I+E MML

FR9403004

CEA-CONF--11818

Xavier MACHURON-MANDARD
Commissariat à l'Energie Atomique
Centre d'Etudes de Saclay
INSTN-SECh
91191 Gif-sur-Yvette; France
Phone : 33-1-69.08.53.00
Fax : 33-1-69.08.77.82

Lecture Abstract (January 25, 1994)

Abstract

The hydrometallurgical processes designed for recovering valuable metals from mineral ores as well as industrial wastes usually require preliminary dissolution of inorganic compounds in aqueous media before extraction and purification steps.

Unfortunately, most of the minerals concerned hardly or slowly dissolve in acidic or basic solutions, which can be a major drawback for the design of efficient industrial processes.

Metallic oxides, sulfides and silicates are among the materials most difficult to dissolve in aqueous solutions. They are also among the main minerals containing valuable metals. Consequently, owing to industrial and scientific interest, many research programs have been undertaken worldwide to gain a better understanding of their dissolution reactions, from both kinetics and mechanism point of view.

The redox properties of such materials sometimes permit to improve their dissolution by adding oxidizing or reducing species to the leaching solution, which leads to an increase in the dissolution rate. Moreover, limited amounts of redox promoters are required if the redox agent is regenerated continuously thanks to an electrochemical device.

Nuclear applications of such concepts have been suggested since the dissolution of many actinide compounds (e.g., UO_2, AmO_2, PuC, PuN,...) is mainly based on redox reactions. In the 1980s, improvements of the plutonium dioxide dissolution process have been proposed on the basis of oxidation-reduction principles, which led a few years later to the design of industrial facilities (e.g., at Marcoule or at the french reprocessing plant of La Hague).

General concepts and well-established results obtained in France at the Atomic Energy Commission (Commissariat à l'Energie Atomique) will be presented and will illustrate applications to industrial as well as analytical problems.

Catalysed Electrolytic Metal Oxide Dissolution Processes

-CEMOD-

Principles and Applications to Actinide Oxide Dissolution or Actinide-Bearing Solid Waste Decontamination

Dr. Xavier MACHURON-MANDARD
Commissariat à l'Energie Atomique
CE-SACLAY; FRANCE

PLAN

- Introduction .
- Historical Background .
- Basic Concepts on Metal Oxide Dissolution Chemistry .
- Applications to Actinide Dioxides .
- Industrial and Analytical Applications .
- Conclusions .

Introduction

Industrial and Scientific Interest of the Dissolution of Metal Bearing Materials

Hydrometallurgical processes devoted to :

Rare metals extraction (Au, Ni, Cu, Co, Mn, Zn, U, . . .)

Au, Ag . . .

$(Ni,Fe)_9S_8$, $CuFeS_2$, $(Co,Ni)_3S_4$ . . .

MnO_2, UO_{2+x} . . .

$Ca(H_3O)_2(UO_2)_2(SiO_4)_2.3H_2O$ . . .

Introduction

Industrial and Scientific Interest of the Dissolution of Metal Bearing Materials

Hydrometallurgical processes devoted to :

- **Substandard nuclear fuel recycling ,**
- **Radioactive wastes treatment ,**
- **Heat exchanger decontamination (LOMI reagents)**
- **Radionuclides preparation ,**
- **Sample preparation for analysis .**

Introduction

Design of New Chemical Processes

What are the problems to solve ?

- Thermodynamics
- Kinetics
- Industrial feasibility (Cost and Safety)
    - Reactor Design ,
    - Monitoring ,
    - Chemicals ,
    - Energy ,
    - Corrosion . . .

