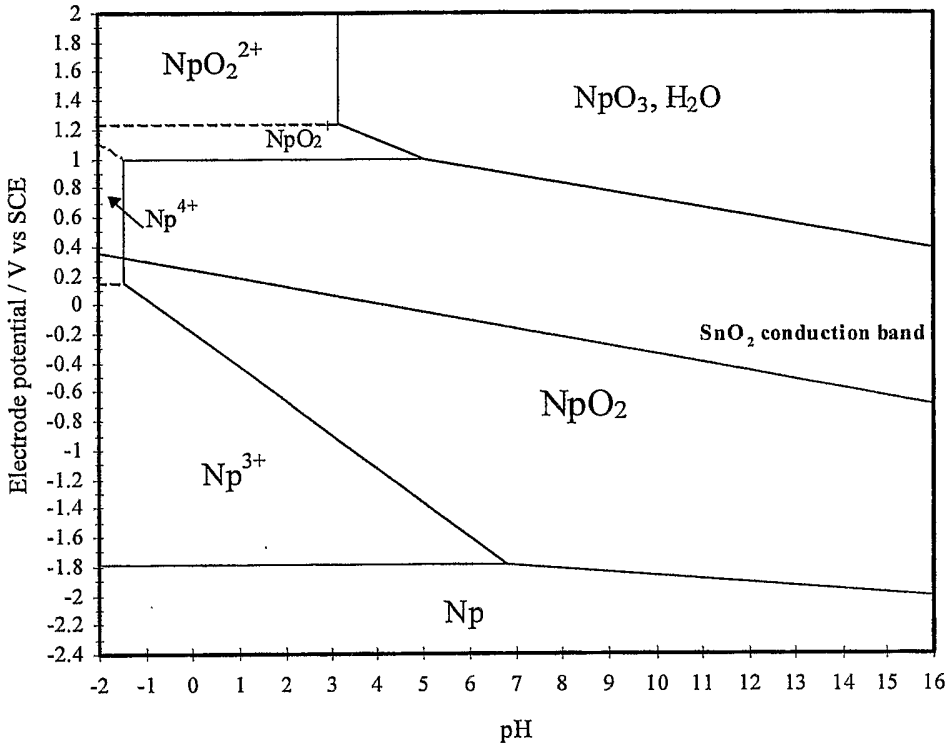


FIGURE 4

Potential-pH diagram of the neptunium-water system at 298K with SnO_2 conduction band edge overlaid. Dissolved neptunium activity = 0.01

