Performance of BDD Anode for Dechlorination of Nitric Acid and Regeneration of Silver (II) in a Tubular Reactor for the Treatment of Solid Wastes Containing Plutonium

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One of the problems frequently encountered in the processing of nuclear fuels is the recovery of plutonium present in solid wastes. The difficulty is to make soluble the plutonium present as the refractory oxide PuO_2. The dissolution of this oxide in nitric acid solutions is easily performed by means of silver(II) a strong oxidizing agent which is usually electrochemically generated on a platinum anode. However, certain solid residues capable of being treated to separate actinides contain important quantities of chloride ions that require an additional electrochemical step to be removed as gaseous chlorine from nitric acid before introducing Ag(I) for Ag(II) electrogeneration. Researches are developed to find electrocatalytic materials being able to replace platinum in view to limit capital costs. In the present work a set-up including a two compartment tubular reactor with recirculation of electrolytes was tested with anodes made of boron doped diamond coated niobium (Nb/BDD) and platinum coated titanium (Ti/Pt) grids for the removal of chloride (up to 0.1 M) and for silver(II) regeneration. The study showed that Nb/BDD anodes eliminate chloride contained in a solution of 6M HNO_3 in gaseous chlorine as well as anodes of Ti/Pt, without producing the unwanted oxoanions of chlorine. Furthermore, the regeneration rate of silver(II) on BDD anode is approximately equal to that obtained on platinum coated titanium anode for the same hydrodynamic conditions in the tubular reactor. Accordingly, dechlorination as well as silver(II) regeneration can be performed in the same electrochemical cell with a Nb/BDD anode. Besides, the service life of Nb/BDD anodes estimated by accelerated life tests conducted in 6M HNO_3 can be considered as very satisfactory compared to that observed with Ti/Pt anodes.

1. Introduction

Electrochemical processes involving Ag(II) regeneration from nitric acid solution of silver nitrate have been developed to treat transuranic wastes. Ag(II) is a strong oxidising agent (E° = 1.98 V/SHE) capable of attacking many organic and inorganic substances. Electrochemical processes involving oxidation of Ag(I) have been developed for the safe low-temperature destruction of a wide variety of contaminated organic waste materials (Steele, 1990). In particular, silver(II) is used for the dissolution of plutonium oxide PuO_2 by its further oxidation to higher valences such as PuO_2^+ and PuO_2^{2+} (Ryan et al. 1990). Dissolution of PuO_2 is of considerable interest, as this process is used in (*i*) aqueous reprocessing of uranium-plutonium fuel, (*ii*) fuel fabrication by reconversion of weapons-grade Pu, and (*iii*) regeneration of Pu from several types of residues produced during conversion processes. But during some of these stages, pyrochemical processes used to recover and purify Pu metal generate ashes rich in chloride salts. Consequently, in the silver(II) process operated by the nuclear industry, chloride contained in solid wastes must be first eliminated before dissolving PuO_2 by chemical attack of Ag(II) in nitric acid solution (Brossard et al. 2003). Indeed, the presence of chloride ions leads to the precipitation of Ag(I) cations to form AgCl, thus making impossible the regeneration of Ag(II) by electrolysis.

Although a chemical process of chloride removal from pyrochemical residues by sparging nitrogen dioxide in the solution was proposed by Pierce et al. (2007) it was considered that the implementation of an electrochemical process involving direct chloride oxidation could be finally simpler:

$$2\ Cl^- \rightarrow Cl_2\ +\ 2\ e \qquad (E° = 1.396\ V/SHE) \tag{1}$$

Thus, in the process of PuO_2 dissolution it would be convenient to use the same electrochemical reactor to first eliminate chloride as gaseous chlorine by electrolysis before dissolving silver nitrate and then to dissolve PuO_2 by regenerating Ag(II). In a previous study, we showed that the Nb/BDD anode can efficiently generate silver(II) in 6 mol L^{-1} nitric acid solution: compared to results found with platinised electrodes (Ti/Pt 2 and 5 μm and Nb/Pt 5 μm) the generation speed of Ag(II) was very similar and the conversion rate was of the same order of magnitude (Racaud et al. 2012). In the aim to use the same anode material to perform the sequential electrochemical steps the study of anodic chlorine evolution on BDD in nitric acid at 6 mol L^{-1} was undertaken in a tubular reactor, a design benefiting from a good experience feedback in nuclear industry (Koehly et al. 1988, 1989)

