ACTA CHEMICA IASI, **17**, 73-84 (2009)

Radioactive Waste Treatment and Disposal: Phosphates for Actinides Conditioning

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Abstract: Phosphates with monazite have been proposed as potential nuclear waste form materials, numerous geochemical studies showing that monazite present a high aqueous durability. The present study is aimed to test the hydrothermal alteration of two natural monazites and of $LnPO_4$ (Ln = La, Ce, Eu, and Gd) end members in extreme condition (very low and very high pH up to 573 K) using a static leaching test. The analyzed specimens show excellent behavior in acidic media. However, the natural as well as synthetic monazites react with KOH, being transformed in an amorphous mixture of phosphates.

Keywords: Nuclear waste forms; Monazites; Aqueous durability.

Introduction

Monazite is a natural orthophosphate mineral containing light rare earth elements, especially Ce, La and Nd. Generally, monazites also contain some Th and U, with the valence being balanced by Ca or Si. The abundance of Th is typically about 10 *wt* % and that of U about 0.5 *wt* %. Monazites were proposed as a high-level nuclear waste form[1-3] because of

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the cumulative favorable chemical and physical characteristics such as the capacity to incorporate a high amount of actinides, very high resistance to aqueous corrosion, resistance to radiation damage and metamictization, among others. Geological evidence indicates that monazites have survived in the earth's crust for about two billion years; this time span exceeds the required stability period for an actinide waste form established at 10^4-10^5 years.[4]

Although most of the recent literature on monazites deals with their application as a nuclear waste form[5], there are few studies on the stability/dissolution rates of the monazites. Oelkers and Poitrasson determined the dissolution stoichiometry of a natural monazite[6] and of synthetic $NdPO_4$[7] in aqueous solution as a function of temperature and pH. Cetiner et al. reported the solubility of end-member $\mathit{REE}PO_4$ (REE = La, Nd, Sm, and Y) with monazite structure in NaCl-HCl and $NaClO_4$-$HClO_4$ for temperatures below 323 K at various ionic strengths.[8] The interaction of some natural monazite specimens with a bicarbonate-carbonate solution was investigated during seven years and the leaching of U and Th was reported by Eyal and Olander.[9] The synthesis, characterization, sintering and leaching of monazite/cheralite solid solution $Ln^{III}_{1-2x}Ca_xTh_{x-y}U_yPO_4$ was presented by Terra et al.[10] We reported the hydrothermal alteration of $Ba_xM^{IV}_xCe_{2-2x}(PO_4)_2$ compounds with monazite structure (M^{IV} = Zr and Hf) in strongly acidic/ basic media as a function of temperature.[11]

In this contribution, we present data on the hydrothermal alteration of two natural monazites and of $LnPO_4$ (Ln = La, Ce, Eu, and Gd) end members in 1 mol·dm^{-3} HCl and 1 mol·dm^{-3} KOH at 573 K for 14 days. Both the altered specimen and the alteration fluids were analyzed, with the aim to explain the stability or chemical alteration of the specimens. The mineral-fluid equilibration was accelerated by using an extreme proton/ hydroxide activity in the starting solution, which hardly occurs on earth and, least of all, in a potential nuclear repository. The question if batch experiments made with solutions having an extreme proton/ hydroxide activity are relevant for the assessment of what will happen with a nuclear waste form in a nuclear repository when it comes in contact with an aqueous fluid is discussed in detail by Pöml et al.[12]

Experimental

The starting materials and the products of the alteration experiments were studied by powder X-ray diffraction analyses (XRD), electron microprobe (EMPA) and electron microscopy (SEM, BSEM). The total surface area was determined by the BET method. The rare earth elements, U, Th and P in the experimental fluids were analyzed by inductive-coupled plasma mass spectrometry (ICP-MS). The sample preparation for EMP was conducted accordingly with the descriptions existing in literature.[13, 14]

Two natural monazite specimens supplied to us by the Mineralogical Museum of the University of Hamburg were studied. They originate from Madagascar (specimen NM1) and from Norway (specimen NM2). The chemical composition as analyzed by EMP of the monazite phase in minerals is presented in Table 1.

