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Thermodynamic Analysis of Precipitation Characteristics of Rare Earth Elements with Sulfate in Comparison with Other Common Precipitants

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Abstract: The selective precipitation of rare earth elements (REEs) in acidic media often plays a key role in the effective extraction of these elements from various sources such as ores and recycling streams. In this study, the precipitation characteristics of REEs with sulfate, a frequently used precipitant, were carefully examined, and the results were compared with those of other precipitants, such as phosphate, oxalate, and fluoride/carbonate systems. Emphasis is given on various forms of precipitates, such as anhydrous sulfate, octa-hydrated sulfate, and sodium double salt, in which the sodium double salt was compared with the anionic double salt precipitation of the fluoride-carbonate system. It was found that anions such as Cl^-, $NO_3{}^-$, and $SO_4{}^{2-}$ play an important role in the precipitation behavior, particularly through complexation with the dissolved REEs. In general, the effectiveness of precipitation follows the order of sodium double salt, a hydrated form of sulfate, and anhydrous sulfate. In this study, it was observed that the synergistic role of a double salt precipitation, either cationic or anionic, is frequently as effective as that of oxalate and phosphate, even in a low pH range.

Keywords: rare earth elements; precipitation; leaching; sodium double salt; complexation

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Citation: Han, K.N.; Kim, R. Thermodynamic Analysis of Precipitation Characteristics of Rare Earth Elements with Sulfate in Comparison with Other Common Precipitants. *Minerals* **2021**, *11*, 670. https://doi.org/10.3390/min11070670

Academic Editor: Jean-François Blais

Received: 20 May 2021
Accepted: 18 June 2021
Published: 23 June 2021

1. Introduction

In general, there are two types of ores containing rare earth elements (REEs), one of which is bastnaesite, one of the predominant REE-bearing minerals found in the Mountain Pass in California, and other common REE minerals are monazite and xenotime, which are often found in beach sands. The former type of mineral consists primarily of Ce and La, forming fluoro-REE carbonate, and the latter are mainly REE phosphates. These minerals are usually refractory and present difficulties in dissolving at normal temperatures and pressures. As a result, these minerals are often treated at a high temperature, mixed with sulfuric acid or sodium hydroxide, making the refractory nature of ores amenable to leaching in mild acid [1–9]. Another method of extracting REEs from refractory ores is to leach in a high concentration of acids such as HCl, HNO_3, H_3PO_4, and H_2SO_4 [10–13].

After leaching REEs from various sources, the solution containing dissolved REEs and many other elements, such as Fe^{3+}, Al^{3+}, and Ca^{2+}, is subjected to precipitation after the pH of the solution was raised to >3–4 to remove the impurity ions. This is followed by the precipitation of REEs using an appropriate precipitant, such as sulfate, carbonate, phosphate, oxalate, and fluoride. Unfortunately, during the first precipitation of impurities, including Fe^{3+} and Al^{3+}, REEs are also co-precipitated or adsorbed on the surface of the precipitated products, resulting in the loss of valuable REEs. To prevent this loss, it would be desirable to be able to preferentially precipitate REEs at low pH values where impurities are still present in the solution.

It is well understood that the choice of sulfate as a precipitant for REEs is a wise strategy in the selective precipitation of REEs from the rest of the impurities in leach liquor. Sulfate is relatively cheap, and the precipitation efficiency with REEs is well established [14–22]. For instance, regardless of the treatment method of REE ores, i.e., either acid or alkali treatment, double sulfate precipitation has been considered a significant step of the REE ore processing to purify REEs from impurity elements or each other [23]. In Bayan Obo, China, bastnaesite is first baked by sulfuric acid and water-leached, and then, REEs are recovered through a double-sulfate precipitation method [24]. In the following steps, REEs are further purified to be a separated element.

In this study, the precipitation behavior of REEs with sulfate was examined carefully and thoroughly, especially in the low pH range. The effects of anions, such as Cl^-, NO_3^-, and SO_4^{2-} that are present because of the inevitable use of acids in the leaching process, will be carefully examined in this study. The significant role of anions in the leaching and precipitation processes has been examined in the past [22,25,26]. It is hoped that a careful and detailed examination of the effect of anions on the precipitation characteristics of REEs will allow the identification of conditions in which REEs can be preferentially separated from impurities at a low pH range. Then, the results will be compared with other precipitants, including phosphate, carbonate, fluoride, and oxalate.

2. Acquisition of Thermodynamic Data

A detailed description of the thermodynamic data has been given in an earlier study by one of the authors [25,26]. Table 1 lists the Gibbs standard free energy formation values of 10 chosen REE complexes that were used in this study. There are 17 REEs, including Sc and Y, in addition to lanthanide group elements. Five light REEs (LREEs: La, Ce, Pr, Nd, and Sm) and five heavy REEs (HREEs: Gd, Tb, Dy, Ho, and Er) were selected as representatives. Other data used in this study and not shown in this table were taken from previous studies. Most data were obtained by HSC [27], and other references as described earlier [28–33]. It should be noted that the Gibbs standard free energy formation values of sodium double salts of the 10 REEs were taken from OLI Studio [34]. These values are consistent with those measured by Lokshin et al. [14,15].

Table 1. The Gibbs standard free energy formation of various compounds in kJ/mol. (Information taken from references [22,25,26] with some modifications).

	Na-D Salt	$RnCl^{2+}$	$RnCl_2^+$	$RnCl_3$	$RnCl_4^-$	$RnNO_3^{2+}$	$Rn(NO_3)_3$	$RnSO_4^+$	$Rn(SO_4)_2^-$	$Rn_2(SO_4)_3$
La	−2745.0	−818.2	−947.8	−1076.4	−1205.4	−799.3	−1016.5	−1450.1	−2201.2	−3668.5
Ce	−2714.6	−808.6	−938.0	−1067.2	−1195.9	−790.1	−1008.8	−1439.8	−2189.1	−3583.6
Pr	−2741.8	−812.8	−941.9	−1071.2	−1192.0	−794.4	−1011.7	−1444.0	−2196.7	−3589.4
Nd	−2754.3	−804.8	−934.0	−1062.8	−1192.0	−786.8	−1003.9	−1435.8	−2187.7	
Sm	−2720.1	−798.1	−927.2	−1056.3	−1185.1	−780.2	−995.4	−1429.6	−2186.9	−3556.8
Gd	−2715.6	−796.1	−925.0	−1054.0	−1182.7	−776.7	−993.0	−1427.5	−2176.8	−3551.9
Tb	−2717.9	−799.5	−928.7	−1057.9	−1186.3	−780.5	−997.8	−1431.3	−2169.6	−3561.7
Dy	−2706.4	−796.0	−925.1	−1054.0	−1182.6	−774.8	−994.7	−1427.3	−2180.3	−3555.4
Ho	−2711.3	−807.4	−936.8	−1065.4	−1194.4	−786.9	−1019.6	−1438.8	−2189.1	−3605.2
Er	−2720.7	−800.7	−930.0	−1058.8	−1187.5	−779.3	−1004.2	−1432.0	−2186.2	−3574.3

Na-D Salt: $NaRn(SO_4)_2 \cdot H_2O$: Data obtained from OLI Studio (the symbol Rn is used throughout this study representing rare earth elements).

3. Process Description of Leaching and Precipitation in Different Acids

As shown in Figure 1, when an ore-bearing REE is dissolved in an acid, it is presumably dissolved first to bring a free REE ion, Rn^{3+}, into the solution. However, as soon as the free REE ions appear in the solution, they are surrounded by anions such as Cl^-, NO_3^-, or HSO_4^- in the leaching process depending on the type of acid used: hydrochloric (HCl), nitric (HNO_3), or sulfuric (H_2SO_4) acid. As these REE species are subjected to precipitation with a precipitant such as sulfate, all these species undergo similar precipitation.

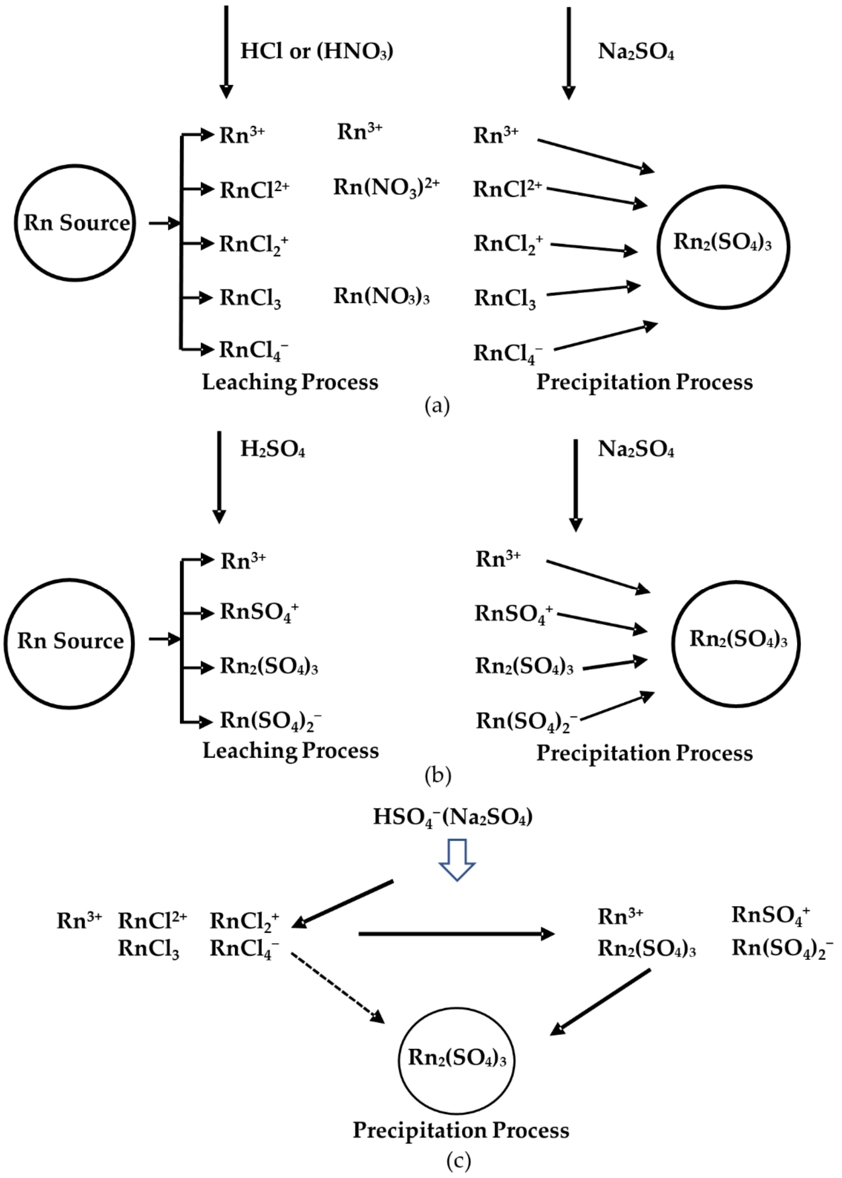


Figure 1. Schematics showing leaching process and precipitation process of (**a**) HCl or HNO_3 system; (**b**) H_2SO_4 system; and (**c**) conversion of Rn-Cl complexes to the Rn-SO_4 complexes and their precipitation.

