Neptunium Chemistry in Environmental Conditions. 2 : $NaNpO_2CO_{3(s)}$ solubility and $NpO_2(CO_3)_3^{5-}$-$NpO_2(CO_3)_2(OH)_2^{-5}$ equilibrium spectophometric studies

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Summary

$NaNpO_2CO_{3(s)}$ is prepared and its X-ray diffraction pattern discussed. This solid solubility in $NaClO_4$ 3 M is interpreted with lg Ks_1=-11.11(0.09) solubility product and lg $Ks_1\beta_i$=-5.77(0.09), -2.98(0.59), -0.55(0.14) for i= 0, 1, 2 and 3 respectively. $NpO_2(CO_3)_i^{1-2i}$ formation constants are deduced : lg β_i=5.34(0.13), 8.13(0.60), 10.56(0.18). Sensitiv analysis is performed to propose maximum values for mixed $NpO_2(CO_3)_i(OH)_j^{1-2i-j}$ and bicarbonate complex formation constants, using different criteria including fitted parameter error distribution histograms, that are computed using "Bootstrap algorthm". $NpO_2(CO_3)_3^{5-}$ prepared in concentrated Na_2CO_3 + $NaClO_4$ media, is dissociated when adding concentrated NaOH, a new species is detected (using its 1010 nm abosorption band) and interpreded as $NpO_2(CO_3)_2(OH)_2^{-5}$, this equilibrium constant, lg($\beta_{2;-2}/\beta_3$)=-27.5(0.5), is used to propose lg $\beta_{2;-2}$=-17.0(0.7). Solubility and spectrophotometric graphical data treatments are also discussed, including "half point reaction" and "sloope at the half point reaction" methods. The formation constants are compared (in part 1 of this work) with other publised data to propose some Np(V) standard thermodynamic constants.

Introduction

In part 1 of present work, we point out that Np can be a major contributor to nuclear waste radiotoxicity and that geochemical codes are extensively used for radioactivity migration predictions : quality data bases (for these codes) are then needed. We are then (in part 1) selecting equilibrium constants for NEA Thermodynamic Data Base [92GRE/LEM]. The aim of the present paper is to present suplementary (unpublished) experimental data needed to validate this selection. We also explain our methodologies for interpretation and quantitative treatments of (our) experimental data, sensitivity analysis and uncertainty assignement with new calculation procedures [90CAC] : the same methodologies are used to (re)interpret some of the published works (see part 1).

$NaNpO_2CO_{3(s)}$ solubility has been measured and interpreted [83MAY] [86GRE/ROB] to compute its solubility product and $NpO_2(CO_3)_i^{1-2i}$ (i=1, 2 and 3) stability constants. We give here experimental details of the preliminary publication [86GRE/ROB] and primary experimental results with new data treatment for sensitive anlysis, i.e uncertainty assignement of the fitted equilibrium constants and interpretation with models (set of chemical species) with new species that was first excluded for qualitative reasons : the idea is to either compute some "minor species" formation constants or to proof that they cannot be detected and in this latter case to propose a mximum value (of their stability constants). Minor species must be consistent with known NpO_2^+ coordination chemistry and reactivity. CO_3^{2-} ligand chemical reactivity toward pentavalent Np is unexpectively high (see part 1) This bidentate ligand probably fit well NpO_2^+ size : NpO_2^+ is a linear cation with usually 6 possible coordination sites in the plan perpendicular to O=Np=O line. Hence, in $NaNpO_2CO_{3(s)}$ solid, NpO_2^+ coordination with 3 bidendate CO_3^{2-} ligands has been proposed [81VOL/VIS3] which is not the case in the smaller NpO_2^{2+} [86GRE/ROB] (or UO_2^{2+}) Rutherfordine structure where only two CO_3^{2-} ligands are bidentate (and two other ones are monodentate). NpO_2^+ coordiantion chemistry in $NaNpO_2CO_{3(s)}$ is probably the same as in the highly charged $NpO_2(CO_3)_3^{-5}$ limiting complex which is strongly stabilised in high ionic strength concentrated carbonat media (see part 1), CO_3^{2-} ligand is probably mainly bidentate in soluble Np(V) complexes, there is certainly no Np(V)-OH^- soluble complex when [OH^-] is less than 1 mM, and OH^- ligand is usually more reactive than HCO_3^- one toward "hard cations" (typically NpO_2^+). We will then restrict our sensitivity analysis to mononuclear soluble complexes where NpO_2^+ central cation is hexacoordinated assuming that CO_3^{2-} ligand is always bidentate.

NpO_2^+ absorption spectrum has got an intense band at 981 nm ($\varepsilon_{981}(NpO_2^+)$=405cm/M [81CAU]) that is shifted to 991 and 998 nm when [CO_3^{2-}] is increased ($\varepsilon_{990}(NpO_2CO_3^-)$=250cm/M ,$\varepsilon_{998}(NpO_2(CO_3)_2^{3-})$=155cm/M, $\varepsilon_{900to1150}(NpO_2(CO_3)_2^{5-})$<8 [89RIG]). In concentrated OH is added to concentrated np(V) carbonate solutions a new absorption band rise at 1010 nm [84VAR/HOB] with molar abosptivity probably more than 60cm/M [89RIG]. There is then a new soluble complex : we are studying Np(V) spectrophotometry in these condtions to measure the stability the new complex. We also give some indications on graphical treatment of data since these methods are used in part 1 to reinterprate publications where experimental data are only shown on some figures. One interpretation directly see on the spectra the half point reaction (when the total absorbance, A_t, is the mean of the maximum and the minimum ones) to compute a stepwise formation constant when the

stoichiometry is known. The shape of the curve $lg(A_t/[Np]_t)$ vs lg[ligand] is mainly due to the reaction stoichiometry, we show how the slope at the half point can be used as a shape criteria to compute stoichiometric coefficients.

Experimental

Spectrophotometry

$(NpO_2)_k(CO_3)_i(OH)_j^{k-2i-j}$ spectrophotometric study is partially published [89RIG], complementary measurements are here performed with the same experimental methodology, experimental conditions are given with the results (table 3). We also tried to add reactants using alternative procedures but they lead to less precise results.

Solubility

The results are already published [86GRE/ROB] ; but with neither experimental nor interpretation details. We give them now with further interpretations. The 35.8 mM $^{237}Np(V)$ mother solution is prepared electrochemically and its purity controled spectrophotometrically using a Cary 17D instrument [81CAU]. The initial solid phase is precipitated out from 16 ml of the mother solution in 25 ml of 0.1 M $NaHCO_3$, I = 3M ($NaNO_3$), $-lg[H^+] = 8.3$. The solid is filtered (after 1 week) and put in a cell or in batches, anyhow the solid phase always changes during the begining of solubility experiments. Other experimental details are with the solubility (table 1) and X-ray (table 2) diffraction results. Solubility is measured using a gamma spectrometer with an Ortec Ge-diod. The 83 keV ray should not be used, probably because the isotopic equilibrium with ^{233}Pa is not achieved quickly enougth, we then use the 29.4 keV ray.

