THE EFFECT OF HUMIC ACID ON THE FORMATION AND SOLUBILITY OF SECONDARY SOLID PHASES OF POLYVALENT METAL IONS

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INTRODUCTION

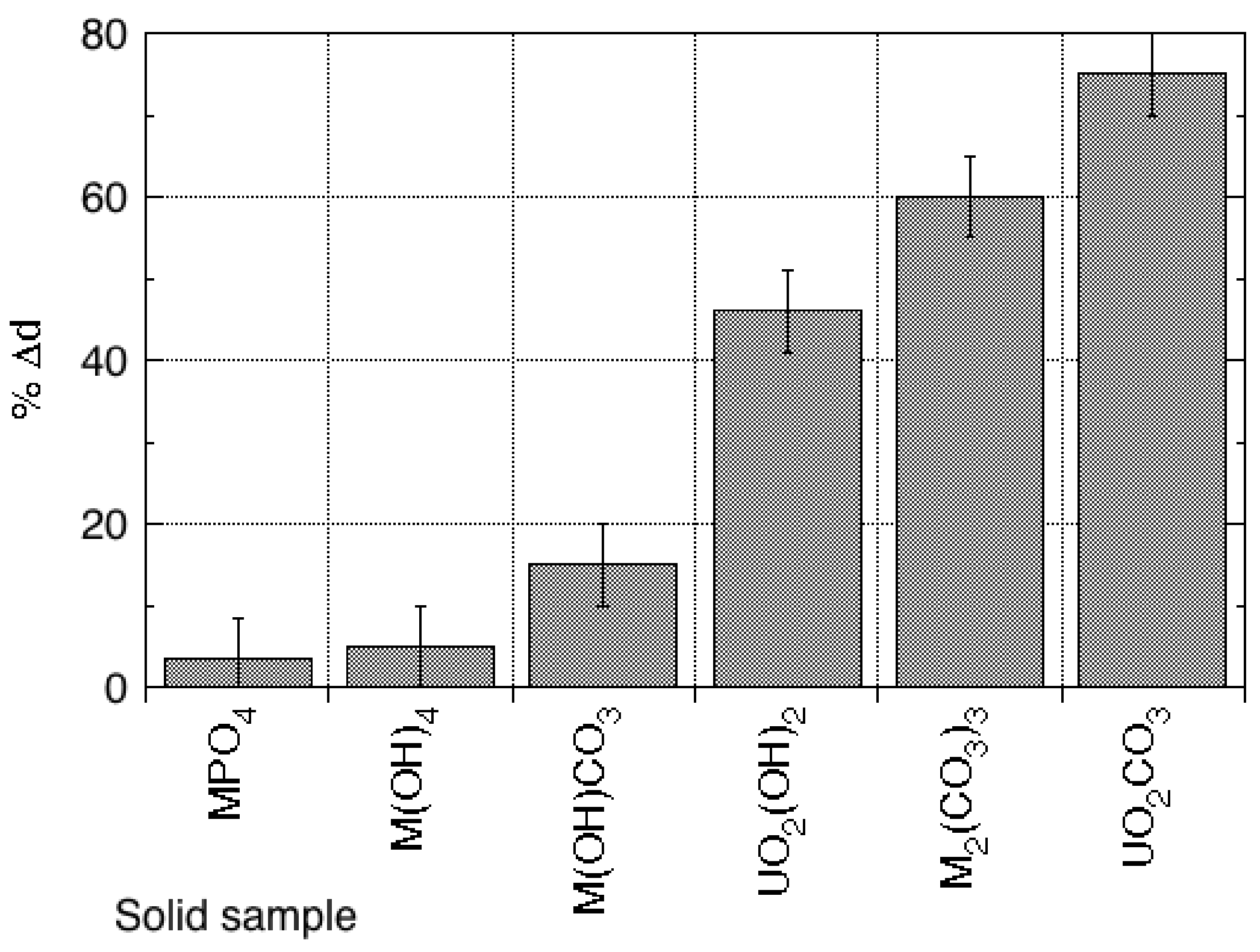
The long-term performance assessment for the safe disposal of (radio)toxic elements (e.g. heavy metal ions) in underground geological formations requires mechanistic knowledge of the chemical behaviour of the metal ions in aquatic systems, because usually only through underground aquifers migration and dispersion of the (radio)toxic elements in the environment is possible [1]. There is particular interest regarding actinides (e.g. U, Pu, Np, Am Cm), because of the amounts produced in fission reactors and their long-lived radionuclides, which are generally highly radiotoxic alpha-radiation emitters. The chemical behaviour of polyvalent metal ions in natural systems is governed by hydrolysis, complexation with naturally occuring ligands, colloid generation, geochemical interaction with mineral surfaces and solid phase formation. The investigation of formed solid phases is of particular interest because secondary phases may represent important sinks for (radio)toxic metal ions within nuclear spent fuel and (radio)toxic waste repositories and determine their solubility and mobility in the geosphere. In this paper we present and discuss data from studies regarding the effect of natural organic matter (NOM) and particularly humic acid (HA) on the solid phase formation of polyvalent metal ions in aqueous solutions. The solid phases, which have been studied are: $M(OH)CO_3$, $M_2(CO_3)_3$, MPO_4, $M(OH)_4$, $UO_2(OH)_2$ and UO_2CO_3.