The three acids, HCl, HNO_3, and H_2SO_4, are commonly used to extract REEs from various sources. When REEs are extracted into solution, there are many forms of REE complexes that are produced during the leaching process [22,25,26]. Examples of Ce speciation in different acid systems are shown in Figure 2. As shown in Figure 2, in HCl, Rn^{3+}, $RnCl^{2+}$, $RnCl_2^+$, $RnCl_3$, and $RnCl_4^-$ (Figure 2a) were formed in the solution depending on the concentration of Cl^- in the solution. It can be noted that the concentration of the free rare earth element, Rn^{3+}, decreases rapidly with an increase in the Cl^- concentration. For the nitrate system, as shown in Figure 2b, Rn^{3+}, $RnNO_3^{2+}$, and $Rn(NO_3)_3$ are present in the system, whereas in the H_2SO_4 system, as shown in Figure 2c, $RnSO_4^+$, $Rn(SO_4)_2^-$, and $Rn_2(SO_4)_3$ are present in the system.

In the species diagrams shown in Figure 2, the most abundant species of REEs is $RnCl^{2+}$ in the Cl^- system and $RnNO_3^{2+}$ in the NO_3^- system, while $Rn(SO_4)_2^-$ is the predominant sulfate species over a wide range of SO_4^{2-} concentrations.

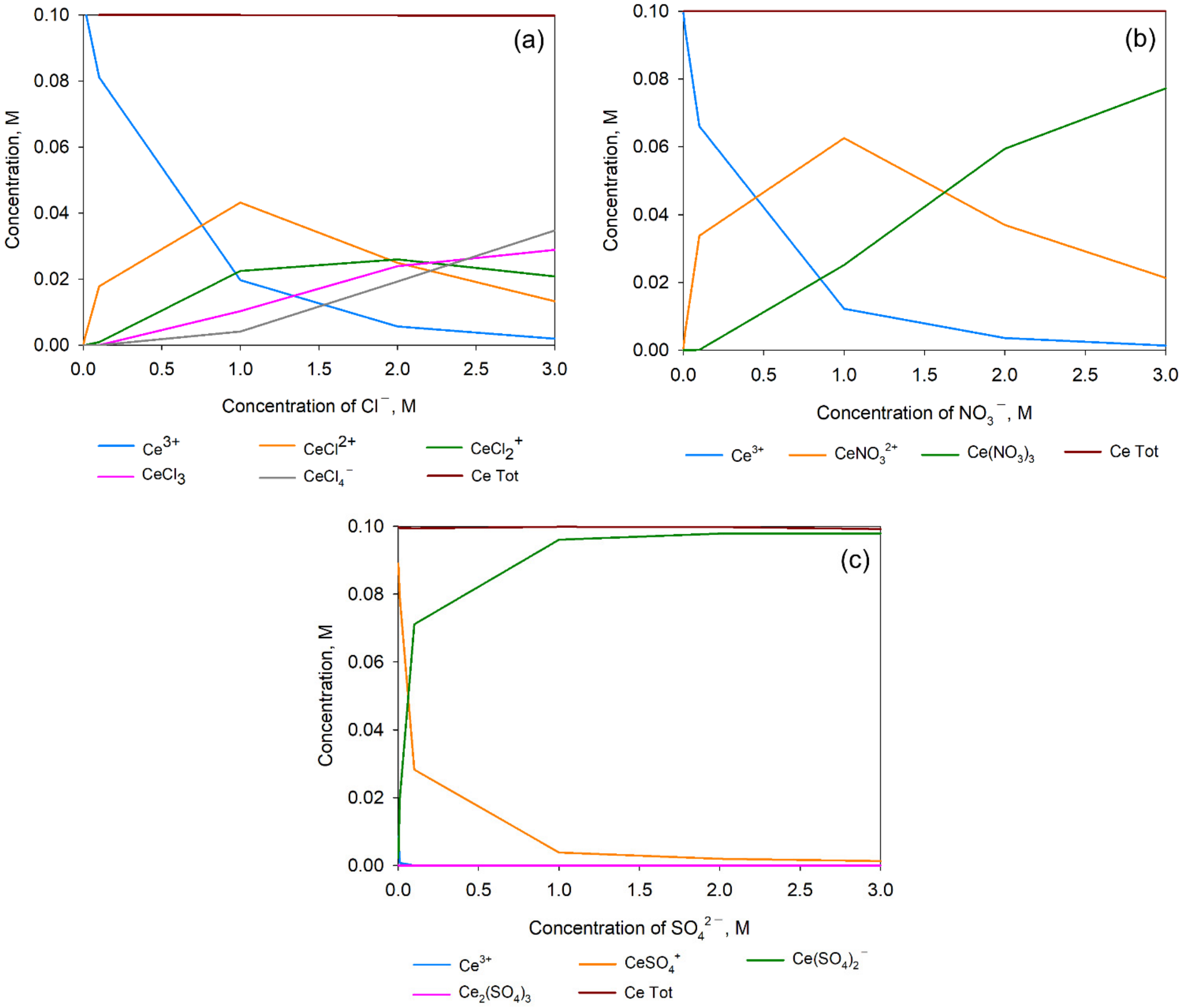


Figure 2. Cerium (III) speciation in (**a**) HCl; (**b**) HNO_3; and (**c**) in H_2SO_4 systems.

The speciation diagrams of 17 REEs generally show remarkably similar behaviors. However, there are differences that should be noted. For example, for the diagrams with Cl^-, most REEs show a similar behavior, as shown in Figure 2 with cerium, in which $RnCl^{2+}$ is the most abundant complex over a wide range of Cl^- concentrations. However, although not covered in this study, it should be mentioned that Sc and Eu show a quite different behavior, in which $RnCl_2{}^+$ is the predominant species. Regarding the $NO_3{}^-$ system, there are more exceptions than in the case of the Cl^- system. Six elements, including Eu, Ho, Er, Tm, Y, and Sc, exhibit $Rn(NO_3)_3$ as the most abundant complex, while the other elements show $Rn(NO_3)^{2+}$ as the most dominant complex over a wide range of $NO_3{}^-$ concentrations, as shown in Figure 2 with cerium. However, for the sulfate system, the exceptions are found with Tb, Ho, Lu, and Sc, in which the predominant complex is $Rn(SO_4)^+$ instead of $Rn(SO_4)_2{}^-$, with all the other elements showing the same trend as seen in Figure 2 with Ce [35].

It can easily be envisaged that the free ion is easily precipitated kinetically because it involves one chemical bonding step with the precipitant, while the other species involve at least two steps, one being dissociation from Cl^- or $NO_3{}^-$ first, before reacting with sulfate, resulting in precipitation. However, when the chemical environment is such that the free ion is scarcely available, as in the case of the sulfate environment (Figure 2c), this may not be possible without two consecutive reactions taking place, namely dissociation and precipitation reactions.

Thermodynamic principles only indicate that the final equilibrium is determined by the reaction that yields the lowest solubility. Therefore, to determine the concentration of the species that is responsible for the final equilibrium status in the precipitation process, each equation must be solved. This is demonstrated in the subsequent calculations to determine the equilibrium concentration of REEs when subjected to precipitation.

4. Precipitation to Various Forms of Sulfates

4.1. Effect of Cl^- on the Precipitation Process

Precipitation of REE species in the HCl environment is considered first. Let us assume that a low-grade REE-bearing ore is subjected to leaching at a low pH—for example, pH 1 with HCl. Consider an ore containing REEs with an overall 1% of REEs and further assume that this ore is placed in a reactor at 30% by weight of solid, as normally practiced in leaching processes. If REEs are dissolved completely in the solution, the total concentration of REEs would be 3.0×10^{-2} mol/L, assuming the average molecular weight of REEs to be 150. Then, the leach liquor would be filtered to remove the solid particles present in the system. As a result, in the following calculations, we assume the initial concentration of total REEs in the solution to be 0.03 mol/L, which has a significant consequence, especially when Cl^- or $NO_3{}^-$ is being released from the REE-complexed species due to precipitation to form a sulfate precipitate. Furthermore, calculations were performed for pH values of 1 and 3 for comparison.

In this section, the precipitation of REE species to anhydrous sulfate, $Rn_2(SO_4)_3$, octahydrated sulfate, $Rn_2(SO_4)_3{\cdot}8H_2O$, and $NaRn(SO_4)_2{\cdot}H_2O$ (Na-double salt) was considered, and the resulting concentrations of REEs in each system were compared to determine the best precipitation reaction under comparable conditions. It has been assumed that the precipitation begins at a given pH (pH 1 or pH 3), which has been predetermined for the chosen acid. Then, sodium sulfate, Na_2SO_4, is added to the solution containing various complexed species of REEs at increments of 0.1, 0.3, 0.5, 1, and 2 mol/L as $HSO_4{}^-$ or $SO_4{}^{2-}$, noting that the solubility of Na_2SO_4 in water is approximately 2 mol/L. For each added concentration of Na_2SO_4, the equilibrium concentration of the reactant, in this case, the chosen REE-complexed species, with respect to the solid precipitate was calculated. It should be noted that the thermodynamic calculations for high ionic strength, especially in the range of 1–2 mol/L of the precipitants added, may not be accurate enough to implement the results directly into practice without further analysis.

As shown in Figure 1a, when HCl or HNO_3 is used in the leaching process of REE-bearing ores, the dissolved free REE ion, Rn^{3+}, is subjected to complexation with either Cl^- or $NO_3{}^-$, and then, the solution is subjected to precipitation into sulfate by adding Na_2SO_4 to the solution. Figure 1b demonstrates the case in which H_2SO_4 is used to leach REE ores. In this case, free REE ion immediately complexes with sulfate to form sulfate complexes, which are then subjected to precipitation by adding Na_2SO_4.

An alternate model is shown in Figure 1c, in which complexed REE species with either Cl^- or $NO_3{}^-$ are re-complexed with sulfate, as Na_2SO_4 is added to precipitate to a desired sulfate. This is possible because chloride or nitrate complexes are easily converted into sulfate complexes under high concentrations of sulfate in the system. Figure 3 shows the ratio of $Rn(SO_4)_2{}^-$ to $RnCl_2{}^+$ as the concentration of $HSO_4{}^-$ increased from 10^{-4} to 2 mol/L. As seen in this figure, the chloride form of the Rn complex is predominant at low sulfate concentrations, while the ratio increases significantly with increasing sulfate concentration. As the concentration of sulfate exceeds 0.01, which is in the range of practical applications, the dominant species becomes the Rn–sulfate complex.

If such a reverse trend occurs before the precipitation, it is possible that the kinetic process of precipitation for such a process could be rather slow. To the best of the authors' knowledge, there is no proof of any of these theories.