-lg[H+], [CO_3^{2-}] and CO_2 partial pressure

The reference compartment of the combined TCBC/11/HS/Sm Tacussel glass electrodes are refilled with a 0.01 M NaCl + 2.99 M $NaClO_4$ solution to lower junction potential : the ionic medium of the solutions is usually I=3 M ($NaClO_4$) in acidic media and, $[Na^+]$=3 M, (ClO_4^-) in carbonate media. It is calibrated (in concentration and not activity units : $-lg[H^+]$ and not pH, for consistency between mass action and mass balance equations) using an ISIS 20000 Tacussel pH-meter and the folowing buffer solutions : 0.01 M $HClO_4$ ($-lg[H^+]$= 2.00), 0.1 M $NaHCO_3$ with CO_2 gas bubbling ($-lg[H^+]$=7.00) and the 0.05 M $NaHCO_3$ + 0.5 M Na_2CO_3 mixture ($-lg[H^+]$=9.62). A N_2-CO_2 mixture is also bubbled in the cell, it is previously equilibrated with a 3 M $NaClO_4$ solution. The pH electrode is used (in the radioactive solutions) just before gamma counting. Reproducibility is notably improved when both shields of the electrode are connected through the plastic glove box with a 4 contact (or later a double shielded tri-axial) Jupiter plug. In batches, pH measurement is performed within a minute without stearing (to avoid equilibration with the air).

Treatment of data

Graphical data treatments of the figures of most published experimental works (including the present one) is often sufficient to determine the dominating chemical reactions and to estimate their equilibrium constants. Statistic treatment of curve fitting results is widely used and it is usually (implicitely) assumed that the error distribution is gaussian. This assomption can easily be demonstrated only when a lot of experimental data (say 10 per fitted parameter) can be measured in conditions sensitive for the model (the set of fitted parameters). We use new algorithms [90CAC] to build the error distribution of each fitted parameter and to performe sensitivity analysis. Graphical methods are still useful to avoid "blind" curve fitting.

Solubility

Working equations

When $NaNpO_2CO_{3(s)}$ precipitates, $(NpO_2)_k(CO_3)_i(OH)_j^{k-2i-j}$ (with this notation, HCO_3^- complexes have negativ stoichiometric coefficients) soluble complex concentration is :

$$s_{ijk} = Ks'_{ijk} [CO_3^{2-}]^{i-k} [H^+]^{-j} \quad (1a)$$

$$s_{ijk} = {}^*Ksp'_{ijk} \; pCO_2^{i-k} [H^+]^{2(k-i)-j} \quad (1b)$$

where $Ks'_{ijk} = Ks'^{k} \beta_{ijk}$, are the (directly) measured parameters,
$*Ksp'_{ijk} = Ks'_{ijk} Kp^{k-i}$
$Ks = Ks' [Na^+] = [Na^+] [NpO_2^+] [CO_3^{2-}]$ is $NaNpO_2CO_{3(s)}$ solubility product,
$\beta_{ijk} = [(NpO_2)_k(CO_3)_i(OH)_j^{k-2i-j}] [H^+]^j / [NpO_2^+]^k [CO_3^{2-}]^i$ are formation constants,
$K_1 = [HCO_3^-] / [H^+] [CO_3^{2-}]$
$Kp_1 = [HCO_3^-] [H^+] / pCO_2$
$Kp = K_1 / K_{p1}$

$$pCO_2 = Kp [H^+]^2 [CO_3^{2-}] \quad (2)$$

The solubility is the summation (on all existing i, j and k) of s_{ijk}. This notation (1a) points out that any solubility measurements data treatment can compute only the sum of the constants having the same (i-k) and j values (and not each Ks'_{ijk}). $[CO_3^{2-}]$ and $[H^+]$ must be independantly varied in a broad enougth domain

(figure 1a). In the air P_{CO_2} is typically $10^{-3.5}$ atm, and when measurements are equilibrated with the air, only the sum of $(*Ksp'_{ijk}\ 10^{-3.5(i-k)})$ constants (1b) having the same 2(i-k)+j values, can then be computed.

Graphical and iterative methods

Graphical methods use the logarithm of an equation (1) to display the experimental results when a 2 dimensional presentation is possible. This occurs when the experimental set up induces a relationship such as (2) or when (in the choosen experimental conditions) the solubility is mainly due to carbonate complexes (j=0). In this last case, the slope of the curve is (i-1) where the predominating soluble complex is $NpO_2(CO_3)_i^{1-2i}$ and an estimation of its formation constant is calculated with (1a). In [86GRE/ROB] we used an improvement of this method : the graphical estimation was the starting point of an iterative procedure where $Ks'_i(m)$ is calculate exactly with (1a) for each experimental points (m) using (execpt for l=i) the previous Ks'_l (figure 3), Ks'_i of each step is the mean of $Ks'_i(m)$ using the ponderation coefficient e_{min} / e.

where e_{min} $= e_s + |i-1|\ e_L$ is the minimum relative error,
e_s is the relative experimental error on solubility measurements,
e_L is the relative experimental error on $[CO_3^{2-}]_m$ measurement,
e = sum (on l) of e_l is the relative error on experimental point (m),
e_l $= (e_s + (l-1)e_L)\ [CO_3^{2-}]_m^{l-i}\ Ks'_l / Ks'_i$

Curve fitting and error distribution histogram building

Here we use the Simplex, Jacknife and Bootstrap [90CAC] procedures. Simplex is a curve fitting algorithm for the data of table 1 ($-lg[H^+]$, $-lg[CO_3^{2-}]$ and $-lg[Np]_t$) that computes the best set of parameters to minimize the summation (on all data) of the square of the residual errors (sre) which is the differrence between the experimental $(-lg[Np]_t)^2$ and its calculated value (using (1)), we are also using the standard deviation, σ : the square root of ((sre)/(number of data)). The Jacknife program takes one of the experimental data out of the original set and then call the Simplex program. This is done for all the data and an "outlier" can be recognize since its σ value is significatively small. The Bootstrap program chooses at random with repetitions, n data from the n original ones and then call the Simplex one. This is done 1000 times. Histograms are then computed (figure 4).