Based on microscopic analysis, the predominant matrix cations in the natural monazites are Ce, La, and Nd. Inclusions of a phase rich in iron (67.57 *wt* %) were determined in NM1 (less than 2 % of the total amount of material) as shown in Figure 1. The thorium content of the monazite phase of NM1 was 11.96 *wt* %, as determined by EMPA.

Table 1. Bulk rock analysis of the investigated samples (*wt* %).

	NM1	NM2
SiO_2	3.15	0.81
P_2O_5	27.07	32.58
CaO	n.d.	1.43
La_2O_3	7.50	12.52
Ce_2O_3	24.23	29.62
Nd_2O_3	14.00	11.54
Sm_2O_3	4.48	2.93
Gd_2O_3	2.38	n.d.
Tb_2O_3	1.61	n.d.
Er_2O_3	1.52	n.d.
Y_2O_3	n.d.	0.66
ThO_2	13.60	8.56

n.d. - not detected

$Ca_3(PO_4)_2$ was detected as a secondary phase in the NM2 sample (about 5 %). It was found that the predominant monazite phase in NM2 (7.52 *wt* % of Th) is associated with huttonite ($ThSiO_4$, 62.69 *wt* % of Th) and xenotime (YPO_4). These results are consistent with the XRD analysis, since the X-ray diffraction patterns indicate only the presence of the above-mentioned crystalline phases in NM1 and NM2 samples.

The synthetic $LnPO_4$ (Ln = La, Ce, Eu, and Gd) end members were obtained by sol-gel reaction, starting from $Ln(NO_3)_3{\cdot}6H_2O$ (for Ln = La and Ce) or Ln_2O_3 (for Ln = Eu and Gd). To obtain the nitrates, the oxides were dissolved in a stoechiometric amount of 63 % HNO_3. The orthophosphates were obtained by adding 85 *wt.* % H_3PO_4 (10 % excess). For $LaPO_4$, $EuPO_4$ and $GdPO_4$, the pH was adjusted to 4.0 using 5 $mol{\cdot}dm^{-3}$ NH_4OH, which initiated the formation of gels. In the $CePO_4$ case, an ageing time of 21 days was necessary to obtain the pure phase. The $LnPO_4$ gels were filtered (Robu-Glas filtering crucible, porosity 5) and washed several times with distilled water.

