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Description of strontium precipitation in highly concentrated nitric acid

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Abstract

The precipitation of strontium in highly concentrated nitric acid is often used in standard radiochemical methods for ^{90}Sr separation. In this work, the description of Sr behavior in such conditions was studied in the point of speciation simulation. Standard speciation method based on Phreeqc software was considered but two problems underlined the limits of this approach to study this process: inappropriate ionic strength correction model (for I>10 M) and the particular dissociation of nitric acid. To overcome these issues, a multipurpose-fitting routine, Minuit, was used to fit chemical model parameters. A polynomial expression was also added to the model in order to take into account nitric acid dissociation. This alternative was proved successful to calculate the Sr precipitate in highly concentrated nitric acid. Comparison was made with the results obtained with Design of Experiment methodology.

Keywords

Concentrated nitric acid, Multipurpose-fitting routine, Phreeqc, Speciation, Strontium

Introduction

The precipitation of strontium in highly concentrated nitric acid is the key step of a standard radiochemical method for isolation of strontium in order to quantify Sr-90 in different types of samples [1–3]. The procedure has been used for decades for environmental, food and radioactive waste samples [4–7]. This step is dedicated to the separation of strontium from its chemical homolog, calcium. If Ca is present in the final precipitate, this non-radioactive interferent leads to error on the Sr precipitation yield, often determined by gravimetry that is then used for activity correction. The separation is based on their different behavior in concentrated nitric acid, as Sr precipitates when Ca stays in solution. However, previous studies have shown that part of Ca could be carried with Sr [8, 9]. Therefore, the precipitation of Sr has to be repeated to insure the complete elimination of Ca [10]. Even with this repetition, this can be still problematic for samples with high Ca content, such as concrete.

In a previous article [11], we demonstrated the advantage of replacing fuming nitric acid, mostly suggested for this method to characterize Sr-90 in radioactive waste. Our study enabled to work with concentrated nitric acid at 69 % (15.9 M), more convenient and less harmful for operators while maintaining similar analytical performance in terms of selectivity and separation yields. An optimal HNO_3 concentration of 63 % (14.2 M), maximizing Sr precipitate while minimizing Ca precipitate, was determined by using Design of Experiment (DoE). Two models describing respectively the percentage of Sr and Ca precipitates depending on the concentration of nitric acid and the total volume of the solution were successfully determined with this methodology. Due to the nature of the models, their validity is strictly limited to the experimental domain studied including nitric acid concentrations between

48 % (10.2 M) and 64 % (14.5 M). Despite the efficiency of this improved method for Sr

quantification, the models obtained are purely empirical and do not give any information about the chemical aspects of the process. Therefore, a better understanding of the chemical phenomena at work in this protocol would be highly desirable, in particular the possible interactions between Sr and Ca precipitations and the role of the very high ionic strength imposed by the nitric acid concentration of the samples.

To this aim, we first performed additional experiments in order to study, under our chemical conditions, two experimental facts previously observed by other authors: Ca carrying [3, 9] and change of the Sr precipitate speciation [12], by introduction of HNO_3 in the solid, as a function of nitric acid concentration. Then, disregarding the Ca carrying effect, we examined the contribution that speciation softwares of different kinds could bring to the understanding of our samples.

Speciation modeling is often implemented in geochemical studies to predict and better understand the behavior of analytes in different environments but has also proven to be efficient to describe radiochemical processes. Gautier et al. [13] and Rosskopfova et al. [14] were able to understand and optimize Ni separation for Ni-63 measurement by studying the effects of pH and ammonia concentration variations. Garcia et al. [15] also presented speciation of Ni in cementitious systems used for nuclear waste immobilization and underlined the influence of different ligands present in the solution on Ni mobility. The focus on key steps of separation allows to understand their mechanisms and determine optimal conditions (pH, concentration, critical interferents, etc.) but can also highlight bias in a protocol and solve it such as shown by Habibi et al. [16] for Cm separation process. In these articles, different softwares have been used, for example Chess, Phreeqc and Medusa, but a great number of other options are available. In this study, we first used a common speciation software, Phreeqc, which performs speciation calculations of complex solutions, based on thermodynamic data compiled in a database and assuming some specific ionic strength corrections. In a second step, adjustment of the ionic strength correction parameters and of the equilibrium constants to the experimental data previously collected was attempted by the use of a multipurpose fitting routine. The results highlighted the inability of these two approaches to correctly describe the speciation of nitric acid as measured experimentally by Ruas et al. [17] and the dramatic consequence this has in view of prediction of the Sr precipitation data. We turned to a hybrid model, which is based on an empirical description of HNO_3 speciation plus a set of chemical equilibria describing Sr complexation and precipitation, including adduct formation. This option proved to be successful, allowing a good description of our experimental results, thus supporting our assumptions. Finally, advantages and disadvantages of this hybrid approach are discussed, under the light of the DoE previous results.

Experimental, speciation and fitting programs

Reagents and equipment

The anhydrous $Sr(NO_3)_2$ (Merck) and the tetrahydrate $Ca(NO_3)_2.4H_2O$ salts (Fisher Chemical) were used as received. For sample preparation, water of ultra-pure quality from a Milli-Q purification system (Millipore, France) and nitric acid (for analysis from Supelco supplier with concentration of 69 %) were used. $Sr(NO_3)_2$ precipitates were washed with n-hexane (Pestipur from Carlo Erba Reagents). pH was measured with a SevenMulti device (Mettler). Ca and Sr yields were determined by ICP-AES (as presented in [11]) or by gravimetry. Nitrate concentrations were determined by ion chromatography (ICS2100, Thermo Fisher Scientific).

