

# Supporting Information

## Crystal structure and stability in aqueous solutions of $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$ and $\text{Na}[\text{NpO}_2(\text{OH})_2]$

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# 1. Experimental

## 1.1 General

All experiments were conducted under controlled Ar atmosphere conditions in a glove box ( $O_2 < 5$  ppm,  $T = 23 \pm 2^\circ\text{C}$ ) in the controlled area of Karlsruhe Institute of Technology – Institute for Nuclear Waste Disposal (KIT-INE). Aqueous solutions were prepared with purified, Ar-purged water (Milli-Q-academic, Millipore). Titrisol® concentrates (Merck) were used to prepare HCl and NaOH stock solutions. NaCl (p.a., Merck) was used to prepare neutral stock solutions with  $[\text{NaCl}] = 1.0 \text{ mol}\cdot\text{L}^{-1}$  ( $1.02 \text{ mol}\cdot\text{kg}^{-1}(\text{H}_2\text{O})$ ). Ion-exchange column purified and oxidation state pure  $^{237}\text{NpO}_2^+$  stock solutions ( $55\cdot 10^{-3} \text{ mol}\cdot\text{L}^{-1}$  Np in  $0.1 \text{ mol}\cdot\text{L}^{-1}$  HCl and  $15\cdot 10^{-3} \text{ mol}\cdot\text{L}^{-1}$  Np in  $0.25 \text{ mol}\cdot\text{L}^{-1}$  HCl) from KIT-INE were used for this study. The latter were thoroughly characterized by liquid scintillation counting (LSC, Tri-Carb 3110 TR, Perkin Elmer), inductively coupled plasma-mass spectrometry (ICP-MS, Elan 6100, Perkin Elmer) and gamma spectrometry (Alpha Analyst spectrometer, Canberra), and their oxidation state were confirmed to be  $\geq 98\%$  in Np(V) by a liquid extraction technique as outlined in section 1.8. Batch solubility experiments were conducted in HD-PE vials, synthesis of the Np solid phases in PTFE vessels or PTFE-lined stainless-steel autoclave. To avoid potential interferences from fluoride traces, PTFE material were cleaned before use according to the ASTM procedure C1285-02.<sup>1</sup>

## 1.2 Synthesis of $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}]\cdot 0.5\text{H}_2\text{O}$ (I)

$\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}]\cdot 0.5\text{H}_2\text{O}$  (I) was synthesized by adding 300  $\mu\text{L}$  of  $0.2 \text{ mol}\cdot\text{L}^{-1}$  NaOH to a 2 mL screw capped PP vessel (Sarstedt) containing 400  $\mu\text{L}$  of the  $55\cdot 10^{-3} \text{ mol}\cdot\text{L}^{-1}$   $^{237}\text{NpO}_2^+$  stock solution in  $0.1 \text{ mol}\cdot\text{L}^{-1}$  HCl (5.2 mg of Np) resulting in the precipitation of greenish  $\text{NpO}_2\text{OH}(\text{am})$ . The latter was separated from the mother liquor by laboratory centrifugation, washed twice with  $0.01 \text{ mol}\cdot\text{L}^{-1}$  NaOH, and equilibrated with 20 mL of  $0.1 \text{ mol}\cdot\text{L}^{-1}$  NaOH (corresponding to  $\text{pH}_m \approx 12.7$ ) in a tightly sealed PTFE-lined stainless-steel autoclave. After 30 days of tempering at  $T = 80 \pm 5^\circ\text{C}$ , the autoclave was gradually cooled down to room temperature within 96 hours. The synthesis resulted in dark-violet crystals.

In a *second synthesis*, additional material of  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}]\cdot 0.5\text{H}_2\text{O}$  (I) used for the *solubility study* were successfully prepared by a very similar procedure. 3.0 mL of the  $15\cdot 10^{-3} \text{ mol}\cdot\text{L}^{-1}$   $^{237}\text{NpO}_2^+$  stock solution in  $0.25 \text{ mol}\cdot\text{L}^{-1}$  HCl (10.7 mg of Np) were added to a screw capped PTFE vessel (50 mL, Vitlab) containing 33 mL of  $0.1 \text{ mol}\cdot\text{L}^{-1}$  NaOH resulting in the precipitation of greenish  $\text{NpO}_2\text{OH}(\text{am})$  and a final solution composition being  $[\text{NaOH}] \approx 0.071 \text{ mol}\cdot\text{L}^{-1}$  and  $[\text{NaCl}] \approx 0.021 \text{ mol}\cdot\text{L}^{-1}$  (corresponding to  $\text{pH}_m \approx 12.5$ ). The closed vessel containing the suspension was equilibrated at  $T = 80 \pm 5^\circ\text{C}$ . After 32 days, the material was cooled down to room temperature within three hours. The synthesis resulted in dark-violet crystals.

### 1.3 Synthesis of Na[NpO<sub>2</sub>(OH)<sub>2</sub>] (II)

Na[NpO<sub>2</sub>(OH)<sub>2</sub>] (II) was synthesized by adding 3.0 mL of the 15 mM NpO<sub>2</sub><sup>+</sup> stock solution in 0.25 M HCl (10.7 mg of Np) to a screw capped PTFE vessel (50 mL, Vitlab) containing 33 mL of 1.0 M NaOH resulting in the precipitation of greenish NpO<sub>2</sub>OH(am) and a final solution composition being [NaOH] ≈ 0.89 mol·L<sup>-1</sup> and [NaCl] ≈ 0.021 mol·L<sup>-1</sup> (corresponding to pH<sub>m</sub> ≈ 13.7). The closed vessel containing the suspension was equilibrated at  $T = 80 \pm 5^\circ\text{C}$ . After 32 days, the material was cooled down to room temperature within three hours. The synthesis resulted in pinkish crystals.

### 1.4 Solid phase characterization

For the analysis by powder X-ray diffraction (XRD; D8 Advance, Bruker), combined scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDX; FEI Quanta 650 FEG, now Thermo Fisher Scientific Inc., equipped with a UltraDry™ Peltier cooled silicon drift X-ray detector and Pathfinder software, version 2.8), solid state Vis/NIR spectroscopy (Lambda 1050+ with a 150 mm integration sphere with InGaAs detector for reflection measurements, Perkin-Elmer), and digital microscopy (VHX-1000, Keyence), a sufficient fraction (about 0.05-1.0 mg, depending on the method) of the synthesized solid phases was separated from the main vessel by centrifugation, washed 2-3 times with 1 mL of ethanol, and placed as a wet paste on the corresponding sample holder, where the material dried within few minutes inside the Ar glove box. For the quantitative analysis of structural Na and Np contents in the solid phases, about 0.5-1 mg of the washed material was digested in 1 mL of 2 % HNO<sub>3</sub>, and the solution analyzed for Na by inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer Inc., Optima 4300 DV), and for Np by liquid scintillation counting (LSC; details see section 1.7). To obtain information about the Np oxidation state distribution, fractions of approx. 0.5 mg of the washed solid phases were digested in 600 μL 1.0 mol·L<sup>-1</sup> HCl and analyzed according to the solvent extraction scheme described in section 1.8. At the termination of the solubility study, solid phases retrieved from selected batch samples were analyzed again by powder XRD.

### 1.5 Single crystal X-ray diffraction (scx)

XRD measurements were performed on a Bruker Apex II Quazar diffractometer collecting minimum one complete full sphere of data. Frames were collected with an irradiation time of several seconds per frame appropriate to size and diffracting abilities of the crystals; a mixed  $\omega$ - and  $\phi$ -scan technique was employed for data collection with  $\Delta\omega = \Delta\phi = 0.5^\circ$ . Data were integrated with SAINT, corrected to Lorentz and polarisation effects and an empirical adsorption correction with SADABS was applied.<sup>2</sup> The structures were solved by direct methods and refined to an optimum R1 value with shelx-2013.<sup>3</sup> Compound (II) was best described as a twinned crystal, integration of the data performed with SAINT and absorption corrections with TWINABS.<sup>2</sup> For more details please see Table 2 and Table 3.

The structures have been deposited at The Cambridge Crystallographic Data Centre (CCDC) with the reference CSD numbers **2160534 (I)** and **2160535 (II)**, they contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the CCDC/CSD via <https://icsd.fiz-karlsruhe.de/search/basic.xhtml>.

## 1.6 Undersaturation solubility study

$\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (I) obtained in the 2<sup>nd</sup> synthesis and  $\text{Na}[\text{NpO}_2(\text{OH})_2]$  (II) were used for the batch solubility study. Appropriate volumes of  $1.02 \text{ mol} \cdot \text{kg}^{-1}(\text{H}_2\text{O})$  NaCl and  $1.0 \text{ mol} \cdot \text{L}^{-1}$  NaOH stock solutions were mixed to obtain NaCl-NaOH matrix solutions with ionic strength  $I = 1.02 \text{ mol} \cdot \text{kg}^{-1}(\text{H}_2\text{O})$  and  $\text{pH}_m = 8\text{--}13$ . About 0.5 to 1.5 mg of the corresponding solid phase were immersed in 5 mL of these  $\text{pH}_m$  adjusted solutions in 6 mL HD-PE vials (undersaturation approach) to make nine independent samples each. 2 to 5 samplings of  $\text{pH}_m$  and  $[\text{Np}(\text{V})]$  were performed within several weeks to months. The results are summarized in Table 7 and Table 8. The stability of the initially added solid phases (**I**) and (**II**), respectively) during the solubility study were confirmed by powder XRD analysis, see Figure 3 and Figure 5. The later was performed at the termination of the solubility study in four samples of each system which were selected in a way that the entire  $\text{pH}_m$  range is covered.