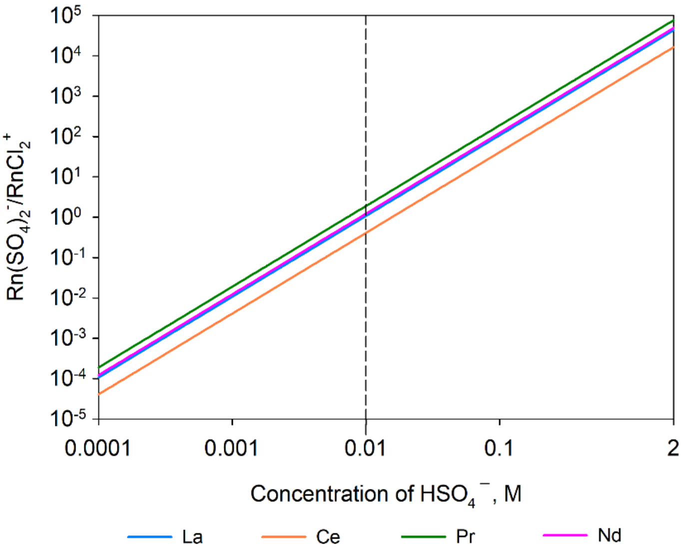


Figure 3. The ratio of $Rn(SO_4)_2^-$ to $RnCl_2^+$ as a function of HSO_4^- concentration at pH 1.

The precipitation of Rn^{3+} to the three sulfate precipitates was considered first, and the relevant equations considered are given in Equations (1)–(3).

$$2Rn^{3+} + 3HSO_4^- = <Rn_2(SO_4)_3> +3H^+ \tag{1}$$

$$2Rn^{3+} + 3HSO_4^- + 8H_2O = <Rn_2(SO_4)_3{\cdot}8H_2O> +3H^+ \tag{2}$$

$$Na^+ +Rn^{3+} + 2HSO_4^- + H_2O = <NaRn(SO_4)_2{\cdot}H_2O> +2H^+ \tag{3}$$

Almost identical equations as Equations (1)–(3) were written for pH 3, except instead of HSO_4^-, SO_4^{2-} was used because the pKa for sulfate is 2. First, the equilibrium constants were calculated. When the pH of the system is determined, the only remaining variables in these three equations are Rn^{3+} and HSO_4^-. As a result, the equilibrium concentration of Rn^{3+} can be calculated for a given concentration of HSO_4^- that is supplied to the system via Na_2SO_4. However, it should be noted that when the calculated equilibrium concentration value of the free REE ion is greater than the initial concentration in the leach liquor, precipitation does not occur.

When species other than free REE ion, such as $RnCl^{2+}$, $RnCl_2^+$, $RnNO_3^{2+}$, $RnSO_4^+$, and $Rn(SO_4)_2^-$ are concerned, the relevant chemical equations are written as follows: for example, $RnCl_2^+$ is precipitated into anhydrous sulfate, octa-hydrated sulfate, and sodium double salt, and the following precipitation equations are considered:

$$2RnCl_2^+ + 3HSO_4^- = <Rn_2(SO_4)_3> +3H^+ + 4Cl^- \tag{4}$$

$$2RnCl_2^+ + 3HSO_4^- + 8H_2O = <Rn_2(SO_4)_3{\cdot}8H_2O> +3H^+ + 4Cl^- \tag{5}$$

$$Na^+ +RnCl_2^+ + 2HSO_4^- + H_2O = <NaRn(SO_4)_2{\cdot}H_2O> +2H^+ +2Cl^- \tag{6}$$

Here, Equations (4)–(6) are analogous to Equations (1)–(3), given earlier. However, the important difference is the fact that these equations contain Cl^- as a product with precipitation, which plays an important role in the calculation of the equilibrium concentrations of REE-bearing species. The source of Cl^- in the system comes from HCl used to adjust the pH of the solution. Therefore, at pH 1, there will be at least 0.1 mol/L of Cl^- present, and as the precipitation proceeds, $RnCl_2^+$ will also produce Cl^-, as shown in Equations (4)–(6). These should be considered in the calculation of the final concentration of $RnCl_2^+$, which is in equilibrium with the precipitate. Therefore, the initial amounts of REEs dissolved in the leaching process are important for the accurate determination of the equilibrium concentrations of REE species. It should be noted that throughout the calculation, the pH of the system was assumed to be constant at a given value of pH 1 or pH 3 in this study.

Another important aspect to be considered in the calculation of the equilibrium concentration of REE-bearing species is that when Na_2SO_4 is added to increase the concentration of the precipitant, HSO_4^- or SO_4^{2-}, there are two moles of Na^+ present for each mole of HSO_4^- or SO_4^{2-}, which should be reflected in the calculation, as in the case of Equation (6).

These calculations were performed for the 10 REEs chosen in this study, as mentioned earlier (Table 1). The average concentration of the 10 elements in each addition of the precipitant, HSO_4^-, was calculated, and the resulting values are given in Table 2 and are also plotted in Figure 4, all of which were performed for pH 1. Similar calculations were carried out at pH 3, and the results were compared with those obtained at pH 1. The resulting plots are shown in Figure 5. Almost identical shapes of plots are given for these two pH values except that the amounts of precipitation are much higher at pH 3 than at pH 1. As seen in Table 3, the amount of precipitate at pH 3 is approximately 3–5 times that at pH 1. The precipitation of REEs into anhydrous and octa-hydrated sulfates was remarkably similar. In general, the degree of precipitation of these two systems is practically the same, although hydrated sulfates seem to be more stable than anhydrous sulfate. Most of the calculations carried out in this study also support the results shown in Figures 4 and 5. Remarkably, the precipitation of REEs as the sodium double salt is significantly more pronounced than in the other two systems, as shown in Figures 4 and 5 (Note that the dashed line shown in the following figures represents a concentration of 1 ppm as a reference).

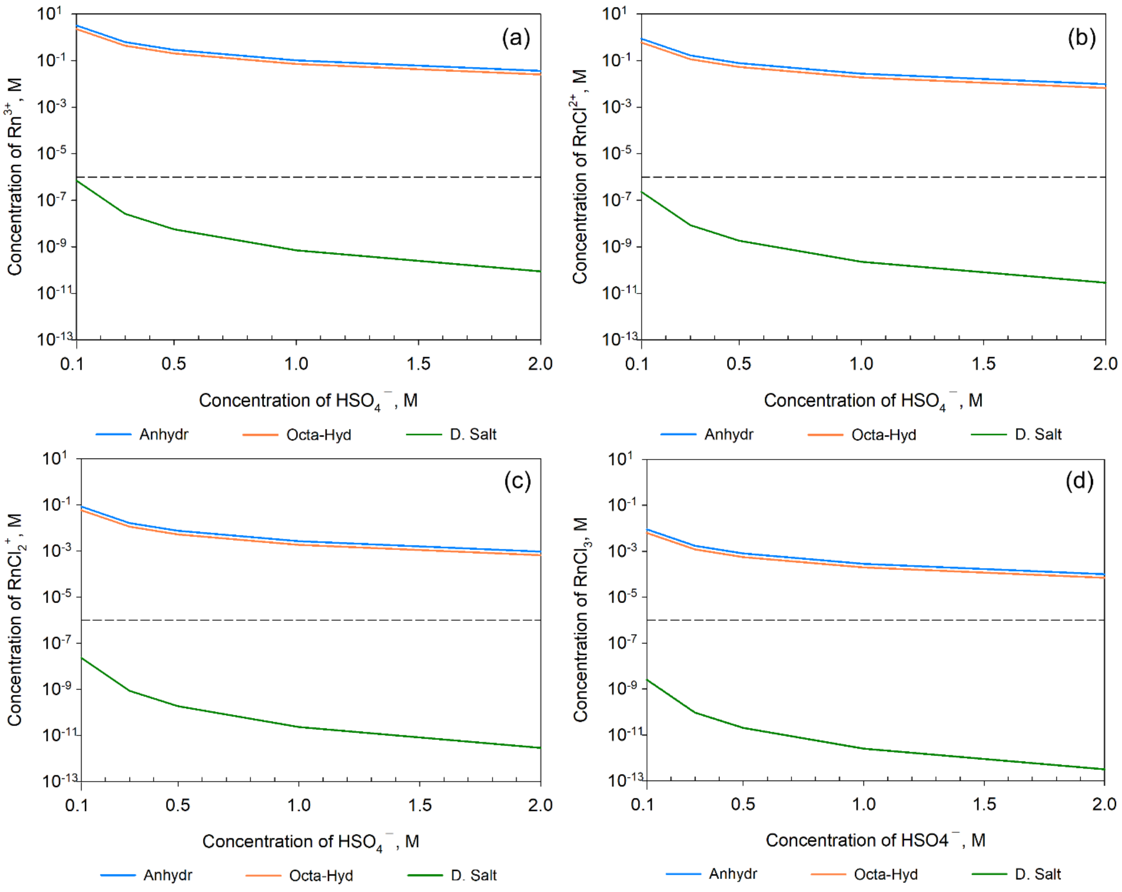


Figure 4. Graphical presentation of precipitation of Rn^{3+}, $RnCl^{2+}$, $RnCl_2^+$, and $RnCl_3$ into three sulfates, anhydrous, octa-hydrated, and sodium double salt at pH 1 with HCl (dashed line: 1 ppm line). (**a**) Rn^{3+} precipitates into the three products. (**b**) $RnCl^{2+}$ precipitates into the three products. (**c**) $RnCl_2^+$ precipitates into the three products. (**d**) $RnCl_3$ precipitates into the three products.

Table 2. Concentrations of Rn^{3+} in equilibrium with three sulfate precipitates; anhydrous, octa-hydrated, and sodium double salt at pH 1 with HCl.