Spectrophotometry ("half point methods")

The data treatment of some of our spectrophotometric results using graphical, Simplex, Jacknife and Bootstrap algorithms are already described [89RIG]. We use 2 types of complementary graphical methods : "half point reaction" determination to estimate equilibrium constant and "slope at the half point reaction" determination to compute (or verify) stoichiometric coefficients.They both rely on the aproximation that only 2 soluble complexes, B and C, are mainly responsable of the the measured absorbance :

$$A_t = k_b\ a_b\ [B] + k_c\ a_c\ [C] \qquad (3)$$

where X $= (NpO_2)_{k_x}(CO_3)_{i_x}(OH)_{j_x}^{\ k_x-2i_x-j_x}$
$k_x\ a_x$ is X molar absorbance, then $A_t = a_x\ [Np]_t$ in a pure X solution,

At half point reaction $$[Np]_{t_{1/2}} / 2 = k_b\ [B]_{1/2} = k_c\ [C]_{1/2} \qquad (4)$$

from (3) and (4) $$A_{t,1/2} / [Np]_{t_{1/2}} = (a_b + a_c) / 2 = (A_{t_{max}} + A_{t_{min}}) / 2 \qquad (5)$$

in these conditions $$K = k_b^{k-1}\ k^{-1}\ [CO_3^{2-}]_{1/2}^{-i}\ [H^+]_{1/2}^{\ j}\ ([Np]_{t_{1/2}} / 2)^{1-k} \qquad (6a)$$

or using (2) $$K = Kp^i\ k_b^{k-1}\ k^{-1}\ (pCO_2)_{1/2}^{-i}\ [H^+]_{1/2}^{2i+j}\ ([Np]_{t_{1/2}} / 2)^{1-k} \qquad (6b)$$

or $$K = Kp^{j/2}\ k_b^{k-1}\ k^{-1}\ [CO_3^{2-}]_{1/2}^{-i-j/2}\ (pCO_2)_{1/2}^{j/2}\ ([Np]_{t_{1/2}} / 2)^{1-k} \qquad (6c)$$

where K $= K_{i_c\ j_c k_c}\ K_{i_b\ j_b k_b}^{\ -k}$, is (k B + j H^+ <-> C + i CO_3^{2-}) equilibrium constant ,
i $= i_c - i_b\ k$ (is changed in -1 when $[OH^-]$ is used instead of $[H^+]$)
j $= j_c - j_b\ k$
k $= k_c / k_b$

Experimental molar absorbances, $A_t / [Np]_t$, are plotted versus $lg[H^+]$ at fixed P_{CO_2} (or $[CO_3^{2-}]_l$) and $[Np]_{t_l}$. The "half point", i.e. $(A_{t_{1/2}} / [Np]_{t_{1/2}}, lg[H^+]_{1/2},)$ is then read on the curve (5) which determines K (6b or (6a) assuming that the stoichiometric coefficients are known. The same type of graphical determinatations are also used when A_t is plotted versus $lg[CO_3^{2-}]$ (or lg P_{CO_2}), at fixed $[H^+]_l$ and $[Np]_{t_l}$. When mixed or polynuclear complexes are involved, the half point is shifted (when different $[Np]_{t_l}$, pCO_{2_l}, $[CO_3^{2-}]_l$ or $[H^+]_l$ are considered), the shift can be easily calculated from (6) : this is a verification of the stoichiometric coefficients or this give an experimental relationship betwen i, j and k when they are unknown. "Slope method" gives other such relationships to determine i, j and k. The "slope at the halh point" is also read on the above curves. Calculation of their theoritical values is straightforward :

$$s([Np]_t)_{[H^+],(P_{CO_2} \text{ or } [CO_3^{2-}])} = (k-1)\,a \quad (7a)$$
$$s([CO_3^{2-}] \text{ or } P_{CO_2})_{[H^+],[Np]_t} = a\,i / (1+k) \quad (7b)$$
$$s([CO_3^{2-}])_{P_{CO_2},[Np]_t} = a\,(i + j/2) / (1+k) \quad (7c)$$
$$s([H^+] \text{ or } pCO_2)_{[CO_3^{2-}],[Np]_t} = -a\,j / (1+k) \quad (7d)$$
$$s([H^+])_{P_{CO_2},[Np]_t} = -a\,(2i + j) / (1+k) \quad (7e)$$
$$s([OH^-])_{y,z} = -\,s([H^+])_{y,z} \quad (7f)$$

where $a = (a_c - a_b) / (a_b + a_c)$ is rougthly 1 when $a_b << a_c$

$s(x)_{y,z} = [d(\lg(A_t/[Np]_t)) / d(\lg x)]_{y,z;1/2}$ is an "half point reaction" slope".

"Slope analysis" is usually consistent with only 1 or very few sets of integer i, j and k values.

Results and interpretations.

Solubility

Solubility results (table 1) can be plotted on a single curve (figure 1b) versus $\lg[CO_3^{2-}]$, hence only CO_3^{2-} are involved in the predominant solubility equilibria in chemical conditions where several data points are obtained at different pH for the same $[CO_3^{2-}]$ (figure 1a).

Solid phases

$NaNpO_2CO_{3(s)}$ is identified from X-ray diffraction patterns (table 2) just after sampling for solubility measurement. $NaNpO_2CO_{3(s)}$ is slowly transformed into $Na_3NpO_2(CO_3)_{2(s)}$ when $[CO_3^{2-}] > 0.03$ M in Na^+ 3 M solutions, this last solid solubility product is then estimated from only the data point leading to its lowest value : this is the highest $[CO_3^{2-}]$ (0.1 M). When $[CO_3^{2-}] > 1$ mM, Np(V) solutions where then oversaturated (figure 1b).

$Na_3NpO_2(CO_3)_{2(s)}$ X-ray diffraction patterns is much more simple that $NaNpO_2CO_{3(s)}$ one, hence this last solid phase is poorly symetrical and precipitates faster than $Na_3NpO_2(CO_3)_{2(s)}$. X-ray diffraction patterns (tables 1 and 2) and solubility results (figure 3) points out that usually more than 3 weeks of equilibration are needed to get $NaNpO_2CO_{3(s)}$ solid phase which is still rather poorly cristalised and that is certainly the main cause of solubility measurement uncertainties. Our $NaNpO_2CO_{3(s)}$ X-ray diffraction pattern correspond to a solid phase obtained [81VOL/VIS3] by heating "$Na_{0.6}NpO_2(CO_3)_{0.8(s)}$" : we then tried to fit $Na_{2x-1}NpO_2(CO_3)_{x(s)}$ solubility product and stoichiometric coefficient, x, (alone or together with $NaNpO_2CO_{3(s)}$) : x cannot be fitted and when it is fixed, the addition of the second solid phase do not improved the fit (as for $NpO_2OH_{(s)}$). Heating effect is then essentially kinetic. For quantitative interpretation, points where poor cristalisation is suspected are then excluded together with those correponding to poor pH buffering of the solution (table 2, figures 1b and 1c). The predominant soluble complexes are then $NpO_2(CO_3)_i^{1-2i}$ (they are monomeric : this is discussed below) and (1a) i=0, 1, 2 and 3.