## 1.7 Determination of pH and Np concentration

The pH values in the solubility samples were determined with a combination glass electrode (Ross type, Orion) calibrated against pH standard buffer solutions (pH 6-12, Merck) before use. The experimentally measured pH values ( $\text{pH}_{\text{exp}}$ ) were converted into the molal proton concentration scale ( $\text{pH}_m = -\log m_{\text{H}^+}$ ) according to  $\text{pH}_m = \text{pH}_{\text{exp}} + A_m$  with  $A_m = +0.08$  for  $1.02 \text{ mol} \cdot \text{kg}^{-1}(\text{H}_2\text{O})$  NaCl-NaOH. Details of this approach are described in Altmaier *et al.*<sup>4</sup> pH measurements with glass electrodes are less reliable in hyperalkaline solutions, *e.g.*, due to the alkali error. The  $\text{pH}_m$  values of solubility samples with  $\text{pH}_m \geq 12$  were therefore calculated from the analytical (initial)  $[\text{OH}^-]$  in these samples according to  $\text{pH}_m = \log m_{\text{OH}^-} - \log K'_w$ , where  $\log K'_w = -13.74$  in  $1.02 \text{ mol} \cdot \text{kg}^{-1}(\text{H}_2\text{O})$  NaCl is the conditional ionic product of water for the reaction  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ .<sup>5</sup> Note, that hydroxide consuming or releasing reactions like the partial dissolution of the added Np(V) solid phases during the equilibration are negligible with respect to the great excess of  $[\text{OH}^-]$  in the samples with  $\text{pH}_m \geq 12$ .

The Np concentration of a sample was routinely measured after a phase separation step by 10 kD ultrafiltration (10 kD  $\approx$  2 nm, nanosep, Pall Corporation) by liquid scintillation counting of the  $^{237}\text{Np}$  alpha activity after  $\alpha/\beta$  discrimination of the beta counts from the daughter  $^{233}\text{Pa}$  on a Tri-Carb 3110 TR liquid scintillation counter (Perkin Elmer) using Ultima Gold XR cocktail (Perkin Elmer). The detection limit for  $^{237}\text{Np}$  is approx.  $1 \cdot 10^{-8}$  M. In some samplings,  $[\text{Np}]$  was also determined in the clear supernatant without an ultrafiltration step. No significant differences were observed between 10kD and supernatant analysis corroborating that sorption of Np(V) on the 10kD ultrafilter is negligible under the experimental

conditions. In hyperalkaline samples with  $\text{pH}_m > \approx 11$  showing low Np solubility close to the LSC detection limit, Np concentrations were determined using a high-resolution sector field ICP-MS (Element XR, Thermo Scientific). The effective detection limit of the later including all dilution steps is about  $3 \cdot 10^{-11}$  M.

## 1.8 Solvent extraction

The oxidation state distribution of Np in the stock solutions, in digested solid phases and in selected solubility samples (especially in the most alkaline ones with  $\text{pH}_m \geq 12$  where certain contributions of Np(VI) can spontaneously form with time) were analyzed by a solvent extraction procedure using  $0.5 \text{ mol} \cdot \text{L}^{-1}$  Di-(2-ethylhexyl) phosphoric acid (HDEHP) (p.a., Merck) in toluene (Emsure®, Merck) with and without a previous oxidation step of the sample solution with  $0.08 \text{ mol} \cdot \text{L}^{-1}$   $\text{K}_2\text{Cr}_2\text{O}_7$  (standard reference material 136e, NIST) in  $2 \text{ mol} \cdot \text{L}^{-1}$  HCl. The  $0.5 \text{ mol} \cdot \text{L}^{-1}$  HDEHP extractant solution was preequilibrated with  $1 \text{ mol} \cdot \text{L}^{-1}$  HCl before use. The basic chemicals HDEHP and toluene were stored inside the Ar box for several months before use to avoid redox artifacts from oxygen traces that may be present in the chemicals when freshly introduced to the Ar box, *c.f.*, Felmy *et al.*<sup>6</sup> As oxidizing agent during the solvent extraction procedure,  $0.01 \text{ mol} \cdot \text{L}^{-1}$   $\text{K}_2\text{Cr}_2\text{O}_7$  in  $1 \text{ mol} \cdot \text{L}^{-1}$  HCl was used. To minimize redox changes of the dissolved Np, the time between the acidification and completion of the extraction was kept as short as possible, namely about 10 minutes. The overall uncertainty of the extraction results is estimated to be about  $\pm 3\%$ .

For the first extraction without oxidation step, an aliquot of the sample solution (typically 250  $\mu\text{L}$ ) was mixed with an equal volume of  $2 \text{ mol} \cdot \text{L}^{-1}$  HCl in a 2 ml screw-capped vial (PP, Sarstedt) to make a solution with  $[\text{H}^+] = 1 \text{ mol} \cdot \text{L}^{-1}$ . This aqueous solution was extracted with an equal volume of the HDEHP extractant solution under intensive agitating. After phase separation by centrifugation, the organic and the aqueous phases were independently analyzed for Np by LSC. Within this procedure, initially present Np(IV)(aq) and Np(VI)(aq) is extracted into the organic phase, while Np(V)(aq), and potentially present Np(III)(aq) and undissolved Np, *i.e.*, Np(IV) particles and colloids, remain in the aqueous phase. In samples with low solubility, where the use of sector field ICP-MS was required, only the aqueous phase containing the Np(V) was analyzed. The second extraction with a previous oxidation step followed the same procedure except that the sample solution was mixed with an equal volume of the oxidation agent solution instead of the  $2 \text{ mol} \cdot \text{L}^{-1}$  HCl. Under these conditions,  $\text{K}_2\text{Cr}_2\text{O}_7$  leads to a rapid oxidation of initial Np(III)(aq) to Np(IV)(aq), and initial Np(V)(aq) to Np(VI)(aq), but leaves initial Np(IV)(aq) and Np(VI)(aq) mainly unaltered. Therefore, initially present Np(III)(aq), Np(IV)(aq), Np(V)(aq), and Np(VI)(aq) are extracted into the organic phase, whereas only Np(IV) particles and colloids remain in the aqueous phase. The extraction scheme applied is virtually the same as described by Nitsche *et al.*<sup>7</sup>

## 2. Solid phase characterization

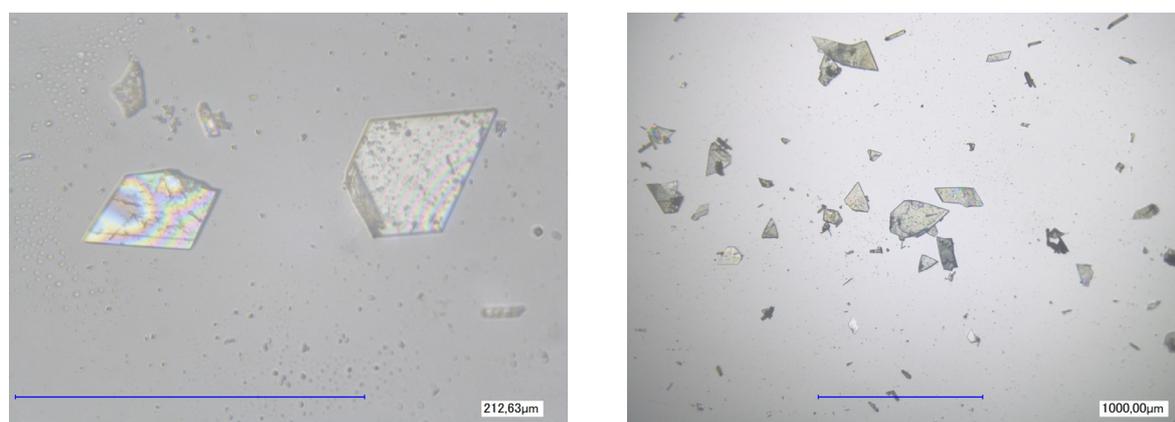
Both Np(V) solid phases were comprehensively characterized by different analytical techniques as summarized in Table 1. The results are briefly discussed in sections 2.1 and 2.2.

**Table 1:** Overview of analytical techniques used for the characterization of  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (I) and  $\text{Na}[\text{NpO}_2(\text{OH})_2]$  (II).

Analytical technique	$\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$	$\text{Na}[\text{NpO}_2(\text{OH})_2]$
Single crystal XRD (washed solid)	Figure 3 and Table 2	Figure 5 and Table 3
Powder XRD (washed solid)	Figure 3	Figure 5
Digital microscopy (washed solid)	Figure 1	n. a.
SEM (washed solid)	Figure 2 and Figure 4	Figure 6
EDX (washed solid)	Na : Np $\approx$ 0.4 : 1 and 0.46-0.52 : 1	Na : Np $\approx$ 1.2 : 1
ICP-OES and LSC (washed digested solid)	Na : Np $\approx$ 0.6 : 1	Na : Np = 0.94 : 1
Solvent extraction (washed digested solid)	$\geq$ 96% Np(V)	$\geq$ 96% Np(V)
Solid state Vis/NIR (washed solid)	Figure 7	Figure 7
Solubility data	Figure 8 and Table 7	Figure 8 and Table 8

### 2.1 $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$ (I)

**Dark-violet crystals obtained within the first synthesis:** the optical appearance and the observation that the material sedimented immediately and quantitatively after stirring the suspension indicated the presence of relatively large crystals. A homogeneous fraction of the washed solid phase material was placed and dried inside a screw capped quartz cuvette (Hellma, 10 mm pathlength). Digital microscopy images of this sample confirmed the presence of single crystals with well-defined platelet-like shape and maximum sizes of up to 400 micrometers, see Figure 1.



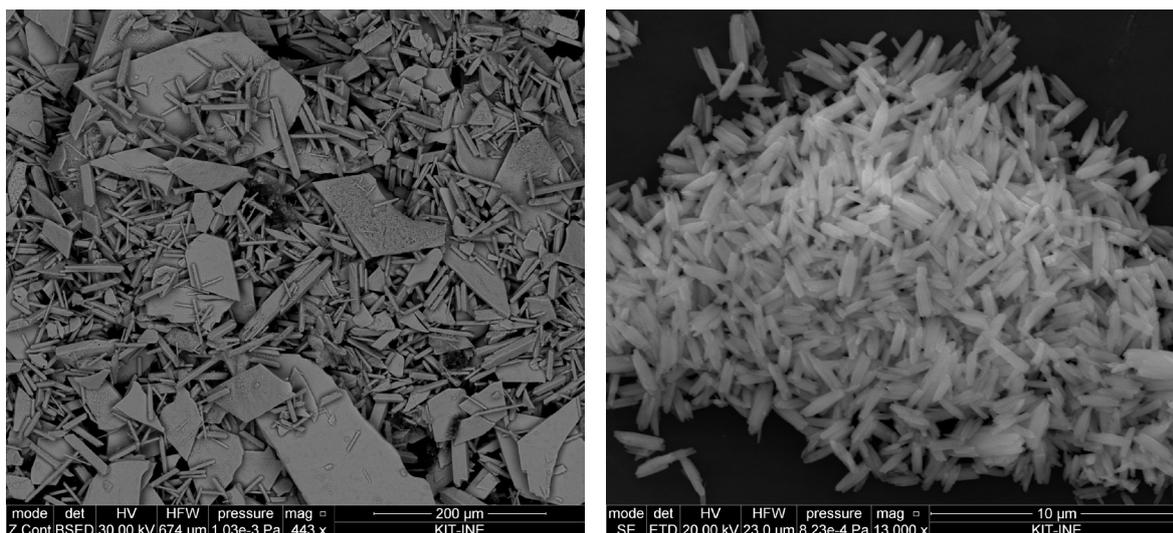
**Figure 1.** Digital microscope images of  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (I) single crystals.

