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Oxychloride–Hydroxychloride–Trihydroxide Phase Relationships of Rare Earths in Aqueous Solution

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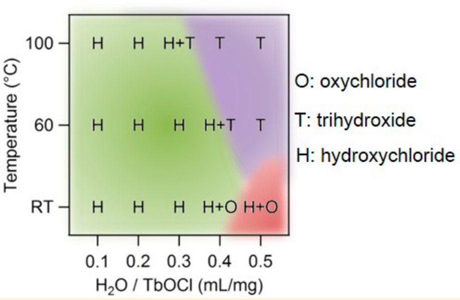
Supporting Information



ABSTRACT: Phase studies were undertaken with PbFCl-type rare earth oxychlorides (REOCls), where RE = La–Dy and Y. Specifically, equilibria in REOCl–H_2O systems were investigated in an effort to describe the interrelationship of the oxychloride, hydroxychloride, and trihydroxide phases of rare earths in water. When lighter rare earths were employed, REOCls were generally stable in basic media, while acidic solutions readily yielded $RE(OH)_3$ by hydrolysis. However, the systematics of equilibrium established in sufficient amounts of water did not continue across the rare earth series and were not particularly relevant to cases in which the oxychloride phase was added to a volume of water smaller than the critical quantity. Difficulties encountered during initial attempts to investigate the hydrolysis of REOCl required that a special parameter, the dilution ratio (D = volume of water/weight of powder), be used for REOCl–$RE_2(OH)_5Cl{\cdot}nH_2O$–$RE(OH)_3$ phase relationships in water at different temperatures. The equilibration of REOCl in solutions of low dilution ratios ($D \leq 0.5$ mL/mg) yielded all three phases depending on the nature of the RE, dilution ratio, and temperature. Interestingly, the addition of salt (NaCl) to systems at similar dilution ratios markedly increased the stability of $RE_2(OH)_5Cl{\cdot}nH_2O$ phases. In contrast, the essential feature of YOCl–water equilibria in the range $0.1 \leq D \leq 1.0$ mL/mg was characterized by spatial stability of the $Y_2(OH)_5Cl{\cdot}nH_2O$ structure. In conclusion, the present investigation provides systematic phase diagrams for rare earth oxychloride–water systems that can be used as guidelines for the preparation and application of REOCls and $RE_2(OH)_5Cl{\cdot}nH_2O$ phases in aqueous media.

1. INTRODUCTION

The majority of the rare earth (La–Ho) oxychlorides (REOCl; RE = rare earths), bromides, and iodides crystallize in a tetragonal PbFCl-structure ($P4/nmm$), while the SmSI- or YOF-structure ($R\bar{3}m$) is adopted by the oxychlorides of heavier rare earths (Tm–Lu) at ambient pressure.[1] YOCl has been reported to have both PbFCl- and YOF-type structures, depending on preparation conditions.[2] For PbFCl-structures, as schematically illustrated in Figure 1a, rare earth ions are located in distorted square antiprismatic sites surrounded by four oxide (O^{2-}) ions and four chloride (Cl^-) ions, and an additional Cl^- in adjacent layer caps the four-Cl^- face of the square antiprism. In the SmSI-structure, the rare earth ion occupies a capped trigonal antiprismatic site composed of a triangle of Cl^- ions and a triangle of O^{2-}, with an additional RE–O bond formed to an O^{2-} in an adjacent O^{2-} triangle. The formation of SmSI-types for heavier rare earths at ambient pressure is usually explained by the small size of their cations relative to chloride, which would otherwise lead to excess Cl–Cl repulsion and a loss of the ninth neighbor in the PbFCl-structure. Although both structures have layered characteristics, some intercalation reactions have been reported for SmSI- or YOF-type REOCls, while PbFCl-type REOCls are not known to undergo topochemical reactions.[3] REOCls have been investigated for catalytic applications in ethane oxidative dehydrogenation, methane coupling, and cracking of *n*-butane and for gas sensor applications such as selective sensing between CO_2 and CO.[4] When doped with activator ions, these materials exhibit efficient UV and cathodoluminescence and up-conversion luminescence, which are useful in lamps, displays, bioapplications, and X-ray intensifying screens.[5] REOCls are also important in pyroelectrochemical processes for reprocessing and fabrication of oxide fuels in eutectic molten chlorides.[6]

Recently, a series of layered rare earth hydroxides (LRHs) with the general formula $RE_2(OH)_5X{\cdot}nH_2O$ (RE = rare earths and X = interlayer organic or inorganic anions) were developed.[7] The structure of $RE_2(OH)_5Cl{\cdot}nH_2O$ (i.e., X = Cl) is schematically represented in Figure 1b, where positively charged rare earth hydroxocation ($[RE_2(OH)_5]^+$) layers and charge-compensating chloride anion layers including water molecules ($[Cl{\cdot}nH_2O]^-$) are alternately arranged. Eight- and nine-coordinated $RE(OH)_m(H_2O)$ (m = 7 and 8, respectively) polyhedra are linked with one another by intralayer μ_3-OH groups. This family of layered rare earth hydroxide materials has attracted increasing attention for its potential applications in heterogeneous catalyst for green chemistry,[8] transparent thin and flexible luminescence films,[9] biomedical contrast agents for magnetic resonance (MR) imaging and probe materials,[10] and

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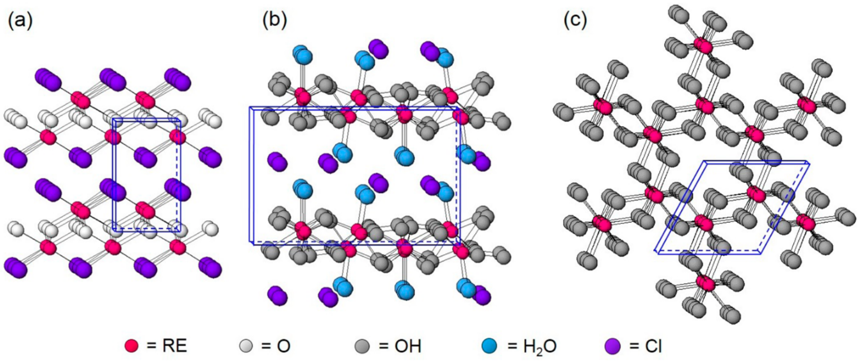

Figure 1. Comparison of the idealized structures for (a) PbFCl-type REOCl, (b) $RE_2(OH)_5Cl\cdot nH_2O$, and (c) $RE(OH)_3$. Corresponding unit cells are outlined by blue lines.

visible detection and separation of thiols and heavy metal-oxoanions.[11]