This attempt is based on the recognized stability and the high oxygen overpotential of diamond electrodes making them excellent candidates for chlorine evolution from dilute chloride solution (Ferro et al. 2000). However, at low solution acidity, at the same time that chlorine is evolved from the anode, a contribution due to oxygen evolution can simultaneously occur. In fact, Ferro et al. (2000) showed by comparison of current-potential curves for chlorine and oxygen evolution that under the same acidic condition (pH = 3.5) the faradaic yield for chlorine evolution was very high on BDD anode. Furthermore, it was shown that oxidation of chloride ions on diamond can form chlorate and perchlorate (Polcaro et al. 2009, Bergmann et al. 2009, Sanchez-Carretero et al. 2011). Although these last observations were made in neutral or alkaline solutions, it was necessary to test if these unwanted products were capable to form under electrochemical dechlorination conditions in concentrated nitric acid.

This paper presents kinetic studies conducted in a tubular reactor to perform (*i*) the electrochemical dechlorination of 6 mol L^{-1} nitric acid solutions containing chloride at concentration up to 0.1 mol L^{-1} and (*ii*) the silver(I) oxidation at initial concentration of 0.1 mol L^{-1}. In addition, the service life of Nb/BDD anodes was estimated by accelerated life tests in nitric acid at 6 mol L^{-1}. The main objective was to test the performance of the promising Nb/BDD anode and to compare its performance to that of Ti/Pt.

2. Materials and method

2.1. Electrochemical reactor

Dechlorination tests were performed under galvanostatic condition in a proprietary electrolysis set-up designed according to sub-critical geometry requirement (Figure 1). Electrolyses were achieved in a tubular reactor consisting of two coaxial compartments separated by a porous ceramic diaphragm (Koehly et al.,1988). The anodic compartment was a temperature-controlled cylinder made of glass. The cathode, in the central compartment was made of stainless steel. Two kinds of anode constituted with rectangular plates of expanded titanium or niobium covered by a layer of Pt (5 μm) or BDD ($\approx$ 1 μm) respectively were used. Plates made of Ti/Pt forming an anode with an active surface of 521 cm^2 were supplied by MAGNETO special anodes B.V. (NL) while the ones made of Nb/BDD (to build anodes of 521 and 260.5 cm^2) were supplied by Condias GmbH (DE). The cell was connected to a direct current supply (Delta Elektronika BV SM 52V-30A; NL).

The cell (Figure 1) was connected in its upper part by a glass pipe with a temperature-regulated glass tank (1.5 L capacity). The anolyte was recirculated at a flow rate up to 25 L min^{-1} to ensure satisfactory renewal of the boundary layer over the full length of the anode. Chlorine evolved in the anodic compartment was trapped in three scrubbers placed in series and containing 5 mol L^{-1} NaOH and 0.05 mol L^{-1} Na$_2$SO$_3$. The atmosphere above the cathodic compartment was swept by a flow of air to trap nitrogen oxides formed by reduction of the concentrated nitric acid (13.6 mol L^{-1}) used as catholyte.

2.2 Chemicals and analysis procedure

Nitric acid 68 % (VWR, AnalaR Normapur®) was used to prepare electrolytic solutions, whereas sodium chloride and silver nitrate (Acros Organics, ACS reagent 99%) were used as model of chloride salt for the dechlorination tests and for the electrogeneration of Ag(II) respectively.