Reaction	**$2Rn^{3+} + 3HSO_4^- = <Re_2(SO_4)_3> +3H^+$**					**$2Rn^{3+} + 3HSO_4^- + 8H_2O = <Rn_2(SO_4)_3 \cdot 8H_2O> +3H^+$**					**$Na^+ +Rn^{3+} + 2HSO_4^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O> +2H^+$**				
HSO_4^- Added (mol/L)	**0.1**	**0.3**	**0.5**	**1**	**2**	**0.1**	**0.3**	**0.5**	**1**	**2**	**0.1**	**0.3**	**0.5**	**1**	**2**
La	1.44×10^{-10}	2.77×10^{-11}	1.29×10^{-11}	4.55×10^{-12}	1.61×10^{-12}	1.38×10^{-14}	2.67×10^{-15}	1.24×10^{-15}	4.38×10^{-16}	1.55×10^{-16}	2.17×10^{-10}	8.05×10^{-12}	1.74×10^{-12}	2.17×10^{-13}	2.72×10^{-14}
Ce	1.04×10^{-9}	2.01×10^{-10}	9.33×10^{-11}	3.30×10^{-11}	1.17×10^{-11}	1.31×10^{-10}	2.53×10^{-11}	1.17×10^{-11}	4.15×10^{-12}	1.47×10^{-12}	4.13×10^{-7}	1.53×10^{-8}	3.31×10^{-9}	4.13×10^{-10}	5.17×10^{-11}
Pr	2.57×10^{-6}	4.94×10^{-7}	2.30×10^{-7}	8.12×10^{-8}	2.87×10^{-8}	2.24×10^{-10}	4.32×10^{-11}	2.01×10^{-11}	7.10×10^{-12}	2.51×10^{-12}	1.96×10^{-10}	7.24×10^{-12}	1.56×10^{-12}	1.96×10^{-13}	2.44×10^{-14}
Nd	6.09×10^{-7}	1.17×10^{-7}	5.45×10^{-8}	1.93×10^{-8}	6.81×10^{-9}	1.16×10^{-8}	2.22×10^{-9}	1.03×10^{-9}	3.65×10^{-10}	1.29×10^{-10}	4.82×10^{-14}	1.78×10^{-15}	3.86×10^{-16}	4.82×10^{-17}	6.02×10^{-18}
Sm	1.18×10^{-8}	2.28×10^{-9}	1.06×10^{-9}	3.74×10^{-10}	1.32×10^{-10}	1.11×10^{-7}	2.14×10^{-8}	9.95×10^{-9}	3.52×10^{-9}	1.24×10^{-9}	3.44×10^{-9}	1.27×10^{-10}	2.75×10^{-11}	3.44×10^{-12}	4.30×10^{-13}
Gd	1.43×10^{-7}	2.75×10^{-8}	1.28×10^{-8}	4.52×10^{-9}	1.60×10^{-9}	2.07×10^{-7}	3.99×10^{-8}	1.85×10^{-8}	6.55×10^{-9}	2.32×10^{-9}	5.33×10^{-9}	1.97×10^{-10}	4.26×10^{-11}	5.33×10^{-12}	6.66×10^{-13}
Tb	7.50×10^{-1}	1.44×10^{-1}	6.71×10^{-2}	2.37×10^{-2}	8.39×10^{-3}	5.00×10^{-1}	9.63×10^{-2}	4.47×10^{-2}	1.58×10^{-2}	5.59×10^{-3}	1.77×10^{-8}	6.55×10^{-10}	1.42×10^{-10}	1.77×10^{-11}	2.21×10^{-12}
Dy	1.64×10^{-3}	3.16×10^{-4}	1.47×10^{-4}	5.19×10^{-5}	1.83×10^{-5}	2.43×10^{-5}	4.68×10^{-6}	2.17×10^{-6}	7.69×10^{-7}	2.72×10^{-7}	4.25×10^{-7}	1.57×10^{-8}	3.40×10^{-9}	4.25×10^{-10}	5.31×10^{-11}
Ho	5.71×10^{0}	1.10×10^{0}	5.10×10^{-1}	1.80×10^{-1}	6.38×10^{-2}	5.00×10^{0}	9.62×10^{-1}	4.47×10^{-1}	1.58×10^{-1}	5.59×10^{-2}	6.20×10^{-6}	2.30×10^{-7}	4.96×10^{-8}	6.20×10^{-9}	7.76×10^{-10}
Er	2.60×10^{1}	5.00×10^{0}	2.32×10^{0}	8.21×10^{-1}	2.90×10^{-1}	1.71×10^{1}	3.29×10^{0}	1.53×10^{0}	5.41×10^{-1}	1.91×10^{-1}	8.69×10^{-9}	3.22×10^{-10}	6.96×10^{-11}	8.69×10^{-12}	1.09×10^{-12}
Avg.	3.24×10^{0}	6.24×10^{-1}	2.90×10^{-1}	1.03×10^{-1}	3.63×10^{-2}	2.26×10^{0}	4.35×10^{-1}	2.02×10^{-1}	7.15×10^{-2}	2.53×10^{-2}	7.08×10^{-7}	2.62×10^{-8}	5.66×10^{-9}	7.08×10^{-10}	8.85×10^{-11}

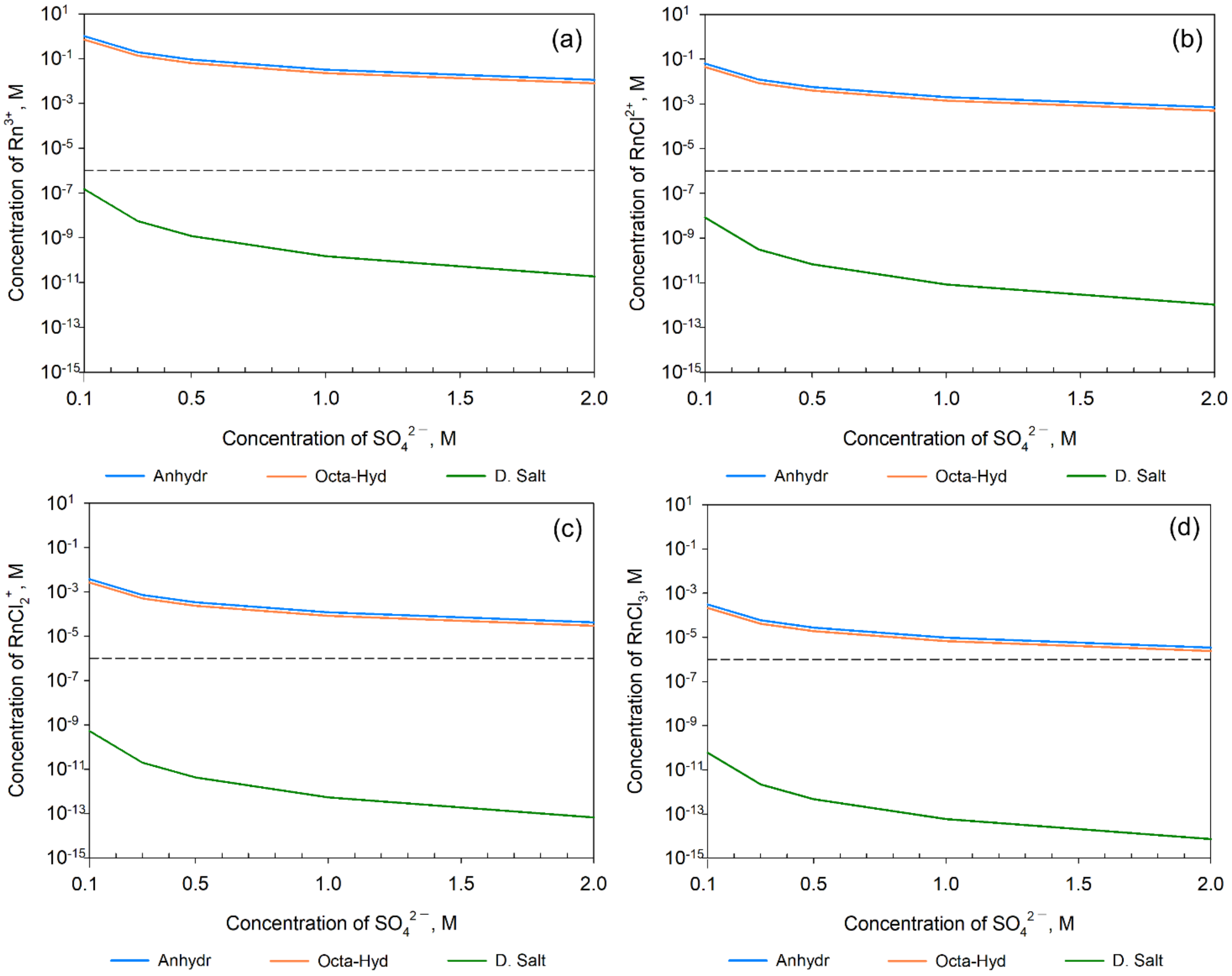


Figure 5. Graphical presentation of precipitation of Rn^{3+}, $RnCl^{2+}$, $RnCl_2^+$, and $RnCl_3$ into three sulfates, anhydrous, octa-hydrated, and sodium double salt at pH 3 with HCl (dashed line: 1 ppm). (**a**) Rn^{3+} precipitates into the three products. (**b**) $RnCl^{2+}$ precipitates into the three products. (**c**) $RnCl_2^+$ precipitates into the three products. (**d**) $RnCl_3$ precipitates into the three products.

Table 3. Average concentration of Rn^{3+} from the ten REEs selected when the concentration of sulfate or bisulfate is 1 mol/L in equilibrium with three sulfate precipitates at pH 1 and 3 with HCl. Concentration ratio at pH 1 to pH 3 are also given.

	pH 1	**pH 3**	**pH1/pH3**
Sulfate	1.03×10^{-1}	3.20×10^{-2}	3.20
Octa-Hyd	7.15×10^{-2}	2.23×10^{-2}	3.20
Double S	7.08×10^{-10}	1.50×10^{-10}	4.72

Sulfate: $Rn_2(SO_4)_3$; Octa-Hyd: $Rn_2(SO_4)_3{\cdot}8H_2O$; Double S:$NaRn(SO_4)_2{\cdot}H_2O$.

In Figure 6, the effect of the concentration of Cl^- is shown. Examples are taken from the precipitation of $RnCl^{2+}$ and $RnCl_3$. It should be noted that for each mole of $RnCl^{2+}$ precipitated, an additional mole of Cl^- would be released from $RnCl^{2+}$, but 3 moles of Cl^- would be added to the system from $RnCl_3$. In this demonstration, we considered the additional Cl^- added to the system to be 0.13, 0.5, 1, and 3, considering that the solubility of NaCl is slightly more than 6 mol/L in water. The value of 0.13 was chosen because at pH 1, 0.1 mol/L of Cl^- is already present, and 0.03 mol/L of Cl^- is added by the dissociation of the complex due to precipitation. It is seen that the adverse effect of this additional chloride on the amount of sulfate precipitation is remarkable.

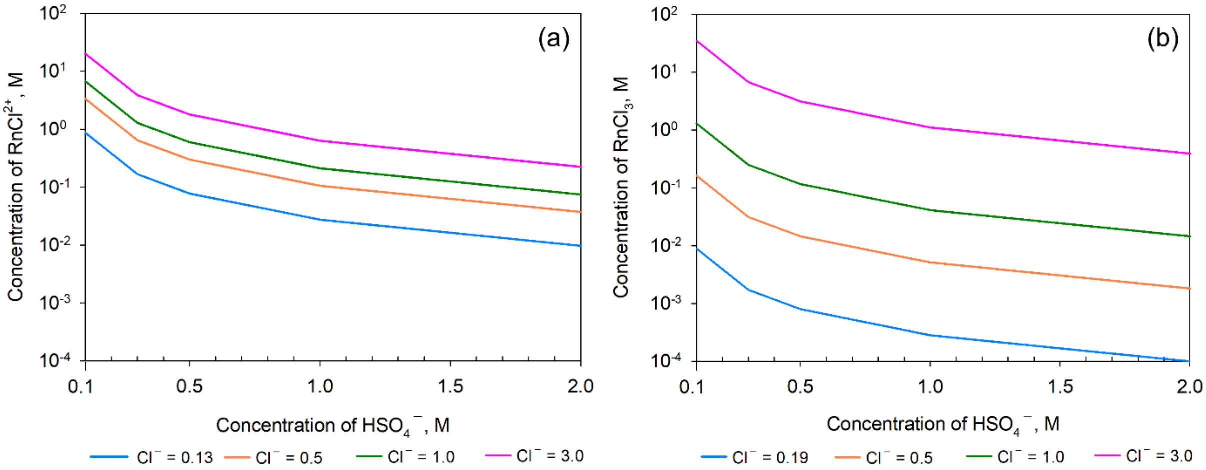


Figure 6. Effect of Cl^- on the precipitation of (**a**) $RnCl^{2+}$; and (**b**) $RnCl_3$.