Sensitivity analysis by plotting fitted parameters and σ versus added minor species formation constant

We trie other models by adding (or taking of) monomeric soluble species, the added species are now called minor species. Curve fitting always computes a result ; but in some cases it is strongly correlated to some mathematical parameters of the algorithm. We then fixe K_{unf}, the formation constant of one species, and compute several times the other parameters to plot (figures 3) them and σ versus $\lg K_{unf}$, the unfitted constant. This is done for all species. The interpretation of such curves is straightforward : when K_{unf} is increased more than say K_{max}, the calculated solubility becomes overestimated (at least in a chemical domain) and σ quickly increases, when K_{unf} is decreased below say K_{min}, it can change neither the solubility (in the whole experimental domain) nor σ. K_{unf} maximum value is then smaller than K_{max}. NpO_2OH^0, $NpO_2CO_3OH^{-2}$, $NpO_2CO_3(OH)_2^{-3}$, $NpO_2(CO_3)_2(OH)_2^{-5}$, $NpO_2(CO_3)_3OH^{-6}$ or $NpO_2(CO_3)_4^{-7}$ minor species addition do not improved the fit : σ minimum value is exactly the same as in the original model (S=0.884). $NpO_2(CO_3)_2HCO_3^{-4}$, $NpO_2CO_3HCO_3^{-2}$, $NpO_2(CO_3)_2OH^{-4}$ or $NpO_2HCO_3^0$ minor species addition improve the fit (S=0.784, 0.812, 0.877 or 0.879 respectively and S=0.767 when the 4 minor species are added) and a K_{unf} optimum value, K_{opt}, ($K_{min}<K_{opt}<K_{max}$) is determine.

Sensitivity analysis from by building fitted parameter distribution of error (histogram)

σ histogram (figure 4f) and statistical tests indicate that σ is not really significatively improved (when minor species are added to the model), the other K values are not significatively modifie by minor species addition. The only improvement in the fit is obtained by suppressing 13 "outliers" data points (from the 68 already selected points) using Jacknife procedure ; this only changes the uncertainties, which are finally estimated from Bootstrap confidence interval on the original (68) data points. We feel (but do not try to demonstrate it mathematically) that when a chemical species is forgoten in the model σ should decrease, and the error distributions (of σ and the fitted parameters) should broaden (since it would now include systematic error). Existing minor species addition should sharpen histogram, this is not the case (figures 4).

Sensitivity analysis conclusions

We then conclude that only K_{max} can be computed for the minor species : $NpO_2CO_3HCO_3^{-2}$ and $NpO_2HCO_3^0$ would predominate when $P_{CO_2} > 1$ atm, extra experimental data in these conditions should then be useful. $NpO_2(CO_3)_2HCO_3^{-4}$ and $NpO_2(CO_3)_2OH^{-4}$ would be stabilized in respectively very concentrated

bicarbonate and carbonate + hydroxide media where extra experimental data do not confirm these asumption : their estimated formation constants are then strictly maximum possible values. These 4 minor species formation constants are fitted mostly from experimental data where the solubility is the less reproducible. Most of the minor species fitted Ks'_{ijk} (if not all of them) then probably fit the uncertainties (figuer 4c) and cannot be considered as formation constants : stability constant maximum values are then proposed (in part 1 table). We only tried minor species assuming hexacoordinated NpO_2^+ in the complexes with bidentate CO_3^{2-} (see the introduction).

Spectrophotometry

Concentrated OH solution additions in concentrated carbonate (Np(V) solutions lead to new complex(es ?)) formation that are easily detected at 1010 nm. The weakly coloured limiting complex, $NpO_2(CO_3)_3^{-5}$, is the predominant starting complex (before OH addition) and its molar absorbance is negligeable ($a_b << a_c$ in (7)). Absorbance is $[CO_3^{2-}]$ and $[OH^-]$ dependant, a mixed $(NpO_2)_k(CO_3)_i(OH)_j^{k-2i-j}$ complex formation is then confirmed [81VOL/VIS3] [89RIG]. Quantitative interpretation and precise measurements are very difficult to obtain : Np(V) concentration have to be quite low to avoid precipitation and the ionic medium is quite correlated to ligand concentrations. "Slope analysis" (7a) on curves where $[Na^+]$=3 M (figures 5), indicates that there is no polymerisation (k=1). The $s([OH^-])_{[CO3^{2-}]}$ slope is unambigeously around 1 and since $a_b << a_c$ (7), a $NpO_2(CO_3)_i(OH)_2^{-2i-1}$ complex is formed (7d). Further slope analysis (7b) suggests (figures 5) direct $NpO_2(CO_3)_2(OH)_2^{-5}$ formation. $NpO_2(CO_3)_2OH^{-4}$ intermediaire complex might well exist, but is hardly detected. The plot of experimental data versus $[OH^-]^2/[CO_3^{2-}]$ (figure 5c) are on a single curve within uncertainties which is consistent with our interpretation. Curve fitting can only confirm the numerical value for the equilibrium constant. The ionic strength effects are within experimental reproducibility, quantitative interpretation are then not tried, the important charges of the 2 major complexes could induce important ionic strength perturbations but since they are the same (-5), they might well balance each other. Anyhow ionic medium cannot be very well controled during reactant addition.

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Table 1 : Np solubility results in carbonate media

T=20°C. $[Na^+]$=3M, in ClO_4^- media. The solubility, $[Np]_{total}$, and $-lg[H^+]$ is measured either in a cell where P_{CO_2} is controlled by bubling CO_2 - N_2 gas mixture for the 65 first points (n=1 to 65), or in batches where $[CO_3]_t$, the CO_3 total concentration, is known from the $NaHCO_3$ or Na_2CO_3 quantity added.

$lg[CO_3^{2-}] = lg(pCO_2)-2lg[H^+]-17.62$
$= [CO_3]_t/(1+10^{9.62+lg[H^+]}(1+10^{6.37+lg[H^+]}))$.

The 65 first points (n=1 to 65) are in chronological order, the time (hour) is set to 0 when CO_2 bubbling is stoped (several days) ; but the solution and the solid in it, are not removed (and are then used again for the following points). Some points(*) are not considered in the treatment of the data, because the experiment is still starting (start), or solubility where not stable for constant solution conditions (wait), or CO_2 stopped bubbling (CO2), or pH was too low to be stable in batches (low pH), or solid phase was changing (solid). Several precipitations and dissolutions are performed in the cell, noted respectively Pi and Di (in the n2 column). Some batches (those with the same n2 number) have been sampled at 2 different times. X ray diffraction results (RX) are named as in table 2 : 1 for $NaNpO_2CO_{3(s)}$, 2 for $Na_3NpO_2(CO_3)_{2(s)}$, and am for amorphous phase.