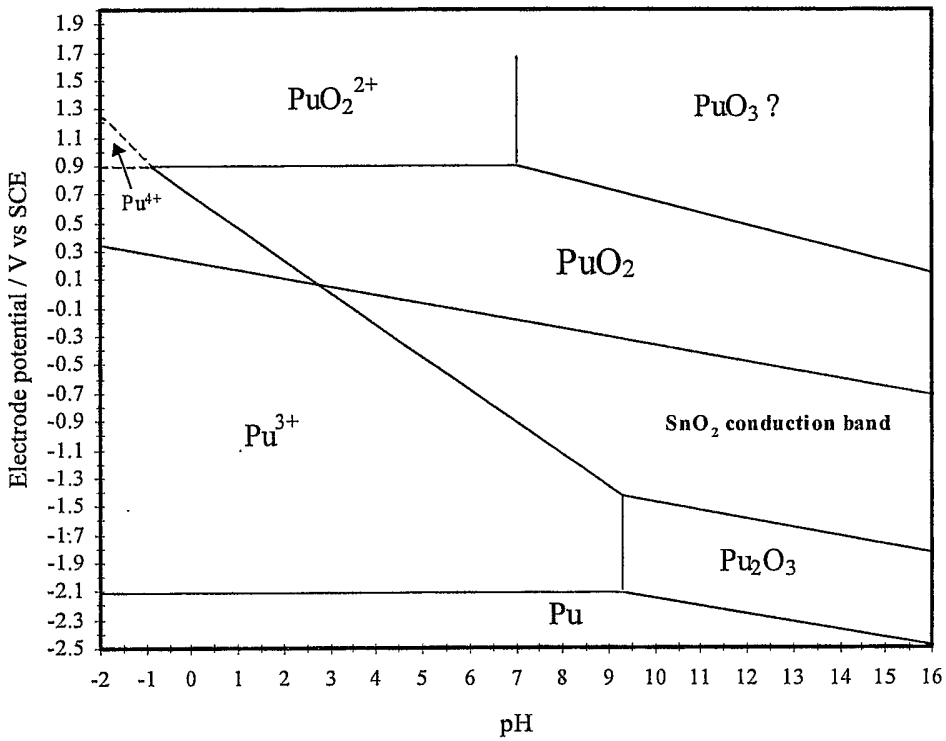


FIGURE 5

Potential-pH diagram of the plutonium-water system at 298K with SnO_2 conduction band edge overlaid. Dissolved plutonium activity = 0.01