In the calculation of the equilibrium concentrations with Rn-Cl complexes, as given in Equations (4)–(6), it has been assumed that the individual Cl complex is the predominant species among the Rn species considered at that time, and therefore all chloride released from the complexes come from that species.

It is generally shown that the precipitation of REEs into anhydrous sulfate is quite significant, especially when the addition of sulfate is more than 0.5 mol/L, which is acceptable from the practical aspect. As seen in Figure 7, LREEs show an acceptable precipitation into anhydrous sulfate, while the precipitation of HREEs is not significant, as their concentrations were calculated to be higher than 1 ppm.

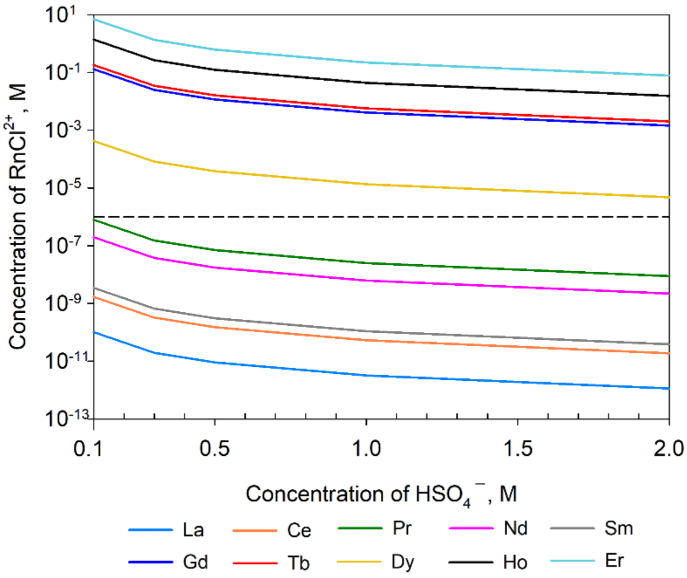


Figure 7. Concentrations of $RnCl^{2+}$ of the ten different REEs in equilibrium with $Rn_2(SO_4)_3$ at pH 1 with HCl.

The effect of sodium concentration on the precipitation of Rn^{3+} to sodium double salt is shown in Figure 8. As the concentration of Na^+ increases from 0.1 to 2 mol/L, the degree of precipitation of the Na double salt increases by nearly one order of magnitude, as seen in Figure 8. The degree of precipitation was more pronounced at pH 3 than at pH 1.

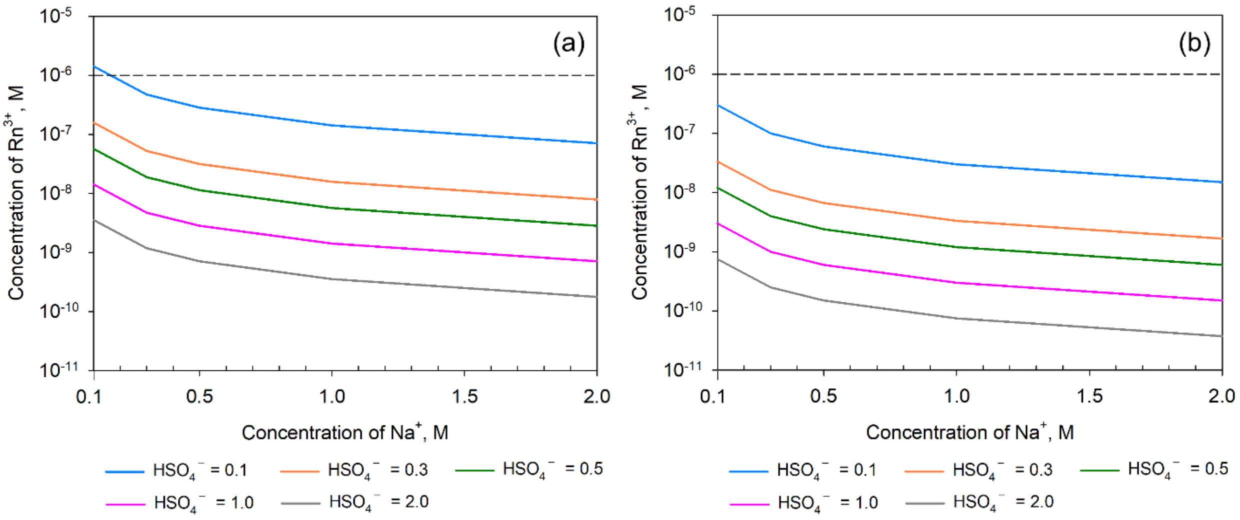


Figure 8. Effect of Na^+ on the precipitation of Rn^{3+} on Na double salt at pH 1 (**a**) and 3 (**b**).

4.2. Effect of NO_3^- on Precipitation Process

As discussed earlier, when HNO_3 is used in the leaching of REE-bearing sources, it is conceivable to assume that Rn^{3+} would be leached out first. However, as soon as the free REE ion is dissolved into the leach liquor, it will form a complex with NO_3^- to give either $RnNO_3^{2+}$ or $Rn(NO_3)_3$, as shown in Figure 1. A similar analysis of the precipitation of these dissolved species with sulfate ions was performed as in the case of the HCl system.

It should be noted that the precipitation of Rn^{3+} is identical for all three forms of sulfate precipitates, namely anhydrous, octa-hydrated, and sodium double salt precipitates. However, the precipitation of $RnNO_3^{2+}$ and $Rn(NO_3)_3$ into the sulfates is different because nitrate, instead of chloride, is involved in the precipitation process. However, the difference is very minor, as shown in Table 4 and Figure 9, where the precipitation of $RnCl^{2+}$ and $RnNO_3^{2+}$ into the sodium double salt are given to demonstrate the difference between these two systems.

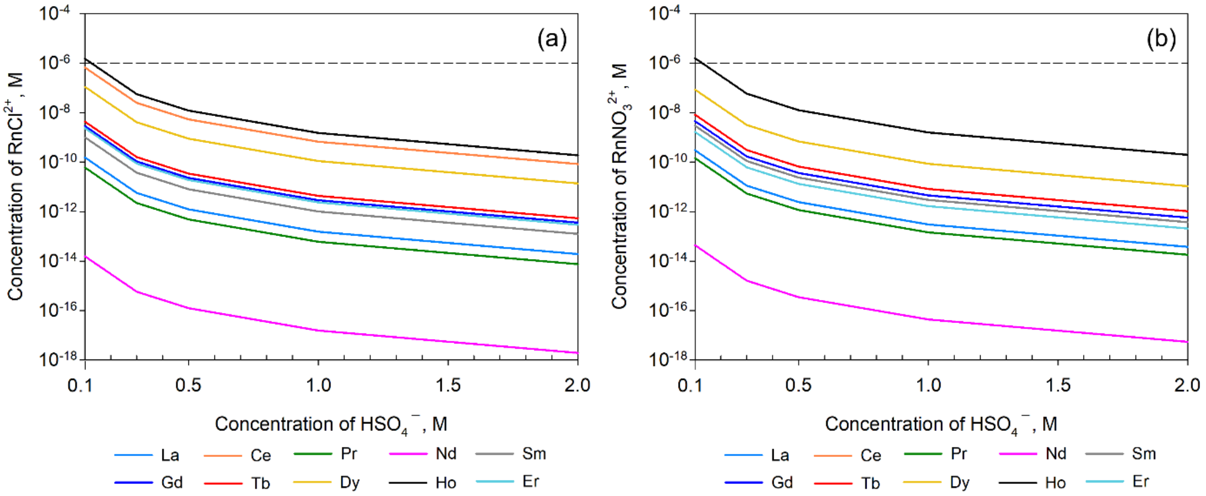


Figure 9. Equilibrium concentrations of (**a**) $RnCl^{2+}$ or (**b**) $RnNO_3^{2+}$ in equilibrium with sodium double salt at pH 1 with HSO_4^- (dashed line: 1 ppm line).

Table 4. Concentrations of $RnCl^{2+}$ or $RnNO_3{}^{2+}$ in equilibrium with sodium double salt at pH 1.

Reaction	**$Na^+ + RnCl^{2+} + 2HSO_4{}^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O> + Cl^- + 2H^+$**					**$Na^+ + RnNO_3{}^{2+} + 2HSO_4{}^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O> + NO_3{}^- + 2H^+$**				
$HSO_4{}^-$ Added (mol/L)	**0.1**	**0.3**	**0.5**	**1**	**2**	**0.1**	**0.3**	**0.5**	**1**	**2**
La	1.53×10^{-10}	5.67×10^{-12}	1.23×10^{-12}	1.53×10^{-13}	1.91×10^{-14}	3.00×10^{-10}	1.11×10^{-11}	2.40×10^{-12}	3.00×10^{-13}	3.75×10^{-14}
Ce	6.66×10^{-7}	2.47×10^{-8}	5.33×10^{-9}	6.66×10^{-10}	8.32×10^{-11}	1.57×10^{-6}	5.82×10^{-8}	1.26×10^{-8}	1.57×10^{-9}	1.96×10^{-10}
Pr	6.00×10^{-11}	2.22×10^{-12}	4.80×10^{-13}	6.00×10^{-14}	7.50×10^{-15}	1.44×10^{-10}	5.34×10^{-12}	1.15×10^{-12}	1.44×10^{-13}	1.80×10^{-14}
Nd	1.55×10^{-14}	5.74×10^{-16}	1.24×10^{-16}	1.55×10^{-17}	1.94×10^{-18}	4.33×10^{-14}	1.60×10^{-15}	3.47×10^{-16}	4.33×10^{-17}	5.42×10^{-18}
Sm	1.00×10^{-9}	3.71×10^{-11}	8.00×10^{-12}	1.00×10^{-12}	1.25×10^{-13}	2.96×10^{-9}	1.10×10^{-10}	2.37×10^{-11}	2.96×10^{-12}	3.70×10^{-13}
Gd	2.87×10^{-9}	1.06×10^{-10}	2.29×10^{-11}	2.87×10^{-12}	3.58×10^{-13}	4.53×10^{-9}	1.68×10^{-10}	3.62×10^{-11}	4.53×10^{-12}	5.66×10^{-13}
Tb	4.29×10^{-9}	1.59×10^{-10}	3.43×10^{-11}	4.29×10^{-12}	5.36×10^{-13}	8.23×10^{-9}	3.05×10^{-10}	6.59×10^{-11}	8.23×10^{-12}	1.03×10^{-12}
Dy	1.10×10^{-7}	4.08×10^{-9}	8.81×10^{-10}	1.10×10^{-10}	1.38×10^{-11}	8.52×10^{-8}	3.15×10^{-9}	6.81×10^{-10}	8.52×10^{-11}	1.06×10^{-11}
Ho	1.50×10^{-6}	5.57×10^{-8}	1.20×10^{-8}	1.50×10^{-9}	1.88×10^{-10}	1.57×10^{-6}	5.82×10^{-8}	1.26×10^{-8}	1.57×10^{-9}	1.97×10^{-10}
Er	2.34×10^{-9}	8.66×10^{-11}	1.87×10^{-11}	2.34×10^{-12}	2.92×10^{-13}	1.65×10^{-9}	6.09×10^{-11}	1.32×10^{-11}	1.65×10^{-12}	2.06×10^{-13}
Avg.	2.29×10^{-7}	8.48×10^{-9}	1.83×10^{-9}	2.29×10^{-10}	2.86×10^{-11}	3.25×10^{-7}	1.20×10^{-8}	2.60×10^{-9}	3.25×10^{-10}	4.06×10^{-11}

4.3. REEs Precipitation in the H_2SO_4 System

As seen in Figure 2, the precipitation of REE complexes in H_2SO_4 is somewhat different from that of the other two, namely HCl and HNO_3 systems. To be consistent, we begin at a given pH, that is, pH 1, but with H_2SO_4 in this case. Therefore, the concentration of HSO_4^- was already 0.1 mol/L, and Na_2SO_4 was added at 0.1, 0.3, 0.5, 1, and 2 mol/L to influence the precipitation of the REE-bearing species. Equilibrium concentrations of Rn^{3+} in equilibrium with the three sulfate precipitates were calculated, and the results are shown in Figure 10 and Table 5. Therefore, in the calculation of the equilibrium concentration with the addition of 0.1 mol/L of the precipitant, HSO_4^- at pH 1 or SO_4^{2-} at pH 3 by adding Na_2SO_4, the concentration of this precipitant was 0.2 in the case of pH 1 and 0.101 mol/L for pH 3.