Figure 1c shows a representative structure of rare earth hydroxides; the hexagonal structure of trihydroxide $RE(OH)_3$ is composed of rare earth atoms coordinated by nine hydroxide ions (tricapped trigonal prism), where the mirror planes are perpendicular to the crystal hexagonal axis.[12] The structure of $RE(OH)_3$ is apparently different from that of $RE_2(OH)_5Cl\cdot nH_2O$. The main difference is that rare earth hydroxo polyhedra form a rectangular net in the hydroxychloride phase, but a hexagonal net in the trihydroxide phase. Rare earth trihydroxides are of great importance because they are good luminescent materials as well as precursors for the preparation of corresponding oxides and sulfides by thermal dehydration and sulfurization, respectively.[13] These materials have been considered as potential candidates for catalyst, sorbent, sensor, energy conversion and storage, and MR contrast agent applications.[14] Furthermore, the photoactivity of $RE(OH)_3$ shows a promising capacity for removal of organic pollutants during wastewater treatment.[15]

We previously reported[16] that LRHs have an interlayer structure sensitive to hydration and hydroxylation reactions. The present investigation was initiated in an effort to characterize the hydroxylation/dehydroxylation behavior of LRHs in aqueous solution systems. Interestingly, hydrolysis reaction studies of LRHs containing interlayer chloride ions, $RE_2(OH)_5Cl\cdot nH_2O$, showed a complex equilibria of three phases, oxychlorides (REOCl), hydroxychlorides ($RE_2(OH)_5Cl\cdot nH_2O$), and trihydroxides ($RE(OH)_3$) that were dependent on several conditions at room temperature and exhibited considerable variation in the phase equilibria across rare earth series. While assessing the stability of each phases in various aqueous conditions, we observed that the amount of water relative to the solid in the reaction system was of critical importance in the structural conversion behavior of oxychloride, hydroxychloride, and trihydroxide formed due to hydrolysis at room temperature. Following this unanticipated result, the dependence on the quantity of water (mL)/powder weight (mg) ratio was systematically examined to establish its role as a parameter for determining the relative stability of the three phases.

Here, we describe the phase equilibria of oxychloride, hydroxychloride, and trihydroxide phases of rare earths and define conditions for the stability of corresponding structures in aqueous solution. In view of the considerable current interest in the structural, catalytic, and optical properties of layered materials containing rare earth elements, it appeared desirable to characterize the rare earth analogues of PbFCl-structure and their layered hydroxychloride derivatives. Since essentially nothing is known about the interrelationship of REOCl, $RE_2(OH)_5Cl\cdot nH_2O$, and $RE(OH)_3$ phases in water, a careful examination of the conditions and the limits of their relative stabilities was deemed worthwhile.

2. EXPERIMENTAL SECTION

2.1. Preparation of REOCl. Rare earth oxychlorides REOCl were prepared by reaction of the respective oxide and ammonium chloride as described previously.[2] In a typical solid-state reaction, the mixture of RE_2O_3 (RE = La, Nd, Sm, Eu, Gd, Dy, and Y), Pr_6O_{11}, or Tb_4O_7 and NH_4Cl (molar ratio RE:Cl = 1:3) was heated at 550 °C for 10 h. After reaching the target temperature, the furnace was programmed to power down to allow for natural cooling. The resulting solid REOCl products were stored in a desiccator.

2.2. Hydrolysis Reaction of REOCls. Powder samples (200 mg) of REOCls were allowed to react in aqueous systems of different water/REOCl ratios (0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 mL/mg) for 24 h at room temperature (RT), 60 °C, and 100 °C. To determine the equilibration of each REOCl with water at different pH values, the initial pH of each aqueous solution was adjusted to the desired value using a solution of 1.0 M KOH. The solution pH was measured *in situ* at every 3 h beginning 5 min after the addition of LaOCl powder to water. Products were then collected by centrifugation, washed with deionized water, and dried at 100 °C.

2.3. Hydrolysis Reaction of REOCl in Aqueous NaCl Solution. To assess the effect of initial $Cl^-(aq)$ concentration, REOCl−water equilibria were investigated in the presence of NaCl (0.2 M) at the same water/REOCl ratios (0.1−1.0 mL/mg) and temperatures (RT−100 °C) for 24 h. Hydrolysis products were collected by centrifugation, washed with deionized water, and dried at 100 °C.

2.4. Characterizations. XRD patterns of REOCl and their hydrolysis products were recorded with a Bruker D8 diffractometer using Cu Kα radiation. Thermogravimetric (TG) analyses of hydroxychloride phases, $RE_2(OH)_5Cl\cdot nH_2O$, were performed at a heating rate of 5 °C/min from RT to 1300 °C. Data was collected in atmospheric air.

3. RESULTS AND DISCUSSION

3.1. General Hydrolysis Behavior of REOCls in Aqueous Solutions with Sufficient Amounts of Water.

Water behaves as an active component for REOCls of light rare earths, allowing it to readily form corresponding trihydroxide phases near RT, while the analogues of heavier rare earths are more stable in aqueous solution.[4b,17] In an effort to obtain comprehensive data on their reactions and stabilities, phase studies were conducted with PbFCl-type REOCl (RE = La−Dy and Y), which are relatively unstable in aqueous media. Specifically, the general equilibria in the system REOCl−H_2O

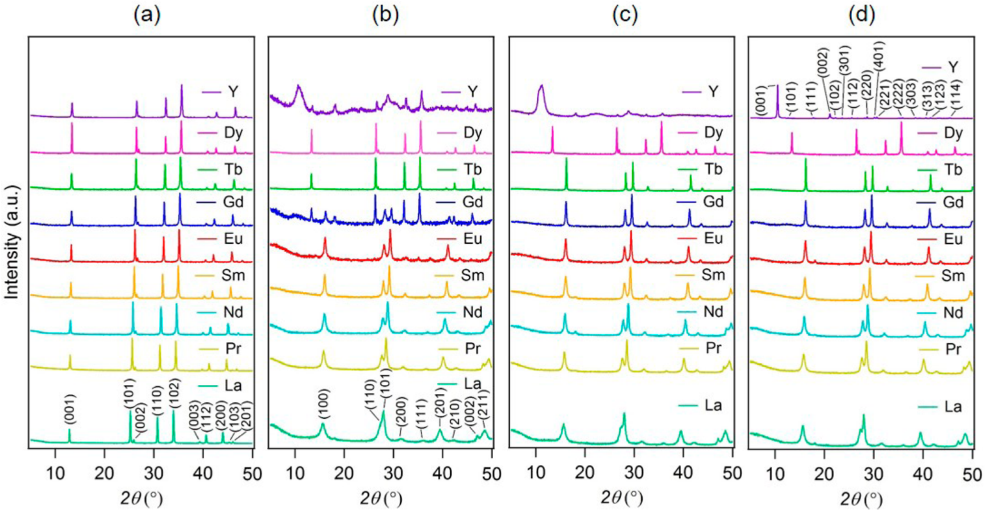

Figure 2. Powder X-ray diffraction patterns of (a) REOCl (RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Y) and products obtained after reacting REOCls (200 mg) with water (200 mL) for 24 h at (b) room temperature, (c) 60 °C, and (d) 100 °C. Reflections from LaOCl, $La(OH)_3$, and $Y_2(OH)_5Cl{\cdot}nH_2O$ are indexed in parts a, b, and d, respectively.

