

COMMISSARIAT A L'ENERGIE ATOMIQUE

CENTRE D'ETUDES NUCLEAIRES DE SACLAY

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CEA-CONF - - 8281

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CHEMICAL EQUILIBRIA IN ACTINOIDE CARBO-
NATE SYSTEMS

I. GRENTHE, P. ROBOUCH, P. VITORCE

CEA CEN Fontenay-aux-Roses, 92 (France).
IRDI, DERDCA/DRDD/SESD

Communication présentée à : Actinides 85 conference
Aix-en-Provence (France)
2-6 Sep 1985

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I. GRENTHE P. ROUBOUCH P. VITORGE

CEA CEN-FAR DRDD/SESD/SCPCS LABORATOIRE DE CHIMIE

S U M M A R Y

By using spectrophotometric and potentiometric methods it is shown that, in media of high ionic strength (NaClO_4 3M) and total concentrations of hexavalent actinoids higher than 10^{-3} M, trimers are formed. The equilibrium constants for the reactions $3\text{MO}_2(\text{CO}_3)_3^{4-} \rightleftharpoons (\text{MO}_2)_3(\text{CO}_3)_6^{6-} + 3\text{CO}_3^{2-}$ are $\log K(\text{U}) = -11,3 \pm 0,1$; $\log K(\text{Np}) = -10,1 \pm 0,1$; $\log K(\text{Pu}) = -7,4 \pm 0,2$. It is demonstrated that one of the cations of the trimer can be exchanged with another actinoid cation : the equilibrium constants for the reactions $2\text{UO}_2(\text{CO}_3)_3^{4-} + \text{MO}_2(\text{CO}_3)_3^{4-} \rightleftharpoons (\text{UO}_2)_2\text{MO}_2(\text{CO}_3)_6^{6-} + 3\text{CO}_3^{2-}$ are $\log K = -11,3 \pm 0,1$; $-10,0 \pm 0,2$; $-8,8$ respectively for M : U, Np, Pu.

Then, polynuclear complexes can be efficient solution "carriers" for other hexavalent actinides in a waste disposal. Some properties of the solid phases $\text{MO}_2\text{CO}_3(\text{s})$ are discussed.

Experimental studies of chemical equilibria of americium (III, IV) are reviewed : in carbonate media Am(III) species are AmCO_3^+ , $\text{Am}(\text{CO}_3)_2^-$, $\text{Am}(\text{CO}_3)_3^{3-}$, $(\text{Am}_2\text{CO}_3)_s$ and $(\text{NaAm}(\text{CO}_3)_2)_s$; for Am(IV), $\log \beta_5 \approx 40$

In NaClO_4 (3M) medium solubility measurements of Np(V) show that $\log \beta_1 = 5,09$, $\log \beta_2 = 8,15$, $\log \beta_3 = 10,46$, $\log K_s(\text{Na Np O}_2 \text{ CO}_3) = 10,56$ and $\log K_s(\text{Na}_3 \text{ NpO}_2(\text{CO}_3)_2) = 12,44$; ionic strength corrections are proposed.

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WHY ACTINOIDE CARBONATES ?

FUNDAMENTAL PROBLEMS

HOW IS THE CARBONATE LIGAND BONDED ? (FIGURE 1)

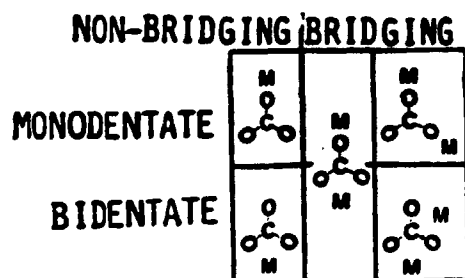


FIGURE 1

HOW IS THE CARBONATE LIGAND BONDED ?

THE MODE OF BONDING MAY BE INFERRED FROM THE COMPOSITION OF THE COMPLEX.

CAN OH^- COMPETE AS A LIGAND WITH THE FAIRLY STRONG BASE CO_3^{2-} ?
 THIS QUESTION IS ANSWERED BY A DETERMINATION OF THE STOICHIOMETRIC COMPOSITION OF THE COMPLEXES.

WILL THE IONIC RADIUS AND/OR THE 5f ELECTRON CONFIGURATION INFLUENCE THE CHEMICAL PROPERTIES OF COMPLEXES IN SOLUTION ?