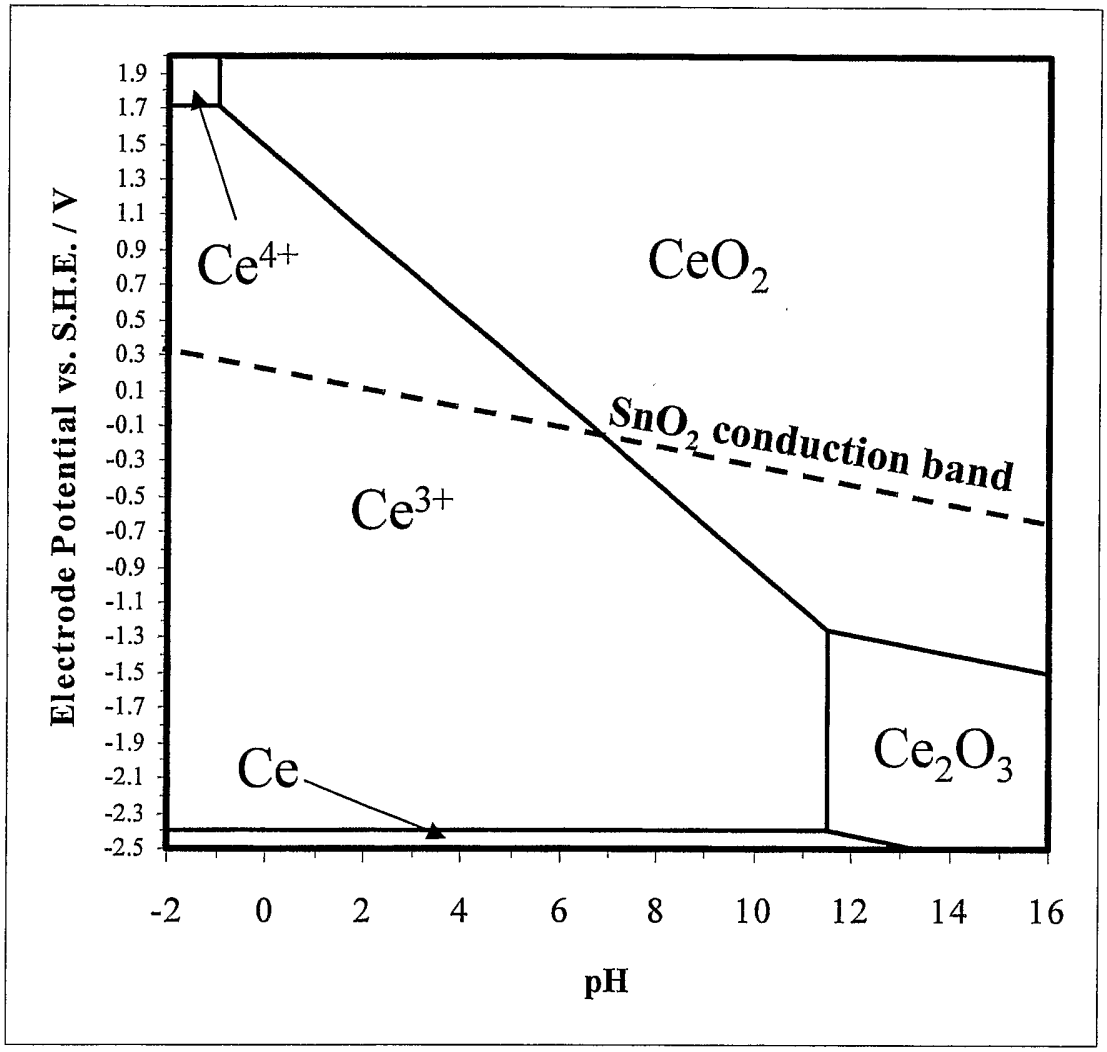


FIGURE 6

Potential-pH diagram of the cerium-water system at 298K with SnO_2 conduction band edge overlaid. Dissolved cerium activity = 0.01

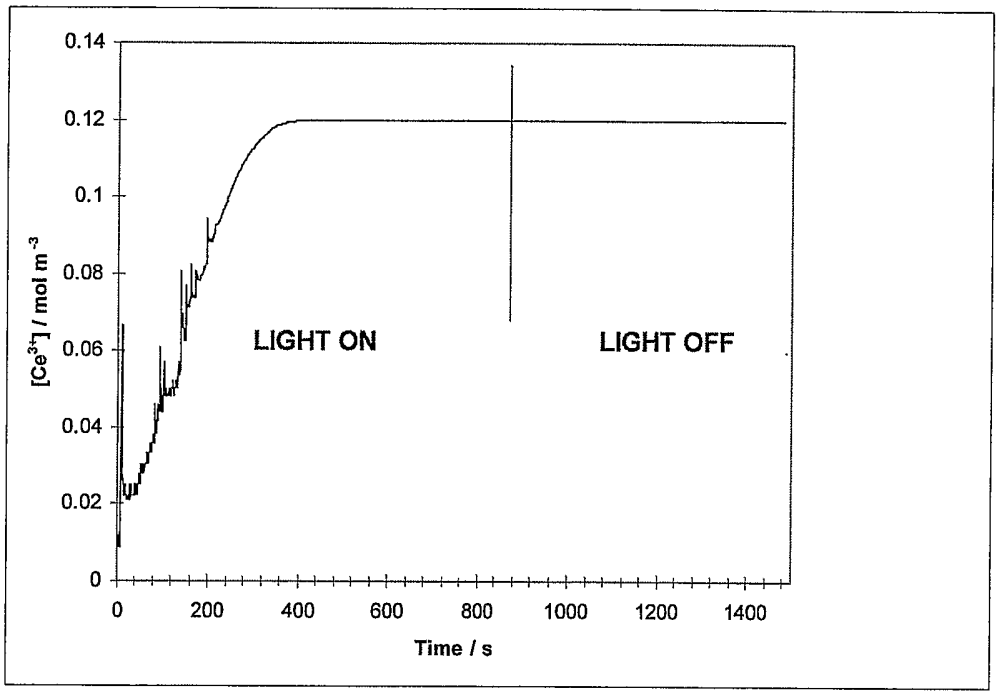


FIGURE 7

Concentration of Ce(III) as a function of illumination time. The Ce^{3+} is generated by photocatalysed reduction of Ce^{4+} achieved through illuminating with light of wavelength 312 nm a solution containing 0.12 mol Ce^{4+} m^{-3}, 55 mol ethanol m^{-3} and 100 g SnO_2 m^{-3}. Illumination is removed at 920 s.