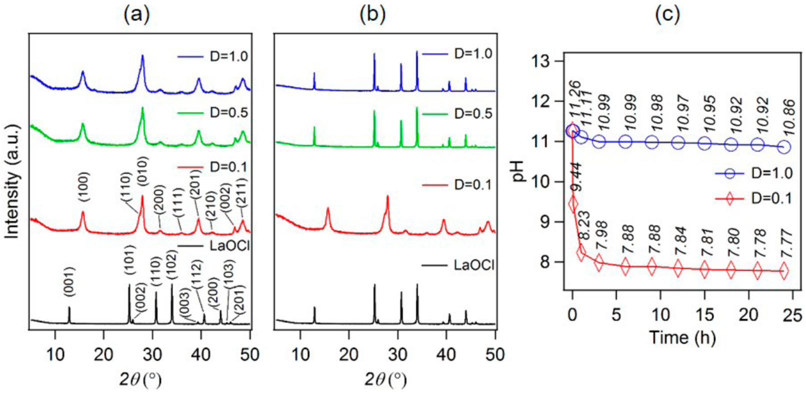

Figure 3. Powder X-ray diffraction patterns of LaOCl after reacting with water of different dilution ratios (D) at room temperature for 24 h. Initial pH was adjusted to (a) ~7 and (b) ~11 by 1.0 M KOH solution. (c) *In situ* pH change curves versus reaction time of aqueous solution of D = 1.0 and 0.1 mL/mg. The initial pH for both solutions was ~11.

were first investigated with 200 mL of water (initial pH ~7) and 200 mg of REOCl at different temperatures.

We first compared the X-ray diffraction (XRD) patterns of REOCl and their products obtained after reaction with water at different temperatures, as shown in Figure 2. Successful synthesis of the different REOCls was confirmed using JCPDS cards (Figure 2a). After reacting REOCl of RE = La–Eu with water at RT–100 °C, all reflections from the products were indexed on the basis of hexagonal $RE(OH)_3$. The absence of reflections due to parent REOCl in XRD patterns within 24 h in water regardless of temperature indicated that the transformation to the trihydroxide form was essentially complete. As shown in Figure 2b, a mixed phase of GdOCl and $Gd(OH)_3$ was obtained after 24 h in water while TbOCl was stable in water at RT. Heating up to a temperature higher than 60 °C was required for complete conversion of the oxychlorides of RE = Gd and Tb to their trihydroxide phases. In contrast, DyOCl was inert between RT and 100 °C in water, with no other phase being observed. It was of particular interest that YOCl formed an unexpected phase completely different from $Y(OH)_3$ after reaction with water. The XRD data of product obtained after reacting YOCl at 100 °C was consistent with the simulated pattern for the layered yttrium hydroxychloride $Y_2(OH)_5Cl{\cdot}nH_2O$ (Figure 2d).[7b] The water content (n) determined by TG analysis was close to 1.5 (Supporting Information Figure S1 and Table S1). Thus, hydroxychlorides and trihydroxides of rare earths can be formed by hydrolysis of corresponding oxychlorides. The hydrolysis reaction of REOCl was characterized by the following equation:

$$2REOCl(s) + 3H_2O(l) \rightarrow RE_2(OH)_5Cl(s) + H^+(aq) + Cl^-(aq) \quad (1)$$

The hydroxychloride products could be subsequently employed as reactants for the second hydrolysis reaction to produce trihydroxide phases.

$$RE_2(OH)_5Cl(s) + H_2O(l) \rightarrow 2RE(OH)_3(s) + H^+(aq) + Cl^-(aq) \quad (2)$$

For instance, Figure 2d suggests that YOCl hydrolyzed to form $Y_2(OH)_5Cl{\cdot}nH_2O$, but additional hydrolysis to $Y(OH)_3$ did not occur even at 100 °C. However, attempts to produce hydroxychloride or trihydroxide forms from REOCl (RE = Tm–Lu) phases with a SmSI-structure were unsuccessful,

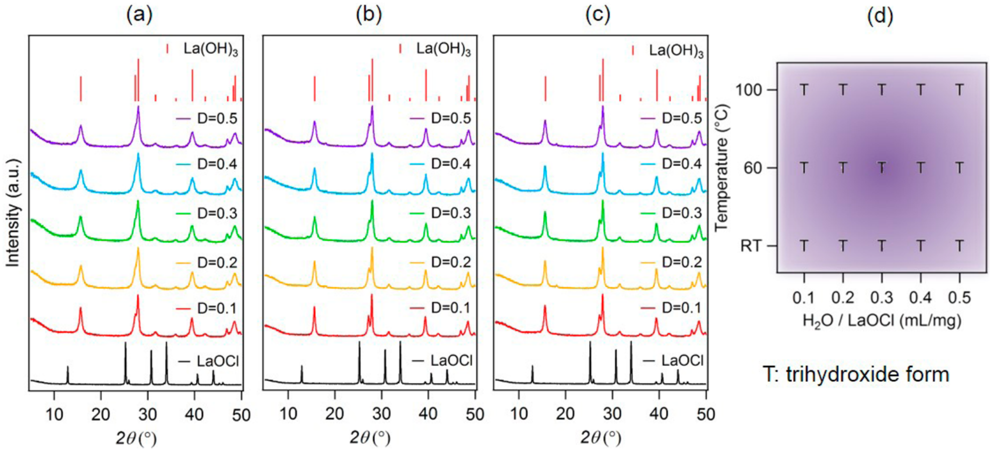

Figure 4. Powder X-ray diffraction patterns of products obtained after reacting LaOCl in aqueous solutions of different dilution ratios (D) at (a) room temperature, (b) 60 °C, and (c) 100 °C for 24 h. The relative diffraction intensities of $La(OH)_3$ according to its JCPDS card (no. 36-1481) are shown for comparison purposes. (d) Phase diagram of the $LaOCl-La_2(OH)_5Cl{\cdot}nH_2O-La(OH)_3$ system in water at $D \leq 0.5$ mL/mg.

although YOCl of similarly sized rare earth did yield a layered hydroxychloride phase.

Compared to the oxide form (La_2O_3), which is sensitive to carbonation or hydration and is consequently unstable in aqueous solutions,[18] the oxychloride form (LaOCl) is much more stable, and its catalytic activity was previously demonstrated for oxidative coupling of methane reactions.[4] However, we previously reported that LaOCl readily hydrolyzes to form $La(OH)_3$ in the pH range 3−7 at RT, and that it is difficult for such hydrolysis to occur at RT with increasing pH.[17] Similarly, REOCls of RE = Pr−Gd are rather stable in basic media, whereas acidic solutions more readily yield $RE(OH)_3$, which is indicative of hydrolysis. Although this rationale was valid in aqueous systems consisting of large amounts of water, it was not particularly relevant to cases in which the oxychloride phase was added into a system containing less water than the critical amount. Difficulties encountered during initial attempts to investigate the effect of pH on hydrolysis of REOCl in aqueous solution required that the special parameter be used for $REOCl-RE_2(OH)_5Cl{\cdot}nH_2O-RE(OH)_3$ phase relationships in water at different temperatures. Here, we defined the dilution ratio (D) as follows:

$$D = \text{the volume of water(mL)/the weight of powder(mg)}$$

Thus, the results shown in Figure 2 were obtained at D = 1.0 mL/mg (i.e., 200 mg of REOCl in 200 mL of water). Figure 3a,b shows our comparison of XRD patterns after hydrolysis of LaOCl at different initial pH values and dilution ratios. It was evident that, at pH ∼7 (Figure 3a), the hydrolysis of LaOCl was consistently accompanied by the transformation to $La(OH)_3$ in the range D = 0.1−1.0 mL/mg. In contrast, at pH ∼ 11 (Figure 3b), LaOCl was stable in water when D = 0.5 and 1.0 mL/mg but hydrolyzed to form $La(OH)_3$ when D = 0.1 mL/mg (i.e., 200 mg of LaOCl in 20 mL of water). Hence, attempts to control the hydrolysis equilibria of LaOCl and $La(OH)_3$ phases by adjusting the initial solution pH were unsuccessful. Although the initial pH values of aqueous solutions were identical, the products differed primarily as a function of dilution ratio (i.e., quantity of water). Furthermore, a consistent dependence of hydrolysis on dilution ratios was observed when pH > ∼8. In further support of this observation, Supporting Information Figure S2 shows, at pH ∼9, the stability of LaOCl in water increased as a function of dilution ratio, and thus, essentially no hydrolysis of LaOCl took place at D = 5.0 mL/mg.

To gain insight into the behavior of LaOCl hydrolysis as a function of dilution ratio, the pH change of aqueous solution was measured *in situ* after adding 200 mg of LaOCl into 200 and 20 mL (D = 1.0 and 0.1 mL/mg, respectively) of water at an initial pH of ∼11. As shown in Figure 3c, the initial pH did not change appreciably even at 24 h after the addition of LaOCl when D = 1.0 mL/mg, whereas a significant decrease in pH was observed for aqueous solutions of D = 0.1 mL/mg. Considering that both reactions of eqs 1 and 2 are accompanied by the increase of $H^+(aq)$ concentration in solution, the change of pH in aqueous media apparently arose from hydrolysis of LaOCl. During the hydrolysis reaction at the surface of LaOCl powder, extensive migration of ions through the solution could result in significant variation of solution pH, the sensitivity being decreased with increasing amounts of water. Diffusion of $H^+(aq)$ ions in solutions with large amounts of water would not strongly influence the solution pH due to sufficient dilution. In contrast, the relative concentration of $H^+(aq)$ ions in solutions with small amounts of water could be sufficiently high such that equilibrium at lower pH was established as the hydrolysis reaction proceeded. Because the initial pH values of aqueous solution were the same (∼11) for both D values, it is clear that initial pH was not the primary determinant of the different product formations, as might be expected. This comparison provides a plausible explanation that the maintenance of pH at ∼11 in the system does not induce hydrolysis of LaOCl while the concomitant decrease of pH to ∼7 results in hydrolysis of LaOCl. The complex variations in phase equilibria observed across the rare earth series also suggested that regions of variable phases could be controlled by adjusting D values. Indeed, the apparent change in pH during hydrolysis of low D systems helped us to understand the difficulties encountered with REOCl−water systems.

3.2. Hydrolysis Behavior of REOCl in Aqueous Solution of Low Dilution Ratios ($D \leq 0.5$).

As demonstrated above, at large dilution ratios ($D \geq$ 1.0 mL/mg), oxychlorides of the light rare earths were sensitive to hydrolysis, resulting in trihydroxide phases near RT. In the heavy rare earth systems, the oxychloride forms were inert to hydrolysis reaction at RT. However, as the quantity of added

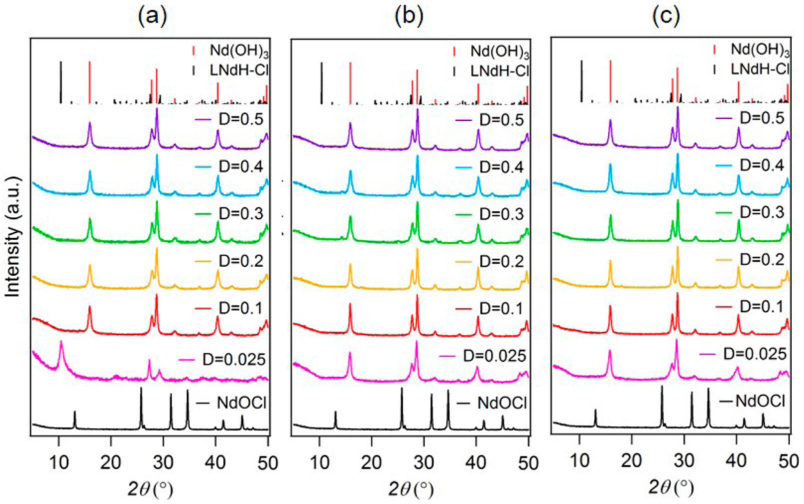

Figure 5. Powder X-ray diffraction patterns of products obtained after reacting NdOCl in aqueous solutions of different dilution ratios (D) at (a) room temperature, (b) 60 °C, and (c) 100 °C for 24 h. Relative diffraction intensities of $Nd(OH)_3$ according to its JCPDS card (no. 83-2035) and simulated intensities of $Nd_2(OH)_5Cl \cdot nH_2O$ (LNdH-Cl) are shown for comparison.

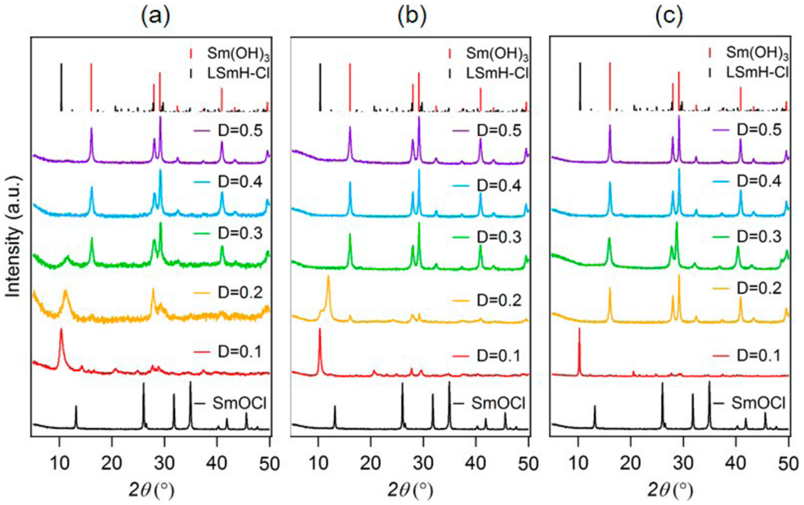

Figure 6. Powder X-ray diffraction patterns of products obtained after reacting SmOCl in aqueous solutions of different dilution ratios (D) at (a) room temperature, (b) 60 °C, and (c) 100 °C for 24 h. Relative diffraction intensities of $Sm(OH)_3$ according to its JCPDS card (no. 83-2036) and simulated intensities of $Sm_2(OH)_5Cl \cdot nH_2O$ (LSmH-Cl) are shown for comparison.