TECHNOLOGICAL AND ENVIRONMENTAL PROBLEMS

WHAT IS THE CHEMICAL BASIS FOR HYDROMETALLURGICAL URANIUM PRODUCTION

WHICH IS THE CHEMICAL BASIS FOR THE USE OF CARBONATE IN NUCLEAR REPROCESSING ?

HOW IS THE MOBILITY OF ACTINOIDS IN GROUNDWATER INFLUENCED BY PH AND PCO_3 ?

PROBLEMS STUDIED

ACTINOIDE(VI) - CARBONATE SYSTEMS

THE LIMITING COMPLEXES ARE $MO_2(CO_3)_3^{4-}$ WITH BIDENTATE COORDINATION AND HEXAGONAL BIPYRAMIDE COORDINATION AROUND M (FIGURE 2)

THE PRECURSOR IS DISCUSSED $MO_2(CO_3)_2^{2-}$ OR $(MO_2)_3(CO_3)_6^{6-}$? IN U(VI) BOTH SPECIES HAVE BEEN IDENTIFIED. THE TRINUCLEAR COMPLEX IS FORMED AT HIGHER IONIC STRENGTH AND TOTAL CONCENTRATION OF URANIUM; ITS GEOMETRY HAS BEEN DETERMINED BY ^{13}C NMR AND XRAY DIFFRACTION /1/ (FIGURE 3)

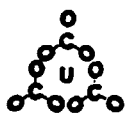


FIGURE 2
STRUCTURE /1/ OF $UO_2(CO_3)_3^{4-}$

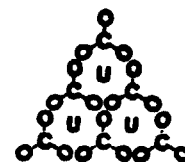


FIGURE 3
STRUCTURE /1/ OF $(UO_2)_3(CO_3)_6^{6-}$

THE FORMATION OF MIXED COMPLEXES HAS BEEN PROPOSED (FIGURES 4-5)

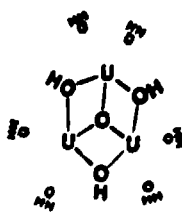
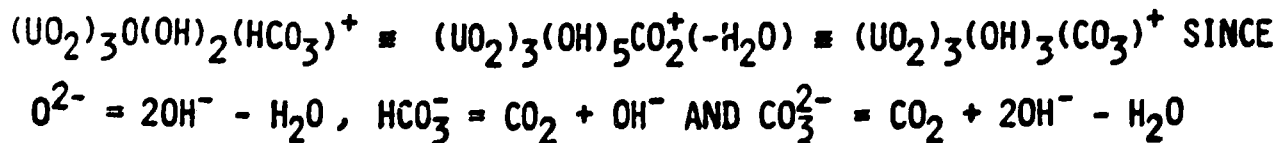


FIGURE 4
STRUCTURE /2/ OF $(UO_2)_3(OH)_5^+$

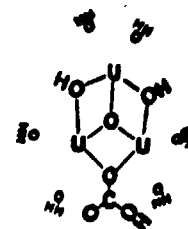


FIGURE 5
POSSIBLE STRUCTURE OF $(UO_2)_3(OH)_3CO_3^+$
 $\rightleftharpoons (UO_2)_3O(OH)_2(HCO_3)^+$

METHOD USED

SPECTROPHOTOMETRY : THERE ARE PRONOUNCED CHANGES IN ABSORPTION SPECTRA AND COLOUR WHEN $[M(VI)]_T$ AND $[CO_3^{2-}]$ ARE CHANGED. AT

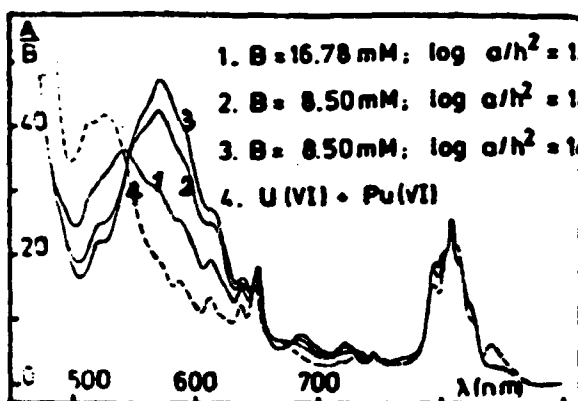


FIGURE 6
PU(VI) SPECTRA IN CARBONATE MEDIA
 $T = 22 \pm 1^\circ C$ $I = 3 M (NaClO_4)$
 $CO_2 + N_2$ GAS BUBBLING

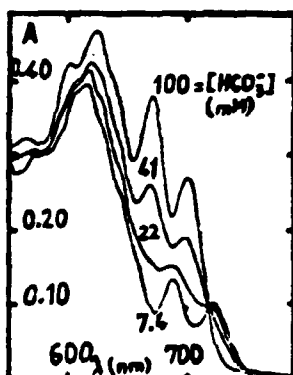


FIGURE 7
NP(VI) SPECTRA IN CARBONATE MEDIA
 $[NP(VI)]_T = 18,65 MM$
 $I = 3 M (NaClO_4)$ $T = 22 \pm 1^\circ C$
 $PCO_2 = 1 ATM$