A single crystal taken from the fraction in the cuvette was subsequently studied by single crystal XRD which revealed the stoichiometry  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$ . The corresponding crystallographic data are summarized in Table 2. The simulated powder XRD pattern is displayed in Figure 3. Neither the stoichiometric composition nor the XRD pattern have been previously reported for a Np(V) compound.

**Table 2.** Crystallographic data for Na<sub>0.5</sub>[NpO<sub>2</sub>(OH)<sub>1.5</sub>] $\cdot$ 0.5H<sub>2</sub>O (**I**).

Empirical formula	H10 Na2 Np4 O16
Formula weight	1260.06
Temperature	183(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2 <sub>1</sub>
Unit cell dimensions	a = 5.9859(2) Å, $\alpha$ = 90° b = 10.1932(3) Å, $\beta$ = 98.8640(10)° c = 12.1524(4) Å, $\gamma$ = 90°
Volume	732.63(4) Å <sup>3</sup>
Z	2
Density (calculated)	5.712 Mg/m <sup>3</sup>
Absorption coefficient	28.270 mm <sup>-1</sup>
F(000)	1064
Crystal size	0.061 x 0.058 x 0.012 mm <sup>3</sup>
Theta range for data collection	1.696 to 38.920°
Index ranges	-10 $\leq$ h $\leq$ 10, -17 $\leq$ k $\leq$ 18, -21 $\leq$ l $\leq$ 21
Reflections collected	30826
Independent reflections	8169 [R(int) = 0.0369]
Completeness to theta = 25.000°	99.9 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	8169 / 1 / 200
Goodness-of-fit on F <sup>2</sup>	1.054
Final R indices [I > 2sigma(I)]	R1 = 0.0197, wR2 = 0.0440
R indices (all data)	R1 = 0.0205, wR2 = 0.0443
Absolute structure parameter	0.17(2)
Largest diff. peak and hole	2.042 and -2.126 e.Å <sup>-3</sup>
CCDC/CSD no.	<b>2160534</b>

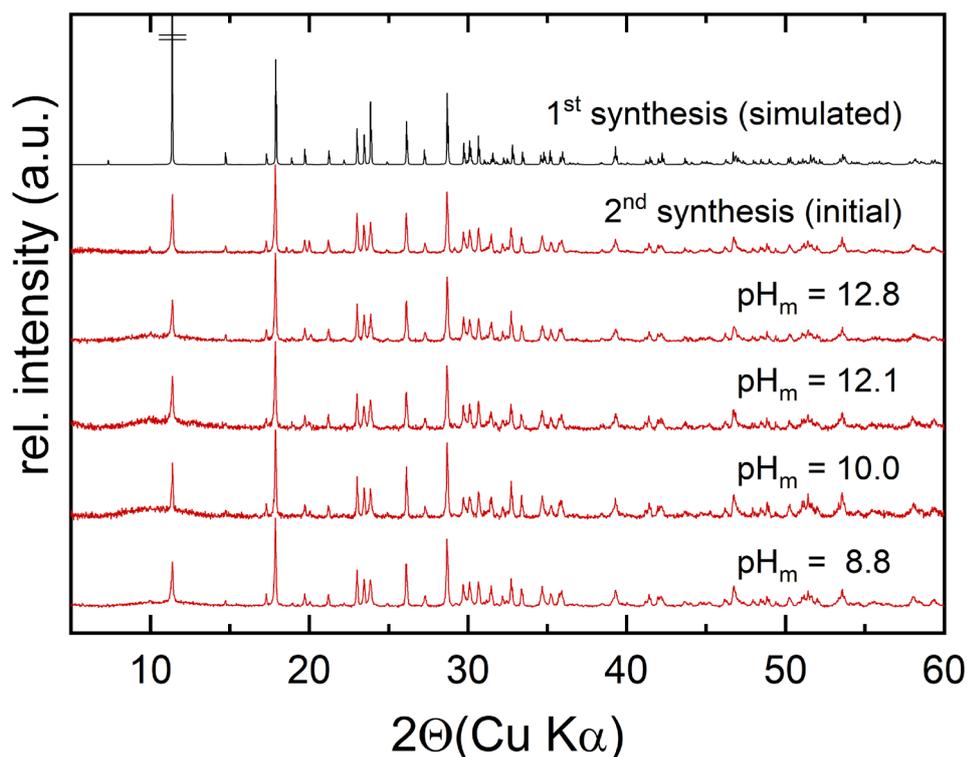
SEM analysis showed that the synthesis had dominantly led to platelet-like single crystals ranging in size from about 5 to 300  $\mu$ m and, to a minor extent, to agglomerated particles consisting of smaller platelets / crystals, see Figure 2. Except the size distribution and agglomeration status, no apparent differences in the morphology between both fractions were observed. SEM-EDX further revealed that the large single crystals and the small agglomerated crystalline particles are chemically not distinguishable, both being Na-Np-O compounds with Na:Np ratio of 0.36-0.41 : 1. Considering the semi-quantitative nature of EDX results under the present setup, the obtained result is in good agreement with the Na : Np ratio in (**I**) based on the single crystal analysis. The SEM-EDX results suggest that the synthesis led to a chemically homogenous crystalline compound differing only in the crystal size.



**Figure 2.** Scanning electron microscope images of  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (**I**). The material was dominantly present as single crystals (left; EDX analysis: ratio Na : Np = 0.41 : 1) and, to a minor extent, as polycrystalline particles (right; EDX analysis: ratio Na : Np = 0.36 : 1).

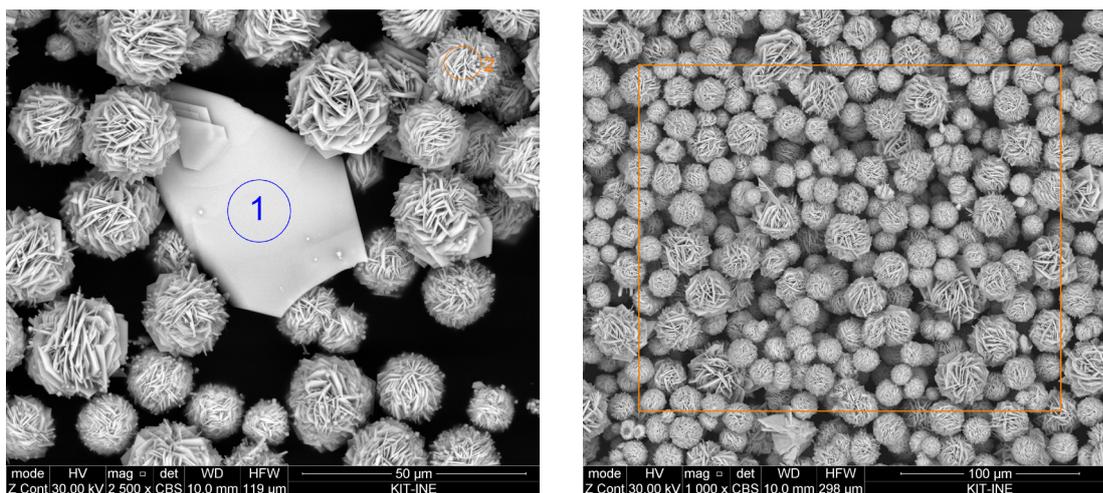
Analysis of the washed, digested solid phase by ICP-OES and LSC (quantitative chemical analysis) revealed molar ratios of Na : Np of about 0.6 : 1 which is close to the expected values for the structural Na- and Np-contents of compound (**I**). The slightly greater Na content may be explained by potential NaOH residues from the mother liquor. On the other hand, the overall uncertainty of this approach which uses two independent analytical methods is just in the order of  $\pm 0.1$ .

**Dark-violet crystals obtained within the second synthesis:** the powder XRD pattern of that material is displayed in Figure 3. It matches very well the simulated pattern from the single crystal analysis performed with  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (**I**) from the initial synthesis, confirming that both synthesis routes have led to the same material.



**Figure 3.** Powder XRD pattern of  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (**I**) used for the solubility study (initial material and the corresponding equilibrium solids retrieved from selected solubility samples with  $\text{pH}_m = 8.8, 10.0, 12.1$  and  $12.8$  at the termination of the solubility study) in comparison to the simulated powder XRD pattern from the single crystal analysis.

Compound (**I**) obtained in the second synthesis was dominantly present as agglomerated crystals and, with significantly smaller contribution, as large single crystals, see SEM images in Figure 4. This is likely due to the faster cooling down phase conducted in the second synthesis compared to the initial one (3 hours versus 96 hours). Analogous to the first synthesis, SEM-EDX confirmed that both fractions (the large single crystals and the agglomerated particles) are chemically not distinguishable showing Na : Np ratios of 0.46-0.52 : 1, *i.e.*, very close to the value found for compound (**I**) in the single crystal analysis. Overall, the material was found to be chemically homogeneous.



**Figure 4.** Scanning electron microscope images of  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (**I**). The material obtained from the second synthesis was dominantly present as agglomerated crystals (EDX analysis 1: ratio Na : Np = 0.46 : 1) and, to a minor extent, as large single crystals (EDX analysis 2: ratio Na : Np = 0.50 : 1). The overview image (right) indicates a chemically homogeneous material (EDX analysis: ratio Na : Np = 0.52 : 1).