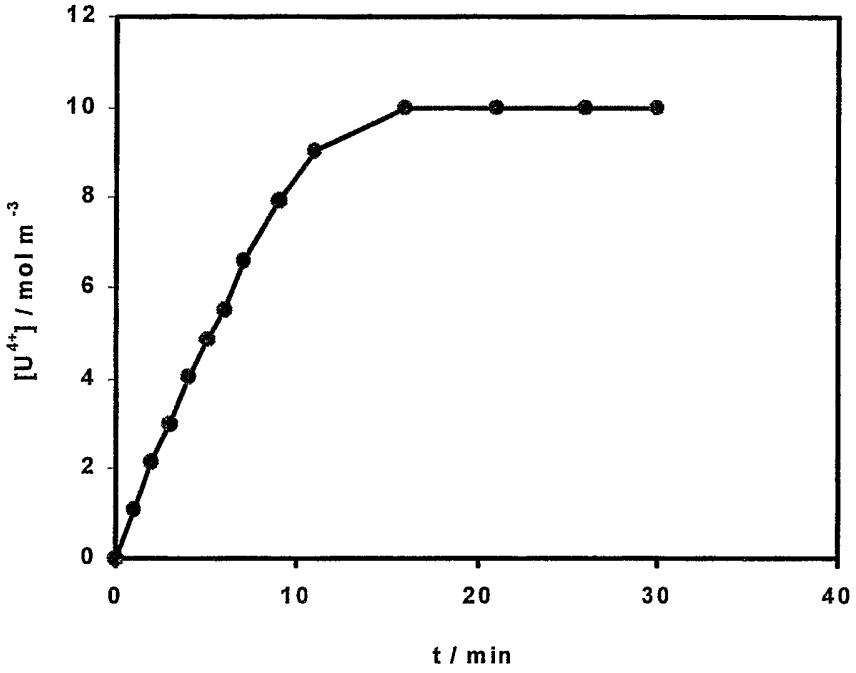


FIGURE 8

Concentration of U(IV) as a function of illumination time. The U^{4+} is generated by photocatalysed reduction of UO_2^{2+} achieved through illuminating with light of wavelength 312 nm a solution containing 10 mol UO_2^{2+} m^{-3}, 55 mol ethanol m^{-3} and 100 g SnO_2 m^{-3}.

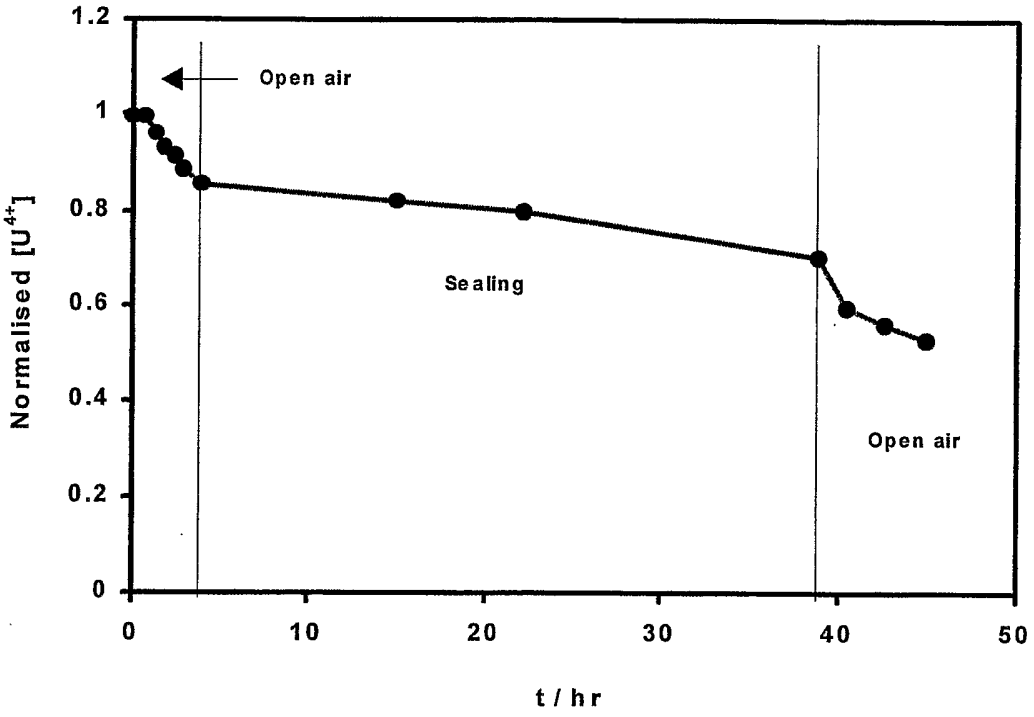


FIGURE 9

The concentration of photogenerated U(IV) as a function of time for the solution of FIGURE 8 after the source of illumination has been removed.