EXPERIMENTAL

M(z) stock solutions were prepared by dissolution of $M(NO_3)_z$ salts (Aldrich Co) in aqueous 0.1 M $NaClO_4$. Solid phases were prepared by alkaline precipitation (pH 10) of a 50 mL M(z) solution. HA solutions used in this study were prepared from Aldrich humic acid, purified and characterized as described elsewhere [2]. The precipitates have been characterized by TGA-50 and XRD. The evaluation of the particle/crystallite sizes was performed using the Scherrer equation [3]. Spectroscopic measurements such as FTIR-ATR, TRLFS, Raman, DR-UV spectroscopy were performed on solid samples after separation by centrifugation as described elsewhere [4]. For solubility studies the solid phases (about 100 mg), prepared in the presence and absence of HA, were conducted with 50 mL of 0.1 M $HClO_4$ solutions. The pH was adjusted by addition of 0.1 M NaOH or 0.1 M $HClO_4$. Following equilibration time (from 2 weeks to one year), pH was measured using a glass electrode and the analytical M(z) concentration in solution was determined spectrophotometrically by means of arsenazo-III according to a previously described method [5]. Prior concentration determination the test solution was ultra-filtrated using 0.45 mm membrane filters to remove any solid phase particulates from the solution.

RESULTS AND DISCUSSION

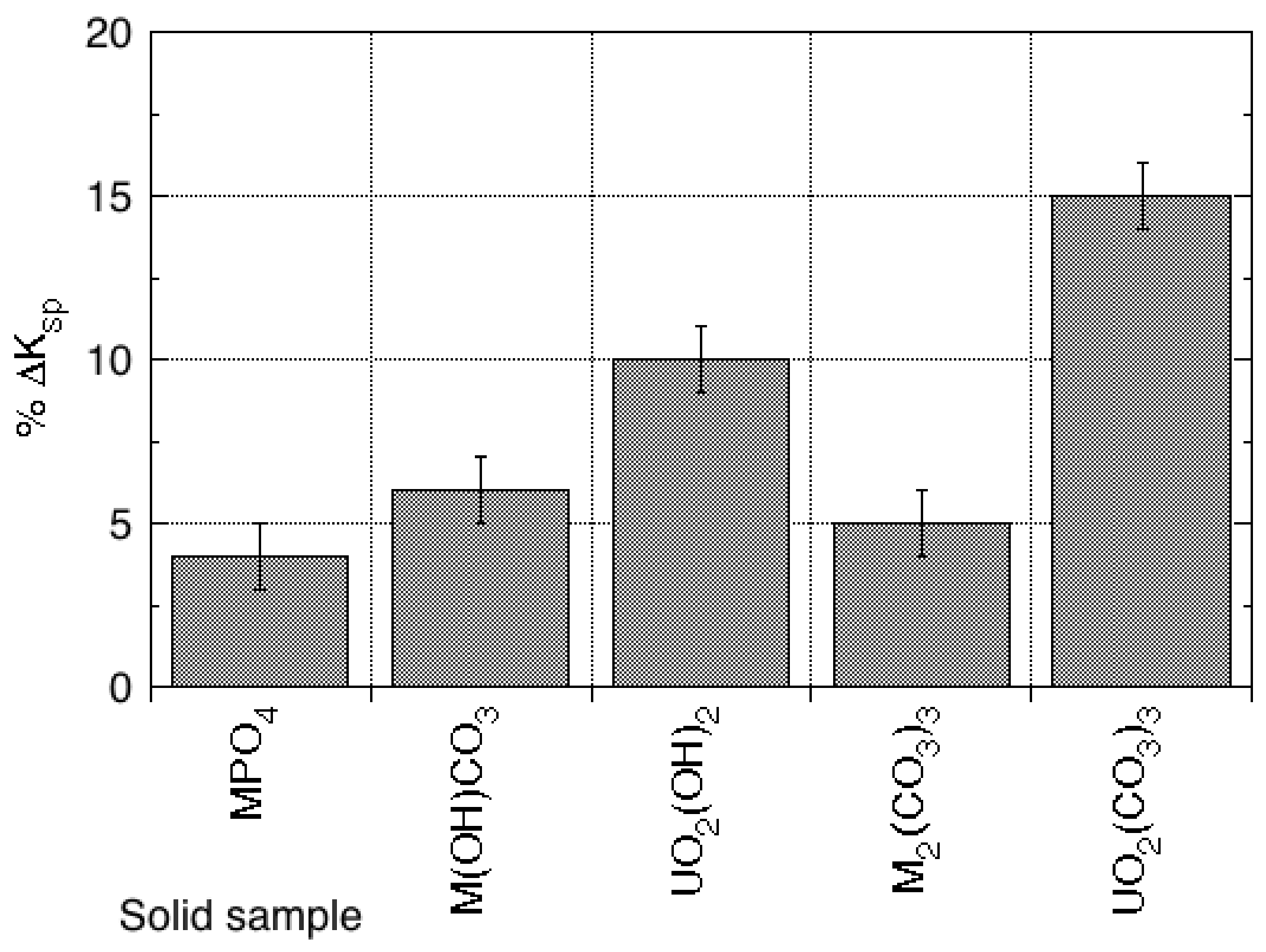
XRD MEASUREMENTS



Relative change in the particle size of the secondary solid phases of polyvalent metal ions precipitated in the presence of humic acid.

The impact of humic acid on the particle size depends strongly on the solid phase stability and is highest for M(VI) and M(III) carbonate and lowest for $LnPO_4$ and $M(OH)_4$ solid phases.