HISTORICAL BACKGROUND

ca. 1000 B.C.
Mediterranean basin

Copper leaching extraction from ores

Mine drainage water containing soluble copper compounds resulting from the action of thiobacillus-like bacteria

HISTORICAL BACKGROUND

South Africa (1890)

Gold extraction by cyanidation

$$4Au + 8NaCN + 2H_2O + O_2 \rightarrow 4Na[Au(CN)_2] + 4NaOH$$

$$2Na[Au(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Au$$

HISTORICAL BACKGROUND

20th Century

Uranium extraction from basic ores

$$UO_2 + 1/2\ O_2 \longrightarrow UO_3$$

$$UO_3 + Na_2CO_3 + 2\ NaHCO_3 \rightarrow Na_4UO_2(CO_3)_3 + H_2O$$

HISTORICAL BACKGROUND

Eugène PELIGOT (Fr)

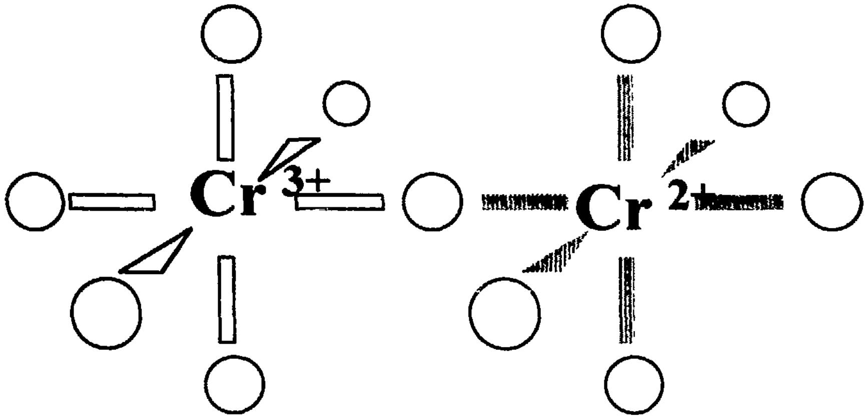
Annales de Chimie Physique , 1845 , vol 14, pp 239-244

$$CrCl_3 \xrightarrow{CrCl_2} Cr^{3+} + 3\ Cl^-$$

Aqueous dissolution of chromium (III) chloride catalysed by minute amounts of chromium (II) ions

HISTORICAL BACKGROUND

1st step : **Chromous ion adsorption and inner sphere coordination structure formation**