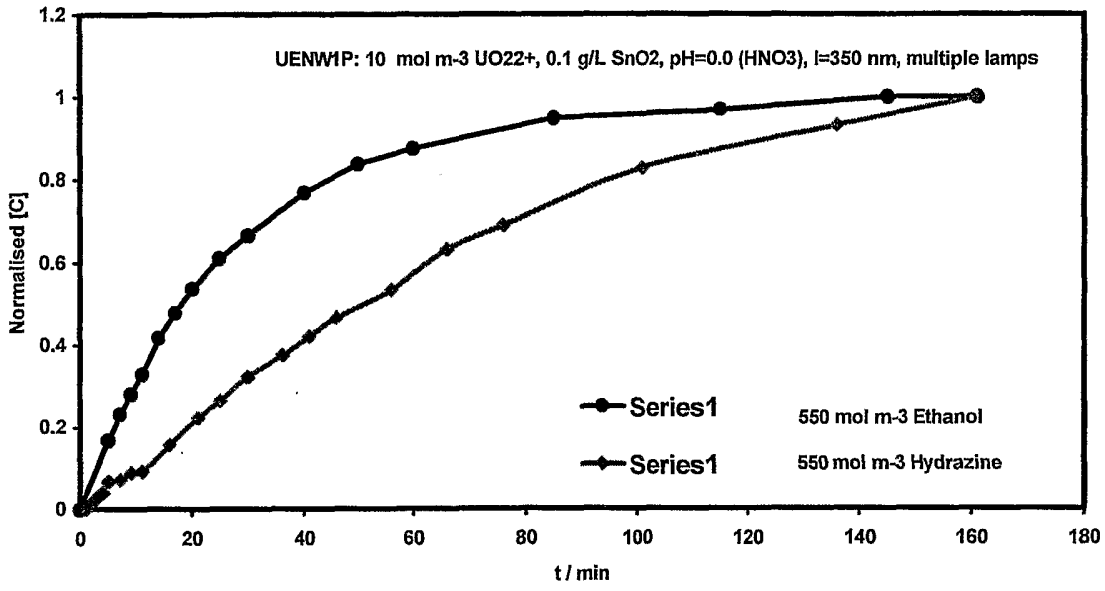


FIGURE 10

Concentration of U(IV) as a function of illumination time. The U^{4+} is generated by photocatalysed reduction of UO_2^{2+} achieved through illuminating with light of wavelength 350 nm a solution containing 10 mol UO_2^{2+} m^{-3}, 100 g SnO_2 m^{-3} and either 1, 550 mol ethanol m^{-3} (Series 1) or 550 mol hydrazine m^{-3} (Series 2).