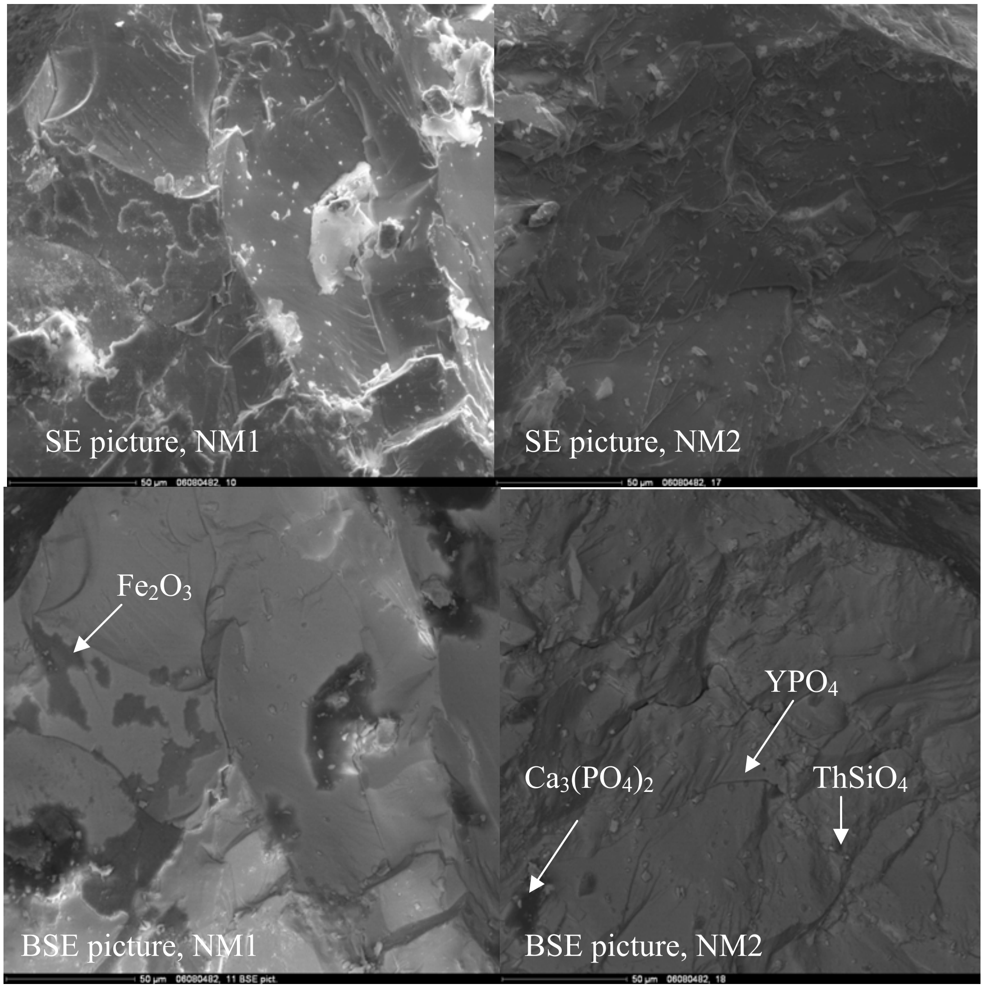

Figure 1. SE and BSE images of NM1 and NM2 monazites used in the hydrothermal alteration experiment

The precipitates were heated in alumina crucibles at 1473 K for 10 h, with heating and cooling ramps of 200 $K \cdot h^{-1}$. The purity of the obtained orthophosphates was verified by XRD at room temperature. A single phase was observed for all $Ln\mathrm{PO}_4$ compounds, having the monoclinic monazite structure ($P2_1/n$). The crystal data of the obtained compounds are presented in Table 2; these data are in good agreement with results reported by Ni et al.[15] We also included the BET surface area of the analyzed powders in this table.

Table 2. The crystal data and the BET surface of the *Ln*PO_4 powders.

	a (nm)	b (nm)	c (nm)	β (°)	V (nm^3)	BET surface area ($m^2 \cdot g^{-1}$)
$LaPO_4$	0.68406	0.70736	0.65126	103°310	0.30512	0.4697
$CePO_4$	0.68009	0.70260	0.64747	103°482	0.30086	0.2559
$EuPO_4$	0.66813	0.68617	0.63491	103°961	0.28248	1.1776
$GdPO_4$	0.66503	0.68466	0.63333	104°003	0.27979	5.7487

The hydrothermal alterations were carried out in nickel autoclaves on grains of natural monazites and powders of synthetic end-members in solutions of 1 $mol \cdot dm^{-3}$ HCl and 1 $mol \cdot dm^{-3}$ KOH at 573 K for 14 days under autogenously pressure. For the synthetic monazites, 0.2 g of the powder (0.1 μm ≤ Ø ≤ 0.125 μm) was contacted with 2 cm^3 HCl/ KOH solutions. For the natural monazites, grains of 0.2086 g (in HCl) and 0.2009 g (in KOH) of NM1 as well as 0.2018 g (in HCl) and 0.2077 g (in KOH) NM2 were contacted with the normalized volume of HCl/ KOH. The reactors were placed in an Ehret TK/L 4105 furnace pre-heated at 573 K.

Results and discussions

The XRD analysis of the altered specimens showed typical monazite diffraction patterns, with no evidence of other crystalline phases. For example, in Figure 2 the X-ray diffraction patterns of NM1 altered in HCl and KOH are presented versus the starting material. The patterns are very similar, with no extra diffractions and with a very small reduction of the intensity of the peaks after alteration.