water was reduced and/or the temperature was increased, the corresponding hydroxychloride forms were produced by hydrolysis of REOCl, the stability boundaries of which were dependent on dilution ratios. Therefore, the equilibrium relationships of $REOCl-RE_2(OH)_5Cl \cdot nH_2O-RE(OH)_3$ phases in aqueous solution were examined over a limited range of low dilution ratios ($D \leq 0.5$ mL/mg) and temperatures (RT−100 °C). In these experiments, initial pHs were fixed to ~7 for all hydrolysis reactions in order to avoid any influence from pH difference. The variation in trends of boundaries between $RE_2(OH)_5Cl \cdot nH_2O$ and $RE(OH)_3$ (for the light rare earths) as well as between REOCls and $RE_2(OH)_5Cl \cdot nH_2O$ (for the heavy rare earths) behaved approximately as expected for the size of rare earths across the series. Importantly, these investigations provided systematic guidelines of the rare earth oxychloride−water systems and may be used as a basis for the preparation and application of REOCl and $RE_2(OH)_5Cl \cdot nH_2O$ phases in aqueous media.

3.2.1. LaOCl and PrOCl. All of the hydrolysis products of LaOCl at $D \leq 0.5$ mL/mg over the range RT−100 °C were identical and readily identified from XRD patterns as the trihydoxide phase $La(OH)_3$, as shown in Figure 4a,c. On the basis of these data, the stable D value and temperature conditions for LaOCl, $La_2(OH)_5Cl \cdot nH_2O$, and $La(OH)_3$ phases in aqueous solution were determined as shown in Figure 4d. These results, coupled with those shown in Figure 2, suggested that hexagonal $La(OH)_3$ is the only stable phase in water up to 100 °C and $D = 1.0$ mL/mg, and that the $LaOCl-La(OH)_3$ phase boundary, if it exists, should be found at a temperature much lower than RT and D value much larger than 1.0 mL/mg. All attempts to isolate the hydroxychloride form $La_2(OH)_5Cl \cdot nH_2O$ at various D values at RT were unsuccessful. In practice, preparation of a layered lanthanum hydroxide (LLaH) phase is difficult in aqueous media, and to date, only $La_2(OH)_5NO_3 \cdot nH_2O$ with NO_3^- as interlayer anions has been successfully prepared under nonaqueous solvothermal conditions.[19] Essentially the identical diagram was obtained for PrOCl in aqueous solution, at least in $D \leq 0.5$ mL/mg and RT−100 °C range (Supporting Information Figure S3).

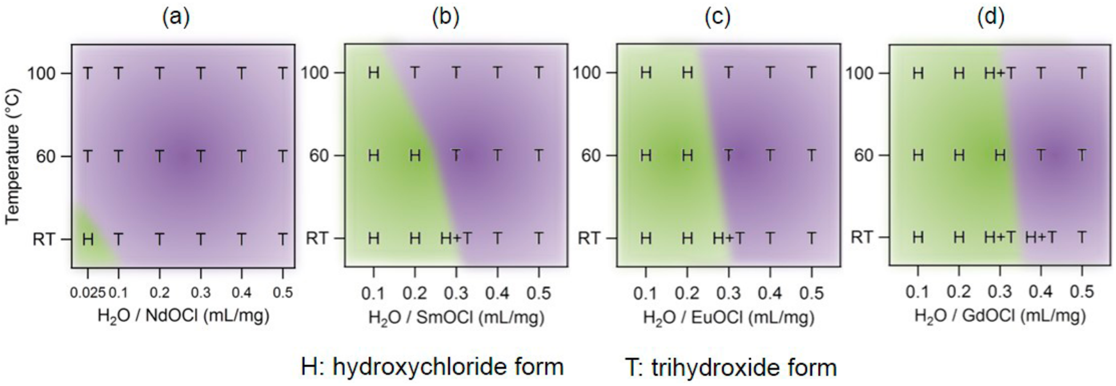

Figure 7. Dilution ratio ($D \leq 0.5$)-dependent phase diagrams for REOCl−$RE_2(OH)_5Cl \cdot nH_2O$−$RE(OH)_3$ systems in water, where RE = (a) Nd, (b) Sm, (c) Eu, and (d) Gd.

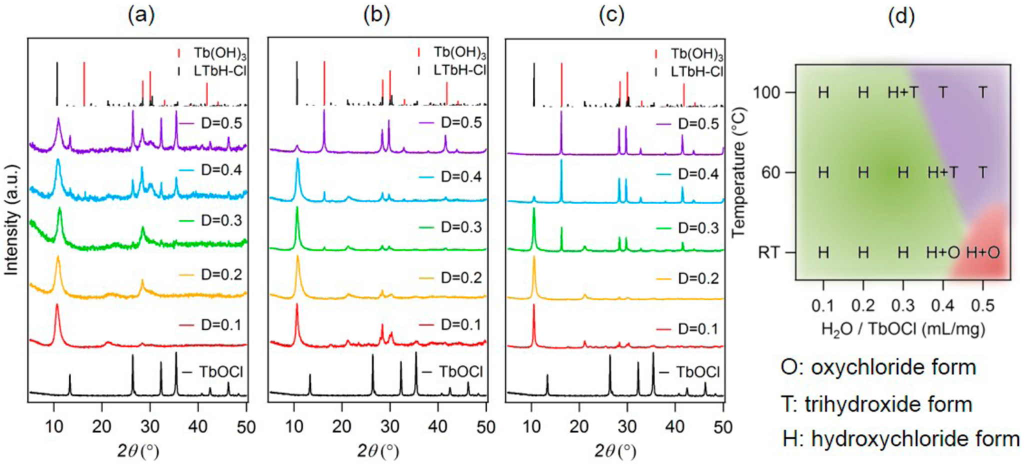

Figure 8. Powder X-ray diffraction patterns of products obtained after reacting TbOCl in aqueous solutions of different dilution ratios (D) at (a) room temperature, (b) 60 °C, and (c) 100 °C for 24 h. Relative diffraction intensities of $Tb(OH)_3$ according to its JCPDS card (no. 76-0800) and simulated intensities of $Tb_2(OH)_5Cl \cdot nH_2O$ (LTbH-Cl) are given for comparison. (d) Phase diagram for the TbOCl−$Tb_2(OH)_5Cl \cdot nH_2O$−$Tb(OH)_3$ system in water at $D \leq 0.5$ mL/mg.

3.2.2. REOCl (RE = Nd−Gd). Oxychlorides of RE = Nd−Gd were also unstable in aqueous media of particularly low D values, and their structures were not maintained after addition in water. Figure 5 compares the XRD patterns recorded after reacting NdOCl in aqueous solutions of $D \leq 0.5$ mL/mg region at different temperatures. When reacted at 60 and 100 °C, the hydrolysis product of NdOCl was the trihydroxide phase $Nd(OH)_3$ regardless of D value. Consequently, the oxychloride−water system for neodymium was very similar to that observed for lanthanum at elevated temperatures. In contrast, when reacted at RT, NdOCl hydrolyzed to form the hydroxychloride phase $Nd_2(OH)_5Cl \cdot nH_2O$ at $D = 0.025$ mL/mg. A number (n) of approximately 1.3 for hydration in the layered hydroxychloride phase was verified by TG analysis (Supporting Information Figure S1 and Table S1). However, a small increase in D value or temperature immediately led to the formation of the trihydroxide phase by additional hydrolysis reaction of hydroxychloride phase (eq 2). These results accounted for the apparently general transformation of REOCl to $RE(OH)_3$ in water for the lighter rare earths (RE = La and Nd).