Samples taken regularly during dechlorination experiments were immediately diluted with pure water (1v/100v). Chloride, chlorate and perchlorate were analysed by ion chromatography (Dionex ICS3000, IonPac® AS19 column 4x250 mm, suppressor and conductometric detection). The flow rate of the pump was set to 1.0 mL min^{-1}. The mobile phase composition was constant (80% of NaOH 5 mmol L^{-1} + 20 % of NaOH 100 mmol L^{-1}) for 1 min and then the gradient was from 20 % to 90 % of NaOH 100 mmol L^{-1} during

27 min to provide good separation of all the peaks in a single chromatogram. Return on initial conditions lasted 4 min. Titration of Ag(II) was described by Racaud et al., 2012.
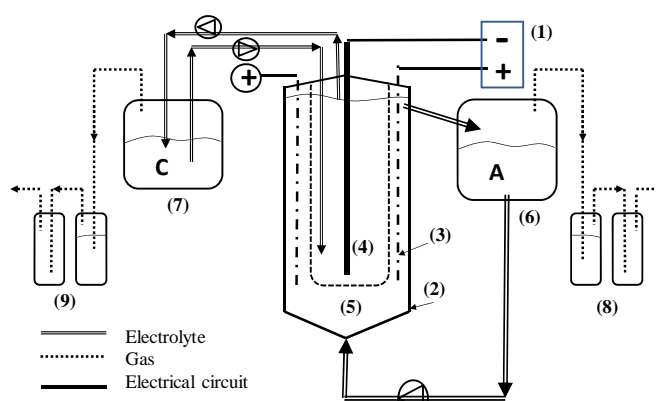

Figure 1: Dechlorination set-up. (1) Power supply (2) Tubular reactor (3) Anode (Nb/BDD or Ti/Pt) (4) Cathode (SS) (5) Diaphragm (6) Tank (anolyte) (7) Tank (catholyte) (8) Chlorine absorber (9) NOx absorber.

The end-point of electrochemical dechlorination was detected by a redox titration on two indicator platinum electrodes (0.28 cm^2 each). In the region of the end-point, when the concentration of chloride reaches a value lower than 10^{-3} mol L^{-1} the voltage (ΔE) between the electrodes varies considerably when they pass a current equal to 50 μA. A sharp change of ΔE arises when the imposed current becomes greater than the oxidation limiting current of Cl$^-$ that marks exactly the end of the electrolysis.

Before each dechlorination experiment the anolyte (1.5 L of 6 mol L^{-1} HNO$_3$ + 0.1 mol L^{-1} NaCl) was recirculated between the anodic compartment and the reservoir during one hour to reach a stationary temperature of 60 °C. A sample of the anolyte was taken for chromatographic analysis just before starting electrolysis.

2.3 Stability of electrodes

The service life of an electrode material is a mattering parameter to estimate its time of use and validate its industrialization. Ageing tests were performed in which the samples were submitted to galvanostatic runs in 6 mol L^{-1} HNO$_3$ at high current density (j = 50 kA m^{-2}) in electrochemical cells of 100 mL capacity, without separator, thermo-regulated at 30°C, under agitation and with a zirconium cathode (7 cm^2). The vapours were evacuated by pumping. Anodes (1.8 cm^2 each; 3 of the Ti/Pt (5μm) type from Magneto and 3 of the Nb/BDD type from Condias) were submitted to tests up to their deactivation. The concentration of nitric acid was straightened every day after concentration control. It was considered that anodes were deactivated when the cell potential exceeded 10 V. We report and discuss here only on the variation of the cell voltage as a function of time.

3. Experimental results and discussion

3.1 Mass transfer rate

Under industrial conditions, concentration of chloride ions in nitric acid can reach 1 mole L^{-1} (Koehly et al., 1989, Pierce et al., 2007) whereas in dechlorination the final concentration should be lower than 10^{-3} mol L^{-1} to avoid AgCl precipitation when AgNO$_3$ is introduced. The rate of reaction (1) may be controlled by charge transfer or mass transport depending on the applied current density, chloride concentration, and hydrodynamic conditions which may depend on the rate of gas evolution at the anode (Racaud et al., 2012). If a sufficient potential, or current intensity, is applied to operate reaction (1) by mass transport control the reaction rate can then be identified to the limiting current I_{lim} that is the maximum reaction rate:

$$I_{lim} = n \, F \, S \, k \, [Cl^-] \tag{2}$$

where n is the number of electrons exchanged, F is the Faraday constant (96498 C mol^{-1}), S the electrode surface (m²) and [Cl$^-$] the chloride concentration (mol m^{-3}).