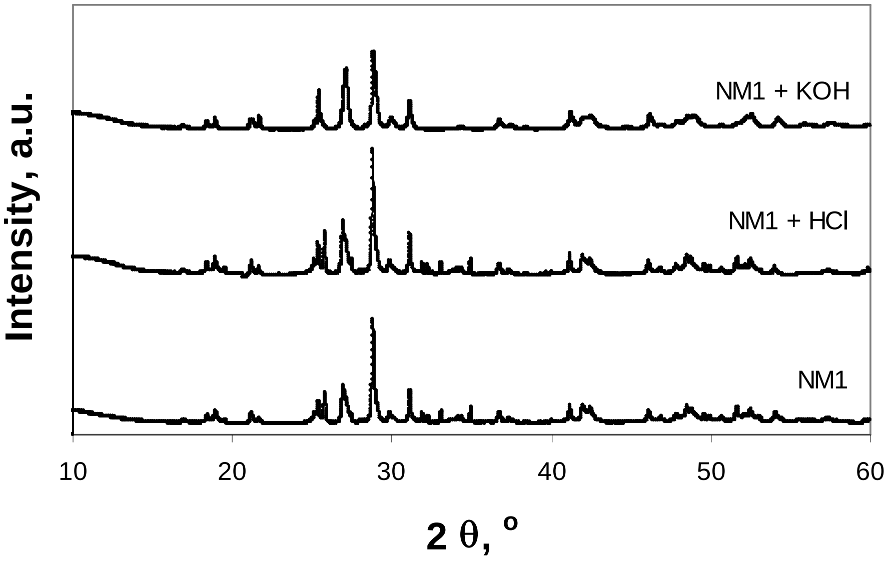

Figure 2. The X-ray diffraction patterns of unaltered and altered NM1 specimen.

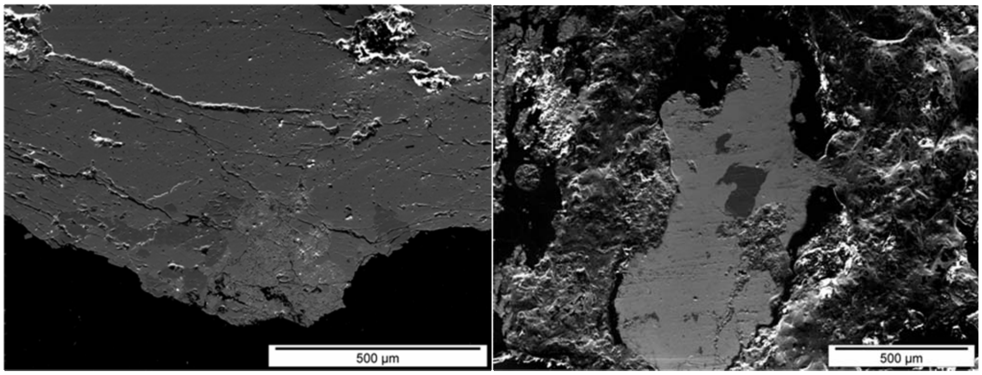

Figure 3. SEM images of the NM1specimens hydrothermally treated in HCl and KOH.

The natural monazites remain un-reacted after 14 days of hydrothermal alteration in HCl, as shown by SEM (Figure 3a) and microprobe analysis. Nevertheless, a newly formed white phase appeared at the surface of the tested materials (less than 1 *wt* %). The chemical analysis reveals that it is $LnCl_3$ (Ln = La, Ce, Nd) formed as the result of a chlorination process. This alteration mechanism was previously described by Poitrasson et al.[16] and the process happens in the presence of halogens, especially fluorine (in the case he described, coming from the alteration of biotite).