○ **Chloride ions**

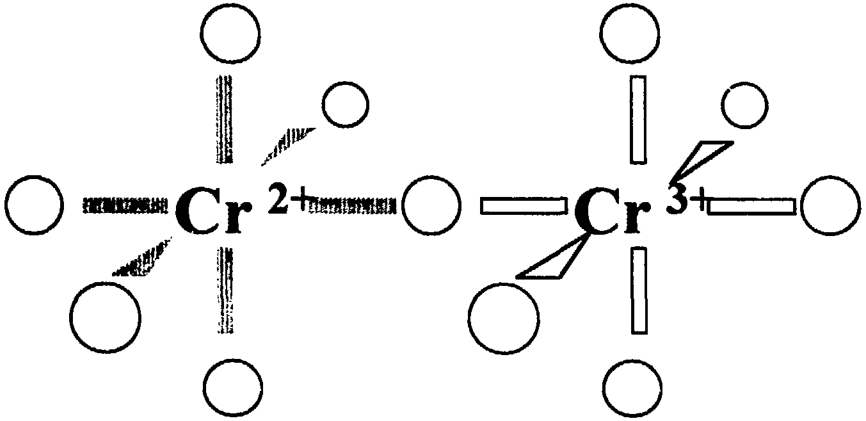
○ **Water molecules**

▭ **Strong chemical bond (inert structure)**

▨ **Weak chemical bond (labile structure)**

HISTORICAL BACKGROUND

2nd step: electron transfer and crystal lattice destruction



○ Chloride ions

◯ Water molecules

▭ **Strong chemical bond (inert structure)**

▬ **Weak chemical bond (labile structure)**

Basic Concepts on Metal Oxide Dissolution Chemistry

Acid-Base reactions

$$M_xO_y + 2y\,H^+ \rightarrow x\,M^{2y/x\,+} + y\,H_2O$$

$$M_xO_y + 2y\,H^+ \xrightarrow{L} x\,(M^{2y/x\,+})\,L + y\,H_2O$$

Complexation can help from Thermodynamics and Kinetics point of view

Basic Concepts on Metal Oxide Dissolution Chemistry

Acid-Base reactions
-example-

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

$$\Delta G° > 30\ \text{kJ/mol}$$

Basic Concepts on Metal Oxide Dissolution Chemistry

Acid-Base reactions

-example-

$$PuO_2 + 4\ H^+ + x\ NO_3^-$$

$$\downarrow$$

$$(Pu^{4+})(NO_3^-)_x + 2\ H_2O$$

$\Delta G° < 0$ kJ/mol (concentrated HNO_3 media)

Basic Concepts on Metal Oxide Dissolution Chemistry

Acid-Base reactions

-example-

$$PuO_2 + 4\,H^+ + F^- \xrightarrow{\text{Concentrated Nitric Acid}} PuF^{3+} + 2\,H_2O$$

$\Delta G° < 0$ kJ/mol

Basic Concepts on Metal Oxide Dissolution Chemistry

Oxidation-Reduction Reactions

combined with acid-base reactions

$$M_xO_y + 2y\ H^+ \rightarrow x\ M^{(2y/x \pm n)} + y\ H_2O$$

-/+ n electrons

Redox reactions can help from Thermodynamics and Kinetics point of view

Basic Concepts on Metal Oxide Dissolution Chemistry

Oxidation-Reduction reactions

-examples-

$UO_2 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2NO_2 + 2H_2O$

$3UO_2 + 8HNO_3 \rightarrow 3UO_2(NO_3)_2 + 2NO + 4H_2O$

$4UO_2 + 10HNO_3 \rightarrow 4UO_2(NO_3)_2 + N_2O + 5H_2O$

$MnO_2 + 2HCl + 2H^+ \rightarrow Mn^{2+} + 2H_2O + Cl_2$

$CeO_2 + 1/2H_2O_2 + 3H^+ \rightarrow Ce^{3+} + H_2O + 1/2O_2$

Applications to Actinide Dioxide Dissolution

Acid-Base Reaction Thermodynamics

$$\underset{\text{Solid}}{MO_2} + 4\,H^+ \longrightarrow \underset{\text{Soluble}}{M^{4+}} + 2\,H_2O$$

MO_2	UO_2	NpO_2	PuO_2	AmO_2
ΔG° kJ/mol	26.54	44.54	32.04	59

Applications to Actinide Dioxide Dissolution

Oxidation Reaction Thermodynamics

$$\underset{\text{Solid}}{MO_2} \xrightarrow{-\ 1\ \text{electron}} \underset{\text{Soluble}}{MO_2^{\ +}}$$

MO_2	UO_2	NpO_2	PuO_2	AmO_2
E° V/SHE ($\Delta G° = -\mathcal{F}E°$)	+ 0.65	+ 1.13	+ 1.43	+ 1.43

Applications to Actinide Dioxide Dissolution

Oxidation Reaction Thermodynamics

$$\underset{\text{Solid}}{MO_2} \xrightarrow{-\,2\text{ electron}} \underset{\text{Soluble}}{MO_2^{\;2+}}$$

MO_2	UO_2	NpO_2	PuO_2	AmO_2
E° V/SHE ($\Delta G° = -2\mathcal{F}E°$)	+ 0.41	+ 1.18	+ 1.22	+ 1.51