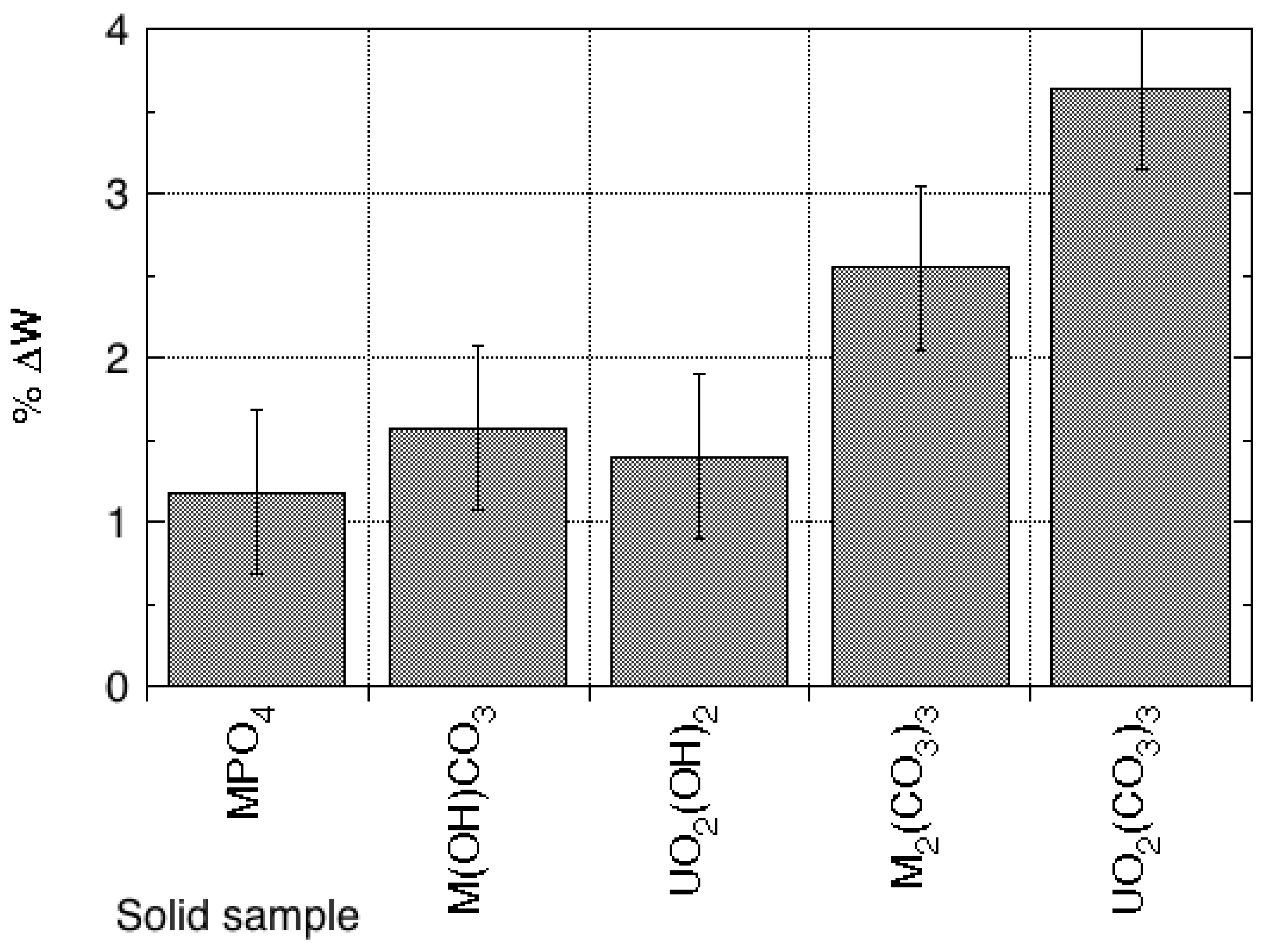
SOLUBILITY MEASUREMENTS



Relative change in the solubility product of the secondary solid phases of polyvalent metal ions precipitated in the presence of humic acid.

Changes in the solid phase solubility because of microsolubility effects are relatively small and within the uncertainties of the solubility product values given in literature for the corresponding solid phases.