Experimental methods

The first set of experiments aimed to verify the impact of Sr amount onto Ca precipitation at different HNO_3 concentrations. Nitric acid was added to aqueous solutions of $Sr(NO_3)_2$ and/or $Ca(NO_3)_2.4H_2O$. Then, the amount of precipitate was quantified by measuring the remaining Sr and/or Ca in the supernatants. The experimental procedure is strictly identical to the one followed previously and which is described in details in [11]. All experiments were done at room temperature.

The second set of experiments intended to confirm the presence of HNO_3 adducts in $Sr(NO_3)_2$ precipitate as described in [12]. Aqueous solutions of $Sr(NO_3)_2$ were prepared and different amounts of nitric acid were added to vary nitric acid concentrations. After shaking of the solutions, the formed precipitates were filtered on disk paper filters placed on a vacuum system. Then the precipitates were washed with 2 x 2 mL of n-hexane and let dried for, at least, 4 h. Known amounts (around 40 mg) of white solids obtained were dissolved in 30 mL of water and the pH was directly measured in the obtained samples. A decrease in pH is indicative of HNO_3 presence in the precipitate. The possibility that the presence of HNO_3 is not due to adduct formation but to occluded solution in crystal cracks, as mentioned in [18], is ruled out by the following test. The effectiveness of the washing was tested by comparing the pH measurement of commercial salt put in nitric acid and washed as described in the method above to the pH measured according to the complete process. The result showed a higher pH (pH = 5.6) for commercial salt which confirmed the efficiency of the washing. After two different dissolutions, in water and in 2 % HNO_3, concentrations of nitrate and Sr were respectively determined by IC and ICP-AES.

Speciation and fitting programs, data set

Speciation programs including databases of thermodynamic constants can be applied to calculate the comprehensive speciation of complex solutions. Two softwares were considered for this work: Chess and Phreeqc [19, 20]. Chess has a user-friendly interface making it easy to handle. The model of ionic strength correction is chosen with a list-box including five options (no correction, Truncated-Davies, Davies, Debye-Hückel and B-dot) and their parameters are given in the database. Even if the different equations are described in [21], calculations are not clear because the program is closed-source which can create difficulties to study complex system. Phreeqc gives more freedom and the parameters used for each calculation are well described and changeable [22]. After tests on the two programs, Phreeqc was chosen for this study.

Several ionic strength corrections are available for use with Phreeqc, in particular the well-known Pitzer or Specific Interaction Theory (SIT) models but also the so-called B-dot and Debye-Hückel empirical equations [23]. These models have different domains of validity, for example the Debye-Hückel equation would not be valid already above 0.1 M, while the B-dot model would diverge above 3 M only [24]. Therefore, none of these models are known to correctly describe the very high ionic strength effects we encounter in our experiments (i.e. above 10 M), even Pitzer is limited at 6 M [25]. Conversely, leaving the question of ionic strength corrections out of the calculations is also bound to fail so a compromise must be found. Among the ionic strength options within Phreeqc, the Pitzer and SIT models require a great number of parameters, most of them not being tabulated in any database (for example mean activity coefficient and ion interaction parameters related to Sr) [26–28]. Therefore, we have chosen the B-dot model, according to Equation 1, because its validity domain is larger than Debye-Hückel, together with the Thermoddem 2017 database [29]:

$$log\gamma_i = \frac{-Az_i^2\sqrt{I}}{1+a_iB\sqrt{I}} + \dot{B}\,I \qquad \text{(Equation 1)}$$

Where γ_i, z_i and a_i are the activity coefficient, the charge and the ionic radius of species i, respectively, while A, B and $\dot{B}$ are parameters tabulated in Thermodddem, as listed in Table 1, and I is the total ionic strength. In the following, equilibrium constants noted with superscript "°" correspond to thermodynamic ones.

Table 1: Parameters of the database Thermoddem 2017 and the fitted values with MINUIT [29], *fixed value (see text)

Parameter	**Thermoddem**	**MINUIT**

	2017	**HNO_3 dissociation**
$K°_{HNO3}$ [M^{-1}]	20.09	170
A [$M^{-1/2}$]	-13.1	-1.43
B [$M^{-1/2}$*$Å^{-1}$]	0.102	1*
$\dot{B}$ [M^{-1}]	-3.56	0.091
$å_{H+}$ [Å]	9.00	9.0
$å_{NO3-}$ [Å]	3.00	2.76
$å_{Sr2+}$ [Å]	5.00	-

Within the configuration including Thermoddem and B-dot, Phreeqc only allows speciation calculations. Adjustments of equilibrium constant values and parameters of Equation 1 present in Thermoddem in order to match experimental data are only possible by a manual lengthy trial and error procedure, which is inapplicable in case of the numerous chemical equilibria and species involved in this work. Eventually, Phreeqc can be connected to scripts (for example in Python or in C++) in order to allow data fittings [30, 31]. However, other solutions do exist and are also relevant according to other experience of model fitting [32, 33].