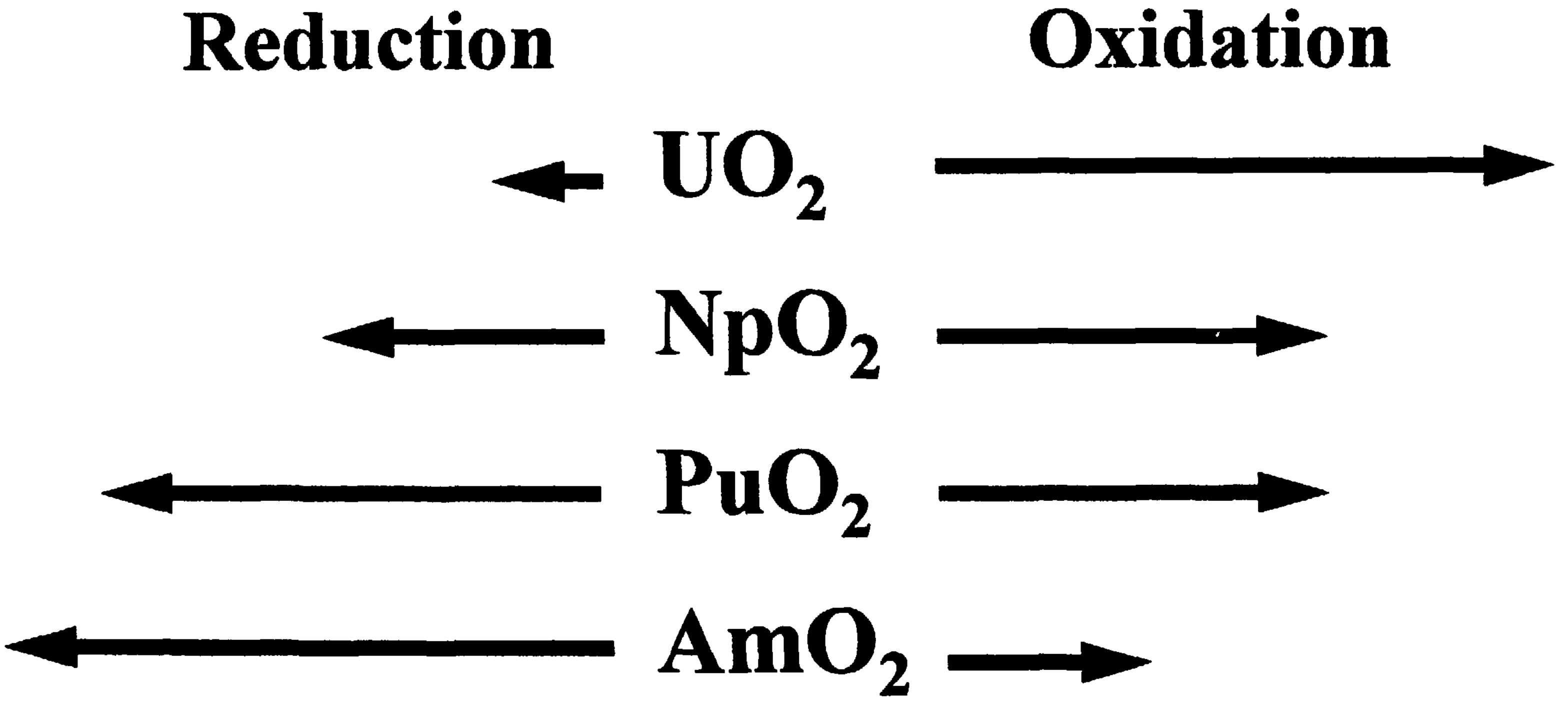
Applications to Actinide Dioxide Dissolution

Reduction Reaction Thermodynamics

$$\underset{\text{Solid}}{MO_2} + 4\,H^+ \xrightarrow{+\,1\ \text{electron}} \underset{\text{Soluble}}{M^{3+}} + 2\,H_2O$$

MO_2	UO_2	NpO_2	PuO_2	AmO_2
E° V/SHE ($\Delta G° = -\mathcal{F}E°$)	- 0.79	- 0.31	+ 0.67	+ 2.01

Applications to Actinide Dioxide Dissolution



Reduction

Oxidation

UO_2

NpO_2

PuO_2

AmO_2

Industrial and Analytical Applications

Oxidative Process

Oxidant	E° (V/SHE)
MnO_4^-/Mn^{2+}	1.51
Ce^{4+}/Ce^{3+}	1.61
Co^{3+}/Co^{2+}	1.83
Ag^{2+}/Ag^{+}	1.98
$S_2O_8^{2-}/HSO_4^-$	2.11