n	time (h)	n1	n2	$-lg[H^+]$	$-lg[CO_3^{2-}]$	$-lg[Np]_t$			RX
1	24			5.10	7.40	3.97	*	start	
2	101			5.10	7.40	3.90	*	start	
3	151			5.09	7.45	4.48	*	start	
4	264	1	P1	5.85	5.93	5.02			
5	439	2	P1	6.21	5.21	5.40			
6	534	3	P1	6.63	4.37	5.70			
7	648	4	P1	6.36	4.91	5.62			
8	792	5	P1	6.58	4.47	5.71			
9	864	6	P1	6.54	4.55	5.70			
10	1157	7		6.64	4.35	5.55		CO2	
11	0			6.62	4.39	5.35	*	start	
12	50			6.53	4.57	5.59	*	start	
13	120			6.44	4.75	5.60	*	start	
14	150			6.29	5.07	5.57	*	start	
15	192	8	D1	5.99	5.65	4.98		start	
16	264	9	D1	5.58	6.47	4.44		start	
17	295		D1	5.08	7.47	3.62	*	wait	
18	312	10	D1	5.12	7.39	3.48		start	
19	341	11	D1	4.73	8.17	2.82		start	
20	432	12	D1	4.78	8.07	2.82		start	
21	439	13	D1	4.72	8.19	2.85			
22	456	14	D1	4.73	8.17	2.81			1d
23	120		P2	5.58	7.42	3.54	*	start	1b
24	164	15	P2	5.57	7.44	3.57			
25	215	16	P2	5.96	6.66	4.41			
26	312	17	P2	6.23	6.12	4.83			
27	384	18	P2	6.39	5.80	5.21			
28	456	19	P2	6.77	4.97	5.63			
29	459	20	P2	6.66	5.19	5.57			
30	500	21	P2	6.65	5.21	5.61			1c
31	548		P2	6.82	4.87	5.43	*	wait	
32	620	22	P2	6.82	4.87	5.72			
33	644	23	P2	6.83	4.85	5.72			
34	692	24	P2	6.98	4.55	5.72			
35	716	25	P2	6.95	4.61	5.61			
36	787		P2	7.00	4.44	5.80	*	CO2	
37	793		P2	7.00	4.51	5.55	*	CO2	
38	817	26	P2	6.94	4.63	5.76			1d
39	955	27	P2	7.33	3.78	5.62			
40	985	28	P2	7.25	3.94	5.61			
41	1031	29	P2	7.25	3.94	5.59		wait	1a
42	1128	30	P2	7.06	4.32	5.80		wait	

43	1147	31	P2	7.07	4.30	5.78		wait	
44	1219	32	D2	6.65	5.27	5.57			
45	1291	33	D2	6.62	5.33	5.55			
46	1321	34	D2	5.92	6.73	4.36		wait	
47	1363	35	D2	5.94	6.69	4.35			
48	1392	36	D2	5.36	7.85	3.28			
49	4			5.42	7.73	3.30	*	start	
50	29			5.46	7.65	3.27	*	start	
51	173	37		5.10	8.37	2.62		start	1a
52	282	38	P3	4.51	8.61	2.61			
53	367	39	P3	4.87	7.89	3.32			
54	431	40	P3	4.86	7.91	3.32			
55	484	41	P3	5.34	6.95	4.32			
56	527	42	P3	5.35	6.93	4.34			
57	576	43	P3	5.68	6.27	5.07		wait	
58	647	44	P3	5.45	6.73	4.42			
59	695	45	P3	5.97	5.69	5.34			
60	767	46	P3	5.95	5.73	5.06			
61	815	47	P3	5.95	5.73	5.34			
62	935	48	P3	6.36	4.91	5.68			
63	1032	49		6.36	4.91	5.47			
64	1175	50		5.85	5.93	5.24			
65	1206	51		5.46	6.71	4.62			
66	672		1	7.65	5.95	4.92	*	low pH	
67	672		2	7.80	5.37	5.68	*	low pH	
68	672	52	3	9.10	3.86	5.86			
69	672	53	4	9.60	3.14	5.72			
70	672	54	5	9.80	2.62	5.26			
71	672	55	6	10.20	2.06	4.48			
72	672	56	7	10.52	1.57	3.66			
73	672		8	10.65	1.04	4.30	*	solid	2
74	672		9	7.85	5.74	4.86	*	low pH	1
75	672		10	7.80	6.35	5.73	*	low pH	
76	1344		1	6.70	7.02	4.88	*	low pH	
77	1344		2	7.70	5.46	4.90	*	low pH	
78	1344		3	8.80	4.11	5.23	*	buffer	
79	1344	57	4	9.60	3.14	5.79			
80	1344	58	5	9.72	2.66	5.17			
81	1344	59	6	10.12	2.08	4.50			
82	1344		7	10.43	1.59	4.54	*	solid	
83	1344		8	10.60	1.04	4.43	*	solid	
84	1344		9	7.80	5.74	4.57	*	low pH	
85	1344		10	8.00	6.12	5.42	*	low pH	
86	672		11	10.50	1.05	3.83	*		
87	672	60	12	10.50	1.27	3.08			
88	672	61	13	10.43	1.46	3.44			
89	672	62	14	10.43	1.70	3.90			
90	672	63	15	10.36	1.85	4.13			
91	672	64	16	10.33	2.08	4.48			
92	672	65	17	10.27	2.29	4.81			
93	672	66	18	10.15	2.51	5.04			
94	672	67	19	10.04	2.75	5.40			
95	672	68	20	9.94	2.97	5.44			
96	336		21	8.54	2.13	4.46	*	solid	am
97	336		22	8.37	2.51	4.69	*	solid	
98	336		23	8.31	2.74	4.88	*	solid	
99	336		24	8.32	2.97	5.14	*	solid	

100	336	25	8.26	3.17	5.32	*	solid	
101	336	26	7.91	3.74	5.59	*	solid	
102	336	27	8.32	3.53	5.64	*	solid	
103	336	28	8.30	3.75	5.78	*	solid	
104	336	29	8.28	3.98	5.59	*	solid	
105	336	30	8.25	4.20	5.78	*	solid	am
106	504	31	8.20	3.45	5.57	*	solid	am
107	504	32	8.30	3.58	5.70	*	solid	
108	504	33	8.25	3.80	5.59	*	solid	
109	504	34	8.21	4.08	5.78	*	solid	
110	504	35	8.13	4.30	5.56	*	solid	
111	504	36	8.09	4.54	4.33	*	solid	
112	504	37	7.99	4.86	5.68	*	solid	
113	504	38	7.93	5.11	5.38	*	solid	
114	504	39	7.85	5.40	5.36	*	solid	
115	504	40	7.73	5.70	5.17	*	solid	am

Table 2 : $NaNpO_2CO_{3(s)}$ X-ray diffraction patterns

λ=1.5405A. Intensities are estimated visually : very strong (S), strong (s), medium (s), weak (w), very weak (vw), and (l) for broad ones. The solid collected with point number n=41 of table 1 is named 1a, its lattice parameters are a=4.784(2)A, b=6.556(4)A, c=4.316(3), and R=0.0017 for 33 rays ; they are fitted using Volkov et col. indexation [79VOL/VIS] of their heated (up to 350°C) "$Na_{0,6}NpO_2(CO_3)_{0,8(s)}$" compound whose difraction patern is significatively different from their other "$NaNpO_2CO_{3(s)},nH_2O$" compounds prepared at various temperature [77VOL/VIS].