In this work, the Minuit routine facility was used to act as a substitute to a fitting script coupled to Phreeqc. Minuit is a multi-purpose fitting routine, developed at CERN [34]. We applied it together with the C++ computer language (Minuit C++ package, implemented on a virtual machine in a PC). This option will be called the Minuit-Phreeqc package in the following. It was checked that the C++ program written could perfectly reproduce the Phreeqc calculations using parameters and values available in the Thermoddem database.

More interestingly, multi-purpose fitting routines such as Minuit also offer the possibility to adjust experimental data sets to any analytical equations, and in particular to models mixing empirical and chemical equations, as the classical mass action law and mass balance equations. This makes a sensible difference as compared to Phreeqc alone, and this option will be termed Minuit-mix. This option can also be realized with the addition of module to Phreeqc with different programming languages (Python, Fortran, C) [30].

In either of the two options Minuit-Phreeqc or Minuit-mix, a system of mathematical equations is written by use of the mass action law and mass balance equations and, eventually, additional empirical equations. The mathematical relationship between the calculated concentrations of species of interest and the chemical conditions (i.e. initial concentrations of reactants, temperature etc.) can be derived, as a function of the parameters of the model, such as thermodynamic equilibrium constants, parameters of the B-dot equation and any other parameters involved in the empirical equations. The Minuit routine then automatically performs adjustments of this analytical equation to the data set by implementation of a multi-parameter least-square procedure. The agreement between the fit and the experimental data is assessed through the χ^2 value as described in Equation 2.

$$\chi^2 = \frac{\sqrt{\sum(X_{exp}-X_{cal})^2}}{n} \qquad \text{(Equation 2)}$$

Where X_{exp} and X_{cal} are the experimental and calculated values, respectively, and n is the number of data points.

Results

New experimental results of this work

Calcium co-precipitation phenomenon

Experiments performed in order to quantify Ca and Sr precipitates under different chemical conditions showed that Sr recovery is similar with or without Ca, while Ca does not precipitate without the presence of Sr, as illustrated in Table 2. These data are a clear evidence that Ca is carried with Sr.

Table 2: Comparison of the precipitation recovery for two different initial conditions with Sr and Ca, Sr only and Ca only. Uncertainties are at 10 % at k=2.

Cations in solution	**HNO_3 [M]**	**Sr^{2+} [M]**	**Ca^{2+} [M]**	**[%] Sr precipitate**	**[%] Ca precipitate**
Sr^{2+}, Ca^{2+}	11.6	0.035	0.028	93	14
	12.6	0.041	0.032	96	9
Sr^{2+}	11.6	0.035	-	87	-
	12.6	0.041	-	97	-
Ca^{2+}	11.6	-	0.028	-	< 1 %
	12.6	-	0.032	-	< 1 %

In early publication, Willard et al. [3] noticed the co-precipitation of Ca with Sr by observing that the proportion of Ca in the precipitate slightly decreased as the standing time before filtration was increased. Co-precipitated Ca would indeed dissolve again in the solution. They also determined the solubility of Ca alone in nitric acid at various concentrations and highlighted that it drops above concentration of 19 M HNO_3 (26 mg/mL at 18 M to 5 mg/mL at 20 M at room temperature) which implies a Ca precipitation only at very high nitric acid concentration. Later, Sunderman and Meinke [9] confirmed the observation and underlined that Ca co-precipitation is more important with Sr than with Ba confirming the strong carrying effect. In their work on HNO_3 dissociation, Ruas and co-workers also observed that $Ca(NO_3)_2$ is fully dissociated up to 11 M [17]. With the nitric acid concentration used in our experiment (maximum of 14.05 M, Table S 1 in Supplementary Information), Ca precipitation would not occur without the presence of Sr.

Presence of HNO_3 adducts

The results of experiments, presented in Table 3, confirmed the presence of different species in the precipitate: $Sr(NO_3)_2$ and HNO_3 adducts. The percentage of adduct is calculated from the NO_3^-/Sr ratio obtained by IC and ICP-AES measurements. The $Sr(NO_3)_2.2HNO_3$ adduct is considered for the calculation presented in Table 3 as it has been highlighted by Mishina et al. in 2014 [18]. The presence of adducts is evidenced through the decrease in pH as the NO_3^-/Sr ratio increases. The HNO_3 adduct is a minority but its fraction increases to approximately 5 % for nitric acid concentration above 12 M. If the simple adduct $Sr(NO_3)_2.HNO_3$ is considered as the only additional species, the calculated fraction of this adduct reaches around 10 % for the nitric acid concentration above 12 M. Also with this experiment, there is no certitude if the adduct contains one or two HNO_3 molecules or a mix of both or even more. However, it shows a low proportion that is not higher than 10 %.

Table 3: Calculated $Sr(NO_3)_2$ and $Sr(NO_3)_2.2HNO_3$ with the ratio of NO_3^-/Sr measured depending on nitric acid concentration. Uncertainties are given in absolute values at k=2.

C HNO_3 [M]	**pH [-]**	**$Sr(NO_3)_2$ [%]**	**$Sr(NO_3)_2.2HNO_3$ [%]**
10	4.6 ± 0.6	98 ± 2	2 ± 2
12	4.3 ± 0.2	94 ± 2	6 ± 2
14	3.6 ± 0.3	95 ± 2	5 ± 2
16	3.9 ± 0.6	95 ± 3	5 ± 3

The results obtained confirmed the work of Mishina et al. [35] on the presence of adducts. Their study of the system Sr-HNO_3-H_2O established a curve describing the solubility of Sr depending on nitric acid concentration [35]. The curve drops to low solubility values (under 0.1 M) above 8 M nitric acid concentration. They also proposed the formation of HNO_3 adducts, which was confirmed in a second publication where they used the measurement of Sr/NO_3^- ratio in a similar concept than in this study but with different techniques [18].