Industrial and Analytical Applications

Reductive Process

Reductant	E° (V/SHE)
I^-/I_2	0.54
$Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$	0.36
V^{3+}/VO^{2+}	0.34
U^{4+}/UO_2^{2+}	0.33
H_2/H^+	0.00

Industrial and Analytical Applications

Reductive Process

Reductant	E° (V/SHE)
$\mathrm{Ti^{3+}/TiOH^{3+}}$	- 0.06
$\mathrm{V^{2+}/V^{3+}}$	- 0.26
$\mathrm{Ti^{2+}/Ti^{3+}}$	- 0.37
$\mathrm{Cr^{2+}/Cr^{3+}}$	- 0.41
$\mathrm{U^{3+}/U^{4+}}$	- 0.61

Catalysed Electrolytic Dissolution Process

- Continuous electrogeneration of the reactant

low mediator concentrations required

- Reaction readily monitored

electrolysis intensity

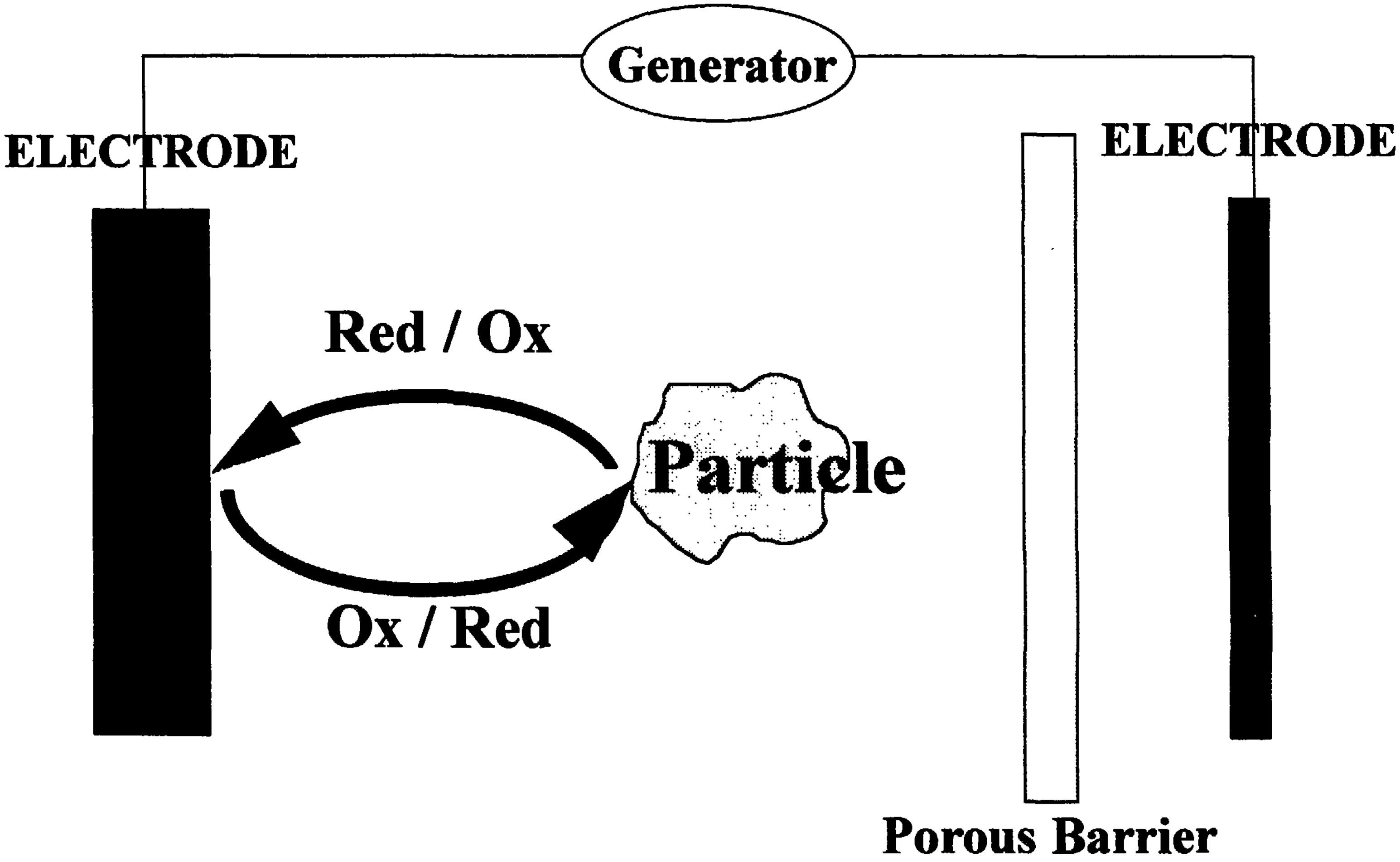
- Soft aqueous media

less corrosive than fluoride ion containing solutions

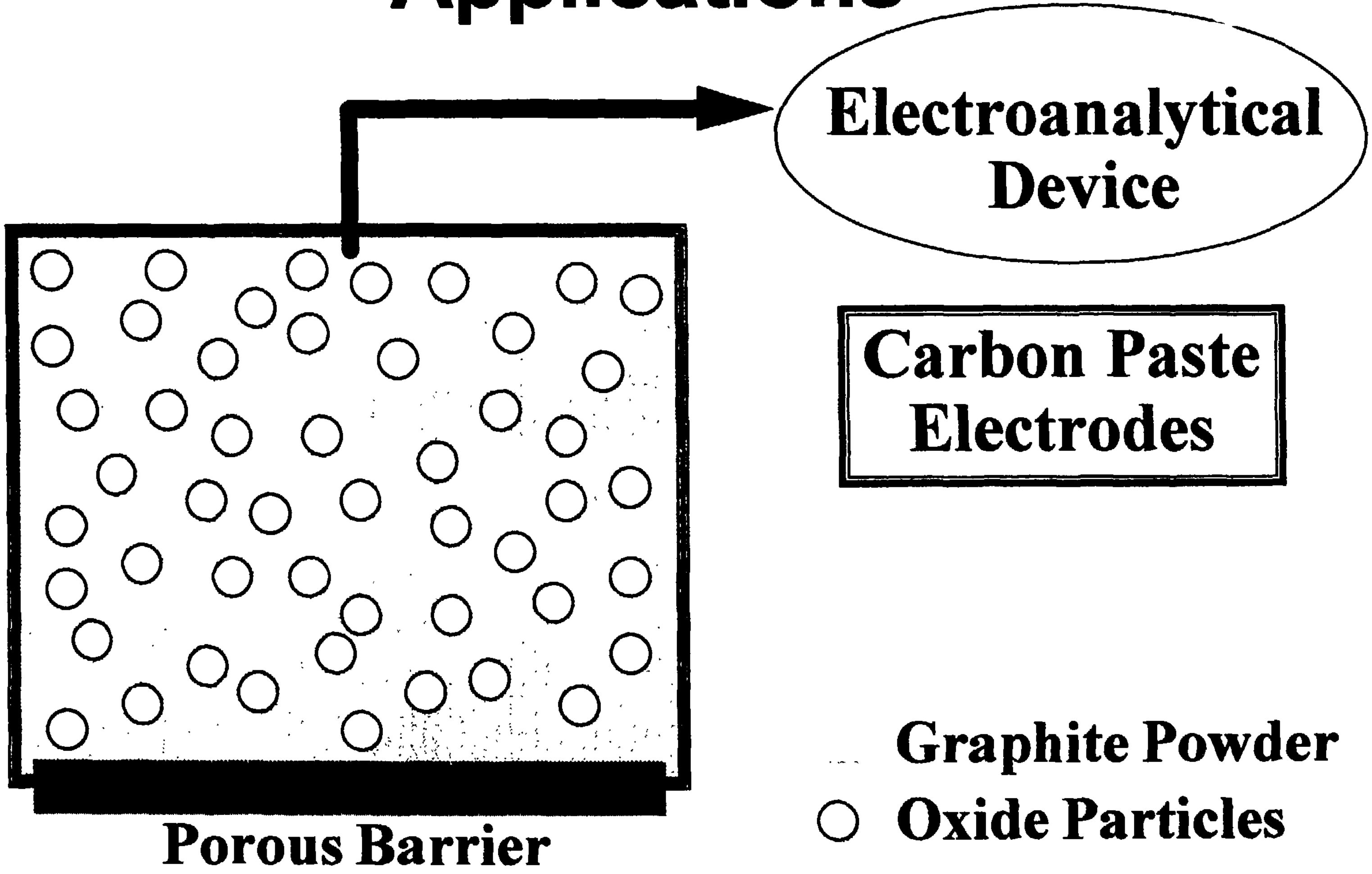
- High dissolution rates

the electrogeneration of the redox species
can be the rate determining step

Industrial and Analytical Applications



Industrial and Analytical Applications



Electroanalytical Device

Carbon Paste Electrodes

Porous Barrier

∙ Graphite Powder