		observed	calculated	
Intensity	hkl	20		d(A)
S(l)	010	13.52	13.49	6.5515
s	100	18.46	18.53	4.7811
s	001	20.55	20.56	4.3129
s	110	23.04	22.99	3.8621
s	011	24.66	24.67	3.6024
m	020	27.14	27.18	3.2758
s	101	27.83	27.81	3.2025
s	111	30.99	31.03	2.8772
vw	120	33.00	33.10	2.7024
vw	021	34.40	34.32	2.6087
w	200	37.54	37.57	2.3906
w	121	39.32	39.28	2.2900
vw	210	40.25	40.09	2.2458
	030		41.28	2.1839
w	002	41.78	41.82	2.1565
w	201	43.07	43.20	2.0909
w	012	44.14	44.14	2.0484
m	211	45.50	45.46	1.9919
	130	45.50	45.60	1.9865
	102	45.50	46.10	1.9658
vw	220	47.05	46.98	1.9311
	112		48.26	1.8829
	131	50.56	50.51	1.8043
w	022	50.56	50.60	1.8013
w	221	51.79	51.79	1.7625
	122		54.34	1.6856
	040		56.06	1.6380
	230		57.03	1.6124
	202	57.73	57.46	1.6013
vw	300	57.73	57.76	1.5938
	212	59.67	59.32	1.5555
	140	59.67	59.57	1.5496
vw	310	59.67	59.61	1.5486
	032		60.22	1.5345
	041		60.36	1.5313
vw	231	61.33	61.28	1.5104
	301		61.98	1.4950
	132	63.67	63.58	1.4611
m	141	63.67	63.72	1.4583
	311	63.67	63.76	1.4575
	222	65.00	64.70	1.4387
	003	65.00	64.74	1.4377
vw	320	65.00	64.97	1.4332

n is table 1 sample number, a, b and c (Ä) are the latice fitted parameters (and uncertainties), R1 and R2 the sdandard deviation computed for the main rays or all of them respectively (and the number of rays used), * low intensity supplementary rays, ** supplementary rays with at least medium intensity and many other ones.

n	name		a	b	c	R1	R2
41	1a		4.784(2)	6.556(4)	4.316(3)	0.0015(27)	0.0017(33)
51	1a		4.779(3)	6.555(4)	4.304(2)	0.0017(22)	0.0024(35)
23	1b	*	4.760(3)	6.573(6)	4.325(2)	0.0013(20)	0.0013(20)
33	1b	*	4.786(3)	6.559(3)	4.295(2)	0.0012(26)	0.0017(34)
30	1c	*	4.788(3)	6.568(4)	4.299(3)	0.0021(25)	0.0026(35)
22	1d	**	4.768(5)	6.544(7)	4.327(3)	0.0016(15)	0.0022(23)
38	1d	**	4.791(2)	6.571(4)	4.312(2)	0.0016(16)	0.0016(33)
	1d	**	4.720(3)	6.622(7)	4.329(3)	0.0011(16)	0.0016(22)

This presentation of the supplementary rays shows the names given to the solid compounds (that might contain mixtures of unstable phases).

name	1b	1b	1c	1d	1d	1d
	*	*	*	**	**	**
20\ n	23	33	30	22	38	
20.255						w
20.645						s
21.405				s		
22.105						m
22.390					w	
25.17					s	
25.275			w	S		
25.325						m
28.805						w
30.225	w	w		m	w	
30.555						w
35.860					w	
37.050						
43.295						
47.605				m		
54.650					w	
54.765				w		

Table 3 : Np(V) spectrophotometry in carbonate hydroxide media.

The initial Np(V) solution compositions are above each bloc of the table. Non indicated concentration concentration unit is M (mole/l). Small volumes of concentrated reactant, R (= NaOH, either Na_2CO_3 or Np(V)) solutions are added directly into the 22ml, 10cm path length cuvette. The slope is $lg(A_t/[Np(V)]_t)$ versus lg[R] linear regression.

$[Na_2CO_3]$ 0.1, $[NaClO_4]$ 2.8				slope 1.23	
NaOH 9.9 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0		1.027		
0.10	0.04	-1.35	1.022	0.088	1.93
0.20	0.09	-1.05	1.018	0.384	2.58
0.30	0.13	-0.88	1.013	0.544	2.73
0.40	0.18	-0.75	1.009	0.688	2.83
0.50	0.22	-0.66	1.004	0.760	2.88
0.60	0.26	-0.58	1.000	0.788	2.90
0.70	0.31	-0.52	0.995		
$[Na_2CO_3]$ 0.49				slope 0.52	
NaOH 9.8 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0		1.027		
0.10	0.04	-1.35	1.022	0.100	1.99
0.20	0.09	-1.05	1.018	0.220	2.33
0.30	0.13	-0.88	1.013	0.296	2.47
0.40	0.18	-0.76	1.009	0.360	2.55
0.50	0.22	-0.66	1.004	0.404	2.60
0.60	0.26	-0.58	1.000	0.436	2.64
0.70	0.30	-0.52	0.995	0.456	2.66
0.80	0.34	-0.46	0.991	0.486	2.69
0.90	0.39	-0.41	0.987	0.492	2.70
1.00	0.43	-0.37	0.982	0.498	2.70
1.25	0.53	-0.28	0.972	0.536	2.74
1.50	0.63	-0.20	0.961	0.540	2.75
1.75	0.72	-0.14	0.951	0.544	2.76
2.00	0.82	-0.09	0.941	0.540	2.76
2.50	1.00	0.00	0.922	0.540	2.77
$[Na_2CO_3]$ 0.5, $[NaClO_4]$ 2				slope 0.69	
NaOH 9.8 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0.00		0.1027		
0.10	0.04	-1.35	0.1022		
0.20	0.09	-1.05	0.1018	0.0184	2.26
0.30	0.13	-0.88	0.1013	0.0256	2.40
0.55	0.24	-0.62	0.1002	0.0452	2.65
0.80	0.34	-0.46	0.0991	0.0536	2.73
1.30	0.55	-0.26	0.0970	0.0664	2.84
1.80	0.74	-0.13	0.0949	0.0736	2.89

$[Na_2CO_3]$ 0.49,	$[NaClO_4]$ 2			slope 0.86	
NaOH 9.9 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0.00	0.00	1.009	0.00	
0.10	0.04	-1.35	1.004	0.00	
0.20	0.09	-1.05	1.000	0.07	1.83
0.30	0.13	-0.88	0.995	0.19	2.27
0.40	0.18	-0.75	0.991	0.27	2.43
0.50	0.22	-0.66	0.987	0.34	2.54
0.60	0.26	-0.58	0.982	0.40	2.61
0.70	0.31	-0.52	0.978	0.44	2.65
0.80	0.35	-0.46	0.974	0.50	2.71
1.00	0.43	-0.37	0.965	0.58	2.78
1.20	0.51	-0.29	0.957	0.68	2.85
1.40	0.59	-0.23	0.949	0.70	2.87
1.90	0.79	-0.10	0.929	0.74	2.90
2.40	0.97	-0.01	0.910	0.75	2.91
2.90	1.15	0.06	0.891	0.72	2.90