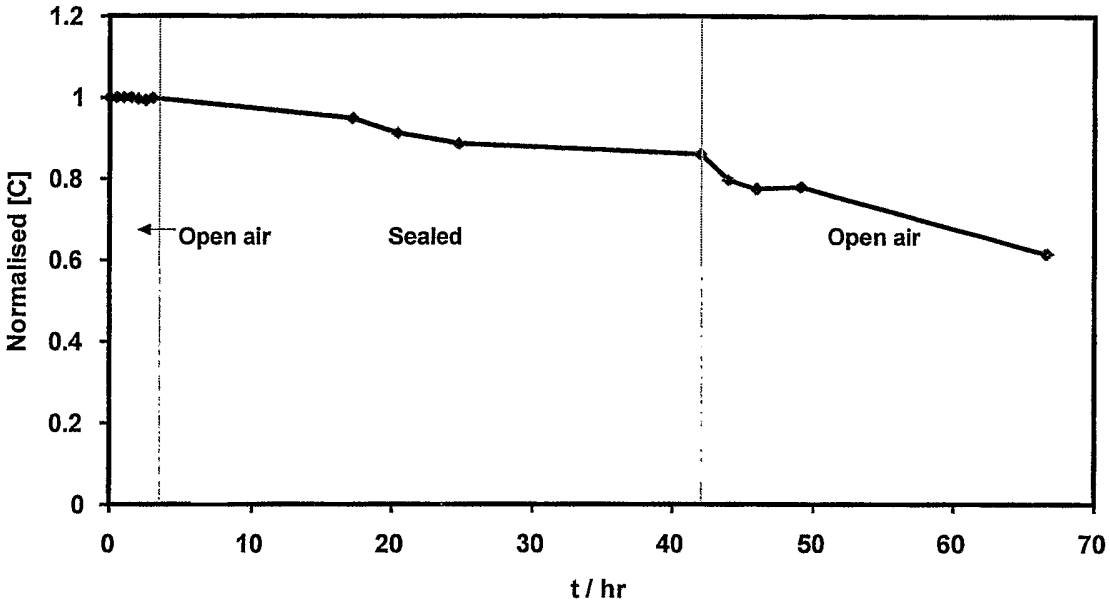


FIGURE 11

The concentration of photogenerated U(IV) as a function of time for the solution of FIGURE 10, Series 1, after the source of illumination has been removed.

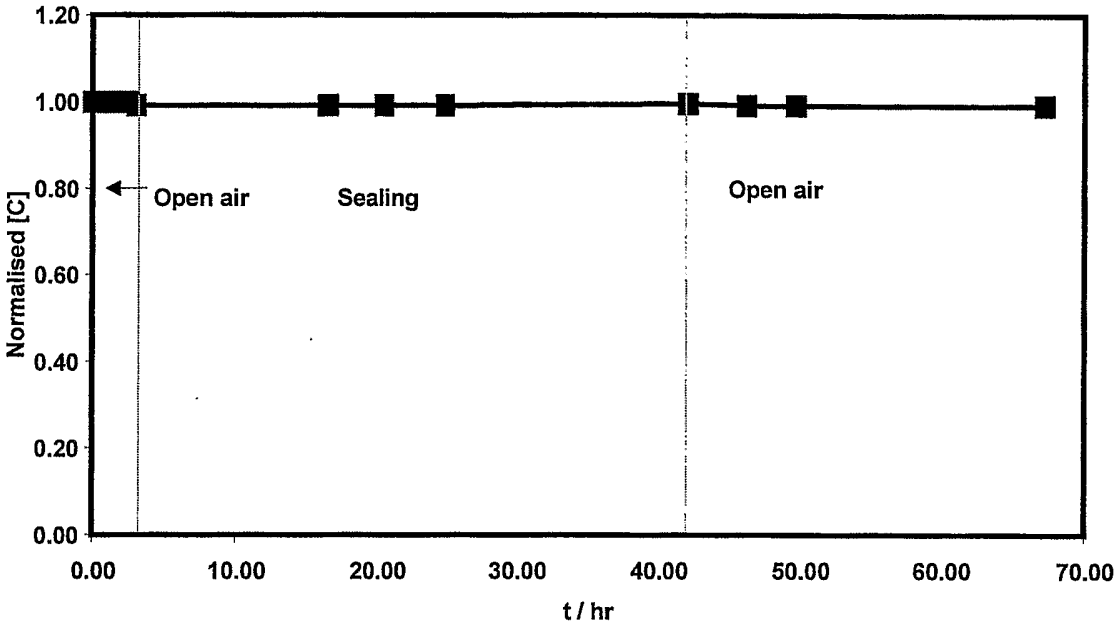


FIGURE 12

The concentration of photogenerated U(IV) as a function of time for the solution of FIGURE 10, Series 2, after the source of illumination has been removed.