The mass transfer coefficient, k, was measured at 60°C for dechlorination in the tubular reactor under anolyte recirculation at a flow rate Φ = 20 L min^{-1} consistent with industrial conditions. Measurements were carried out in 6 mol L^{-1} nitric acid with sodium chloride at initial concentration of 0.040 mol L^{-1} and 0.050 mol L^{-1} lower than that used typically in the industrial process ([Cl$^-$]$_0$ = 0.1 mol L^{-1}) in view to obtain current-

potential curves presenting a net diffusion plateau. Plots (not shown) of the electro-oxidation of chloride were obtained point by point under galvanostatic conditions: for successive controlled current intensity values the electrode potential was registered after 3 seconds. Chloride oxidation appears distinctly before water discharge as a short plateau of 150 mV length. The mass transfer coefficient k was then determined using the limiting current intensity measured at 1.45 V/SCE on Ti/Pt, and 2.5 V on Nb/BDD. Current intensities were corrected by the residual current measured in nitric acid at 6 mol L^{-1}. The mass transfer coefficient k, measured at 60 °C, was equal to 6.01×10^{-5} m s^{-1} at the Ti/Pt 5µm anode, whereas it was equal to 4.84×10^{-5} m s^{-1} at the Nb/BDD anode. The discrepancy between the two values of k results probably from different induced hydrodynamic conditions established by the different expended metals. The mass transfer coefficient k was determined at the same flow rate for Ag(I) oxidation at 25 °C; values of k were 5.0×10^{-5} m s^{-1} and 4.2×10^{-5} m s^{-1} respectively at Ti/Pt and Nb/BDD electrode. The k values were used to calculate the $[Cl^-] = f(t)$ curves (see below).

3.2 Dechlorination

Dechlorination experiments were conducted under galvanostatic condition at applied current lower, equal or higher to the initial limiting current. Figure 2a shows that 6 mol L^{-1} nitric acid solutions, initially containing 0.1 mol L^{-1} of chloride, can be dechlorinated until 10^{-3} mol L^{-1} in less then 2500 s at I = 30 A on the Ti/Pt anode. Figure 2b shows that under the same conditions, chloride can be removed in 3000 s on Nb/BDD.

During an electrolysis started at a current intensity I lower than the initial limiting current $I°_{lim}$ ($\alpha = I / I°_{lim} < 1$), when $[Cl^-]$ reaches a critical concentration defined by $[Cl^-]_c = I/nFkS$, the potential of the anode increases and oxygen evolution starts. A critical time t_c can be defined by: $t_c = \tau (1-\alpha) / \alpha$, where $\tau = V_{sol}/(S\,k)$ (Walsh, 1993). Figure 2a shows a case where $\alpha = 1$, that is for which the process is all along mass transfer limited; thus, the chloride concentration varies as: $C(t) = C_0 \exp(-t / \tau)$. A similar case is represented with curve I in Figure 2b (for the same ratio V_{sol}/ S), whereas for a surface of electrode reduced by half (Figure 2b, curve II) an increase of the ratio α to 2.47 has no accelerating effect.

According to the value of the mass transfer coefficient of these two electrodes, electrolysis times to reach the final chloride concentration of 10^{-3} mol L^{-1} were slightly higher for the Nb/BDD anode than for Ti/Pt.

The series of dechlorination tests assessed also that perchlorate and chlorate were always in concentration lower than the detection limit of the analytical protocol (perchlorate < 10^{-3} and chlorate < 2×10^{-3} mol L^{-1}).

In summary, in this device characterized by a (S / V_{sol}) ratio of 35 m^{-1}, electrochemical dechlorination can be performed satisfactorily in 40 minutes under standard industrial conditions; therefore, the process carried out with the Nb/BDD could be adapted for industrial application.
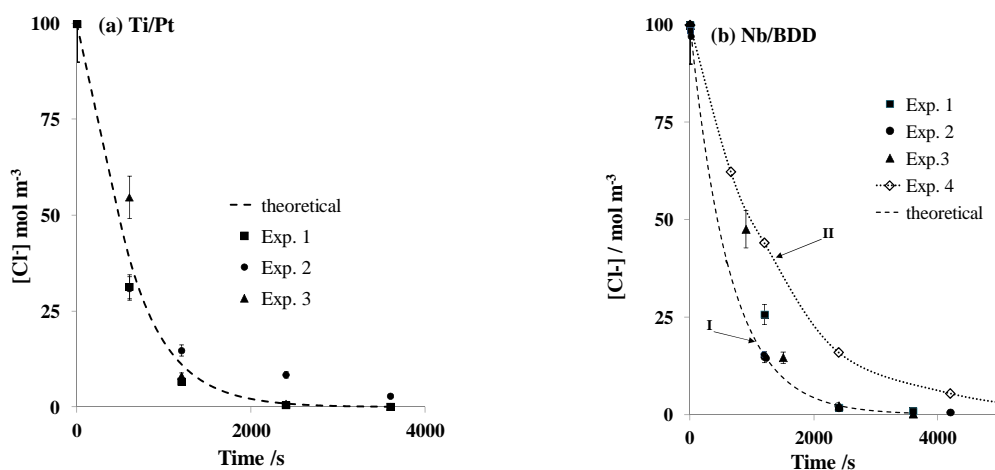

