

Am(OH)_{3(s)}, AmOHCO_{3(s)}, Am₂(CO₃)_{3(s)} Stabilities in Environmental Conditions.

Pierre Vitorge

CEN-FAR, CEA DCC/DSD/SCS/SGC LAT, FONTENAY-AUX-ROSES, FRANCE

Summary

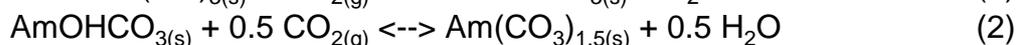
These three solid phases have been proposed to calculate Am solubility in environmental conditions, predicted solubility can hence differ by several orders of magnitude. Thermodynamic considerations are here used to predict the stability domains of these solid phases in contact with aqueous solutions of various chemical compositions : it is only p_{CO_2} (carbonic gas partial pressure equilibrated with the solution) dependent, which is consistent with all published works about Am solid phases (preparation and solubility).

Introduction

Radioelement solubility limits are sometimes used for safety assessment of nuclear waste disposal. Am solubility has hence been measured in basic and carbonate media where the pure solid phases Am(OH)_{3(s)} [1], AmOHCO_{3(s)} [2] [3] [4] [5] and Am₂(CO₃)_{3(s)} [6] have been characterized. It has been shown [6] that the chemical model (set of Am soluble complex stability constants) used to interpret Am₂(CO₃)_{3(s)} solubility gave also an interpretation consistent with all the published works about Americium in carbonate media (the same Am speciation model has been confirmed [7] and independently proposed [5]), and that it is not the case for one of the AmOHCO_{3(s)} model [2]. One of the authors of [2] recently published [8] Am solubility measurement interpreted with Am₂(CO₃)_{3(s)} solid phase ; but they did not give much comments about their previous interpretations and there is indeed recent convincing evidence [5] that Am solubility can be controlled by AmOHCO_{3(s)} solid phase at least when $p_{\text{CO}_2} = 0.001$ atm. We have then reexamined this problem : it is clear that the aqueous solution chemical conditions were not the same in the above Am solubility works, correct soluble Am speciation might then be needed. Still we present here some thermodynamic considerations that only use implicit speciation (and then do not rely on it) to show a way to predict the stability of these three solid phases : we will show that p_{CO_2} is the only important aqueous phase chemical parameter (it was 0.001 atm for AmOHCO_{3(s)} [5] and 0.1 to 1 atm for Am₂(CO₃)_{3(s)} [6] careful preparation, characterization and solubility studies).

Thermodynamic approach

When in contact with the air (where there is some CO₂ gas) or with carbonate or bicarbonate solutions, Am(OH)_{3(s)} can be transformed to AmOHCO_{3(s)} and/or Am₂(CO₃)_{3(s)}. We write these possible equilibria the following way:



the equilibrium constants of (1) and (2) are respectively

$$pCO_{2,0,1} = p_{CO_2}/a_{H_2O} \quad (3)$$

$$(pCO_{2,1,1.5})^{0.5} = (p_{CO_2}/a_{H_2O})^{0.5} \quad (4)$$

where a_{H_2O} is the activity of water (1 in standard conditions)

$pCO_{2,i,j}$ is an equilibrium constant (noted this way to point out that it is only p_{CO_2} dependent in standard conditions).

It is then clear that AmOHCO_{3(s)} is stable in contact with an aqueous solution, only when :

$$pCO_{2,0,1} < p_{CO_2}/a_{H_2O} < pCO_{2,1,1.5} \quad (5)$$

From known solubility products $Ks_0 = [Am^{3+}](a_{H_2O}/[H^+])^3 \quad (6)$

$$Ks_1 = [Am^{3+}][CO_3^{2-}]a_{H_2O}/[H^+] \quad (7)$$

$$Ks_{1.5} = [Am^{3+}][CO_3^{2-}]^{1.5} \quad (8)$$

carbonate CO₂ gas equilibrium constant

$$K_p = (p_{CO_2} a_{H_2O})/([CO_3^{2-}][H^+]^2) \quad (9)$$

and definitions (3) and (4) we predict the numerical values of the equilibrium (1) and (2) constants :

$$pCO_{2,0,1} = K_p Ks_1/Ks_0 \quad (10)$$

$$pCO_{2,1,1.5} = K_p(Ks_{1.5}/Ks_1)^2 \quad (11)$$

If now AmOHCO_{3(s)} is not stable (i.e inequality (5) is not true at the considered temperature) the constant

$$(pCO_{2,0,1.5})^{1.5} = (p_{CO_2}/a_{H_2O})^{1.5} \quad (12)$$

of the only stable equilibrium



is also deduced as (10) or (11) :

$$pCO_{2,0,1.5} = K_p(Ks_{1.5}/Ks_1)^{2/3} \quad (14)$$

A temperature, T_{tr} , might also exist where the three solid phases are stable, inequalities (5) would then be equalities, from (5), (10) and (11) or (14)