Analogues containing Sm−, Eu−, and Gd−water systems behaved in a consistent manner. Specifically, when REOCl (RE = Sm−Gd) were reacted at low D values, their hydrolysis products consisted of the hydroxychloride phases $RE_2(OH)_5Cl \cdot nH_2O$ even after 24 h at 100 °C. As shown in Figure 6, the hydrolysis product of SmOCl at $D = 0.1$ mL/mg was $Sm_2(OH)_5Cl \cdot nH_2O$ phase, and was stable even at 100 °C, while the XRD patterns after reaction in solutions of $D \geq 0.3$ mL/mg indicated that only $Sm(OH)_3$ was present. Oxychlorides of Eu and Gd also hydrolyzed to form well-crystallized hydroxychloride phases even at elevated temperatures, when $D \leq 0.2$ and 0.3 mL/mg, respectively (Supporting Information Figures S4 and S5). The numbers of hydration (n) determined by TG analyses were in the range 1.5−2.0 (Supporting Information Figure S1 and Table S1).

The results obtained from the equilibration of REOCl (RE = Nd−Gd) with water ($D \leq 0.5$ mL/mg) in the temperature range RT−100 °C are summarized schematically in Figure 7. The two phase equilibria of REOCl−water systems of RE = Nd−Gd contrasted with the single phase ($La(OH)_3$) found for the LaOCl−water system. The identities of each phase, namely, hydroxychlorides and hexagonal trihydroxides, were established by evaluating the respective XRD data. The equilibration of NdOCl with water produced a hydroxychloride phase $Nd_2(OH)_5Cl \cdot nH_2O$ only at a narrow range of temperature (near RT) and D (≤0.025 mL/mg), and otherwise formed the trihydroxide phase $Nd(OH)_3$. The phase equilibria of Sm, Eu, and Gd systems were quite similar, exhibiting only slight differences in the boundaries between stable regions for the

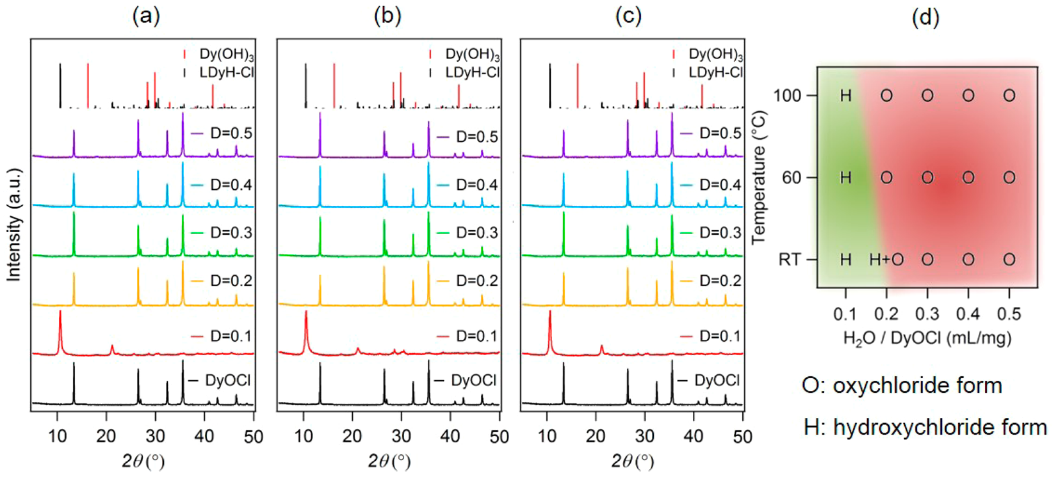

Figure 9. Powder X-ray diffraction patterns of products obtained after reacting DyOCl in aqueous solutions of different dilution ratios (D) at (a) room temperature, (b) 60 °C, and (c) 100 °C for 24 h. Relative diffraction intensities of $Dy(OH)_3$ according to its JCPDS card (no. 83-2039) and simulated intensities of $Dy_2(OH)_5Cl\cdot nH_2O$ (LDyH-Cl) are given for comparison. (d) Phase diagram for the $DyOCl-Dy_2(OH)_5Cl\cdot nH_2O-Dy(OH)_3$ system in water at $D \leq 0.5$ mL/mg.

corresponding hydroxychloride and trihydroxide phases, which were identified at D of ~0.3 mL/mg. No significant temperature dependence was observed for the favorable regions for the two phases. At lower D values, the hydrolysis products of REOCls consisted of hydroxychloride phases in the range RT−100 °C; however, as the D values increased, trihydroxides comprised an increasingly larger fraction of the diagrams, regardless of temperature. A slight increase in D value boundary between hydroxychlorides and trihydroxides was induced during the change from Sm to Eu and Gd, and therefore, the region for the hydroxychloride phase was enlarged.

3.2.3. TbOCl and DyOCl. In general, the systematics of equilibrium established by the first half of the rare earth series did not continue across the series. As shown in Figure 2, for solutions with D = 1.0 mL/mg, TbOCl was stable at RT and then underwent increasing hydrolysis to form the trihydroxide phase as the temperature increased. DyOCl was inert to hydrolysis, and its trihydroxide phase was not produced, even after heating the oxychloride phase at 100 °C in water. However, marked variations in the equilibria of TbOCl and DyOCl−water systems were observed with decreasing D values.

Figure 8 shows the XRD patterns of products obtained after reacting TbOCl in water in the range $0.1 \leq D \leq 0.5$ mL/mg at different temperatures. At somewhat lower D values, the hydrolysis products of TbOCl consisted of the hydroxychloride phase, and measurable effects were not induced by temperature changes in the RT−100 °C range, which was similar to the observations made for RE = Sm, Eu, and Gd. As the value of D increased, chloride was only partially replaced by hydroxide to produce a mixture of oxychloride and hydroxychloride forms at RT, but hydrolysis of TbOCl was complete, and thus, the only product was the trihydroxide phase at high temperatures. An overview of the phases observed for different D values and temperatures is presented in Figure 8d. TbOCl can either exist in an unreacted form or hydrolyze to produce both hydroxychloride and trihydroxide phases in water. Thus, the phase equilibria of $TbOCl-Tb_2(OH)_5Cl\cdot nH_2O-Tb(OH)_3$ in water were the most complex that were encountered for the rare earth series, and substantial variations were observed as a function of changes in D value and temperature. The hydroxychloride phase was stable at $D <$ ~0.3 mL/mg, whereas all three phases could be identified at D values between 0.4 and 0.5 mL/mg, depending on temperature.