Other candidates for the actinide conditioning suffer much more dramatic transformations in similar reaction conditions. An almost fully amorphous zircon ($ZrSiO_4$) re-crystallizes as function of experimental temperature/ duration.[17] The pyrochlore is transformed in a more stable phases (anatase, rutile etc.) in similar alteration conditions at only 448 K.[18]

During the alteration in 1 $mol\cdot dm^{-3}$ KOH at 573 K, the natural monazites (NM1 and NM2) and $EuPO_4$ react with the liquid, no solution being found after 14 days of hydrothermal alteration. In the case of the natural monazite, the SEM analysis show a "core" of the original material in a big amount of a spongy phase (Figure 3b). The microprobe analysis suggests that the main constituent of this newly formed amorphous phase is $K_3Ln(PO_4)_2$ (Ln = La, Ce, and Nd). This result shows that the chemical reaction occurs at the interface solution/monazite, potassium being included in the $LnPO_4$ structure. A similar result was obtained in the case of the alteration of the $Ba_xZr_xCe_{2-2x}(PO_4)_2$, when crystalline $K_3Ce(PO_4)_2$ formed.[11]

In Table 3 we present the normalized release rate of the materials released in solutions ($mol\cdot m^{-2}\cdot d^{-1}$) after 14 days of hydrothermal alteration as function of alteration medium, as measured by ICP-MS. The dissolution rate of the monazites is very low (several $\mu g\cdot m^{-2}\cdot d^{-1}$), being in good agreement with the data reported previously.[6, 19] This is due to the very strong condition we applied during the alteration. The dissolution of all the altered materials in HCl is congruent $\left[\sum(REE+Th)/P \cong 1\right]$; in the case of the alteration in KOH this ratio is closer to the value 0.5. This is consistent with the proposed mechanism of insertion of potassium in the *Ln*PO_4 structure.

Table 3. The amount of material released in solutions after 14 days of hydrothermal alteration as a function on alteration media.

	Alteration medium[a]	Dissolved material, $(mol \cdot m^{-2} \cdot d^{-1}) \cdot 10^6$						
		La	Ce	Eu	Nd	Gd	Th	P
NM1	HCl	0.65±0.10	1.18±0.19	-	0.62±0.10	0.05±0.02	1.61±0.12	3.89±0.29
NM2	HCl	0.89±0.12	1.31±0.25	-	0.82±0.13	-	1.83±0.14	4.17±0.32
$LaPO_4$	HCl	3.39±0.22	-	-	-	-	-	3.91±0.25
	KOH	3.21±0.19	-	-	-	-	-	6.69±0.40
$CePO_4$	HCl	-	2.81±0.21	-	-	-	-	3.19±0.29
	KOH	-	3.02±0.19	-	-	-	-	6.16±0.18
$EuPO_4$	HCl	-	-	3.34±0.29	-	-	-	3.21±0.18
$GdPO_4$	HCl	-	-	-	-	3.01±0.18	-	2.96±0.21
	KOH	-	-	-	-	3.22±0.21	-	5.98±0.23

[a] in the systems NM1/KOH, NM2/KOH and $EuPO_4$/KOH no solution after 14 days of alteration.

Conclusions

The obtained results on the hydrothermal alteration of two natural monazites and *Ln*PO_4 (*Ln* = La, Ce, Eu, and Gd) synthetic end-members at 573 K at very low/ very high pH are in good agreement with one another and with our previous results on the $Ba_xM^{IV}_xCe_{2-2x}(PO_4)_2$ solid solutions: all the studied compounds are very stable in hydrochloric acid, the amount of REE/Th released in solution being negligible and with no indications for chemical effects on the solids. Contrarily, the two studied natural monazites as well as the $EuPO_4$ end member strongly react with potassium hydroxide, no solution being found after 14 days of hydrothermal alteration. This aspect has to be considered before choosing the monazites as a possible waste matrix for the actinides and the justification of monazite-based ceramics as actinide waste forms requires additional investigations.

These results indicate that even under extremely acidic conditions monazite is a stable waste form. Our results for alkaline conditions show a limited stability but the dissolved lanthanides precipitate in a secondary phase. There is no significant difference in the amount of dissolved materials.

Acknowledgements

The authors thank Dr. P. Pöml and B. Cramer for the characterizations of the samples.

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