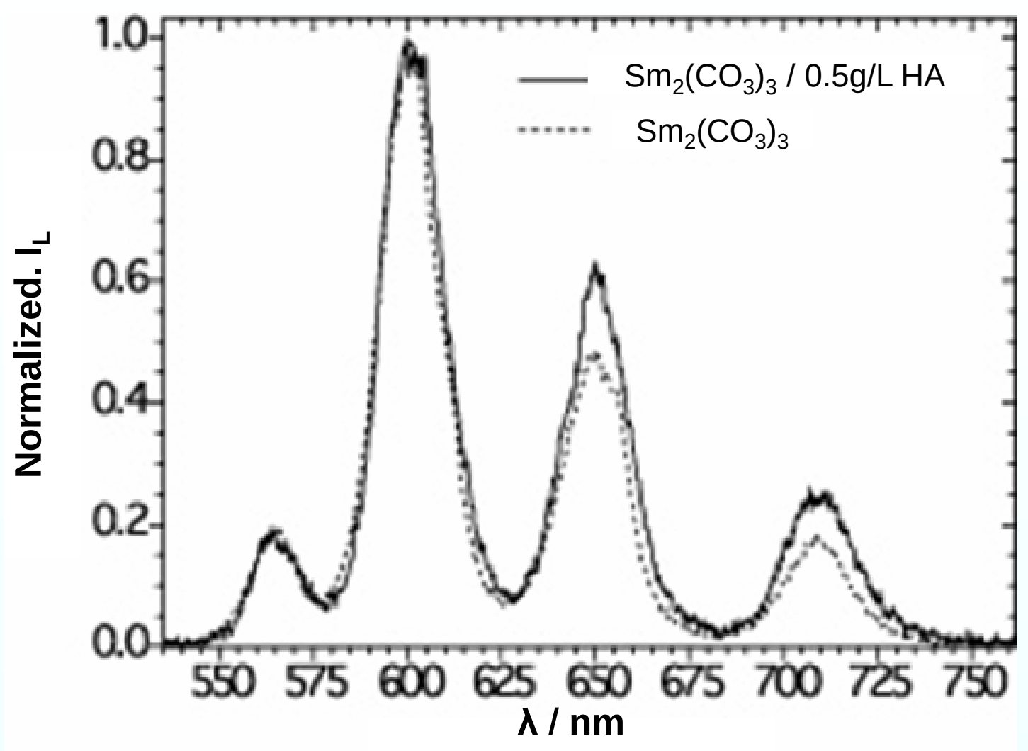
THERMOGRAVIMETRIC ANALYSIS



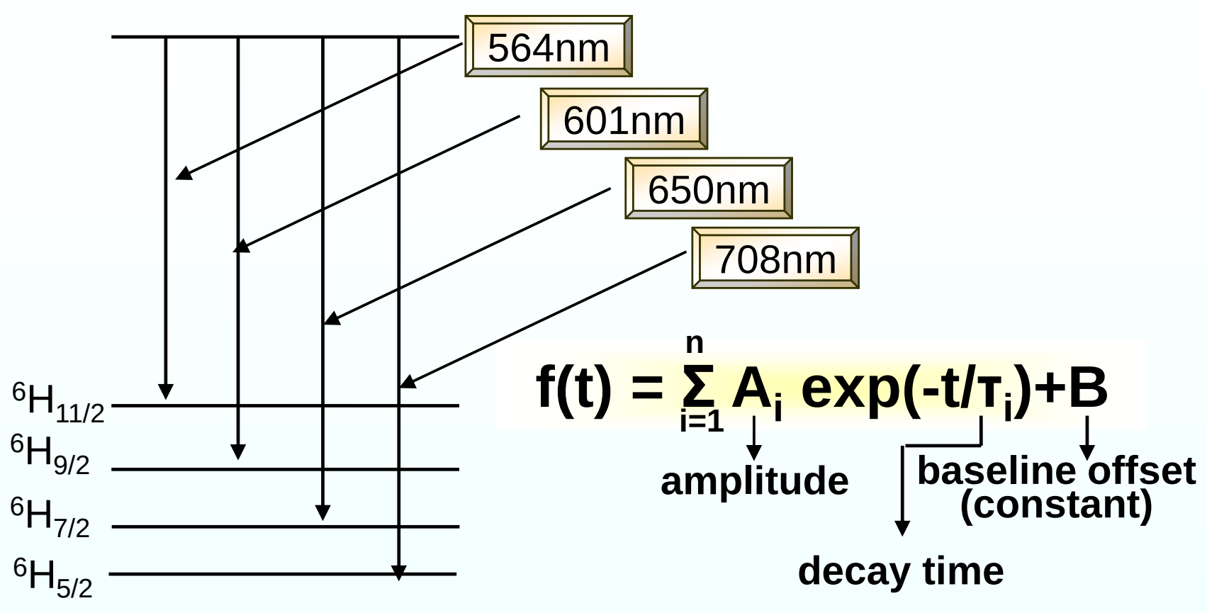
Relative change in the water loss of the secondary solid phases of polyvalent metal ions precipitated in the presence of humic acid.