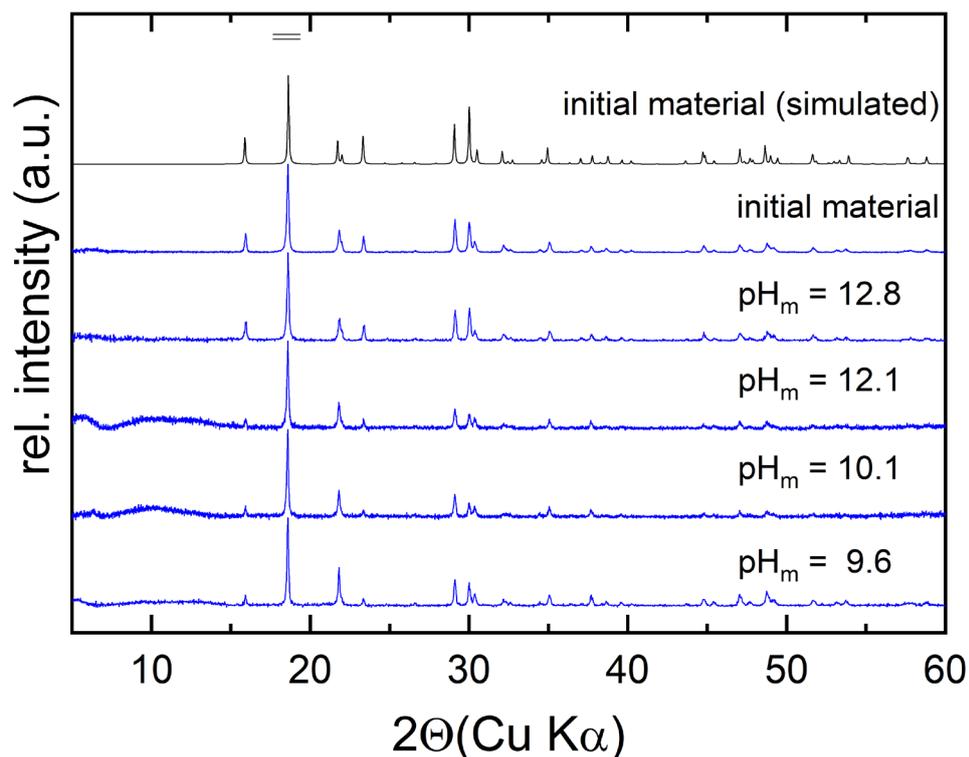
Information about the Np oxidation state distribution in  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (**I**) was obtained by liquid extraction of a digested solid phase fraction. The results of the HDEHP extraction after the oxidation step with  $\text{K}_2\text{Cr}_2\text{O}_7$  revealed that 99.4% of the Np were extracted with HDEHP, confirming that nearly all the Np was present as aqueous  $\text{Np}(\text{aq})$ . Without the oxidation step, only  $\approx 3.4\%$  of the Np (*i.e.*,  $\text{Np}(\text{IV})(\text{aq})$  and  $\text{Np}(\text{VI})(\text{aq})$ ) were extracted by HDEHP, while  $\approx 96.6\%$  of the Np remained in the aqueous phase (*i.e.*,  $\text{Np}(\text{III})(\text{aq})$ ,  $\text{Np}(\text{V})(\text{aq})$  and undissolved Np). Combining the results with the fact that contributions of  $\text{Np}(\text{III})(\text{aq})$  did not play any role under the experimental conditions, the oxidation state of the digested solid phase is  $\approx 96.0\%$   $\text{Np}(\text{V})(\text{aq})$ . This confirms that  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (**I**) is a  $\text{Np}(\text{V})$  compound.

## 2.2 Na[NpO<sub>2</sub>(OH)<sub>2</sub>] (II)

A single crystal taken from a washed fraction of this material was analyzed by single crystal XRD which revealed the stoichiometry Na[NpO<sub>2</sub>(OH)<sub>2</sub>]. The corresponding crystallographic data are summarized in Table 3. The simulated powder XRD pattern is displayed in Figure 5. The stoichiometric composition and the diffraction data are in very good agreement with the ones previously reported for Na[NpO<sub>2</sub>(OH)<sub>2</sub>] by Almond *et al.* (hydrothermal reaction of Np(V) and NaOH in an aqueous solution with a pH of 14 over 3 days at 120 °C).<sup>8</sup>

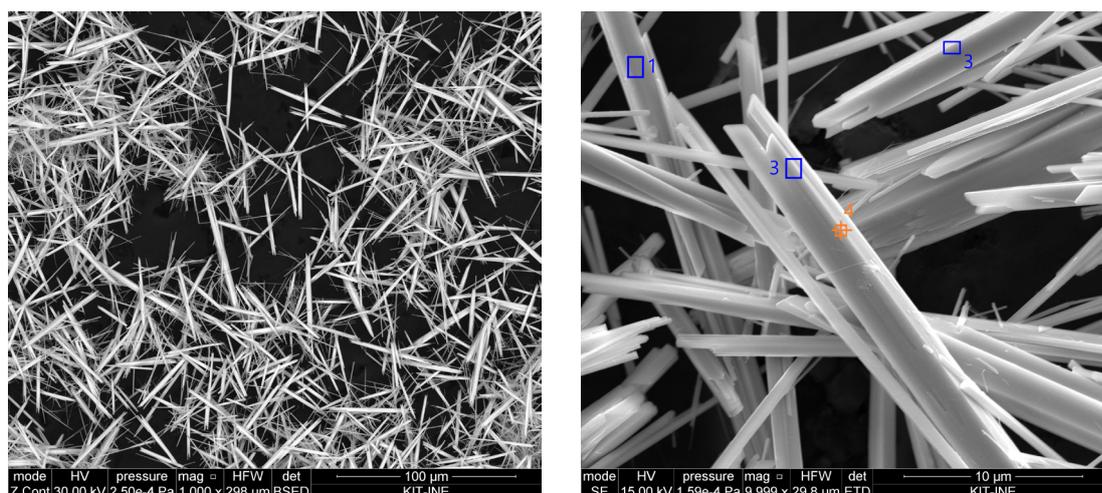
**Table 3.** Crystallographic data for Na[NpO<sub>2</sub>(OH)<sub>2</sub>] (II).

Empirical formula	H2 Na Np O4
Formula weight	326.01
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Unit cell dimensions	a = 5.856(7) Å, α = 90° b = 7.621(9) Å, β = 90° c = 8.174(9) Å, γ = 90°
Volume	364.8(7) Å <sup>3</sup>
Z	4
Density (calculated)	5.936 Mg/m <sup>3</sup>
Absorption coefficient	28.451 mm <sup>-1</sup>
F(000)	552
Crystal size	0.050 x 0.005 x 0.005 mm <sup>3</sup>
Theta range for data collection	3.655 to 28.766°.
Index ranges	-7 ≤ h ≤ 7, -10 ≤ k ≤ 10, -10 ≤ l ≤ 10
Reflections collected	880
Independent reflections	880
Completeness to theta = 25.000°	100.0 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	880 / 0 / 55
Goodness-of-fit on F <sup>2</sup>	0.920
Final R indices [I > 2sigma(I)]	R1 = 0.0590, wR2 = 0.0981
R indices (all data)	R1 = 0.1113, wR2 = 0.1101
Absolute structure parameter	0.08(19)
Largest diff. peak and hole	3.267 and -2.934 e.Å <sup>-3</sup>
CCDC/CSD no.	<b>2160535</b>



**Figure 5.** Powder XRD pattern of  $\text{Na}[\text{NpO}_2(\text{OH})_2]$  (II) used for the solubility study (initial material and the corresponding equilibrium solids retrieved from selected solubility samples with  $\text{pH}_m = 9.6, 10.1, 12.1$  and  $12.8$  at the termination of the solubility study) in comparison to the simulated powder XRD pattern from the single crystal analysis.

SEM analysis of compound (II) showed that the synthesis had quantitatively led to thin crystalline needles of up to  $100\ \mu\text{m}$  length, see Figure 6. Qualitative SEM-EDX analysis confirmed the presence of structural Na and Np with a ratio of  $1.2 \pm 0.2 : 1$  based on nine analyses, *i.e.*, close to the expected value.



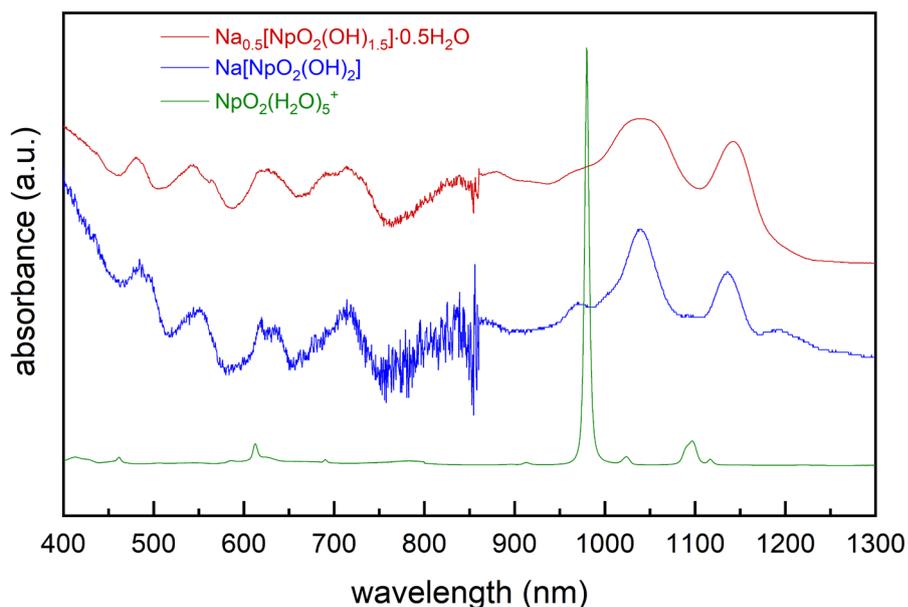
**Figure 6.** Scanning electron microscope images of  $\text{Na}[\text{NpO}_2(\text{OH})_2]$  (II). The material obtained in the synthesis crystallized as thin needles. Exemplary SEM-EDX analyses 1 to 4 (right) reveals ratios of  $\text{Na} : \text{Np} = 1.14 : 1 / 1.42 : 1 / 1.19 : 1 / 1.07 : 1$ .