○ Oxide Particles

Industrial and Analytical Applications

- Aged PuO_2 dissolution for transuranium element production (Np , Am , Cm) .
- Decontamination of Pu-Bearing materials .

Metallic wastes (dismantling of hot-cells)
PuO_2 stainless steel cans (MELOX plant)
Incineration ashes (UP1 plant of Marcoule)
Cryotreatment sludges (technological wastes)
Zircaloy hulls (PWR)

Ag^{II} Oxidative Process

Application to PuO_2

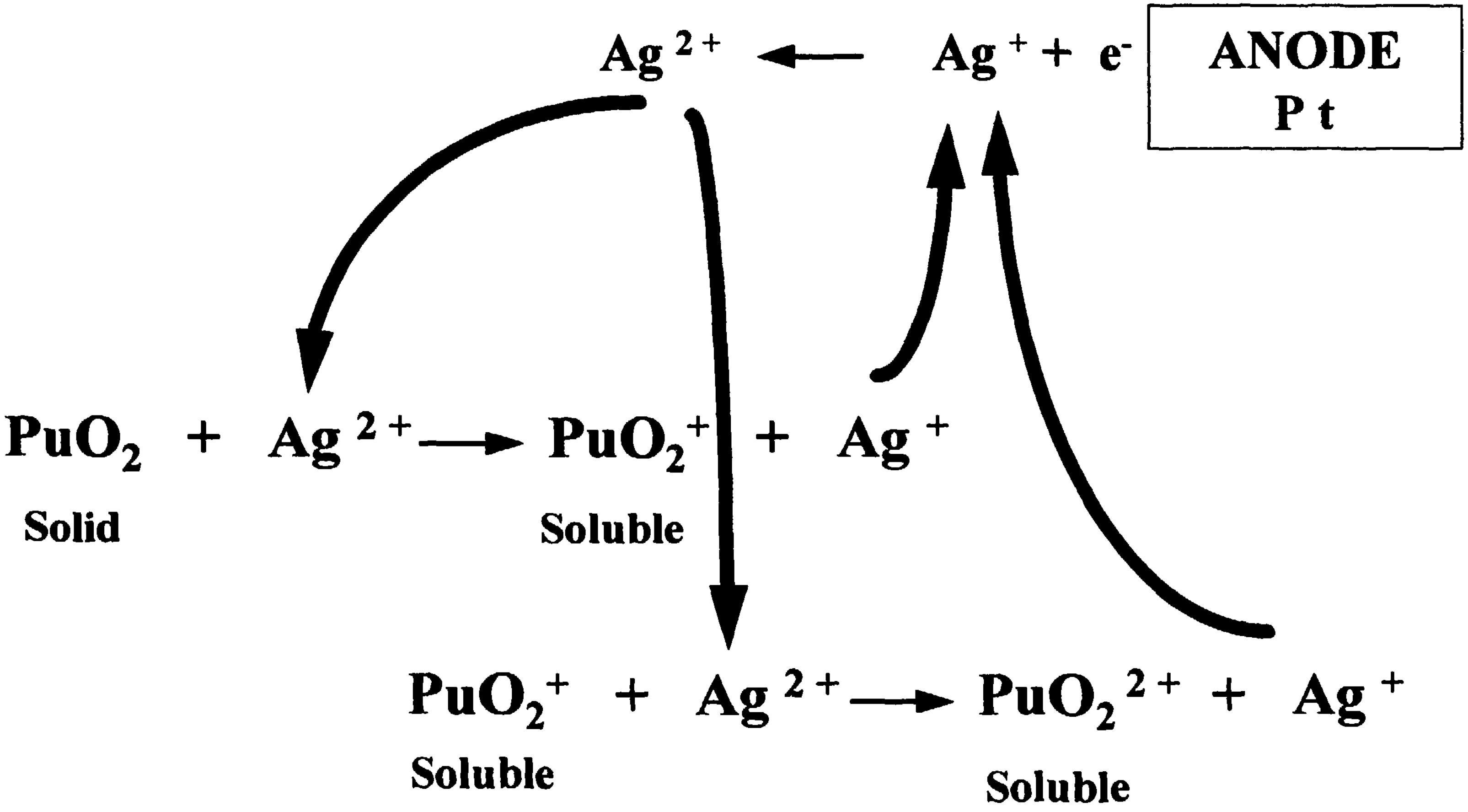
$$PuO_2 + 2\ Ag^{2+} \longrightarrow PuO_2^{2+} + 2\ Ag^{+}$$