Consequently, the presence of HNO_3 adducts is confirmed but the ratio compared to the simple salt was found low. Mishina et al. [18] highlighted that the complex formed with HNO_3 is not stable. It was confirmed in this work by the observation of acid release already after one night with humidified pH paper placed above the salt in a sealed flask. The instability of the compound could explain the fact that no equilibrium constant has been determined yet.

Speciation results using Phreeqc or Minuit-Phreeqc

Nitric acid dissociation description

Within the frame of radiochemical measurements, the nitric acid concentration in the samples is rather high (> 10 M) as compared to Sr amounts (< 0.04 M). The presence of Sr(II) as a soluble species or Sr precipitation have thus a negligible influence on the overall ionic strength (less than 1 % under the chemical conditions of the present work). Therefore, the chemistry at work in the samples is driven by the ionic strength imposed by HNO_3. The particular behavior of nitric acid in solution is highlighted by the experimental data of Ruas et al. [17] where the concentration of free NO_3^- species as a function of the total concentration of HNO_3 is deduced from Raman spectroscopy. It was shown that HNO_3 is a weak acid, which dissociation constant can be modelled by use of the BIMSA (BIding Mean Spherical Approximation) theory, with a very good accuracy up to 6 M. However, between 7 M and 13.6 M, which is the maximum HNO_3 concentration investigated by Ruas and co-workers, even the BIMSA approach cannot reproduce the variation of free and associated nitrate species as a function of the initial concentration of HNO_3. This discrepancy was ascribed, at least in part, to the appearance of species such as NO_2^+ and HNO_2 [17, 36]. Therefore, in the range of initial HNO_3 concentrations of our work (from 10.53 M up to 14.05 M), it is unlikely that Phreeqc would be able to properly describe the data of Ruas and co-workers by only considering H^+, NO_3^- and HNO_3 species in solution, according to the chemical equilibrium below:

$$HNO_3 \leftrightarrows H^+ + NO_3^- \qquad \text{(Equilibrium 1)}$$

As a first obvious reason for this expected discrepancy, note that the dissociation constant value inserted in Thermoddem for eq. 1 ($\log_{10} K°_{HNO3\text{-}TD} = 1.303$ M^{-1}, i.e. $K°_{HNO3\text{-}TD} = 20.09$ M^{-1}) [37] is more than a factor 1.5 higher than the one derived by Ruas et al. ($K°_{HNO3\text{-}Ruas} = 11.9$ M^{-1}) [17]. Phreeqc speciation calculations performed with $K°_{HNO3\text{-}TD} = 20.09$ M^{-1} and using Equation 1 for ionic strength corrections together with the tabulated parameters as in **Erreur ! Source du renvoi introuvable.** clearly evidenced this expected disagreement, already above 4 M HNO_3, as displayed in Figure 1**Erreur ! Source du renvoi introuvable.** ($\chi^2 = 0.4459$). Even by changing $K°_{HNO3\text{-}TD}$ to the value derived by Ruas and co-workers, the discrepancy between the experimental data of Ruas et al. and Phreeqc calculations remains high (see Figure 1, $\chi^2 = 0.3332$). As described by Ruas et al. [17], until approximately 4 M, HNO_3 behaves as a strong acid and then as a weak acid to reach a maximum dissociation at 9 M. The parameters of Thermoddem are then well suited to describe the dissociation up to 9 M with a χ^2 of 0.2126 on this portion (Figure 1, green curve). The $K°_{HNO3\text{-}Ruas}$ value gives an even better fit for this part with a χ^2 of 0.1084 (red curve). However, above 9 M, the model with both equilibrium constant values fails to calculate the experimental dissociation.

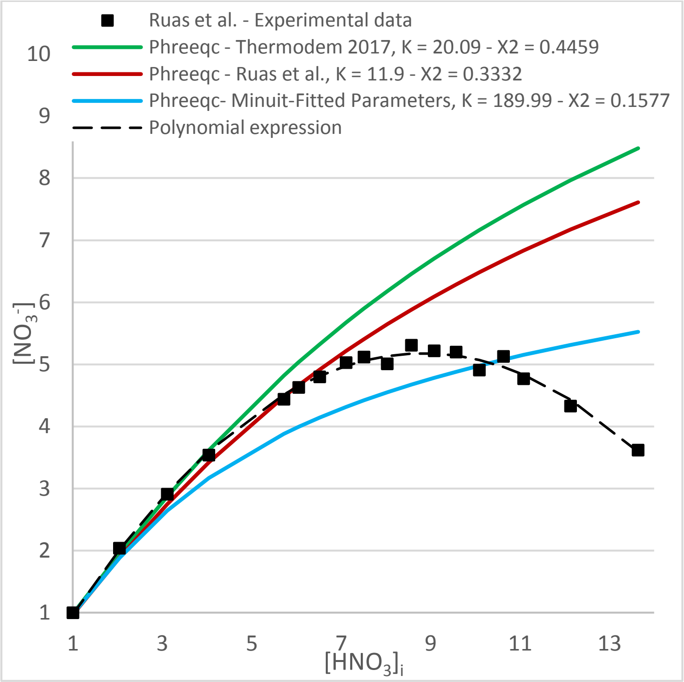

Figure 1: Comparison between Phreeqc calculated values with the database Thermoddem 2017 (green curve), with $K°_{HNO3\text{-}Ruas}$ *(red curve), with MINUIT fitted parameters (blue curve), with empirical polynomial function (dotted curve) and with the experimental data from Ruas et al. (black squares) of* HNO_3 *dissociation*