Quantitative chemical analysis of the digested solid phase by ICP-OES and LSC revealed a molar ratio of Na : Np of 0.94 : 1 which further corroborates the stoichiometric composition of compound **(II)** based on the single crystal XRD results. 99.4% of the Np of the digested solid phase **(II)** were extracted with HDEHP after the oxidation step with  $K_2Cr_2O_7$ , confirming that nearly all the Np was present as aqueous Np(aq). Without the oxidation step, only  $\approx 3.2\%$  of the Np (*i.e.*, Np(IV)(aq) and Np(VI)(aq)) were extracted by HDEHP, while  $\approx 96.8\%$  of the Np remained in the aqueous phase (*i.e.*, Np(III)(aq), Np(V)(aq) and undissolved Np). As contributions of Np(III)(aq) did not play any role under the experimental conditions, and as undissolved Np was shown to be practically absent, the non-extracted  $\approx 96\%$  of Np corresponded to Np(V)(aq) which confirms that  $Na[NpO_2(OH)_2]$  **(II)** is a pure Np(V) compound.

### 2.3 Solid state Vis/NIR of $Na_{0.5}[NpO_2(OH)_{1.5}] \cdot 0.5H_2O$ **(I)** and $Na[NpO_2(OH)_2]$ **(II)**

The solid state Vis/NIR absorption spectra of compounds **(I)** and **(II)** are displayed in Figure 7 in comparison to the spectrum of the  $NpO_2(H_2O)_5^+$  aquo ion in 2%  $HNO_3$  solution. The latter is characterized by its prominent NIR band at  $\lambda_{max} = 980.2$  nm with  $\epsilon \approx 395$   $L \cdot mol^{-1} \cdot cm^{-1}$  and FWHM  $\approx 7$  nm.<sup>9,10</sup> Analogous to solution complexes of Np(V) with ligands such as  $OH^-$ ,  $CO_3^{2-}$  or carboxylates, this prominent NIR band is red-shifted and broadened in both hydroxide solid phases.<sup>11,12,13</sup> It is further apparent that the intensity of the less intense absorption bands of the Np(V) aquo ion are significantly enhanced in the solid phases relative to the prominent NIR band. In compound **(I)**, the prominent NIR band appears as splitted band consisting of two overlapped singlet bands of very similar intensity. These two singlet bands – Gaussian curve fitting reveals  $\lambda_{max} \approx 1023$  nm with FWHM  $\approx 43$  nm and  $\lambda_{max} \approx 1057$  nm with FWHM  $\approx 42$  nm, respectively – are indicative for two *distinguishable* neptunyl(V) sites in compound **(I)**. Based on the single crystal results, the structure of compound **(I)** contains four crystallographically distinct neptunium sites, Np(1) to Np(4). As discussed in the main paper, Np(1) and Np(4) have formally the same coordination environment, namely  $(NpO_2)(O)_2(OH)_3$  pentagonal bipyramids<sup>i</sup>, with only marginal differences in the crystallographic features. Likewise, Np(2) and Np(3) show formally the same coordination environments, namely  $(NpO_2)O(OH)_4$  pentagonal bipyramids<sup>i</sup>, that have again very similar crystallographic features. It is, therefore, very likely, that these two pairs of Np sites with distinguishable chemical environments just represent the two singlet contributions to the prominent NIR band. In  $Na[NpO_2(OH)_2]$  **(II)**, the prominent NIR band appears as a singlet band at  $\lambda \approx 1041$  nm with FWHM  $\approx 38$  nm. This is in full agreement with the fact that compound **(II)** only contains one crystallographically unique neptunyl(V) sites, namely  $(NpO_2)O(OH)_4$  pentagonal bipyramids<sup>i</sup>.

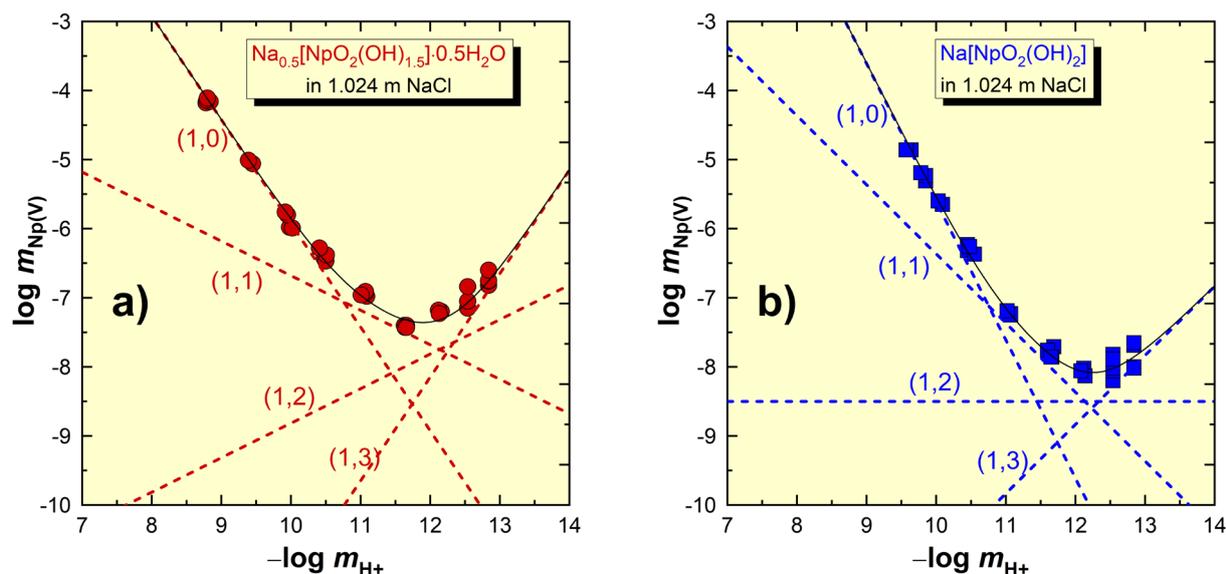
<sup>i</sup> More precise expressions of the coordination sites are  $(Np(O_{ax})(O_{ax\_2-center\ CCl})(O_{eq\_2-center\ CCl})_2(OH_{eq\_2-center\ BL})_2(OH_{eq\_3center\ BL}))$  for Np(1) and Np(4) in compound **(I)**,  $(Np(O_{ax\_2-center\ CCl})_2(O_{eq\_2-center\ CCl})(OH_{eq\_2-center\ BL})_2(OH_{eq\_3center\ BL})_2)$  for Np(2) and Np(3) in compound **(I)**, and  $(Np(O_{ax})(O_{ax\_2-center\ CCl})(O_{eq\_2-center\ CCl})(OH_{eq\_2-center\ BL})_4)$  for Np(1) in compound **(II)**.



**Figure 7.** Solid state Vis/NIR absorption spectra of  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (I) and  $\text{Na}[\text{NpO}_2(\text{OH})_2]$  (II) in comparison to the one of the  $\text{NpO}_2(\text{H}_2\text{O})_5^+$  aquo ion.

### 3. Additional information on the solubility study and the thermodynamic evaluation

The experimentally determined solubility data for  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (I) and  $\text{Na}[\text{NpO}_2(\text{OH})_2]$  (II) are listed in Table 7 and Table 8 and displayed in Figure 8 together with the results of model calculations with the specific ion interaction theory (SIT), as outlined in the following. The fact, that no significant trend with time in  $\log [\text{Np}(\text{V})]$  was observed, indicate that the samples of both systems reached quickly a steady state. Furthermore, two results make it very likely that both Np(V) solids were indeed in a real equilibrium with the corresponding Np(V) aqueous species, namely the consistency of the two sets of  $\log \beta$  values acquired from the two independent solubility studies, and the reasonable slope-behavior observed in both solubility curves. Accompanying experiments from oversaturation could have further demonstrated that an equilibrium had been reached in the samples. These were, however, not performed in the present work, as the formation of crystalline Na-Np(V)-OH phases is kinetically slow at room temperature, particularly at  $\text{pH}_m < 11$ , and are typically accompanied by the initial formation of metastable phases like  $\text{NpO}_2\text{OH}(\text{am})$  or other Na-Np(V)-OH phases with Na:Np  $\approx 0.2:1$  to  $1.6:1$ .<sup>11</sup> To overcome the challenge of slow transformation processes observed at room temperature, the crystalline Na-Np(V)-OH phases were synthesized in the present work at elevated temperature conditions, and subsequently studied at room temperature.

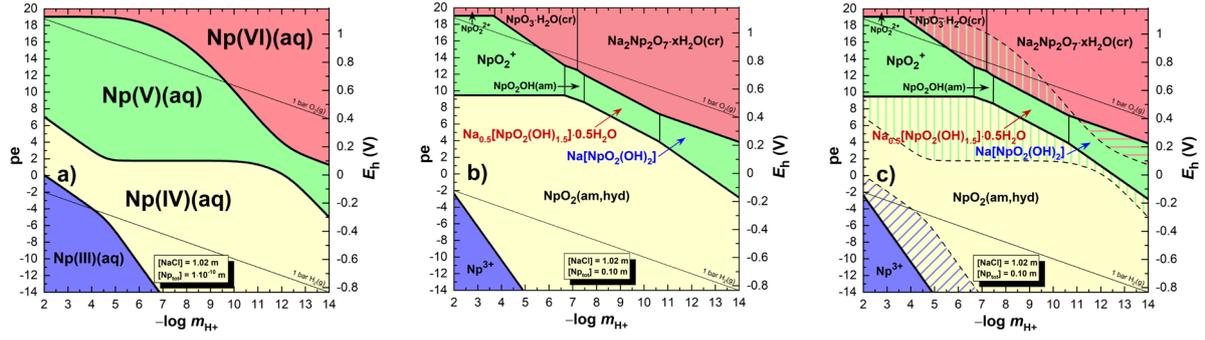


**Figure 8.** Experimental molal Np(V) solubility of  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (a) and  $\text{Na}[\text{NpO}_2(\text{OH})_2]$  (b) in 1.024 mol·kg<sup>-1</sup>(H<sub>2</sub>O) NaCl-NaOH solution at  $T = 23 \pm 2^\circ\text{C}$ . Solid lines representing the overall solubility and dotted lines representing the contribution of the species  $\text{NpO}_2^+$  (1,0),  $\text{NpO}_2\text{OH}(\text{aq})$  (1,1),  $\text{NpO}_2(\text{OH})_2^-$  (1,2) and  $\text{NpO}_2(\text{OH})_3^{2-}$  (1,3) were calculated with the *SIT* model.