Figure 2. Calculated (dotted lines) and experimental (symbols) [Cl⁻] = f(t) curves on (a) Ti/Pt, and (b) Nb/BDD anodes. V_T (anolyte) = 1.5 L; $[NaCl]_0$ = 100 mol m^{-3} in 6 mol L^{-1} HNO_3; T = 60 °C; flow rate Φ = 20 L min^{-1}; I = 30 A. Modelling using (a) k = 6.1×10^{-5} m s^{-1} and α = 1 for Ti/Pt (S = 521 cm^2; $I°_{lim}$ = 30.2 A), and (b) k = 4.84×10^{-5} m s^{-1} for Nb/BDD. Exp. 1-3 (curve I): anode surface S = 521 cm^2; α = 1.23; $I°_{lim}$ = 24.3 A. Exp. 4 (curve II): anode surface S = 260.5 cm^2; α = 2.47; $I°_{lim}$ = 12.2 A.

3.3 Silver(I) oxidation

In the anodic compartment, Ag^{2+} generated in aqueous nitric acid solution at 6 mol L^{-1} is stabilized by nitrate ion; thus in the absence of a reducing agent, silver(II) is present as a dark brown nitrate complex:

$$Ag^+ + NO_3^- \rightarrow Ag(NO_3)^+ + e^- \hspace{4cm} (3)$$
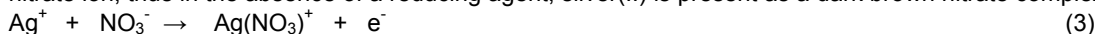
However, the increase of the Ag(II) concentration gives a rise to the rate of oxidation of the water according to reaction (2):

$$2\,Ag(NO_3)^+ + H_2O \rightarrow 2\,Ag^+ + 2\,HNO_3 + \tfrac{1}{2}\,O_2 \hspace{3cm} (4)$$
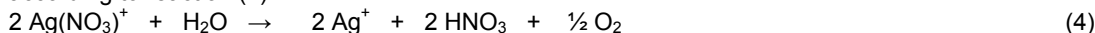
Thus, the concentration of Ag(II) reaches a quasi-stationary value.

Table 1 presents values of the initial rate of generation of Ag(II) for different current intensities just as the conversion of Ag(I) at the stationary state. The Nb/BDD electrode presents performance slightly lower than that of the Ti/Pt electrode of platinum for the most important both currents (15A and 30A). For the current intensity lower than 15 A, the generation speeds of Ag(II) obtained with Nb/BDD are similar to those obtained with Ti/PT. By increasing the current, the speeds of generation of Ag(II) and the conversion rate increase. However, at current intensity higher than I_{lim}, competitive reactions between hydroxyl radicals (and hydrogen peroxide) and Ag(II) slow down the production rate of Ag(II) as shown in Table 1 for I = 30 A (α = 2.8). Thus, using a BDD anode needs a perfect control of the current to optimise Ag(II) generation.

Table 1: Ag(II) generation rate and conversion at stationary state as functions of current intensity for Nb/BBD and Ti/Pt anodes in the tubular reactor. [Ag(I)]$_0$=0.05 mol L^{-1}, [HNO$_3$]=6 mol L^{-1}, T=30°C, Ø=20 L min^{-1}, S=521 cm^2.