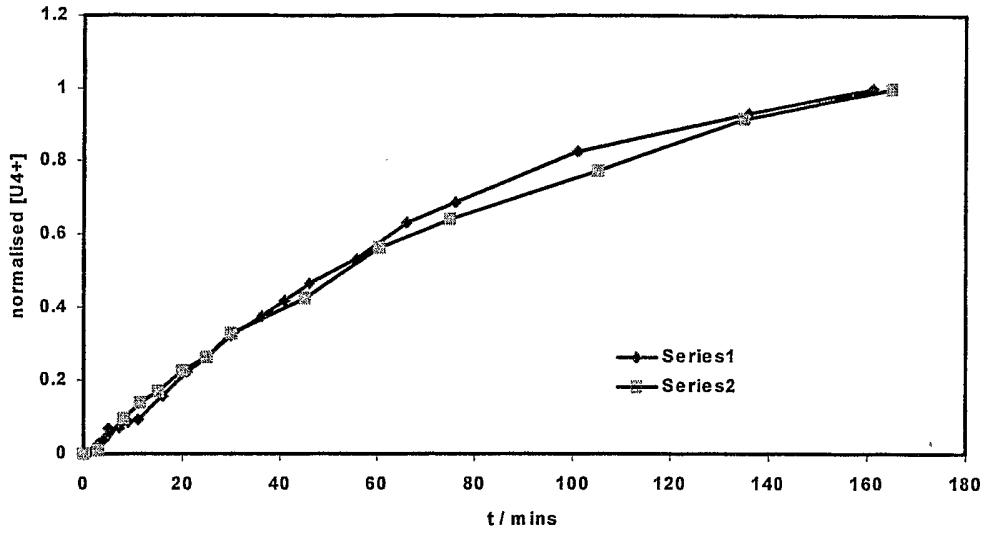


FIGURE 13

Series 1: Concentration of U(IV) as a function of illumination time. The U^{4+} is generated by photocatalysed reduction of UO_2^{2+} achieved through illuminating with light of wavelength 350 nm a one solvent phase, aqueous solution containing 10 mol UO_2^{2+} m^{-3}, 100 g SnO_2 m^{-3} and 550 mol hydrazine m^{-3}.

Series 2: Concentration of U(IV) in tributyl phospahate as a function of illumination time. The U^{4+} is generated by photocatalysed reduction of UO_2^{2+} achieved through illuminating with light of wavelength 350 nm a two solvent phase system – one solvent phase being an aqueous solution initially containing 10 mol UO_2^{2+} m^{-3}, 100 g SnO_2 m^{-3} and 550 mol hydrazine m^{-3}, the other solvent phase initially containing only tributyl phosphate.