The powder XRD analysis performed with solid phase fractions in selected samples at the termination of the solubility study (*c.f.*, Figure 3 and Figure 5) gave no indications for a transformation of the initially added solid phases **(I)** and **(II)**. This corroborates, that **(I)** and **(II)** were the solubility controlling solid phases in the corresponding batch series. The results of the liquid extraction performed in the supernatant solution of the solubility samples revealed that Np(V) is practically the only Np oxidation state in the aqueous phase for  $\text{pH}_m \leq \sim 12.0$ . However, in samples with greater  $\text{pH}_m$ , we additionally observed minor contributions of dissolved Np(VI)(aq) (about 10% at  $\text{pH}_m \approx 12.5$  and 15% at  $\text{pH}_m \approx 12.8$ ). All Np(V) solubility data shown in the graphs and tables of the present work were corrected for Np(VI) contributions.

From a thermodynamic perspective the (partial) formation of Np(VI) in the hyperalkaline Np(V) solubility samples is actually not unexpected, and can be explained by the closeness (partial overlap) of the stability fields of aqueous Np(VI) and solid Np(V). This is in particular apparent when the Pourbaix diagram for the entire Np redox state (which includes all relevant solid and aqueous Np species in the calculation) is superimposed with the Pourbaix diagram for aqueous Np species<sup>ii</sup>, see Figure 9.

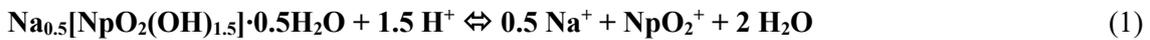
<sup>ii</sup> The Pourbaix diagram for aqueous Np species is calculated by neglecting contribution from Np solid phases. Still, it represents the thermodynamic stability fields of *aqueous* Np species not only in system without Np solid phases but also systems with Np solid phases.



**Figure 9.** Pourbaix diagrams for neptunium in  $1.02 \text{ mol}\cdot\text{kg}^{-1}(\text{H}_2\text{O}) \text{ NaCl}$ . a) represents only the stability fields of aqueous Np species and b) of the entire Np system considering solid and aqueous Np species. Stability fields of a) and b) are superimposed in diagram c). Calculations were performed with thermodynamic data reported in NEA-TDB extended by the constants derived in the *p.w.*

Figure 9 reveals that parts of the stability field of solid Np(V) fall together with the stability field of aqueous Np(VI) for  $\text{pH}_m \geq 11$  (indicated as horizontal pinkish stripes). This particular area represents a pe-pH domain where solid Np(V) is the predominant Np species in the entire system, and Np(VI) is the predominant aqueous Np species. Here, the general redox equilibrium  $\text{Np(V)(s)} \Leftrightarrow \text{Np(VI)(aq)}$  controls the Np solubility. In the remaining pe-pH domains where solid Np(V) is the predominant Np species in the system, aqueous Np(V) is the prevailing aqueous Np species. Here, the “classical” solubility equilibrium, without changes in the pentavalent Np oxidation state,  $\text{Np(V)(s)} \Leftrightarrow \text{Np(V)(aq)}$  controls the Np solubility. From the experimentally determined oxidation states distribution, it is evident that the latter equilibrium was relevant for the solubility samples of the present work (which is expected for systems with an initial large inventory of Np(V) that are free of redox holding agents). However, the partial overlap, *i.e.* the closeness of the stability fields of solid Np(V) and aqueous Np(VI) can explain the formation of certain levels of Np(VI) in such hyperalkaline Np(V) systems.

As already outlined in the main paper, the shapes of the solubility curves of **(I)** and **(II)** can be explained by equilibria between the solid phases **(I)** and **(II)** and the species  $\text{NpO}_2^+$ ,  $\text{NpO}_2\text{OH}(\text{aq})$ ,  $\text{NpO}_2(\text{OH})_2^-$  and  $\text{NpO}_2(\text{OH})_3^{2-}$ . Detailed expressions of all relevant equilibrium reactions are listed in Eqs. (1) to (9). The dissolution equilibria of solids **(I)** and **(II)** with respect to the  $\text{NpO}_2^+$  aquo ion are defined as



with

$$\log *K'_{s,0} = 0.5 \log [\text{Na}^+] + \log [\text{NpO}_2^+] - 1.5 \log [\text{H}^+] \quad (1a)$$

and

$$\log *K^{\circ}_{s,0} = \log *K'_{s,0} + 0.5 \log \gamma_{\text{Na}^+} + \log \gamma_{\text{NpO}_2^+} + 2 \log a_w - 1.5 \log \gamma_{\text{H}^+} \quad (1b)$$

and



with

$$\log *K'_{s,0} = \log [\text{Na}^+] + \log [\text{NpO}_2^+] - 2 \log [\text{H}^+] \quad (2a)$$

and

$$\log *K^{\circ}_{s,0} = \log *K'_{s,0} + \log \gamma_{\text{Na}^+} + \log \gamma_{\text{NpO}_2^+} + 2 \log a_w - 2 \log \gamma_{\text{H}^+} \quad (2b)$$

where  $\log {}^*K'_{s,0}$  and  $\log {}^*K^\circ_{s,0}$  are the conditional (valid for a given medium with  $I > 0$ ) and the thermodynamic (valid for infinite dilution,  $I = 0$ ) solubility constants, respectively,  $\gamma_i$  are the activity coefficients of species  $i$ , and  $a_w$  the water activity in a given medium. Eqs. (1) and (2) describe the solubility behavior of (I) and (II) reasonably well for  $\text{pH}_m$  conditions where  $\text{Np(V)}$  hydrolysis species is negligible. The latter becomes predominate at  $\text{pH}_m \geq \sim 10.7$ . The corresponding equilibria are defined as



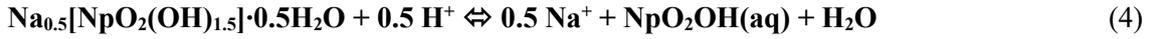
with

$$\log {}^*\beta'_b = \log [\text{NpO}_2(\text{OH})_b^{1-b}] + b \log [\text{H}^+] - \log [\text{NpO}_2^+] \quad (3a)$$

and

$$\log {}^*\beta^\circ_b = \log {}^*\beta'_b + \log \gamma_{\text{NpO}_2(\text{OH})_b^{1-b}} + b \log \gamma_{\text{H}^+} - \log \gamma_{\text{NpO}_2^+} - b \log a_w \quad (3b)$$

where  $\log {}^*\beta'_b$  and  $\log {}^*\beta^\circ_b$  are the conditional (valid for a given medium with  $I > 0$ ) and the thermodynamic (valid for infinite dilution,  $I = 0$ ) hydrolysis constants, respectively. For a comprehensive thermodynamic description of the solubility curves of (I) and (II), the equilibria between the solid phases and the  $\text{Np(V)}$  hydrolysis species have, therefore, to be considered as well, and can be obtained by combining Eqs. (1) and (2), respectively, with Eq. (3):

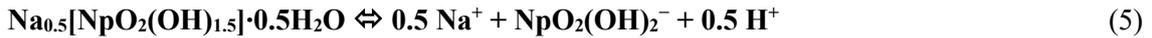


with

$$\begin{aligned} \log {}^*K'_{s,1} &= \log {}^*K'_{s,0} + \log {}^*\beta'_1 \\ &= 0.5 \log [\text{Na}^+] + \log [\text{NpO}_2\text{OH}(\text{aq})] - 0.5 \log [\text{H}^+] \end{aligned} \quad (4a)$$

and

$$\begin{aligned} \log {}^*K^\circ_{s,1} &= \log {}^*K^\circ_{s,0} + \log {}^*\beta^\circ_1 \\ &= \log {}^*K'_{s,1} + 0.5 \log \gamma_{\text{Na}^+} + \log \gamma_{\text{NpO}_2\text{OH}(\text{aq})} + \log a_w - 0.5 \log \gamma_{\text{H}^+} \end{aligned} \quad (4b)$$

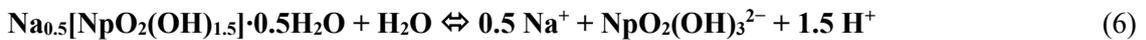


with

$$\begin{aligned} \log {}^*K'_{s,2} &= \log {}^*K'_{s,0} + \log {}^*\beta'_2 \\ &= 0.5 \log [\text{Na}^+] + \log [\text{NpO}_2(\text{OH})_2^-] + 0.5 \log [\text{H}^+] \end{aligned} \quad (5a)$$

and

$$\begin{aligned} \log {}^*K^\circ_{s,2} &= \log {}^*K^\circ_{s,0} + \log {}^*\beta^\circ_2 \\ &= \log {}^*K'_{s,2} + 0.5 \log \gamma_{\text{Na}^+} + \log \gamma_{\text{NpO}_2(\text{OH})_2^-} + 0.5 \log \gamma_{\text{H}^+} \end{aligned} \quad (5b)$$