The adsorption of humic acids on the particle surface affects the water holding capacity of the solid phase as indicated by TGA measurements.

Spectroscopic Measurements (TRLFS)



Emission spectra of $Ln_2(CO_3)_3$ (dashed line) and $Ln_2(CO_3)_3$ with 0.5 g/L HA (solid line) at dt = 100 ns, λex= 464 nm.



$$f(t) = \sum_{i=1}^{n} A_i \exp(-t/\tau_i)+B$$

The fluorescence decays for all samples were monoexponential.

Sample	(ns) at 464 nm
$Sm_2(CO_3)_3$	946
$Sm_2(CO_3)_3$ + 0.1 g/L HA	1013
$Sm_2(CO_3)_3$ + 0.3 g/L HA	1019
$Sm_2(CO_3)_3$ + 0.5 g/L HA	1011

The decay times (τ) for all Sm(III) samples are very similar (946ns<τ<1011ns) and no systematic influence of the HA on τ could be observed.

Compared to the Sm(III) decay time in water (2.3 μs < τ_{H2O} < 2.7 μs) [6] or in other solids such as Sm(III) doped glasses, oxides or even organic complexes (500 μs < τ < 3.1 ms) the decay times determined for the $Sm_2(CO_3)_3$ and $Sm_2(CO_3)_3$-xHA solids are distinctly shorter. This may be explained by fast (phonon-assisted) relaxation pathways provided by the coordinating CO_3^{2-} ions in the solids.

CONCLUSIONS

- The formation of secondary solid phases of polyvalent metal ions is not significantly affected by the presence of HA in an aqueous system. However, if redox-sensitive (oxidizing) species are present, these may be reduced by HA leading to the formation of solid phases corresponding to lower oxidation states of the oxidazing metal species.
- Spectroscopic data obtained by FTIR spectroscopy clearly show that only the pure solid phases are formed and the HA is just coprecipitated, most probably adsorbed onto the solid particles.
- The adsorption HA on the particle surface affects the texture of the solid phase formed, resulting in different particle sizes and different water holding capacity of the solid phase. The impact on the texture and particle size depends strongly on the solid phase stability and is highest for M(VI) and M(III) carbonate and lowest for $LnPO_4$ and $M(OH)_4$ solid phases.
- The changes in the solid phase solubility because of microsolubility effects are relatively small and within the uncertainties of the solubility product values given in literature for the corresponding solid phases.
- Coating of nano-sized solid phase particles with HA colloids could increase their stability in the aqueous phase and result in enhanced contaminant mobility.

LITERATURE

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ACKNOWLEDGEMENT

The research leading to these results has received funding from the Cyprus Research Promotion Foundation (Grant agreement No. PENEK/ENISC/0308/05 and PROSBASH/ERUEX/0308/02) and partially by the University of Cyprus.

3rd INTERNATIONAL NUCLEAR CHEMISTRY CONGRESS 18-23 SEPTEMBER 2011, TERRASINI – PALERMO – SICILY - ITALY