Since neither the hydroxychloride nor trihydroxide phase of dysprosium was observed at D = 1.0 mL/mg and 100 °C (Figure 2), the stability field of DyOCl appeared to extend to much higher temperature and beyond the range of dilution ratios tested in this study. However, as shown in Figure 9, the hydroxychloride phase $Tb_2(OH)_5Cl\cdot nH_2O$ was found when DyOCl was equilibrated in an aqueous solution of D = 0.1 mL/mg between RT and 100 °C. Although a mixture of the oxychloride and hydroxychloride phases was observed at RT when D = 0.2 mL/mg, the hydrolysis of DyOCl was considerably reduced with increasing D values. Furthermore, the trihydroxide phase was not observed, as shown in the phase diagram for the DyOCl−water system (Figure 9d). The observation of remaining oxychloride phases in RE = Tb and Dy systems and absence of trihydroxide phases in the Dy system are probably due to the increased inertness of smaller rare earth ions to hydrolysis. These results are consistent with a previous study showing that lighter rare earth oxides more readily form the corresponding trihydroxides.[20] Similar behavior has been observed for binary rare earth hydroxide systems. Specifically, the stabilities of hexagonal trihydroxides decrease across the series, and a trihydroxide for lutetium adopts the cubic structure.[21] Indeed, REOCls of smaller rare earths (RE = Dy−Lu) were found to be essentially inert to hydrolysis, and no evidence of $RE(OH)_3$ phases was detected even after heating up to 100 °C for extended periods in water. These consistent observations confirmed that the hydrolysis reaction of REOCl is preferable at lower dilution ratios and the rate of hydrolysis is slower for smaller rare earth ions.

3.2.4. YOCl. The Tb system was characterized by existence of all three phases, oxychloride, hydroxychloride, and trihydroxide, indicating a complicated hydrolysis reaction sensitive to the experimental conditions. In the smaller Dy system, the enlarged stable region for the oxychloride phase resulted in a narrower region for hydroxychloride phase and absence of trihydroxide phase. Considering that the ionic radius of Y^{3+} is smaller than that of Dy^{3+} (Tb^{3+} = 1.095 Å, Dy^{3+} = 1.083 Å, Y^{3+} = 1.075 Å), YOCl might be anticipated to have a wider range of stability

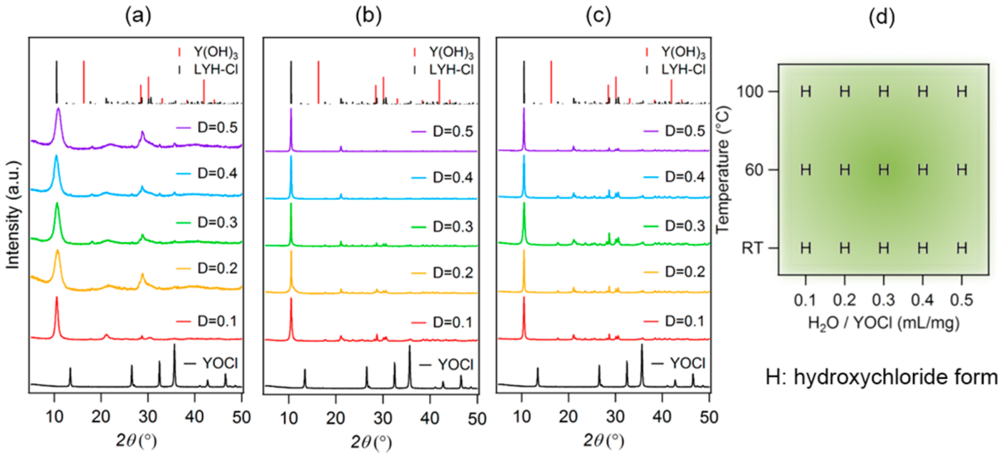

Figure 10. Powder X-ray diffraction patterns of products obtained after reacting YOCl in aqueous solutions of different dilution ratios (D) at (a) room temperature, (b) 60 °C, and (c) 100 °C for 24 h. Relative diffraction intensities of $Y(OH)_3$ according to its JCPDS card (no. 83-2042) and simulated intensities of $Y_2(OH)_5Cl \cdot nH_2O$ (LYH-Cl) are given for comparison. (d) Phase diagram for the $YOCl-Y_2(OH)_5Cl \cdot nH_2O-Y(OH)_3$ system in water at $D \leq 0.5$ mL/mg.

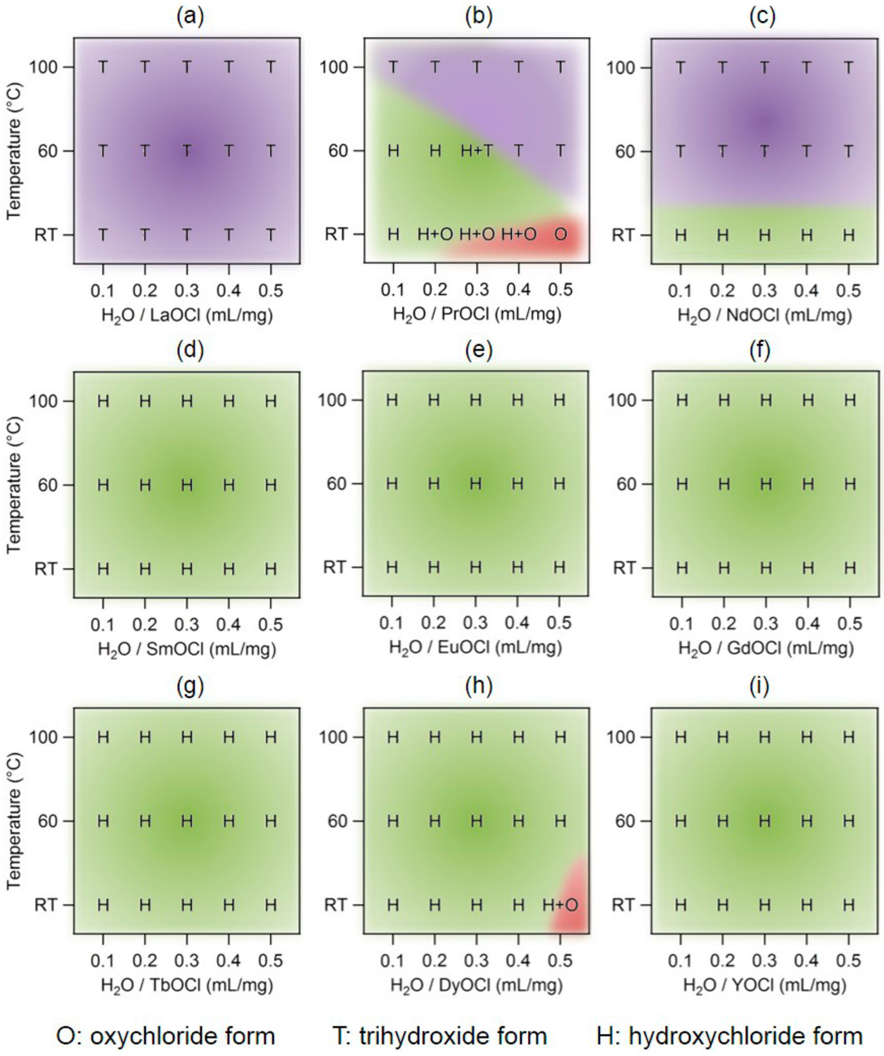

Figure 11. Dilution ratio ($D \leq 0.5$)-dependent phase diagrams for $REOCl-RE_2(OH)_5Cl \cdot nH_2O-RE(OH)_3$ systems in 0.2 M NaCl solution, where RE = (a) La, (b) Pr, (c) Nd, (d) Sm, (e) Eu, (f) Gd, (g) Tb, (h) Dy, and (i) Y.

than DyOCl; however, the observed results exhibited an opposite trend.

