Appendix 3
Electrochemical reduction of U(VI)

Contents

A3.1 Introduction

The preparation of U(IV) is required to achieve the precipitation of a suitable U(IV) amorphous phase. Different preparation methods exist to obtain tetravalent uranium from hexavalent uranium: chemical reduction by reducing agents such as dithionite and metallic zinc or electrochemical reduction. However, electrochemical reduction presents the main advantage that the introduction of undesirable chemical impurities in the solution is avoided.

A3.2 Material

The equipment required for an electroreduction is rather simple (Figure A3.1). A three electrodes system is used to maintain the cathodic potential at a constant and fixed value throughout the electrolysis. The electrolysis cell includes a working electrode where the reduction reaction occurs (cathode), a counter-electrode (anode) needed for the current flow and a reference electrode against which the potential at the cathode is measured. Platinum electrodes are used as working and counter-electrodes since platinum is relatively non-reactive. By means of a potentiostat (CMS 100, Gamry Instruments, version 2.40a), the potential difference applied between the working electrode and the counter-electrode is varied in function of the measured current in such a way that the potential between the working and the reference electrode is maintained constant (cathodic potential working mode). The potential at the cathode is measured against a saturated silver/silver chloride reference electrode (Ag/AgCl reference electrode). The measured values were corrected to be expressed with respect to the standard hydrogen electrode (SHE):

$$E \text{ cathode (SHE)} = E \text{ cathode (Ag/AgCl electrode)} + E \text{ (Ag/AgCl electrode)}$$

At 25°C, the potential of the Ag/AgCl electrode (Metrohm) in 3 M KCl electrolyte solution is 0.207 V *versus* SHE.

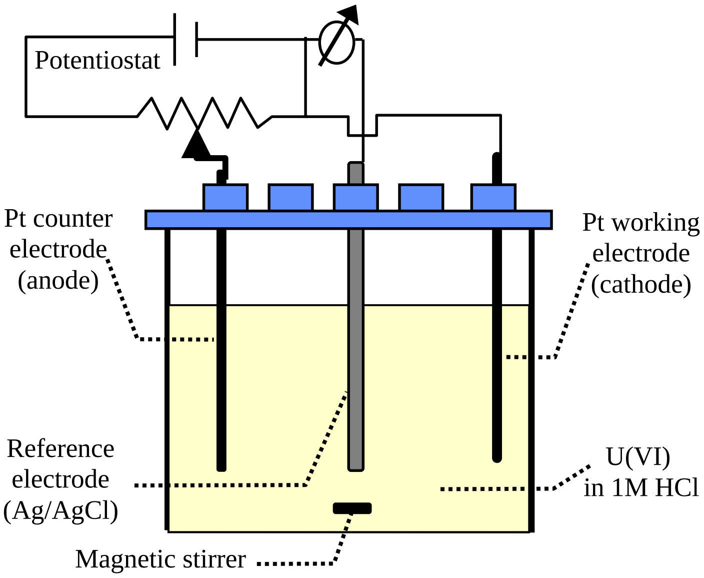

Figure A3.1. Experimental set-up for the electrochemical reduction of U(VI).

A3.3 Experimental conditions

The U(VI) reduction is promoted in acidic medium as described by the reaction:

$$UO_2^{2+} + 2e^- + 4H^+ \rightleftharpoons U^{4+} + 2H_2O \qquad E^0 = 0.267\ V \text{ (Grenthe } et\ al.\text{, 1992)}$$

Consequently, the electroreduction was performed in 1M HCl background solution. Unlike HNO_3, H_2SO_4 and $HClO_4$, HCl is not an oxidised acid and was thus selected. Moreover, U(IV) remains stable in 1M HCl for several hours in air (Dierckx *et al.*, 2000).

The formal potential (E) at 25°C and 1 atm of the UO_2^{2+}/U^{4+} couple in HCl medium is given in Grenthe *et al.* (1992, Table V.3, p.93). The reported values vary from 0.310 to 0.337 V *versus* NHE[1] at HCl molality between 0.2 and 2 $mol{\cdot}kg^{-1}$. However, the potential required to reduce U(VI) to U(IV) is higher than the theoretical potential. An overpotential is needed to overcome the cell resistance and the activation barrier of the reaction itself.