CONSTANT $[M(VI)]_T$ THE MOLAR ABSORPTIVITY IS DEPENDENT ONLY ON $PCO_2/[H^+]^2 \sim CO_3^{2-}$ INDICATING THAT THE ONLY LIGAND IS CO_3^{2-} (PCO_2 IS CONTROLLED BY BUBBLING CO_2-N_2 GAS MIXTURE IN THE SOLUTIONS). WHEN $[CO_3^{2-}]$ IS CONSTANT AN INCREASE OF $[M(VI)]_T$ INDUCES THE DIMINUTION OF THE MOLAR ABSORPTIVITY OF $MO_2(CO_3)_3^{4-}$, THIS INDICATES THAT $[MO_2(CO_3)_3^{4-}]$ DECREASES WHILE POLYNUCLEAR SPECIES ARE FORMED.

RESULT LOG K(M) FOR REACTION (1)

M	SPECTROPHOTOMETRY	E.M.F MEASUREMENTS
U	- 11,3 \pm 0,1	
NP	- 10,1 \pm 0,1	
PU	- 7,4 \pm 0,2	- 7,6

HEIEROATOMIC ACTINOIDE (VI) CARBONATE COMPLEXES

IN CARBONATE SOLUTIONS WHERE THE RATIO $[U(VI)]/[M(VI)] > 5$
ONE OBSERVES THAT

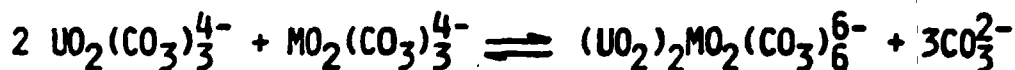
THE SPECTRA OF THE MO_2 PART IS PRACTICALLY THE SAME AS IN A PURE
 $M(VI)$ -CARBONATE SOLUTION. THE MOLAR ABSORPTIVITY OF THE $Np(VI)$
PRECURSOR IS 1/3 OF THAT OF $(NpO_2)_3(CO_3)_6^-$

THE SPECTRA FOR A GIVEN TOTAL CONCENTRATION OF $M(VI)$ ARE DISPLACED
TOWARD HIGHER VALUES OF $\log pCO_2/[H^+]^2$ WHEN $U(VI)$ IS PRESENT

THESE FACTS INDICATE THE FORMATION OF $(UO_2)_2MO_2(CO_3)_6^-$

RESULTS SPECTRA OF $(UO_2)_2NpO_2(CO_3)_6^-$
 $(UO_2)_2PuO_2(CO_3)_6^-$

LOG K(M) FOR THE REACTION



U	- 11,3
Np	- 10,0
Pu	- 8,8

THE $U(VI)$ ACTS AS A SOLUTION CARRIER FOR $Np(VI)$ AND $Pu(VI)$, A FACT
WHICH MIGHT BE OF IMPORTANCE FOR THE TRANSPORT OF ACTINOIDE (VI) ION
BY GROUNDWATER E.G AT A SITE FOR RADIOACTIVE WASTE DISPOSAL.

SOLID $(MO_2CO_3)_s$ PHASES

THE COORDINATION OF $U(VI)$ BY CO_3^{2-} IS SIMILAR IN THE SOLUBLE
COMPLEXES $UO_2(CO_3)_3^{4-}$ $(UO_2)_3(CO_3)_6^-$ AND THE $(UO_2CO_3)_s$ SOLID /3/

THEN WE HAVE VERIFIED THAT $(\text{PuO}_2\text{CO}_3)_s$ AND $(\text{NpO}_2\text{CO}_3)_s$ CAN BE OBTAINED BY PRECIPITATION OF M(VI) EITHER FROM ACIDIC MEDIUM BY HCO_3^- ADDITION OR FROM BICARBONATE MEDIUM BY H^+ ADDITION.