	$[Na_2CO_3]$ 0.98			slope 0.66	
NaOH 9.9 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0		1.027		
0.20	0.09	-1.05	1.018		
0.40	0.18	-0.75	1.009	0.2	2.30
0.60	0.26	-0.58	1.000	0.34	2.53
0.80	0.35	-0.46	0.991	0.42	2.63
1.00	0.43	-0.37	0.982	0.524	2.73
1.20	0.51	-0.29	0.974	0.556	2.76
1.40	0.59	-0.23	0.966	0.58	2.78
1.60	0.67	-0.17	0.957	0.616	2.81
1.80	0.75	-0.13	0.949	0.628	2.82
2.00	0.83	-0.08	0.941	0.648	2.84
2.20	0.90	-0.05	0.934	0.676	2.86
3.20	1.26	0.10	0.897	0.68	2.88

[Na	$_2CO_3$] 1,	$[NaClO_4]$ 1		slope 0.99	
NaOH 9.8 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0.00		1.027		
0.10	0.04	-1.35	1.022		
0.20	0.09	-1.05	1.018	0.076	1.87
0.30	0.13	-0.88	1.013	0.124	2.09
0.40	0.18	-0.76	1.009	0.144	2.15
0.50	0.22	-0.66	1.004	0.212	2.32
0.70	0.30	-0.52	0.995	0.316	2.50
0.90	0.39	-0.41	0.987	0.348	2.55
1.10	0.47	-0.33	0.978	0.428	2.64
1.30	0.55	-0.26	0.970	0.472	2.69
1.50	0.63	-0.20	0.961	0.52	2.73
1.70	0.70	-0.15	0.953	0.536	2.75

	$[Na_2CO_3]$ 1.5				slope 0.90
NaOH					y =
9.8 M	x =		$[Np]_t$	absorb.	$A/[Np]_t$
(ml)	[OH]	lg x	(mM)	A	lg y
0.00	0.00		0.1027		
0.25	0.11	-0.96	0.1015		
0.50	0.22	-0.66	0.1004	0.0184	2.26
0.75	0.32	-0.49	0.0993	0.0304	2.49
1.00	0.43	-0.37	0.0982	0.0368	2.57
1.25	0.53	-0.28	0.0972	0.0424	2.64
1.50	0.63	-0.20	0.0961	0.0504	2.72
1.75	0.72	-0.14	0.0951	0.0512	2.73

	$[Na_2CO_3]$ 1.47				slope 0.95
NaOH					y =
9.9 M	x =		$[Np]_t$	absorb.	$A/[Np]_t$
(ml)	[OH]	lg x	(mM)	A	lg y
0			1.027		
0.25	0.11	-0.95	1.015	0.04	1.60
0.50	0.22	-0.66	1.004	0.20	2.31
0.75	0.33	-0.49	0.993	0.28	2.44
1.00	0.43	-0.37	0.982	0.36	2.56
1.25	0.53	-0.27	0.972	0.42	2.63
1.50	0.63	-0.20	0.961	0.47	2.69
1.75	0.73	-0.14	0.951	0.51	2.73
2.00	0.83	-0.08	0.941	0.51	2.73
2.25	0.92	-0.04	0.932	0.56	2.78
2.50	1.01	0.00	0.922	0.56	2.78
2.75	1.10	0.04	0.913	0.58	2.81
3.00	1.19	0.07	0.904	0.58	2.81
3.25	1.27	0.11	0.895	0.60	2.83
4.25	1.60	0.20	0.861	0.59	2.84

$[Na_2CO_3]$ 0.5,	$[NaClO_4]$ 2,	$[NaOH]$ 0.43			slope	0.26
				y =		
Na_2CO_3	x =		absorb.	$A/[Np]_t$		
(ml)	$[CO_3]$	lg x	A	y	[OH]	lg[OH]
	0.2940	-0.53	0.086	837.39	1.20	0.08
15.00	0.1764	-0.75	0.078	759.49	1.32	0.12
10.00	0.1176	-0.93	0.072	701.07	1.38	0.14
9.00	0.1058	-0.98	0.068	662.12	1.39	0.14
8.00	0.0940	-1.03	0.064	623.17	1.40	0.15
5.00	0.0588	-1.23	0.048	467.38	1.44	0.16
3.00	0.0350	-1.46	0.038	370.01	1.46	0.16
1.70	0.0200	-1.70	0.030	292.11	1.48	0.17
	1.0000	0.00	0.074	720.55	0.50	-0.30

$[Na_2CO_3]$ 0.498, $[NaClO_4]$ 2, [NaOH] 0.43				slope 0.09
Np 10.27mM	$x=[Np]_t$		absorb.	$y = A/[Np]_t$
(ml)	(mM)	lg x	A	lg y
0.00	0.1027	-3.99	0.04	2.61
0.10	0.1492	-3.83	0.05	2.56
0.20	0.1952	-3.71	0.07	2.58
0.30	0.2409	-3.62	0.09	2.57
0.40	0.2861	-3.54	0.10	2.56
0.60	0.3754	-3.43	0.13	2.53
0.80	0.4631	-3.33	0.16	2.55
1.00	0.5492	-3.26	0.21	2.58
1.20	0.6339	-3.20	0.27	2.62
1.40	0.7171	-3.14	0.30	2.62
1.60	0.7990	-3.10	0.34	2.63
1.80	0.8794	-3.06	0.39	2.65
2.00	0.9585	-3.02	0.44	2.66
2.20	1.0363	-2.98	0.49	2.67

$[Na_2CO_3]$ 1.497, [NaOH] 0.515				slope 0.01
Np 10.27mM	$x=[Np]_t$		absorb.	$y = A/[Np]_t$
(ml)	(mM)	lg x	A	lg y
0	0.1027	-4.0	0.048	2.67
0.1	0.1492	-3.8	0.064	2.63
0.2	0.1952	-3.7	0.069	2.55
0.3	0.2409	-3.6	0.100	2.62
0.4	0.2861	-3.5	0.120	2.62
0.5	0.3309	-3.5	0.147	2.65
0.7	0.4194	-3.4	0.180	2.63
0.9	0.5063	-3.3	0.228	2.65

Figures 1 : Np(V) solubility results

Table 1 results are plotted here ($[Na^+]$ = 3 M, ClO_4^-, T = 20 +/- 1°C). The solid is precipitated by adding HCO_3^- (P1), it is then dissolved with H^+ (D1) and precipitated again (P2) etc... in a cell at controled CO_2 partial pressure. Np(V) is also equilibrated in batches (series a and b) during 4 (a4 and b4) or 8 (a8) weeks.

Figure 1a : Experimental domain

On lg $[CO_3^{2-}]$ vs. -lg$[H^+]$ presentation, $[HCO_3^-]$ or P_{CO_2} constant values are on straight lines with slope 1 (HCO_3) or 2 (CO_2) ; lg $[HCO_3^-]$ and lg P_{CO_2} values are written above or below on the figure. The 68 solubility experimental points used for curve fitting are here indicated together with spectrophotometric Np(V) mixed complex experimental conditions (spec).