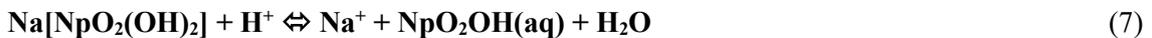
with

$$\begin{aligned} \log {}^*K'_{s,3} &= \log {}^*K'_{s,0} + \log {}^*\beta'_3 \\ &= 0.5 \log [\text{Na}^+] + \log [\text{NpO}_2(\text{OH})_3^{2-}] + 1.5 \log [\text{H}^+] \end{aligned} \quad (6a)$$

and

$$\begin{aligned} \log {}^*K^\circ_{s,3} &= \log {}^*K^\circ_{s,0} + \log {}^*\beta^\circ_3 \\ &= \log {}^*K'_{s,3} + 0.5 \log \gamma_{\text{Na}^+} + \log \gamma_{\text{NpO}_2(\text{OH})_3^{2-}} + 1.5 \log \gamma_{\text{H}^+} - \log a_w \end{aligned} \quad (6b)$$

and



with

$$\begin{aligned} \log {}^*K'_{s,1} &= \log {}^*K'_{s,0} + \log {}^*\beta'_1 \\ &= \log [\text{Na}^+] + \log [\text{NpO}_2\text{OH}(\text{aq})] - \log [\text{H}^+] \end{aligned} \quad (7a)$$

and

$$\begin{aligned}\log *K^{\circ}_{s,1} &= \log *K^{\circ}_{s,0} + \log *\beta^{\circ}_1 \\ &= \log *K'_{s,1} + \log \gamma_{\text{Na}^+} + \log \gamma_{\text{NpO}_2(\text{OH})(\text{aq})} + \log a_w - \log \gamma_{\text{H}^+}\end{aligned}\quad (7b)$$

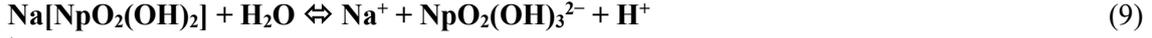


with

$$\begin{aligned}\log *K'_{s,2} &= \log *K'_{s,0} + \log *\beta'_2 \\ &= \log [\text{Na}^+] + \log [\text{NpO}_2(\text{OH})_2^-]\end{aligned}\quad (8a)$$

and

$$\begin{aligned}\log *K^{\circ}_{s,2} &= \log *K^{\circ}_{s,0} + \log *\beta^{\circ}_2 \\ &= \log *K'_{s,2} + \log \gamma_{\text{Na}^+} + \log \gamma_{\text{NpO}_2(\text{OH})_2^-}\end{aligned}\quad (8b)$$



with

$$\begin{aligned}\log *K'_{s,3} &= \log *K'_{s,0} + \log *\beta'_3 \\ &= \log [\text{Na}^+] + \log [\text{NpO}_2(\text{OH})_3^{2-}] + \log [\text{H}^+]\end{aligned}\quad (9a)$$

and

$$\begin{aligned}\log *K^{\circ}_{s,3} &= \log *K^{\circ}_{s,0} + \log *\beta^{\circ}_3 \\ &= \log *K'_{s,3} + \log \gamma_{\text{Na}^+} + \log \gamma_{\text{NpO}_2(\text{OH})_3^{2-}} + \log \gamma_{\text{H}^+} - \log a_w\end{aligned}\quad (9b)$$

Eqs. 1 to 9 represent the principal chemical model to describe the solubility and hydrolysis behavior of solids **(I)** and **(II)** as a function of  $\text{pH}_m$ . The code *fiteql* was used to evaluate values for the conditional solubility constants  $\log *K'_{s,0}$  for **(I)** and **(II)** and hydrolysis constants  $\log *\beta'_n$  with  $n = 1,2,3$  from both experimental data sets, see Table 4.<sup>14</sup>

**Table 4.** Summary of the experimental equilibrium constants in 1.02 mol·kg<sup>-1</sup>(H<sub>2</sub>O) NaCl solution independently evaluated from the solubility data for Na<sub>0.5</sub>[NpO<sub>2</sub>(OH)<sub>1.5</sub>]·0.5H<sub>2</sub>O (**I**) and Na[NpO<sub>2</sub>(OH)<sub>2</sub>] (**II**) using the model-code *fiteql* (2σ error values).<sup>14</sup>

constant	compound (I)	compound (II)
$\log *K'_{s,0}$	9.08 ± 0.03	14.40 ± 0.03
$\log *\beta'_1$	-10.82 ± 0.09	-10.70 ± 0.11
$\log *\beta'_2$	-22.85 ± 0.16	-22.93 ± 0.17
$\log *\beta'_3$	-35.18 ± 0.10	-35.27 ± 0.11

For the extrapolation of the conditional equilibrium constants (valid for 1.02 mol·kg<sup>-1</sup>(H<sub>2</sub>O) NaCl solution) to zero ionic strength, the *SIT* was applied in the present work.<sup>15,16</sup> According to the *SIT*, activity coefficients  $\gamma_i$  are defined as

$$\log \gamma_i = -z_i^2 D + \sum \varepsilon(i,k) m_k$$

where  $z_i$  is the charge of the ionic species  $i$ ,  $\varepsilon(i,k)$  is the ion interaction parameter between ion  $i$  and an unlike charged counterion  $k$ ,  $m_k$  is the molal concentration of the counterion  $k$ ,  $D$  is the Debye-Hückel term,

$$D = 0.509\sqrt{I} / (1+1.5\sqrt{I})$$

at  $T = 25^\circ\text{C}$  with  $I$  being the molal ionic strength. The ion interaction parameters and the calculated activity coefficients valid for 1.02 mol·kg<sup>-1</sup>(H<sub>2</sub>O) NaCl solution used in the present work are

summarized in Table 5. The resulting thermodynamic equilibrium constants (valid for  $I = 0$ ) are summarized in Table 6.

**Table 5.** SIT ion interaction parameters and calculated activity coefficients  $\log \gamma_i$  for the species X in 1.02 mol·kg<sup>-1</sup>(H<sub>2</sub>O) NaCl used for the evaluation of the thermodynamic constants at  $I = 0$ .

species	$\varepsilon(\text{i}^+, \text{Cl}^-)$ and $\varepsilon(\text{i}^-, \text{Na}^+)$	$\log \gamma_i$ (1.02 m NaCl)	reference
Na <sup>+</sup>	0.03 ± 0.01	-0.174 ± 0.01	NEA-TDB <sup>16</sup>
H <sup>+</sup>	0.12 ± 0.01	-0.082 ± 0.01	NEA-TDB <sup>16</sup>
OH <sup>-</sup>	0.04 ± 0.01	-0.164 ± 0.01	NEA-TDB <sup>16</sup>
NpO <sub>2</sub> <sup>+</sup>	0.09 ± 0.05	-0.113 ± 0.05	NEA-TDB <sup>16</sup>
NpO <sub>2</sub> OH(aq)	0	0	NEA-TDB <sup>16</sup>
NpO <sub>2</sub> (OH) <sub>2</sub> <sup>-</sup>	-0.05 ± 0.1	-0.26 ± 0.1	Hummel <i>et al.</i> (estimate) <sup>17</sup>
NpO <sub>2</sub> (OH) <sub>3</sub> <sup>2-</sup>	-0.10 ± 0.1	-0.92 ± 0.1	Hummel <i>et al.</i> (estimate) <sup>17</sup>
H <sub>2</sub> O	$a_w = 0.9661$		Pitzer <sup>5</sup>

**Table 6.** Summary of the thermodynamic equilibrium constants at  $I = 0$  ( $2\sigma$  error values) calculated from the conditional constants using the specific ion interaction theory (SIT) in comparison to the current NEA-TDB selection.<sup>16</sup> Recommended values are highlighted in bold.

constant	compound (I)	compound (II)	mean values	NEA-TDB
$\log {}^*K_{s,0}^\circ$	<b>9.06 ± 0.03</b>	<b>14.47 ± 0.03</b>	-	-
$\log {}^*\beta_1^\circ$	-10.77 ± 0.09	-10.65 ± 0.11	<b>-10.71 ± 0.14</b>	-11.3 ± 0.3
$\log {}^*\beta_2^\circ$	-23.13 ± 0.16	-23.21 ± 0.17	<b>-23.17 ± 0.23</b>	-23.6 ± 0.6
$\log {}^*\beta_3^\circ$	-36.19 ± 0.10	-36.28 ± 0.11	<b>-36.23 ± 0.16</b>	-

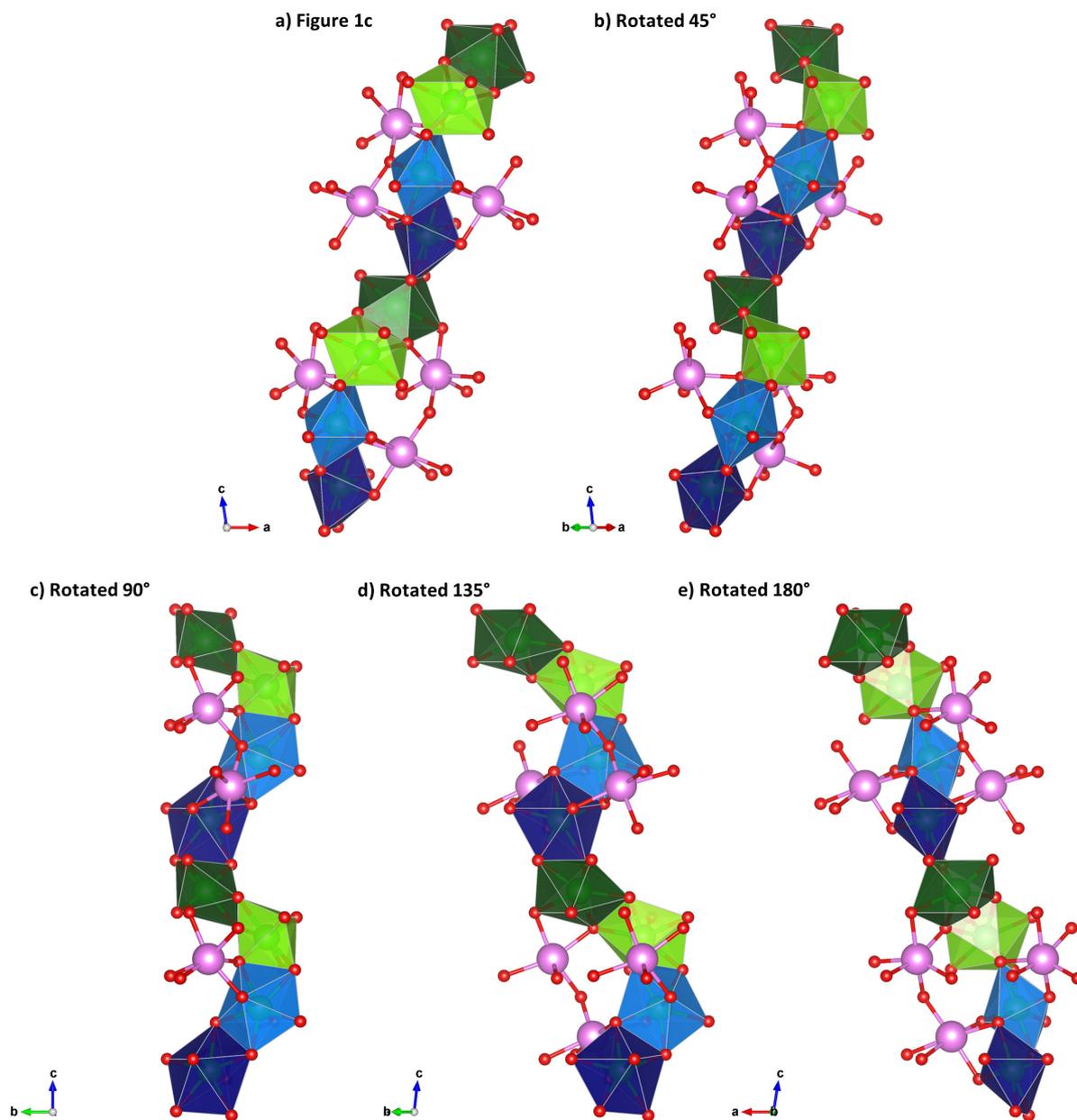
**Table 7.** Experimental solubility data for  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (**I**) in  $1.02 \text{ mol} \cdot \text{kg}^{-1}(\text{H}_2\text{O})$  NaCl solutions.