XRD patterns measured after reaction of YOCl in water at different temperatures are shown in Figure 10. On the basis of comparison of crystallographic data with simulated intensities, all of the products of the hydrolysis reaction of YOCl were identified as layered hydroxychloride $Y_2(OH)_5Cl \cdot nH_2O$ ($n \sim 1.5$, Supporting Information Figure S1 and Table S1). No reflections that could be assigned as basal reflections of the trihydroxide form were observed. As summarized in the phase diagram in Figure 10d, the essential features of YOCl−water equilibria in the range of $0.1 \leq D \leq 1.0$ mL/mg may be explained by the spatial stability of the $Y_2(OH)_5Cl \cdot nH_2O$ structure. Analogous to TbOCl− and DyOCl−water systems with an RE size similar to Y, formation of the trihydroxide phase or remaining as the oxychloride phase of Y should be feasible, at least at high *D* ratios. Interestingly, no evidence was obtained for either the oxychloride and trihydroxide phases; only the hydroxychloride phase was observed over the range of *D* values and temperatures investigated. Because the decreased stabilities of the trihydroxide forms were consistent with the size-dependent trend across the rare earth series, the absence of the trihydroxide phase for small Y was not particularly surprising. However, the remarkable stability of hydroxychloride phase of Y observed for a substantial range of *D* value and temperature was not anticipated. Although this observation is not well-understood, several interrelated factors may be responsible. Because different reaction times provided identical results and no YOCl remained, the equilibria did not appear to be kinetically limited. Here, it could be considered that the lanthanum hydroxychloride decomposed to form LaOCl by liberating H_2O, whereas the yttrium hydroxychloride does not yield YOCl due to loss of HCl over a similar temperature region.[22] The apparent difference in thermal decomposition behaviors of these two compounds would account for the failure to observe the oxychloride phase of Y in Figure 10d. As shown in Figure 2b, the observed small amount of remaining YOCl suggests that the stable field of YOCl is probably enlarged with increasing *D* values higher than 1.0 mL/mg at RT.

3.3. Effects of Salt on the Hydrolysis of REOCls in Aqueous Solutions with Low Dilution Ratios. According to eqs 1 and 2, the hydrolysis reaction of REOCl is accompanied by liberation of $Cl^-(aq)$ ions into the aqueous solution system. Therefore, it was anticipated that, despite having the same *D* value and temperature conditions, initial $Cl^-(aq)$ ion concentrations could be another factor determining the degree of hydrolysis, and consequently, the boundaries of oxychloride, hydroxychloride, and trihydroxide phases of rare earths in water. To gain additional insight into the stabilities of each phase, we expanded our investigation to include sodium chloride (NaCl), which is of particular importance for assessing salt effects.

When NaCl was added to REOCl−water systems, even in low concentrations, the equilibrium at given dilution ratio and temperature was actually affected by the salt concentration, although these effects varied depending on the nature of the RE. Figure 11 shows a schematic diagram demonstrating the effects of a 0.2 M solution of NaCl on REOCl−water equilibria. Compared with Figures 4d and 10d, LaOCl− and YOCl−water systems did not exhibit any noticeable differences in the presence of NaCl. Attempts to isolate the La analogue of $RE_2(OH)_5Cl \cdot nH_2O$ were unsuccessful; only the trihydroxide was obtained despite testing in the presence of salt over a wide range of temperatures and *D* ratios. The apparent stability of the $Y_2(OH)_5Cl \cdot nH_2O$ phase was also maintained in the 0.2 M NaCl solution. In contrast, in the PrOCl−water system, the hydroxychloride form that was not obtained in aqueous media without NaCl (Supporting Information Figure S3) was observed at low *D* value and low temperature range in NaCl solution. Similarly, the hydroxychloride region in NdOCl−water system that was narrow in aqueous media without NaCl (Figure 7a) was also enlarged significantly to $D > 0.5$ mL/mg at RT following addition of NaCl.

The dramatic effect of salt on the equilibrium relationships of $REOCl{-}RE_2(OH)_5Cl \cdot nH_2O{-}RE(OH)_3$ systems in aqueous solution was most apparent for RE = Sm−Dy. Equilibration of these REOCls in solution without salt yielded oxychloride, hydroxychloride, and/or trihydroxide phases depending on the specific RE, *D* value, and temperature (Figures 7−9); however, in the 0.2 M solution of NaCl, hydroxychloride was practically the only phase observed at least for $D \leq 0.5$ mL/mg. Although experiments in which DyOCl was equilibrated in 0.2 M NaCl solution produced a mixed phase of hydroxychloride and oxychloride at $D = 0.5$ mL/mg and RT, only the hydroxychloride phase was observed above 40 °C. The addition of salt and resulting increase of anions amenable to charge compensation in the interlayer galleries may actually be the origin of the increase in stability of the layered hydroxychloride structure. Although not the primary purpose of this study, the effect of salt to markedly reinforce the stability of layered hydroxychlorides in REOCl−water systems was nevertheless an interesting observation. Thus, hydrolysis of REOCls appears to provide an alternative route for preparing layered $RE_2(OH)_5Cl \cdot nH_2O$ at ambient pressure and room temperature.

■ CONCLUSIONS

We performed in-depth exploration of the hydrolysis behavior of REOCls to generate phase diagrams that define the stabilities of oxychloride, hydroxychloride, and trihydroxide phases of rare earths in water. The observed phase equilibria differed from those expected on the basis of merely conventional pH values. The newly described phase diagrams will likely allow for the use of dilution ratios (*D*) to prevent hydrolysis or to achieve efficient synthesis of the desired phases. Stability of REOCls in water should not be expected when the RE is large, with LaOCl being particularly unstable to completely hydrolyze to $La(OH)_3$ in aqueous solutions with low *D* values. In contrast, the stability of $RE_2(OH)_5Cl \cdot nH_2O$, except RE = La, was significantly increased in the presence of salt over a wide range of *D* values. The existence of such stable phases is consistent with recent reports of layered rare earth hydroxide families. Although the corresponding phase equilibria are rather complex, these results should greatly enhance our understanding of the behavior of rare earths in aqueous media.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

TGA profiles, table of analysis data for the amounts of water in the hydroxychloride phases, additional XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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