Figure 1b : Solubility and curve fitting results

Curves are calculated using lg β_{101} = 5.33, lg β_{201} = 8.22, lg β_{301} = 10.56 formation constant and either (1(s)) $NaNpO_2CO_{3(s)}$ (lg(Ks_{001}/3) =-10.63) or (3(s)) $Na_3NpO_2(CO_3)_{2(s)}$ (lg(Ks_3/9) = 1.98) solubility product.

Figure 1c : Time dependency

The error, er = lg$[Np]_t$ -lg$[Np]_{calculated}$ is plotted versus time. The solid is never remove from the cell solution ; but the time is set to 0, when CO_2 bubbling is stopped. Experimental points not included in the curve fitting (out) are also plotted.

Figures 2 : Fitted constants $[CO_3^{2-}]$ and $[H^+]$ dependency

lg Ks_{ij1}' are computed for each experimental ($[Na^+]$ = 3 M, ClO_4^-, T = 20 +/- 1°C) point assuming that Ks_{kl1}' have their (previously) fitted (now fixed) values. This is meaningless when $[NpO_2(CO_3)_i(OH)_j^{1-2i-j}]$ is negligeable and Ks_{1kl}' can then be very big and even negative (not plotted in this last case which explains that the divergent parts of the curve are not symetrical). These figures would detect wether Ks_{ij1}' determinations are correlated to some experimental conditions ($[CO_3]^{2-}$ or $[H^+]$), indicating possible systematic error : this is never the case. Only 2 examples are presented here. Ks_{ij1}' symbol is refered i;j on the legenda.

Figures 3 : Sensibility analysis on Np(V) solubility interpretations in carbonate media

Ks_{ij1}', are fitted while one formation constant, Ks_{pq1}', is fixed, to plot lg Ks_{ij1}' and σ versus lg Ks_{pq1}'. σ minimum (when it exists) is indicated (dark point), 4 typical cases are shown. When too high values are choosen for Ks_{pq}', σ increases dramatically and some other constants decrease or even cannot be fitted.

Figure 3a : $NpO_2(CO_3)_2^{3-}$

There is a slight σ minimum ; and $NpO_2(CO_3)_2^{3-}$ exists : it has been detected using spectrophotometry [RIG89].

Figure 3b : NpO_2OH^0

This species cannot be detected (no σ minimum) and there is no experimental evidence that it exists ; but since there is mixed $NpO_2(CO_3)_i(OH)_j^{1-2i-j}$ complex evidence, $NpO_2(OH)_j^{1-j}$ hydroxide complexes should exist in some chemical conditions.

Figure 3c : NpO_2HCO3^0

There is a σ minimum ; but it is probably too low to be interpreted as an $NpO_2HCO_3^0$ evidence : Ks_{1-11}' fitted value is probably overestimated.

Figures 4 : "Bootstrap" error distribution histograms

Some random perturbations of the original data set are induced (using Bootstrap algorithms) to fit 1000 times the Ks_{ij1}' constants. The results are presented as histograms : the surface of each class is constant (and includes 20 events) and the height is arbitrary. All the equilibrium constant graduations (on the histograms) are the same (to allow visual comparison). Each class Ks_{ij1}' mean value is also indicated with a symbol. Different models are presented : the original one (with no minor sprcies), models with one minor species addition ($NpO_2HCO_3^0$, $NpO_2CO_3HCO_3^{2-}$, $NpO_2(CO_3)_2OH^{4-}$, $NpO_2(CO_3)_2HCO_3^{4-}$), or without $NpO_2(CO_3)_2^{3-}$, and the original model where 13 "Jacknife outliers" (55 data) are not considered. Only some typical plotted of some of the tested models are plotted here.

Figure 4a : σ

Taking $NpO_2(CO_3)_2^{3-}$ species of the original model quite significatively increases σ. Minor species additions do not improve the fit. "Jacknife outliers" are also outliers here.

Figure 4b : $NpO_2(CO_3)_2^{3-}$

The histogram is not symetrical, it is then clear that the error distribution can hardly be assumed to be a gaussian one. Fitted lg Ks_{201}' values that cannot be shown on this figure (they are very negative) are interpreted as Ks_{201}' = 0 values : $NpO_2(CO_3)_2^{3-}$ stability domain is very narrow which explains this behaviour.

Figure 4c : $NpO_2(CO_3)_3^{5-}$

Taking $NpO_2(CO_3)_2^{3-}$ species of the original model, significatively increases β_3, the $NpO_2(CO_3)_3^{5-}$ formation constant : chemical interpretation is straightforward.

Figures 5 : Mixed $NpO_2(CO_3)_i(OH)_j^{1-2i-j}$ complex spectrophotometric evidence.

Molar abosorbance at 1010 nm (see table 3), $A/[Np(V)]_t$, is plotted versus some concencentrations in lg-lg units. A concentrated $[NaOH]_{in}$ (M) solution is usely added in a [Np(V)] (mM) concentrated $[Na_2CO_3]_{in}$ (M) + $[NaClO_4]_{in}$ (M) solution (in some cases Na_2CO_3 or Np(V) solutions are used for additions). The legenda symbols refer to the initial concentrations : $[Na_2CO_3]_{in}$, $[NaOH]_{in}$, $[NaClO_4]_{in}$, [Np(V)]. $NpO_2(CO_3)_3^{5-}$ extinction coefficient is very small, total molar aborbance increases with NaOH additions : (at least) one new complex containing OH ligand is then formed.

Figure 5a : experimental results

The slope of the curves (with constant $[Na^+]$ and $[CO_3^{2-}]$) is 1 wich is consistent with $NpO_2(CO_3)_3^{5-}$ transformation into $NpO_2(CO_3)_i(OH)_2^{-1-2i}$ (with OH addition). These curves are shifted toward higher [OH] when $[Na_2CO_3]_{in}$ is higher : there are less CO_3 ligand in the new complex ($i < 3$). The shift is 0.5 (lg[OH] unit) when $lg[Na_2CO_3]_{in}$ is increased from -1 to 0 hence $0.5 = (3 - i)/2$: $i = 2$ ($NpO_2(CO_3)_2(OH)_2^{-5}$ is formed).

Figure 5b : $NpO_2(CO_3)_2(OH)_2^{-5}$ evidence

To verify that 2 OH and 1 CO_3 are involved in the $NpO_2(CO_3)_3^{5-}$<>$NpO_2(CO_3)_2(OH)_2^{-5}$ equilibrium, $lg(A/[Np(V)]_t)$ is plotted versus $(2\ lg[OH^-] + lg[CO_3^{2-}])$: the points with constant $[Na^+]$ are on a single curve (within experimental uncertainties) and ionic strength effects are hardly detected.

These figures are not available in electonic version, some were later published in Ref.[98VIT/CAP]