Solid

Soluble

[HNO_3] : 4 to 6 M ; [Ag] : 0.1 M; T : 20 to 40 °C

Ag^{II} Oxidative Process



$Ag^{2+} \longleftarrow Ag^{+} + e^{-}$

ANODE
Pt

$PuO_2 + Ag^{2+} \longrightarrow PuO_2^{+} + Ag^{+}$

Solid — Soluble

$PuO_2^{+} + Ag^{2+} \longrightarrow PuO_2^{2+} + Ag^{+}$

Soluble — Soluble

Cr^{II} Reductive Process

Application to PuO_2

$$PuO_2 + Cr^{2+} + 4\,H^+$$

Solid

$\downarrow$ **Sulfuric Acid medium**

$$Pu^{3+} + Cr^{3+} + 2\,H_2O$$

Soluble

Basic kinetics and mechanism data are now available

Cr^{II} Reductive Process

Application to PuO$_2$

- **Empirical rate law formulation and heterogeneous kinetics modelling**
- **The study of the reaction mechanism by ^{18}O-labelling experiments provided a striking evidence of the heterogeneous nature of the electron transfer**

PuO_2 Dissolution Process using other Reducing Species

- **Empirical kinetics experiments have been performed with : V^{3+}, V^{2+}, U^{3+}, U^{4+} , Ti^{3+}**

- **Reaction rates**

Cr^{2+}, V^{2+}, U^{3+} >> Ti^{3+} >> V^{3+}, U^{4+}

Strong reductants **Weak reductants**

PuO_2 Dissolution Processes using Redox Species

Oxidative process : very efficient for pure PuO_2
and oxidizing or inert matrices

Reductive process : more suitable for matrices
having reducing properties
such as cellulosic wastes

Conclusions

- CEMOD processes are very interesting from both scientific and industrial point of view .
- They can be applied to many ores or materials refractory to dissolution in acidic media but having redox properties.
- Consequently, nuclear materials such as oxide fuels or radioactive compound bearing wastes can be treated by using such a method .