$$Ks_{1,1.5}^3 = Ks_{0,1.5} Ks_{1.5,1.5}^2 \quad (15)$$

Thermodynamic data

$Ks_{1.5}$ [6] and Ks_1 [5] values have been measured in different media, $pCO_{2,i,j}$ constant has very little ionic medium dependence ; but when they are calculated from (10) and (11), Ks_i values have to be corrected for ionic strength effects : we use

the SIT [9] [6] [12] for these corrections. We have shown [10] that standard values might be correlated to the procedure used for extrapolation to 0 ionic strength which finally induces uncertainties, typically all Pitzer's parameters cannot always be fitted when there are not enough experimental data [10] and the same observation has been made [5] for Am systems. K_{s0} published values are quite scattered [6].

We have then measured Am(III) solubility in basic aqueous solutions (KOH 0.05 to 10 M) where CO₂ partial pressure is maintained very low by Ca(OH)_{2(s)} additions. Similar calculations as above (where Ca²⁺ is used instead of Am³⁺) indicate that calcium solid phases buffer a much lower p_{CO_2} (10^{-13} atm) than Am solid phases. It takes 1 to 6 months to obtain constant Am solubility which is $10^{-11.1}$ when KOH is less than 1 M. This corresponds to the lowest published values of Am(OH)_{3(s)} solubility product and the interpretation is straightforward : Am(OH)_{3(s)} is amorphous and is slowly transformed into a more stable, then less soluble phase. Careful reading of Am₂(CO₃)_{3(s)} and AmOHCO_{3(s)} published studies also indicates that these crystalline phases are not obtained at once at room temperature.

Results and conclusion

The solubility product and equilibrium constant discussed above, are used to compute $\lg pCO_{2,i,j}$ (table 1).

Table 1 : Characteristic pCO_2 calculation.		
	Our estimation	Our calculation ^(a)
$\lg pCO_{2,0,1}$	-7.8 +/- 2	-7.4 +/- 2
$\lg pCO_{2,1,1.5}$	-1.5 +/- 4	-2.22 +/- 0.90

(a) (At "Migration 91", Kim's and coworkers have presented again [11] some experimental results that confirms the present interpretation : they have measured Am₂(CO₃)_{3(s)} and AmOHCO_{3(s)} solubility products in 0.1 M NaClO₄ medium and we are using the numerical values that they have published in the abstracts of the conference for this calculation, since they did not discuss the thermodynamic relative stability of the solid phases).

The three solid phases are then probably stable, which is consistent with the preparation conditions of the solid phases which also controlled Am solubility (table 2).

Table 2 : Preparation conditions of Am solid phases which also controlled Am solubility.		
Solid phases	pCO_2 range (atm)	Ref.
Am ₂ (CO ₃) _{3(s)}	0.1 to 1	[6]
AmOHCO _{3(s)}	0.001	[5]
Am(OH) _{3(s)}	10^{-13}	this work

Acknowledgements :

Solubility measurements were performed by Patrick Tran The. Financial support was received from CCE, contract FI1W0190. This is a joint CEA DCC-ANDRA program.

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Figure : Am solid phases predominance diagram in carbonate/water system. $pX = -\lg a_X$ where

a_X is ion X^{z_X} activity, z_X is its charge : $pH = -\lg a_{H^+}$, $-pHCO_3 = \lg a_{HCO_3^-}$,

$-pCO_3 = \lg a_{CO_3^{2-}}$. Activity units are mol/l. Constant CO_2 partial pressure, p_{CO_2} , (and also $a_{HCO_3^-}$) are straight lines with slope 2 (and 1 respectively) on this representation ; p_{CO_2} , (and also $-pHCO_3$)

values are written beside the corresponding lines. Hence one can read on this diagram which solid should be in equilibrium with an aqueous solution where, typically pH and p_{CO_2} are known. The 2 equilibria between the 3 solid phases are written on the figure. Each equilibrium induces constant p_{CO_2} (see text) which is then a limit of a range of predominance. These limits are estimated in text

(bold lines $\lg p_{CO_2,1} = -7.8 \pm 2$,

$\lg p_{CO_2,1.5} = -1.5 \pm 4$) or calculated from reference [11] (dashed bold line

$\lg p_{CO_2,0.1} = -7.6 \pm 2$, $\lg p_{CO_2,1.5} = -2.22 \pm 0.90$ where $p_{CO_2,i,j} = p_{CO_2}/a_{H_2O}$ is an equilibrium constant in atm./mol. unit ; it is p_{CO_2} (atm) in standard conditions or when a_{H_2O} variations with the ionic medium can be neglected).

Key words : Americium, Solubility, Carbonate, Hydroxide, Environment.