Current / A	Nb/BDD		Ti/Pt 5µm	
	Generation rate mol m^{-2} min^{-1}	Conversion %	Generation rate mol m^{-2} min^{-1}	Conversion %
7.3	5.99×10^{-2}	34.4	6.19×10^{-2}	36.83
15	7.31×10^{-2}	33.04	9.36×10^{-2}	41.82
30	6.59×10^{-2}	-	1.29×10^{-1}	-

Referring to a batch recirculation reactor system, a study was developed to simulate the galvanostatic electrolysis. The theoretical modelling is based on a mass balance in which the rate of Ag(II) generation is expressed as the difference between the production rate by electrolysis and the destruction rate by reaction with water (Racaud et al., 2012). Figure 3 presents experimental results for an electrolysis performed in the tubular reactor.

3.4 Electrode stability

Figure 4 shows the variation of the cell potential during electrolysis under very high anodic current density for six electrodes. The relative jump of potential indicates the total deactivation of an electrode. The life expectancy of three Ti/Pt anodes were respectively of 880, 1280 and 1550 hours whereas those of the anodes of diamond were 1620, 1720 and >1810 hours. A theoretical extrapolation based on a practical current density of 1500 A m^{-2} leads to a minimal life expectancy of more than 3 years for Ti/Pt (value in agreement with the industrial experience on the TiPt) and approximately 6 years for Nb/BDD.
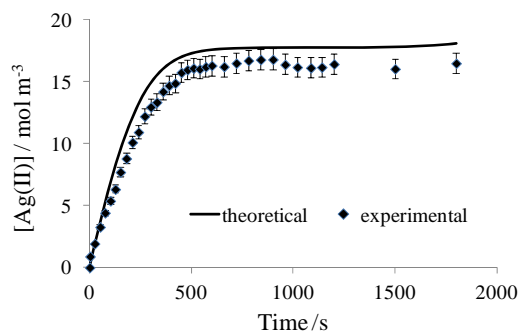

Figure 3: Theoretical (line) and experimental (symbol) variation of Ag(II) concentration during electrolysis. Electrolysis conditions: [Ag(I)]$_0$=0.05 mol L^{-1}; T=30°C, [HNO$_3$]=6mol L^{-1}; k = 4.24 x 10^{-5} m s^{-1}; I=15A, anode Nb/BDD; error bars = ± 10%. Theoretical values are obtained from Equations 4-14 in Racaud et al. (2012).
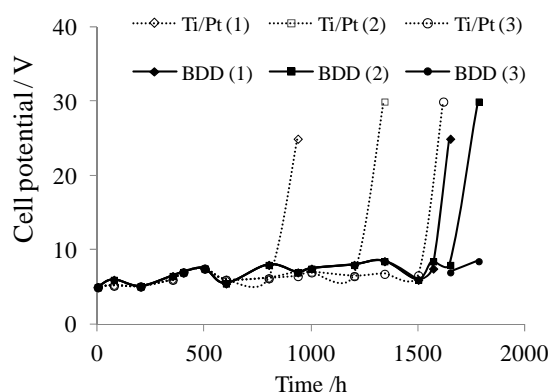
Figure 4: Accelerated life tests of Ti/Pt electrodes (empty symbols) and BDD electrodes (full symbols) in 6 mol L^{-1} HNO$_3$ solution with current densities of 50 kA m^{-2} at 30°C.

Conclusions

This study developed with a tubular electrochemical cell has shown that the Nb/BDD anode represents an interesting alternative in the Ti/Pt anode for the dechlorination as well as for the regeneration of Ag(II) in nitric acid solution. Therefore, sequence of both steps in the same reactor is possible because conductive diamond shows a kinetic performance comparable to that of platinised titanium. Results obtained with Ti/Pt 5µm and Nb/BDD anodes were satisfactory since dechlorination reached 99 %, value in accordance with the practical objective. Furthermore, the formation of oxoanions of chlorine was not detected during electrochemical dechlorination. The specific particularity of the Nb/BDD electrode lies in the service life practically double than that of Ti/Pt. Monitoring the rate of Ag(I) oxidation on the BDD anode imposes however the current density to be controlled to avoid the generation of hydroxyl radicals susceptible to slow down the rate of the Ag(II) electrochemical regeneration.

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