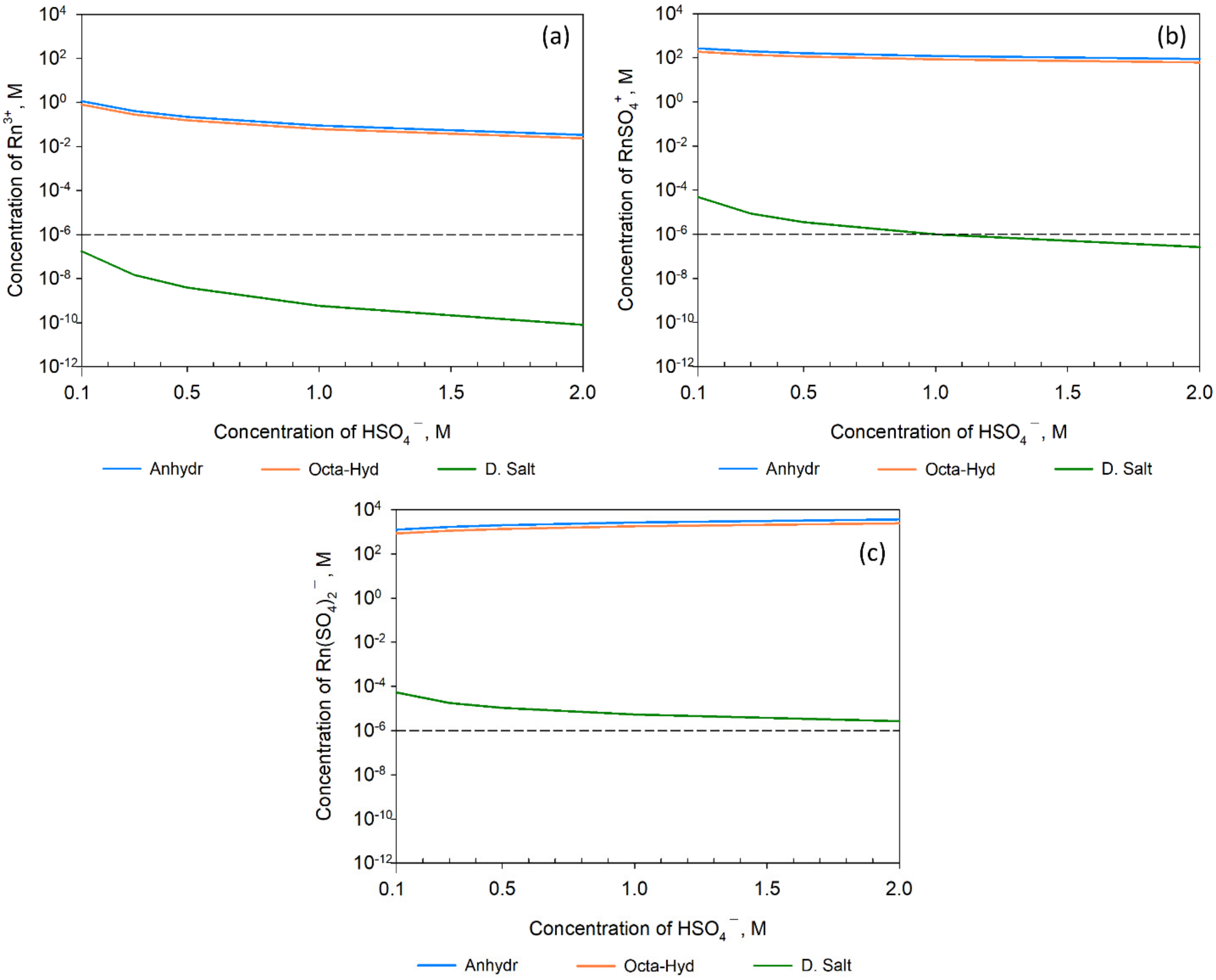


Figure 10. Graphical presentation of precipitation of Rn^{3+}, $Rn(SO_4)^+$, and $Rn(SO_4)_2^-$ into three sulfates, anhydrous, octa-hydrated, and sodium double salt at pH 1 with H_2SO_4. (**a**) Rn^{3+} precipitates into the three products. (**b**) $Rn(SO_4)^+$ precipitates into the three products. (**c**) $Rn(SO_4)_2^-$ precipitates into the three products.

Table 5. Concentration of Rn^{3+} in equilibrium with three sulfate precipitates; anhydrous, octa-hydrated, and sodium double salt at pH 3 with H_2SO_4.

Reaction	**$2Rn^{3+} + 3HSO_4^- = <Re_2(SO_4)_3> + 3H^+$**					**$2Rn^{3+} + 3HSO_4^- + 8H_2O = <Rn_2(SO_4)_3 \cdot 8H_2O> + 3H^+$**					**$Na^+ + Rn^{3+} + 2HSO_4^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O> + 2H^+$**				
SO_4^{2-} Added (mol/L)	**0.1**	**0.3**	**0.5**	**1**	**2**	**0.1**	**0.3**	**0.5**	**1**	**2**	**0.1**	**0.3**	**0.5**	**1**	**2**
La	4.42×10^{-11}	8.60×10^{-12}	4.00×10^{-12}	1.42×10^{-12}	5.02×10^{-13}	4.26×10^{-15}	8.29×10^{-16}	3.86×10^{-16}	1.37×10^{-16}	4.83×10^{-17}	4.52×10^{-11}	1.70×10^{-12}	3.67×10^{-13}	4.60×10^{-14}	5.76×10^{-15}
Ce	3.21×10^{-10}	6.24×10^{-11}	2.91×10^{-11}	1.03×10^{-11}	3.64×10^{-12}	1.19×10^{-10}	2.32×10^{-11}	1.08×10^{-11}	3.83×10^{-12}	1.35×10^{-12}	8.59×10^{-8}	3.22×10^{-9}	6.98×10^{-10}	8.75×10^{-11}	1.09×10^{-11}
Pr	7.90×10^{-7}	1.54×10^{-7}	7.15×10^{-8}	2.53×10^{-8}	8.96×10^{-9}	2.05×10^{-10}	3.98×10^{-11}	1.85×10^{-11}	6.55×10^{-12}	2.32×10^{-12}	4.06×10^{-11}	1.53×10^{-12}	3.30×10^{-13}	4.14×10^{-14}	5.18×10^{-15}
Nd	1.88×10^{-7}	3.65×10^{-8}	1.70×10^{-8}	6.01×10^{-9}	2.13×10^{-9}	1.05×10^{-8}	2.03×10^{-9}	9.47×10^{-10}	3.35×10^{-10}	1.19×10^{-10}	1.00×10^{-14}	3.76×10^{-16}	8.14×10^{-17}	1.02×10^{-17}	1.28×10^{-18}
Sm	3.64×10^{-9}	7.07×10^{-10}	3.29×10^{-10}	1.17×10^{-10}	4.13×10^{-11}	3.43×10^{-8}	6.66×10^{-9}	3.10×10^{-9}	1.10×10^{-9}	3.88×10^{-10}	7.15×10^{-10}	2.68×10^{-11}	5.81×10^{-12}	7.28×10^{-13}	9.11×10^{-14}
Gd	4.40×10^{-8}	8.54×10^{-9}	3.98×10^{-9}	1.41×10^{-9}	4.98×10^{-10}	6.38×10^{-8}	1.24×10^{-8}	5.77×10^{-9}	2.04×10^{-9}	7.23×10^{-10}	1.11×10^{-9}	4.16×10^{-11}	9.00×10^{-12}	1.13×10^{-12}	1.41×10^{-13}
Tb	2.31×10^{-1}	4.49×10^{-2}	2.09×10^{-2}	7.40×10^{-3}	2.62×10^{-3}	1.54×10^{-1}	2.99×10^{-2}	1.39×10^{-2}	4.94×10^{-3}	1.75×10^{-3}	3.68×10^{-9}	1.38×10^{-10}	2.99×10^{-11}	3.74×10^{-12}	4.68×10^{-13}
Dy	5.05×10^{-4}	9.82×10^{-5}	4.57×10^{-5}	1.62×10^{-5}	5.73×10^{-6}	7.48×10^{-6}	1.45×10^{-6}	6.77×10^{-7}	2.40×10^{-7}	8.48×10^{-8}	8.83×10^{-8}	3.31×10^{-9}	7.18×10^{-10}	8.99×10^{-11}	1.12×10^{-11}
Ho	1.76×10^{0}	3.41×10^{-1}	1.59×10^{-1}	5.63×10^{-2}	1.99×10^{-2}	1.54×10^{0}	2.99×10^{-1}	1.39×10^{-1}	4.93×10^{-2}	1.74×10^{-2}	1.29×10^{-6}	4.84×10^{-8}	1.05×10^{-8}	1.31×10^{-9}	1.64×10^{-10}
Er	7.99×10^{0}	1.55×10^{0}	7.24×10^{-1}	2.56×10^{-1}	9.06×10^{-2}	5.27×10^{0}	1.02×10^{0}	4.77×10^{-1}	1.69×10^{-1}	5.98×10^{-2}	1.81×10^{-9}	6.78×10^{-11}	1.47×10^{-11}	1.84×10^{-12}	2.30×10^{-13}
Avg.	9.98×10^{-1}	1.94×10^{-1}	9.03×10^{-2}	3.20×10^{-2}	1.13×10^{-2}	6.96×10^{-1}	1.35×10^{-1}	6.30×10^{-2}	2.23×10^{-2}	7.90×10^{-3}	1.47×10^{-7}	5.52×10^{-9}	1.20×10^{-9}	1.50×10^{-10}	1.87×10^{-11}

Two equations relevant to Figure 10c are given as follows, Equations (7) and (8):

$$2Rn(SO4)_2^- + H^+ = <Rn_2(SO_4)_3> + HSO_4^- \tag{7}$$

$$2Rn(SO4)_2^- + H^+ + 8H_2O = <Rn_2(SO_4)_3 \cdot 8H_2O> + HSO_4^- \tag{8}$$

The characteristics of precipitation described by these two equations are those of the decomposition reaction. As a result, adding HSO_4^- deters the precipitation reaction, resulting in an increase in the equilibrium concentration of $Rn(SO_4)_2^-$. This is clearly shown in Figure 10c.