<b>sample</b>	<b>pH<sub>m</sub></b>	<b>log [Np(V)]<sub>m</sub></b>	<b>comment</b>
(I)_A	8.78	-4.18	4 samplings within $t_{eq} = 197$ d. Powder XRD after termination.
	8.84	-4.16	
	8.79	-4.14	
	8.80	-4.11	
(I)_B	12.54	-7.05	4 samplings within $t_{eq} = 22$ d. pH <sub>m</sub> calculated from analytical = initial $[\text{OH}^-]$ .
	12.54	-7.15	
	12.54	-7.05	
	12.54	-6.84	
(I)_C	11.09	-6.98	4 samplings within $t_{eq} = 208$ d.
	11.07	-6.93	
	11.07	-6.91	
	11.01	-6.96	
(I)_D	10.48	-6.43	4 samplings within $t_{eq} = 22$ d.
	10.50	-6.47	
	10.51	-6.38	
	10.41	-6.28	
(I)_E	9.98	-5.98	4 samplings within $t_{eq} = 26$ d. Powder XRD after termination.
	10.02	-5.99	
	9.95	-5.80	
	9.92	-5.76	
(I)_F	12.84	-6.82	4 samplings within $t_{eq} = 22$ d. pH <sub>m</sub> calculated from analytical = initial $[\text{OH}^-]$ . Powder XRD after termination.
	12.84	-6.76	
	12.84	-6.75	
	12.84	-6.60	
(I)_G	12.16	-7.20	4 samplings within $t_{eq} = 48$ d. Powder XRD after termination.
	12.12	-7.18	
	12.13	-7.23	
(I)_H	9.45	-5.06	2 samplings within $t_{eq} = 14$ d.
	9.39	-5.01	
(I)_I	11.63	-7.40	4 samplings within $t_{eq} = 26$ d.
	11.66	-7.40	
	11.64	-7.43	
	11.66	-7.43	

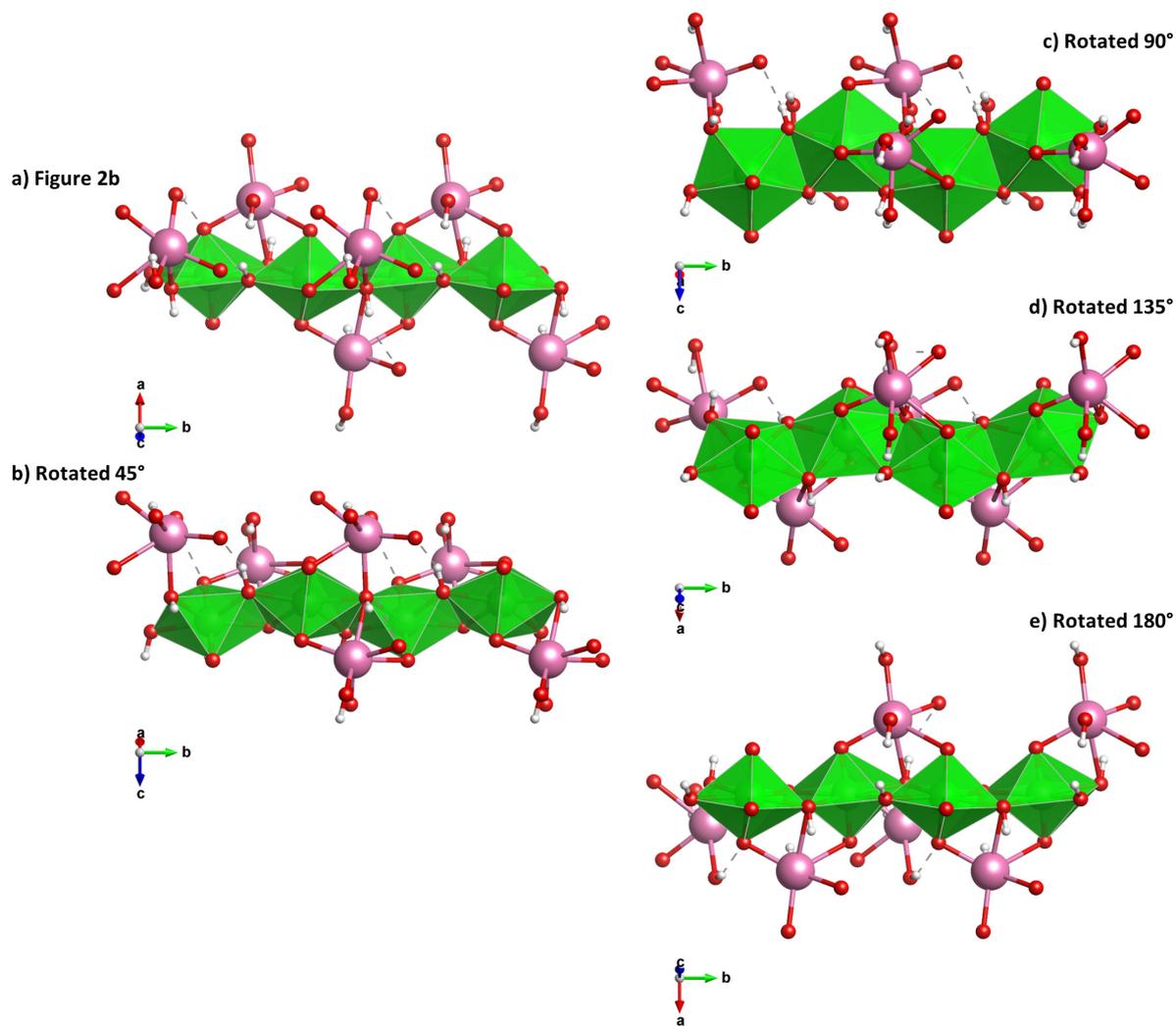
**Table 8.** Experimental solubility data for Na[NpO<sub>2</sub>(OH)<sub>2</sub>] (**II**) in 1.02 mol·kg<sup>-1</sup>(H<sub>2</sub>O) NaCl solutions.

<b>sample</b>	<b>pH<sub>m</sub></b>	<b>log [Np(V)]<sub>m</sub></b>	<b>comment</b>
(II)_A	10.45	-6.32	4 samplings within $t_{eq} = 169$ d.
	10.45	-6.23	
	10.55	-6.37	
	10.48	-6.26	
(II)_B	11.07	-7.23	3 samplings within $t_{eq} = 208$ d.
	11.07	-7.25	
	11.02	-7.19	
(II)_C	11.69	-7.71	4 samplings within $t_{eq} = 142$ d.
	11.66	-7.86	
	11.60	-7.76	
	11.65	-7.86	
(II)_D	12.84	-8.00	4 samplings within $t_{eq} = 142$ d. pH <sub>m</sub> calculated from analytical = initial [OH <sup>-</sup> ]. Powder XRD after termination.
	12.84	-8.02	
	12.84	-7.69	
	12.84	-7.65	
(II)_E	12.12	-8.02	3 samplings within $t_{eq} = 48$ d. Powder XRD after termination.
	12.14	-8.13	
	12.08	-8.06	
(II)_F	12.54	-8.20	5 samplings within $t_{eq} = 142$ d. pH <sub>m</sub> calculated from analytical = initial [OH <sup>-</sup> ].
	12.54	-8.06	
	12.54	-8.02	
	12.54	-7.82	
	12.54	-7.89	
(II)_G	10.09	-5.65	2 samplings within $t_{eq} = 48$ d. Powder XRD after termination.
	10.03	-5.60	
(II)_H	9.85	-5.31	3 samplings within $t_{eq} = 14$ d.
	9.85	-5.23	
	9.78	-5.19	
(II)_I	9.64	-4.86	2 samplings within $t_{eq} = 14$ d. Powder XRD after termination.
	9.57	-4.86	

#### 4. Additional depictions of the structures of $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$ and $\text{Na}[\text{NpO}_2(\text{OH})_2]$



**Figure 10.** Additional depictions of the chain composed of  $\{[\text{Np}(1)\text{-Np}(4)]\text{-}[\text{Np}(2)\text{-Np}(3)]\}_n$  dimer polymerization along the 101 plane in  $\text{Na}_{0.5}[\text{NpO}_2(\text{OH})_{1.5}] \cdot 0.5\text{H}_2\text{O}$  (I), *c.f.* Figure 1 of the main paper.<sup>18</sup> (Na, pink; Np(1), dark blue; Np(2), light green; Np(3), dark green; Np(4), light blue; O, red).



**Figure 11.** Additional depictions of the  $(\text{NpO}_2)\text{O}(\text{OH})_4$  pentagonal bipyramid chain in  $\text{Na}[\text{NpO}_2(\text{OH})_2]$  (II) from the side view, *c.f.* Figure 2 of the main paper.<sup>18</sup> (Na, pink; Np, light green; O, red; H, white).

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