In a second step, adjustment of the experimental data with the Minuit-Phreeqc package was attempted, considering Equilibrium 1 above. The mathematical solution of the problem is based on the system of equations including the law of mass action (with Equation 1) and the conservation of matter. In this frame, $K°_{HNO3}$ is the thermodynamic equilibrium constant, and up to five independent parameters can be fitted: $K°_{HNO3}$, A, a_{H+}, a_{NO3-} and $\dot{B}$. This comes from the fact that it is not possible to adjust the a_i and B independently because they are directly correlated in Equation 1. Consequently, in this work, parameters a_{H+} and a_{NO3-} have been fitted, while B was set to 1 for all fits. Several trials were performed showing that the fitting procedure is rather sensitive to the initial values of the parameters and that very similar χ^2 values can be obtained with very different parameter sets. This is an indication that the mathematical function used is not appropriate. The values of one possible parameter set are presented in Table 1 ($\chi^2 = 0.1577$) and the corresponding fitted curve is displayed in Figure 1. Although a significant improvement in the overall χ^2 value is obtained as compared to that of the χ^2 values for Phreeqc trials discussed above (a factor around 3), it is clear from Figure 1 that the obtained fit is not able to recover all the domain of experimental data.

Other trials with Phreeqc were attempted by introducing the contribution of HNO_2, as suggested by Ruas et al. [17], through the chemical equations presented below.

$$\mathrm{NO_2^-} + \mathrm{H^+} \rightleftarrows \mathrm{HNO_2} \qquad \text{(Equilibrium 2)}$$

$$HNO_2 + 0.5\, O_2 \rightleftarrows HNO_3 \qquad \text{(Equilibrium 3)}$$

Figure 2 presents two of the Phreeqc speciation results, where the two equilibrium constants $K°_{NO2-}$ and $K°_{HNO2}$ (Equilibrium 2 and Equilibrium 3) have been varied manually up to extreme values (0.0001 to 2000 M^{-1}) in the database. Again, χ^2 values and general behavior of the calculated NO_3^- variations are incompatible with the experimental data of Ruas and co-workers, whatever the values used. Similarly, none of the trials performed with the Minuit-Phreeqc package (data not shown) and considering HNO_2 and NO_2^- were able to reproduce the decreasing trend of NO_3^- at high initial nitric acid concentrations.

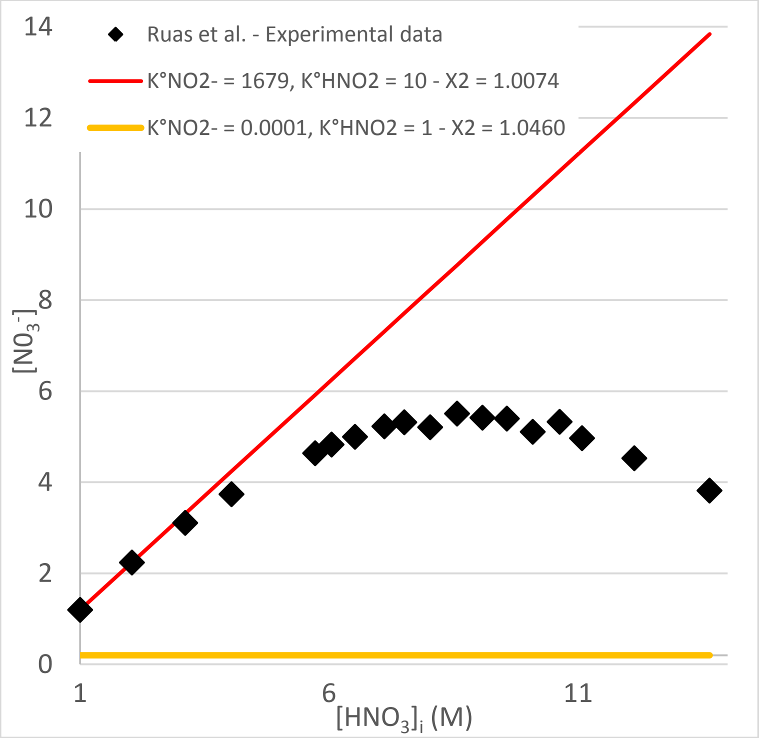

Figure 2: Effect of the integration of the contribution of HNO_2 to the model of the system studied with Phreeqc with different equilibrium constants and comparison with experimental values from Ruas et al.

At this stage, it is clear that the experimental free NO_3^- variations cannot be described within Phreeqc or Minuit-Phreeqc, which consequently sheds serious doubts on the ability of these two options to correctly describe our other experimental data.