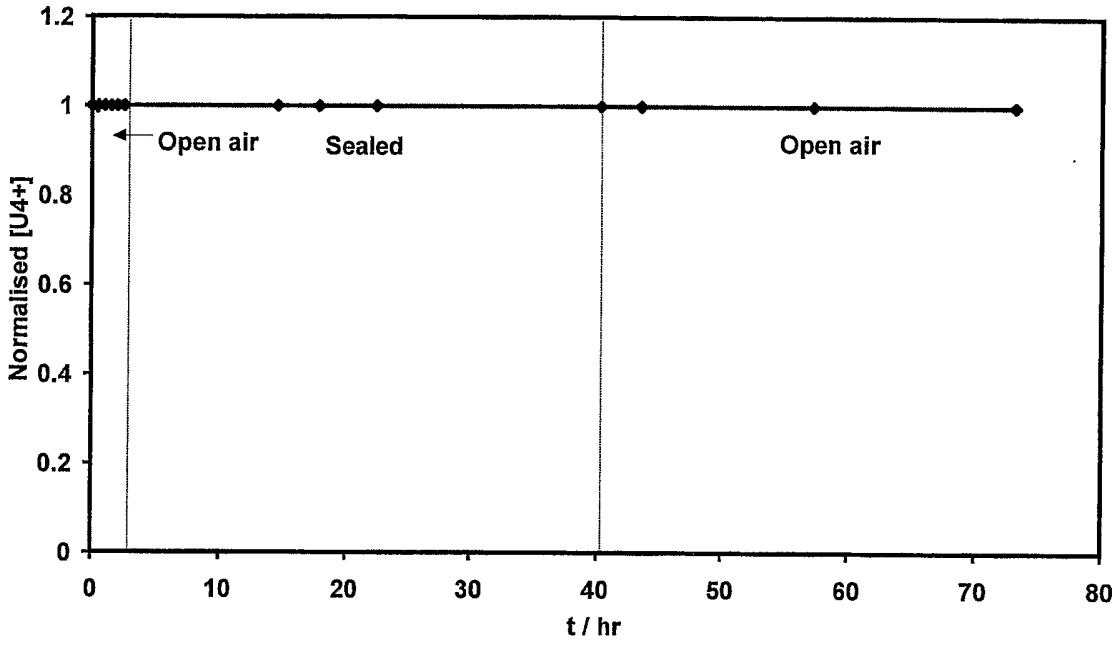


FIGURE 14

The concentration of photogenerated U(IV) as a function of time for the non-aqueous solvent phase of FIGURE 13, Series 2, after the source of illumination has been removed.

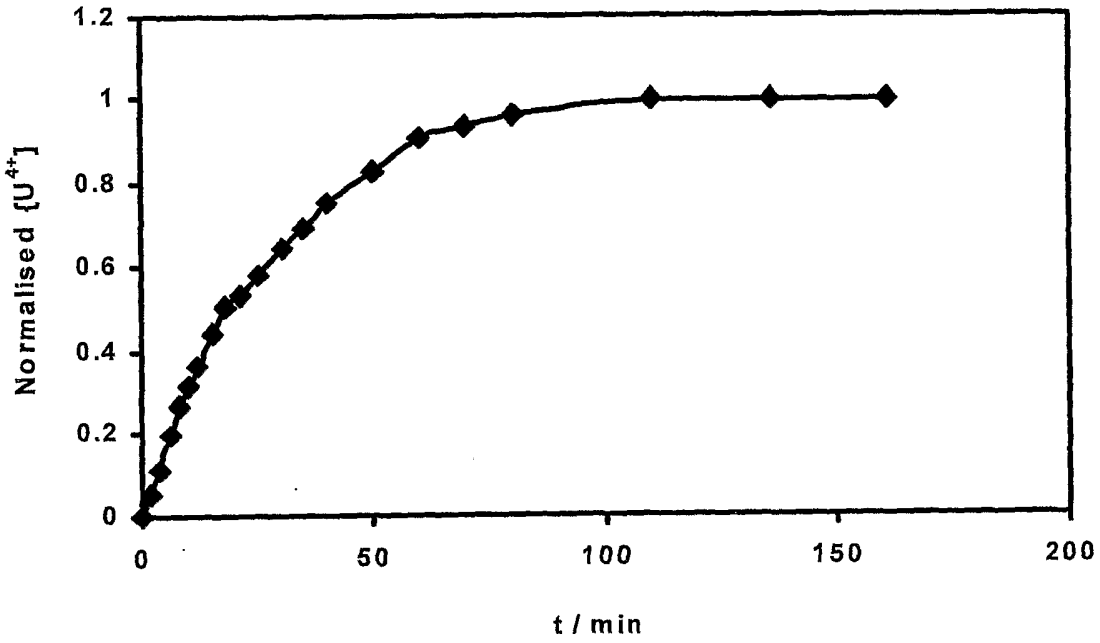


FIGURE 15

Concentration of U(IV) as a function of illumination time. The U^{4+} is generated by photocatalysed reduction of UO_2^{2+} achieved through illuminating with light of wavelength 350 nm an aqueous solution containing 10 mol UO_2^{2+} m^{-3}, 0.05 mol Ce^{4+} m^{-3}, 100 g SnO_2 m^{-3} and 550 mol hydrazine m^{-3}.