It is noted that there are as many equilibrium concentrations as REE-bearing species in each system, including Cl^-, NO_3^-, or SO_4^{2-}. However, thermodynamic principles indicate that there should be only one equilibrium concentration for a given system. To answer this question, let us consider the precipitation of these complexes into the sodium double salt as an example. Figure 11 shows the precipitation from the three different acid systems based on the equations provided in Table 6 (Equations (9)–(17)), namely HCl, HNO_3, and H_2SO_4. As shown in this figure, there is no clear pattern in the precipitation order. The species that gives the lowest equilibrium concentration represents the final concentration for precipitation. The equilibrium concentration should also satisfy the relationships that determine the distribution of these species, as shown in Figure 2.

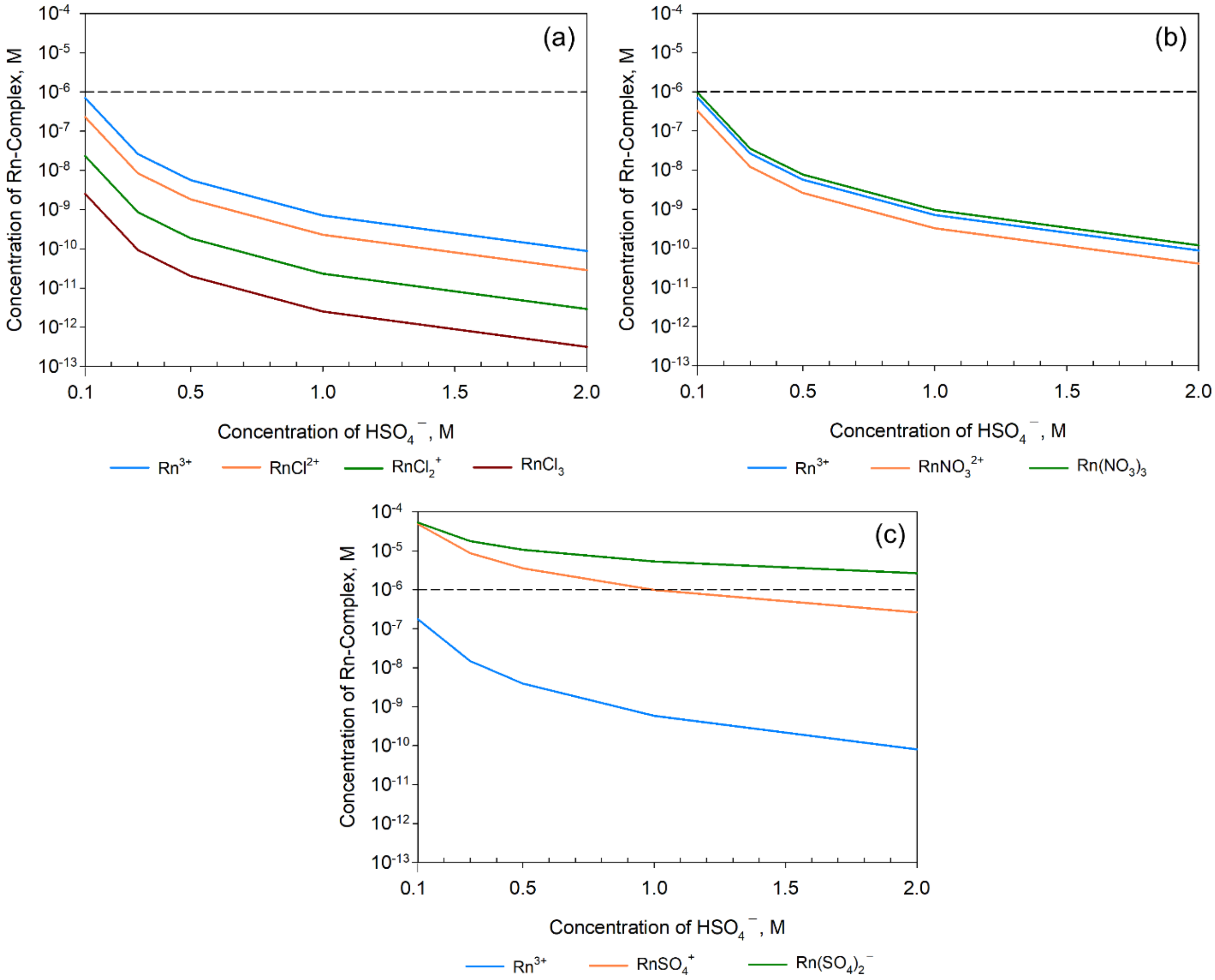


Figure 11. Equilibrium concentration of REE complexes with Na double salt at pH 1 in (**a**) HCl; (**b**) HNO_3; and (**c**) H_2SO_4 systems (dashed line: 1 ppm line).

Table 6. Precipitation equations for various REE complexes into Na double salt as shown in Figure 11.

$Na^+ + RnCl^{2+} + 2HSO_4^- = <NaRn(SO_4)_2 \cdot H_2O> + Cl^- + 2H^+$	(9)
$Na^+ + RnCl_2^+ + 2HSO_4^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O> + 2Cl^- + 2H^+$	(10)
$Na^+ + RnCl_3 + 2HSO_4^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O> + 3Cl^- + 2H^+$	(11)
$Na^+ + Rn^{3+} + 2HSO_4^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O> + 2H^+$	(12)
$Na^+ + RnNO_3^{2+} + 2HSO_4^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O> + NO_3^- + 2H^+$	(13)
$Na^+ + Rn(NO_3)_3 + 2HSO_4^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O> + 3NO_3^- + 2H^+$	(14)
$Na^+ + Rn^{3+} + 2HSO_4^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O> + 2H^+$	(15)
$Na^+ + Rn(SO_4)^+ + HSO_4^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O> + H^+$	(16)
$Na^+ + Rn(SO_4)_2^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O>$	(17)

As seen in Figure 11, the equilibrium concentration of REE-bearing species in the sodium double salt varies with different species. Again, the values given here are the averages of ten different REEs, as mentioned earlier. Figure 11a shows the equilibrium concentrations of various REE species in the Cl^- system. The precipitation of $RnCl_3$ yielded the lowest concentration, followed by $RnCl_2^+$, $RnCl^{2+}$, and Rn^{3+}. In contrast, in the NO_3^- system, the order was $RnNO_3^{2+}$, Rn^{3+}, and $Rn(NO_3)_3$. It is noted that in the nitrate system, the spread of the concentrations is very narrow, while for the Cl^- system, the spread is very wide, giving orders of magnitude difference between various species. In the SO_4^{2-} system, Rn^{3+} precipitates very well, followed by $Rn(SO_4)^+$ and $Rn(SO_4)_2^-$.

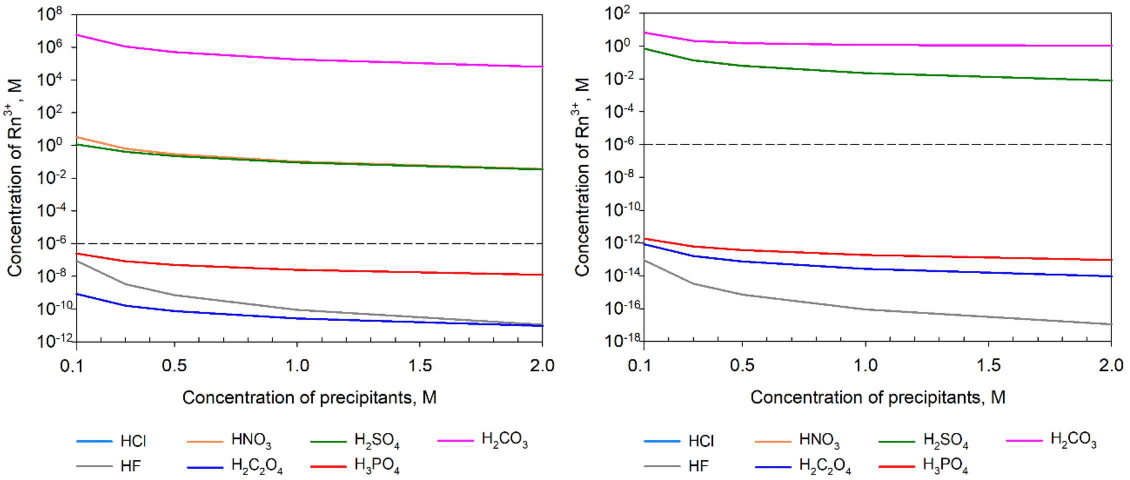
5. Comparison of Sulfate to Other Precipitants: Carbonate, Fluoride, Oxalate, and Phosphate Systems

The results obtained from various forms of REE precipitates with sulfate as the precipitant were compared with those of other precipitants, including carbonate, fluoride, phosphate, and oxalate. These precipitants have been used by numerous investigators and/or practitioners within the industry [36–47]. It is of particular interest to compare the unusual precipitation behavior of sodium double salt, which is a cationic double salt with an anionic double salt, fluoro-carbonate precipitate, which is frequently observed in real situations via a bastnaesite configuration.

The equations used in this section of the study were arranged to be comparable to those used in sulfate systems. For the convenience of the readers, the equations used in this section of the study were tabulated and listed immediately after relevant figures.

Carbonate or CO_2 is commonly used to precipitate REEs from the solution after increasing the pH of the solution to remove iron and other impurities prior to REE precipitation. When carbonate or CO_2 is added to water, the most stable species is H_2CO_3 at pH 1 or 3 because the pKa value for the system is 6.38 [22]. For comparison, the above three acid systems are chosen at pH 1 and pH 3, and the concentration of REEs in the solution is approximately 1000 ppm (i.e., 0.03 mol/L), as discussed earlier. H_2CO_3 was added at the same rate as done in the sulfate system.

The relevant equations for Rn^{3+} precipitates to carbonate are given in Table 7 as Equations (21) and (28) for pH 1 and 3, respectively. As can be seen in Figure 12, the precipitation of the three acid systems and carbonate system is impractical at these pH values because the equilibrium concentration of REEs is far above the critical line (1 ppm line), as shown in Figure 12.



(a) (b)

Figure 12. Equilibrium concentrations of Rn^{3+} for precipitation into $Rn_2(SO_4)_3$ at (**a**) pH 1; and (**b**) pH 3, and the results are compared with those of carbonate, fluoride, oxalate, and phosphate (dashed line: 1 ppm line).

Table 7. Precipitation equations of Rn^{3+} for precipitation into $Rn_2(SO_4)_3$ at pH 1 (a) and pH 3 (b) and the results are compared with those of carbonate, fluoride, oxalate, and phosphate (equations used in Figure 12).