Sr precipitation data

The Thermoddem basic configuration does not contain information about Sr(II) mono- and dinitrato- complexes, in terms of equilibrium constants and a_i values. Therefore, the chemical equilibria and associated equilibrium constants added for this work, are presented below.

$$Sr^{2+}\, NO_3^- \rightleftarrows\; Sr(NO_3)^+ \qquad \text{Equilibrium 4}$$

$$Sr(NO_3)^+ + NO_3^- \;\rightleftarrows Sr(NO_3)_{2\,solid} \qquad \text{Equilibrium 5}$$

For a_{SrNO3}, the value of 4 Å has been chosen because it corresponds to similar ions present in the database and most of the values for this parameter are comprised between 3.6 and 5.7 Å. For $K°_{SrNO3+}$ and $K°_{Sr(NO3)2}$, the values have been fixed to 6.4 M^{-1} and 0.4 M^{3} respectively according to [38]. For the Sr adduct, no data could be found in the literature so in a first approach, this compound has been neglected in the Phreeqc calculation, which is reasonable considering its low experimental ratio (see Table 3). Phreeqc speciation (data not shown) were not able to predict Sr precipitation while precipitation occurs experimentally. The PHREEQC software alone with the database Thermoddem 2017 has shown its limits. Similarly, trials with the Minuit-Phreeqc package also proved unsuccessful, with no precipitation, either by considering the existence of HNO_3 adducts or not (data not shown).

Modelling using Minuit-mix

Nitric acid dissociation description

The disappointing results discussed above in section 3.2. are clearly an argument in favor of the use of multipurpose fitting programs. More precisely, it can be assumed that the main reason for such inadequate calculations or fits are mainly ascribable to an incorrect description of HNO_3 dissociation. It was therefore decided to model the experimental data of Ruas and collaborators empirically, by use of an *ad hoc* polynomial expression, following Equation 3 and as illustrated in Figure 2. In this frame, only HNO_3, H^+ and NO_3^- species were considered.

$$Y = -0.0686\, X^2 + 1.2117\, X - 0.1727 \qquad \text{(Equation 3)}$$

where X is the initial HNO_3 concentration in M and Y is the free NO_3^- concentration, in M.

Describing the dissociation of nitric acid according to an empirical polynomial function is actually a change of paradigm as compared to the use of Phreeqc. It does not imply any hypothesis on the reason leading to such a decrease of free ions NO_3^- in solution. Possible explanations exist to justify this phenomenon, for example as mentioned earlier with HNO_2

formation [17], but in this case, none of them are taken into consideration within this approach. As the values calculated by the polynomial expression have a chemical meaning, the limit of the approach is determined by chemical significance and experimental data. Therefore, in principle, no extrapolation of the polynomial should be made out of the HNO_3 initial range of 1 M – 13.64 M. However, considering our Sr precipitation data set, the polynomial calculation for H^+ was extended up to 14.05 M of initial HNO_3 concentration in order to include data of Table S1. Obtaining experimental data at higher concentration would imply using fuming nitric acid that is avoided as much as possible because of its harmfulness.

Calcium co-precipitation phenomenon

Ca carrying has been evidenced in previous works and has been confirmed through our experiments (see section 3.1.1). In the context of the use of multipurpose fitting programs, the question arises of trying to model precipitation by an empirical approach (in addition to that used for HNO_3 dissociation), as carrying cannot be described through a set of chemical equilibria. In order to compare performances on common grounds, and in line with the Phreeqc study, it was decided not to model calcium carrying at all.

Sr precipitation data

Before any fitting, the general philosophy of this hybrid model, mixing empiricism for HNO_3 dissociation and description through chemical equilibria for Sr nitrate ions interactions, should be checked and the basic assumptions of the model should be fixed. First, considering the trace amounts of Sr involved in our experiments, and the very large HNO_3 initial concentration, the ionic strength will be equalized to the concentrations of NO_3^- as derived from Equation 3. H^+ and NO_3^- concentrations will be considered equal to each other. These two assumptions derive from neglecting the concentration of all nitrato-Sr species in these calculations, which is a reasonable assumption.

Second, Sr complexation and precipitation with nitrates are chemically described according to the previous Equilibrium 4 and Equilibrium 5, plus the following one:

$$Sr^{2+} + 2\,NO_3^- + 2\,HNO_3 \rightleftarrows Sr(NO_3)_2.\mathrm{XHNO_3} \quad \text{(Equilibrium 6)}$$

where X is a positive integer as the stoichiometry of the adduct and its nature (one or multiple adducts) is not confirmed. Thermodynamic precipitation constants are written as:

$$\mathrm{K°_{Sr(NO3)2}} = (\mathrm{Sr}^{2+})(\mathrm{NO_3^-})^2 \quad \text{(Equation 4)}$$

$$\mathrm{K°_{Sr\text{-}adduct}} = (\mathrm{Sr}^{2+})(\mathrm{NO_3^-})^2(\mathrm{HNO_3})^2 \quad \text{(Equation 5)}$$

where parentheses stand for activities of species.

It is obvious from Equation 4 and Equation 5 that $\mathrm{K°_{Sr\text{-}adduct}} = \mathrm{K°_{Sr(NO3)2}}\,(\mathrm{HNO_3})^{\mathrm{X}}$.Note that the experimental data set from our previous publication does not distinguish between the two types of Sr precipitates, as only the global Sr(II) concentration in the supernatant was measured.

The mathematical resolution method is summarized below. The mass balance for Sr is written:

$$[Sr^{2+}] + [Sr(NO_3)^+] + [Sr(NO_3)_2] + [Sr(NO_3)_2.XHNO_3] = [Sr]_{init} \quad \text{(Equation 6)}$$

Where [A] is the concentration of species A and $[\mathrm{Sr}]_{\mathrm{init}}$ is the initial concentration of Sr in the sample. Although this is not a common usage, the concentration of solid species is defined as their number of moles divided by the sample volume.