RESULT: $(\text{MO}_2\text{CO}_3)_s$ FOR M = U, NP AND PU ARE ISOSTRUCTURAL

EXTRA LINES IN THE XRAY DIFFRACTION PATTERN APPEAR SEVERAL DAYS AFTER THE PRECIPITATION OF NpO_2CO_3 AND PuO_2CO_3

$(\text{MO}_2\text{CO}_3)_s$ SOLIDE PHASE ; LATTICE PARAMETERS (Å)

M	A	B	C	REF.
U	4,85 (1)	9,205(8)	4,296(6)	/3/
NP	4,80 (2)	9,37 (6)	4,20 (3)	THIS WORK
PU	4,803(7)	9,31 (2)	4,23 (1)	THIS WORK

Np(V)-CARBONATE SYSTEMS

SOLUBILITY MEASUREMENTS OF Np(V) IN CARBONATE MEDIA WITH NaClO_4 3M CAN BE INTERPRETED WITH NpO_2CO_3 , $\text{NpO}_2(\text{CO}_3)_2^{3-}$ AND $\text{NpO}_2(\text{CO}_3)_3^{5-}$ SOLUBLE SPECIES, $\text{Np}_2\text{O}_7\text{CO}_3$ AND $\text{Na}_2\text{NpO}_2(\text{CO}_3)_2$ SOLID PHASES. THE LIMITING COMPLEX $\text{NpO}_2(\text{CO}_3)_3^{5-}$ IS FORMED ONLY AT HIGH IONIC STRENGTH (FIGURES 8-9)

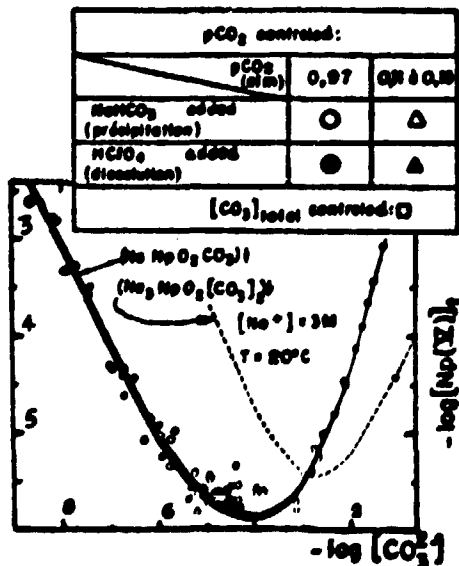


FIGURE 8

SOLUBILITY OF Np(V) IN CARBONATE MEDIA

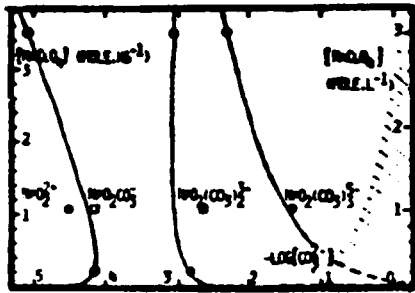


FIGURE 9

NP(V) CARBONATE COMPLEXES IN NaClO_4 MEDIA

$$\text{LOG}\beta_1(M) = \text{LOG}\beta_1(0) + \Delta Z_1^2 \frac{0.5107 M}{I+1.5 M} - \epsilon_1 M$$

$$M = [\text{NaClO}_4] \text{ (MOLE.KG}^{-1}\text{)}$$

1	$\text{LOG}\beta_1$	ΔZ_1^2	$-\epsilon_1$
1	4.62	-4	0.42
2	6.93	0	0.35
3	5.80	12	0.47

● THIS WORK

○ MAYA L. INORG. CHEM. 22 (1983) 2093-5

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AM-CARBONATE SYSTEMS

SOLUBILITY MEASUREMENTS OF Am(III) IN CARBONATE MEDIA CAN BE INTERPRETED BY AmCO_3^+ , $\text{Am}(\text{CO}_3)_2^-$, $\text{Am}(\text{CO}_3)_3^{3-}$ SINCE THE SOLID PHASES HAVE BEEN IDENTIFIED BY XRAY DIFFRACTION, TO BE $(\text{Am}_2(\text{CO}_3)_3)_s$ AND $(\text{NAAm}(\text{CO}_3)_2)_s$

FROM PUBLISHED E.M.F MEASUREMENTS /4/ WE PROPOSE

$$\text{LOG}\beta_5 (\text{Am(IV)}) = 40$$

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