$2Rn^{3+} + 3\,HSO_4^{-} = <Rn_2(SO_4)_3> +3H^{+}$	(18)
$2Rn^{3+} + 3\,HSO_4^{-} = <Rn_2(SO_4)_3> +3H^{+}$	(19)
$2Rn^{3+} + 3\,HSO_4^{-} = <Rn_2(SO_4)_3> +3H^{+}$	(20)
$2Rn^{3+} + 3\,H_2CO_3 = <Rn_2(CO_3)_3> +6H^{+}$	(21)
$Rn^{3+} + 3\,HF = <RnF_3> +3H^{+}$	(22)
$2Rn^{3+} + 3\,HC_2O_4^{-} = <Rn_2(C_2O_4)_3> +3H^{+}$	(23)
$Rn^{3+} + H_3PO_4 = <RnPO_4> +3H^{+}$	(24)
$2Rn^{3+} + 3\,SO_4^{2-} = <Rn_2(SO_4)_3>$	(25)
$2Rn^{3+} + 3\,SO_4^{2-} = <Rn_2(SO_4)_3>$	(26)
$2Rn^{3+} + 3\,SO_4^{2-} = <Rn_2(SO_4)_3>$	(27)
$2Rn^{3+} + 3\,H_2CO_3 = <Rn_2(CO_3)_3> +6H^{+}$	(28)
$Rn^{3+} + 3\,HF = <RnF_3> +3H^{+}$	(29)
$2Rn^{3+} + 3\,HC_2O_4^{-} = <Rn_2(C_2O_4)_3> +3H^{+}$	(30)
$Rn^{3+} + H_2PO_4^{-} = <RnPO_4> +2H^{+}$	(31)

Fluoride is one of the strong precipitants for REEs [45,46]. The relevant equations for the free REE ion precipitate with HF are given in Table 7, Equations (22) and (29) for pH 1 and pH 3, respectively. It shows the strongest precipitant for REEs at pH 3 and the second strongest at pH 1, as shown in Figure 12.

It should be noted that the REE precipitation with a mixture of fluoride and carbonate, often referred to as the fluoro-carbonate precipitate, resembles the precipitation of sodium double sulfate, in which the anions are responsible for the double salt precipitation, unlike the sodium double salt with sulfate, where two cations are responsible. In either case, synergy works to help the overall precipitation more effectively. This is illustrated in Figure 13.

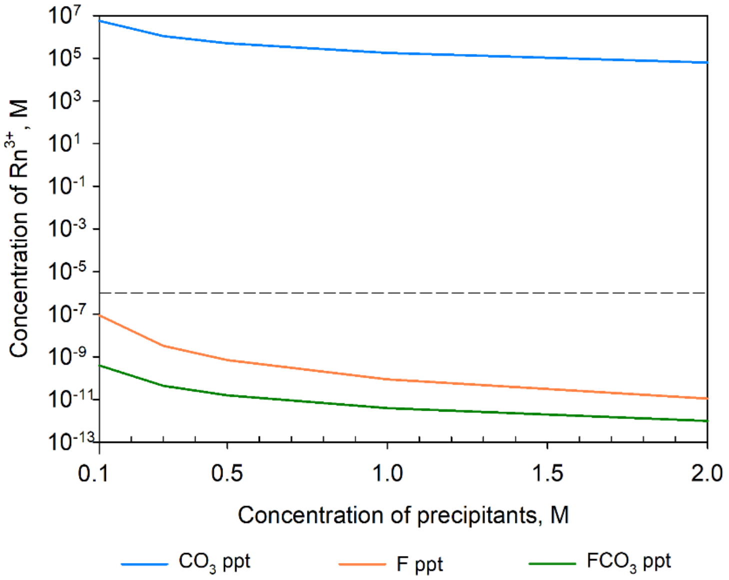


Figure 13. Equilibrium concentration of Rn^{3+} with carbonate, fluoride, and fluoro-carbonate precipitate at pH 1 (dashed line: 1 ppm line).

Oxalate and phosphate are also well known as strong precipitants of REEs. The precipitation equations are given as Equations (23) and (24) at pH 1 and Equations (30) and (31) at pH 3 for oxalate and phosphate, respectively. At pH 1, oxalate is the strongest precipitant considered in this study, and phosphate results in about 10^{-8} mol/L of the dissolved Rn^{3+} concentration, which is less than the 1 ppm level. At pH 3, these two precipitants gave almost similar precipitation powers for REEs, leaving 10^{-13} to 10^{-14} mol/L of dissolved Rn^{3+}.

As shown in Figure 13, REE carbonate precipitation is not as effective, and it is performed only at high pH values, with the advantage that the precipitated products are easily re-dissolved in mild acid [22,36]. Therefore, no attempt has been made to precipitate REEs at low pH with carbonate. However, fluoride is known to be one of the most effective precipitants of REEs, and numerous investigators and practitioners have shown its effectiveness in the past [17,45–47]; this has been demonstrated in this study, as shown in Figure 13. Table 8 presents the relevant equations used in the analysis (Equations (32)–(34)). It is clear that fluoro-carbonate is an effective anionic double salt exhibiting a synergistic characteristic in the precipitation of REEs.

Table 8. Precipitation equations of Rn^{3+} into various precipitants used in Figure 13.

$2Rn^{3+} + 3\,H_2CO_3 = \langle Rn_2(CO_3)_3\rangle + 6H^+$	(32)
$Rn^{3+} + 3\,HF = \langle RnF_3\rangle + 3H^+$	(33)
$Rn^{3+} + HF + H_2CO_3 = \langle RnFCO_3\rangle + 3H^+$	(34)

Based on the analysis of different precipitants, the selected precipitants that showed good precipitation ability, i.e., less than 1 ppm dissolved REE level, were compared, as shown in Figure 14. For practical purposes, only the results at pH 1 were considered. Oxalate and phosphate are the two efficient precipitants for REEs, as shown in Figure 14. Oxalate may be the most widely and frequently used precipitant for REEs, especially at low pH values. The solubility of sodium oxalate is rather low, approximately 0.3 mol/L. However, the solubility of oxalic acid is relatively high, more than 1 mol/L in water, and its pKa values are 1 and 4.2 [22].

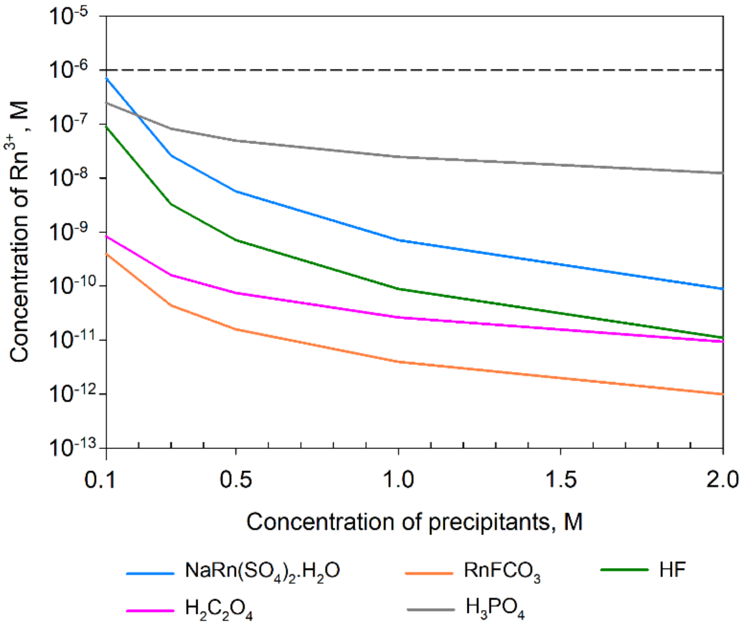


Figure 14. Equilibrium concentrations of Rn^{3+} for precipitation into $NaRn(SO_4)_2 \cdot H_2O$ at pH 1, and the results are compared with those of fluoride, fluoro-carbonate, oxalate, and phosphate (dashed line: 1 ppm line).

As seen in Figure 14, the precipitation of REEs of carbonate and sulfate is not likely to be a candidate for the preferential precipitation of REEs at low pH values. However, the double salt forms, either anionic or cationic, are very strong candidates for use in the separation of REEs from other elements at low pH, such as pH 1, as demonstrated in Figure 14. The equations used in these calculations are listed in Table 9 (Equations (35)–(39)).

Table 9. Precipitation equations Rn^{3+} for precipitation into $NaRn(SO_4)_2$ H_2O at pH 1 and the results are compared with fluoride, fluoro-carbonate, oxalate, and phosphate (equations used in Figure 14).

$Na^+ + Rn^{3+} + 2HSO_4^- + H_2O = <NaRn(SO_4)_2 \cdot H_2O> + 2H^+$	(35)
$Rn^{3+} + 3\,HF = <RnF_3> + 3H^+$	(36)
$Rn^{3+} + HF + H_2CO_3 = <RnFCO_3> + 3H^+$	(37)
$2Rn^{3+} + 3\,HC_2O_4^- = <Rn_2(C_2O_4)_3> + 3H^+$	(38)
$Rn^{3+} + H_3PO_4 = <RnPO_4> + 2H^+$	(39)

6. Conclusions

Ores and secondary sources bearing REEs are often treated with acids such as HCl, HNO_3, and H_2SO_4 to extract REEs into the solution. When free REE ions are dissolved in aqueous media, they are easily subjected to complexation with anions, such as Cl^-, NO_3^-, and SO_4^{2-}, present in the system derived from acids used in the leaching process. These anions play an important role in the subsequent precipitation processes and can help or hamper the precipitation process with various precipitants.

This study focused on the precipitation behavior of REEs with sulfate into three common precipitates, namely anhydrous, octa-hydrated, and Na double salt sulfate. Emphasis has been given on the synergistic effect of cationic and anionic double salts and their effectiveness in the precipitation of REEs at low pH values. It has been found that Na double salt sulfate is the most preferred precipitate among the three sulfate precipitates, whose degree of precipitation is comparable with other strong precipitants such as fluoride, oxalate, and phosphate.

Author Contributions: Conceptualization, K.N.H. and R.K.; methodology, K.N.H. and R.K.; software, K.N.H. and R.K.; validation, K.N.H. and R.K.; formal analysis, K.N.H. and R.K.; investigation, K.N.H. and R.K.; resources, R.K.; data curation, K.N.H. and R.K.; writing—original draft preparation, K.N.H.; writing—review and editing, K.N.H. and R.K.; visualization, K.N.H.; supervision, K.N.H.; project administration, K.N.H. and R.K.; funding acquisition, R.K. All authors have read and agreed to the published version of the manuscript.

Funding: Part of the study has been supported by the Korea Evaluation Institute of Industrial Technology funded by the Ministry of Trade, Industry and Energy in Korea (Project No.: 20010817, 21-9806).

Acknowledgments: The authors extend their appreciation to the Minerals staff, especially Anker He, for their assistance and encouragement throughout the process. Rina Kim is also grateful for the support of the Korea Evaluation Institute of Industrial Technology funded by the Ministry of Trade, Industry and Energy in Korea (Project No.: 20010817, 21-9806).

Conflicts of Interest: The authors declare no conflict of interest in relation to this paper.

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