The mass action law for the Sr-mono nitrato complex is written:

$$K°_{SrNO3+} = \frac{(Sr(NO_3^+))}{(Sr^{2+})(NO_3^-)} \quad \text{(Equation 7)}$$

Then, in case of Sr precipitation, one derives:

$$[Sr(II)] = \frac{K^{\circ}_{Sr(NO3)2}}{[NO_3^-]^2}\,\frac{1}{\gamma_{Sr}\gamma_{NO3-}^2} + \frac{K^{\circ}_{Sr(NO3)+}K^{\circ}_{Sr(NO3)2}}{[NO_3^-]}\,\frac{1}{\gamma_{Sr(NO3)+}\gamma_{NO3-}} \quad \text{(Equation 8)}$$

Where [Sr(II)] is the total concentration of Sr(II) in the supernatant. In this last equation, parameters to be fitted are the thermodynamic equilibrium constants, plus the various parameters to be found in the expressions of the activity coefficients. Thus, adjustment of the parameters is obtained by comparing the experimental [Sr(II)] values to the calculated ones. The thermodynamic equilibrium constant of the adduct ($K°_{Sr\text{-}adduct}$) is not directly obtained with the fit. Therefore, the stoichiometry of the adduct is not essential to define in this case. If experimental data could confirm a stoichiometry, there would be an interest to calculate the $K°_{Sr\text{-}adduct}$ from $K°_{Sr(NO3)2}$ determined with the fit to get more knowledge on the precipitate. However, the unstability of the adduct complicates the experimental data collection.

As already mentioned, the value of B has been fixed to 1. It should be kept in mind that there is not a unique best fit, because by changing B and adjusting the a_i so to keep the products Ba_i constant, an infinite number of best fits can be obtained. One possible set of parameters is listed in Table 4 and the results are presented in Figure 3, where the fitted total Sr(II) concentration of the supernatant is plotted as a function of the experimental values. The χ^2 obtained with this model is 45.76.

Table 4: Parameters used for the Minuit mix model with their values. * indicates fixed parameters

Parameter	**MINUIT** **Sr precipitation**
$K°_{SrNO3+}$ [M^{-1}]	0.756
$K°_{Sr(NO3)2}$ [M^{3}]	1.44×10^{8}
A [$M^{-1/2}$]	-14.2
B [$M^{-1/2}*Å^{-1}$]	1*
$\dot{B}$ [M^{-1}]	-2.84
$å_{NO3-}$ [Å]	0.3*
$å_{Sr}$ [Å]	0.5*

$å_{SrNO3+}$ [Å]	0.41*

The values of $K°_{SrNO3+}$ and $K°_{Sr(NO3)2}$ obtained with MINUIT-mix model (respectively 0.756 M^{-1} and $1.44x10^8$ M^3) do not correspond to the values found in the literature (6.4 M^{-1} and 0.4 M^3) [38]. As the MINUIT-mix model constants are calculated from a model based on thermodynamic and experimental equations, the discrepancies with the literature can be expected.

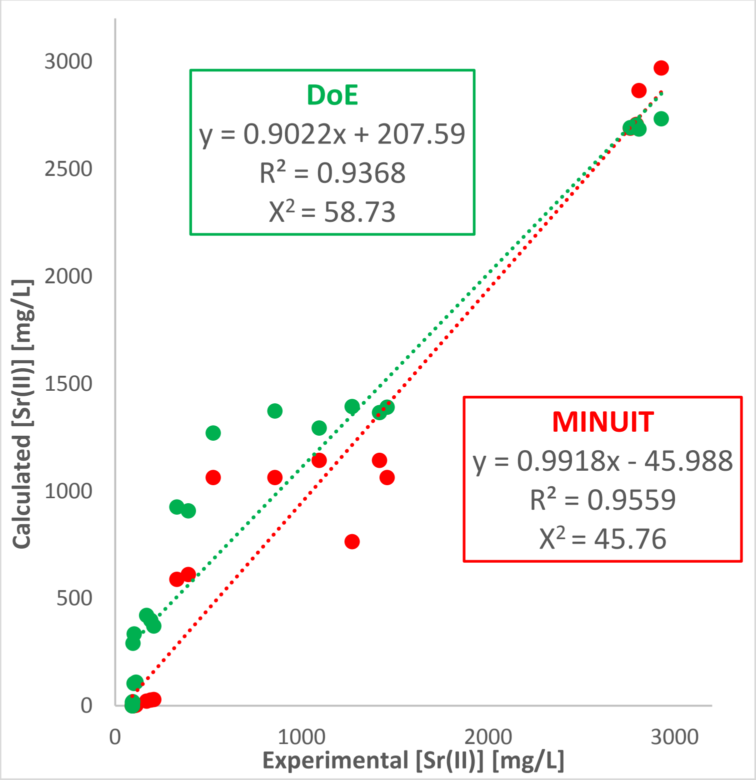

Figure 3: Correlation between the calculated and the experimental values for MINUIT-mix model and DoE model [11]

The intermediate values are less reliable because their experimental deviations are more important. As they are at the limit of precipitation, slight variations during the experiment could have a greater influence on the result, for example the waiting time before centrifugation (normally around 20 min). It means higher uncertainties (than the 10 % for data close to 0 % and 100 % Sr precipitate) should be considered on the intermediate points. However, for the process, the real interest is to determine at which nitric acid concentration the yield approaches 100 % and the Minuit-mix model successfully recovers the experimental data in this range.