To resume, the optimal potential for the uranium electroreduction has to be lower than about 300 mV (the theoretical value for the reduction) but sufficiently high to avoid the massive production of gaseous hydrogen, $H_2(g)$, at the cathode. In 1 M HCl solution (*p*H = 0), the reduction of H^+ to form gaseous H_2 occurs at 0 V *versus* SHE:

$$2\,H^+ + 2e^- \rightleftharpoons H_2(g) \qquad E^0 = 0\ V$$

Therefore, the selected value to perform the U(VI) electroreduction in 1 M HCl was -200 mV *versus* Ag/AgCl reference electrode, *i.e.* 7 mV *versus* SHE just above the reduction potential of the protons. This value of cathodic potential was also used by Dierckx *et al.* (2000).

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[1] NHE: normal hydrogen electrode is a synonym of SHE (standard hydrogen electrode).

The U(VI) solution was prepared by weighing 0.136 g of $UO_2(NO_3)_2 \cdot 6H_2O$, removing nitrate by heating the salt in concentrated HCl and dissolving the residue in 27 ml 1M HCl to obtain an U(VI) solution at a concentration of 10^{-2} $mol \cdot l^{-1}$. If the uranium salt was directly dissolved in 1M HCl, the presence of nitrate (2×10^{-2} $mol \cdot l^{-1}$) could introduce interferences during the electrolysis. To avoid any possible complications, nitrate was removed before electroreduction. The uranyl nitrate salt was first dissolved in 3 ml of concentrated HCl (37%). The solution was then evaporated until dryness under an infra-red-lamp. The process of dissolution in concentrated HCl and evaporation was repeated three times. Finally, the solid residue was dissolved in 1M HCl. An aliquot of 1 ml was sampled and analysed by UV-Vis spectrophotometry as reference spectra of U(VI). The remaining 26 ml were electroreduced for 25 hours under atmospheric conditions at a constant cathodic potential of –200 mV *versus* Ag/AgCl reference electrode under constant stirring to enhance the transport of the reactive species towards the electrodes.

The oxidation state of uranium was controlled by UV-Vis spectrophotometry (Varian Cary 500 spectrophotometer) at the wavelength range of 350-750 nm.

A3.4 Problems

Several problems were encountered with the electrochemical reduction technique.

Although the reduction of natural uranium was possible, the electroreduction of the 233-uranium isotope was not successfully achieved. The specific activity of 233-uranium (357 $Bq \cdot \mu g^{-1}$) is much higher than that of natural uranium (0.01 $Bq \cdot \mu g^{-1}$). A likely explanation is that the oxidising species produced by radiolysis of the solution caused by the radioactivity of 233-uranium may prevent the reduction.

Since the electroreduction occurs under atmospheric conditions, the U(IV) acidic solution was degassed by bubbling with pure Ar prior to its titration by NaOH. To avoid this step of degassing, we attempted to electrochemically reduce natural U(VI) in degassed 1 M HCl under an Ar-0.4% CO_2 atmosphere (< 5 ppm O_2) but without success. Under these anaerobic conditions, the formation of a black layer at the cathode was noticed. The reduction of U(VI) was probably inhibited by this layer.

Finally, unexpected problems were met with the electrochemical reduction technique. The spectrophotometric controls of the acidic U(IV) solution showed that the absorbance at 648 nm characteristic for U(IV) was about 30-40 % lower than the value measured for the electroreduced U(IV) stock solutions used in the study of the time evolution of the solubility (see 6.2). A systematic study of the different parameters was performed: change of 3M KCl electrolyte solution of the Ag/AgCl reference electrode, change of working, counter- and reference electrodes, preparation of fresh 1M HCl background solution, change of potentiostat (minipotentiostat MP 95, Bank elektronik), variation of the stirring velocity and addition of reducing agent such as hydrazine. Unfortunately, we did not succeed in solving the problem. Therefore, U(IV) was produced by the oxidative dissolution of uranium metal in concentrated HCl.

A3.5 References

Dierckx, A., Put, M., De Cannière, P., Wang, L., Maes, N., Aertsens, M., Maes, A., Vancluysen, J., Verdickt, W., Gielen, R., Christiaens, M, Warwick, P., Hall, A., van der Lee, J. 2000. Transport of radionuclides due to complexation with organic matter in clay formations (Trancom-Clay). European Commission Nuclear Science and Technology. Final report **EUR 19135** EN.

Grenthe, I., Fuger, J., Konings, R.J.M., Lemire, R.J., Muller, A.B., Nguyen-Trung Cregu, C., Wanner H. 1992. *Chemical Thermodynamics of Uranium,* Vol. 1 (H. Wanner and I. Forest, eds). OECD-Nuclear Energy Agency, North-Holland Elsevier Science Publishers B.V., Amsterdam.