Discussion

The different simulation methods, DoE, Phreeqc, Minuit-Phreeqc and Minuit-mix can be compared because they were used for the same process. Except Phreeqc, all the methods required experimental results for parameters or coefficients fitting. Minuit-Phreeqc, such as Phreeqc, was not able to calculate any precipitation. For DoE, the dataset used for the complete studies of the process is more important than the one presented in Table S 1 in Supplementary Information. Indeed, before focusing on the two influencing parameters, prior experiments had to be realized for parameters screening studies. In opposite, the Minuit-mix method used Ruas et al. dataset for nitric acid dissociation. Even with these variations, the fit for the coefficients of the final models were made with the dataset presented in Table S 1**Erreur ! Source du renvoi introuvable.** in Supplementary Information.

Unlike Phreeqc and Minuit-Phreeqc, the Minuit-mix model is able to simulate the precipitation observed experimentally. As presented in Figure 3, the Minuit-mix model reproduced successfully both the low and high values of [Sr(II)], corresponding to high quantity of precipitate (around 200 mg which represents almost 100 % of initial Sr precipitate) and the absence of precipitation, respectively. Compared to the two cited methods using Phreeqc, the main difference is the introduction of the polynomial expression to calculate HNO_3 dissociation. The particular behavior of HNO_3 is confirmed to cause the incapacity to simulate the precipitation with purely speciation methods.

Compared to the result of DoE model (R^2 = 0.9368 and χ^2 = 58.73), the correlation between the calculated values and the experimental ones for Minuit-mix is improved with a R^2 of 0.9559, a χ^2 of 45.76 and a slope closer to the expected value of 1 in case of a perfect fit. With a better chemical understanding of the process and a better correlation to experiment, the Minuit-mix model is an improvement compared to DoE method for Sr precipitation. However, DoE keeps an advantage as it is able to determine a model for Ca precipitation depending on the parameters studied. As the two models were determined based on experimental data, both are limited to the experimental domain of the dataset.

Conclusion

Speciation modeling has been proven useful to better understand radiochemical separations. The precipitation in nitric acid is often implemented to isolate Sr from Ca for the analysis of Sr-90 in radioactive waste. However, little work dealt with a deep comprehension of Sr chemical behavior in such conditions. In this study, speciation simulation was investigated to describe Sr behavior in nitric acid. The modeling of Sr precipitation in highly concentrated nitric acid has presented challenges for two main reasons: the high ionic strength and the particular behavior of nitric acid. The program Phreeqc has shown its limits as it was not able to calculate nitric acid dissociation as measured by Ruas and co-workers. To overcome the problem, the routine Minuit was preferred as it is able to fit the parameters of the chemical model of the process and to introduce the dissociation of nitric acid as a polynomial expression depending on initial nitric acid concentration determined by the experimental data from Ruas and co-workers. This Minuit-mix option has been proven successful as the results of our calculation corresponded rather well to the experimental values. Moreover, it confirmed the reliability of the dataset obtained by Ruas et al. To improve this Minuit-mix model, the proportion of adduct, $Sr(NO_3).2HNO_3$, could be introduced in the calculation. A new set of experimental data should then be acquired and for each point, the proportion of adduct should be measured.

Compared to the DoE models obtained in our previous study, the results have been improved in terms of correlation with experimental values. The limitations remain the same for both models as their validity is limited to the experimental domain of the dataset used.

Considering the chemical understanding of the process, for Sr precipitation, the Minuit-mix model is advantageous. If Ca is taken in consideration, the Minuit-mix option is not adapted as it has been proven in this study that the precipitation of Ca is due to carrying. Also, no model based on mass action law and mass balance equations would be able to calculate this phenomenon. In opposite, DoE method with its model based purely on experimental values is able to represent this phenomenon as long as the process is robust, repeatable and the influencing parameters correctly identified.

Being able to simulate a process in high concentrated medium gives great possibilities to use Minuit-mix method for other radiochemical studies, for example to improve ^{107}Pd radiochemical method in which both high concentrated nitric and hydrochloric acids are implemented to isolate palladium from interferents.

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Supplementary Information

Table S 1 : Experimental data used for determination of models with DoE [11] and for speciation models. Uncertainties are at 10% at k=2

Points	HNO_3 [M]	$Sr(NO_3)_2$ [M]	[%] Sr precipitate
1	10.53	0.0309	<1
2	10.56	0.0307	<1
3	10.60	0.0339	2
4	10.83	0.0327	2
5	12.30	0.0357	53
6	12.28	0.0353	54
7	12.39	0.0341	58
8	12.28	0.0389	68
9	12.30	0.0351	72
10	12.30	0.0388	85
11	12.45	0.0385	88
12	12.46	0.0395	90
13	13.21	0.0344	93
14	13.23	0.0378	94

15	13.28	0.0413	95
16	14.03	0.0312	96
17	13.75	0.0359	96
18	14.02	0.0317	97
19	14.05	0.0340	97
20	13.76	0.0374	97
21	14.05	0.0358	97
22	14.05	0.0409	97
23	14.03	0.0408	97