



Spectroscopic investigation on the formation of hypochlorite by alpha radiolysis in concentrated NaCl solutions

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Abstract

The hypochlorite formation induced by alpha radiation in saline solutions is studied by UV/VIS spectroscopy. Experiments are carried out in NaCl solutions of various concentrations between 1 and 5 mol/l and with volume alpha activities in the range of 20–444 GBq/l. The concentration of radiolytically formed hypochlorite is measured over a period of up to 200 days. The build-up of hypochlorite to an equilibrium concentration is found to depend on both, the chloride and the activity concentration and is calculated by means of a kinetic reaction model. Experimental results for the formation of hypochlorite are compared with the model calculation. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Alpha radiolysis; Chloride brine; Hypochlorite; Kinetic model

1. Introduction

In a final disposal for nuclear waste the speciation of dissolved radionuclides define closely their mobility and thus their potential hazard. In this way redox and complex formation reactions govern primarily the chemical behaviour of actinides in aquatic systems (Kim, 1993). Investigations in saline solutions show that under alpha radiation both redox and complex formation reactions of actinides are strongly affected by radiation effects which depend on the chloride and the activity concentration of the solution

(Bueppelmann et al., 1986, 1988; Lierse and Kim, 1986; Kim et al., 1987; Pashalidis and Kim, 1992; Pashalidis et al., 1993). Under α -irradiation solutions with a chloride content of more than 2 mol/l generate not only radiolytic gases like H₂ and O₂ (Reed et al., 1993; Gray and Simonson, 1985; Jenks, 1972) but also chlorate (Jenks, 1972), hypochlorite, chlorine (Pashalidis and Kim, 1992; Vladimirova et al., 1972) and chlorite. The formation of hypochlorite is associated with a high redox potential, which can reach about 1300 mV (Bueppelmann et al., 1988; Kim et al., 1987; Pederson et al., 1984) in acidic solutions. Under such conditions Am(III) is oxidized to Am(V) (Kim et al., 1987; Bueppelmann et al., 1986; Magirius et al., 1985) and Pu(IV) to Pu(VI) (Bueppelmann et al., 1986, 1988; Lierse and Kim, 1986; Kim et al., 1987). Besides its oxidizing properties, hypochlorite has the ability to

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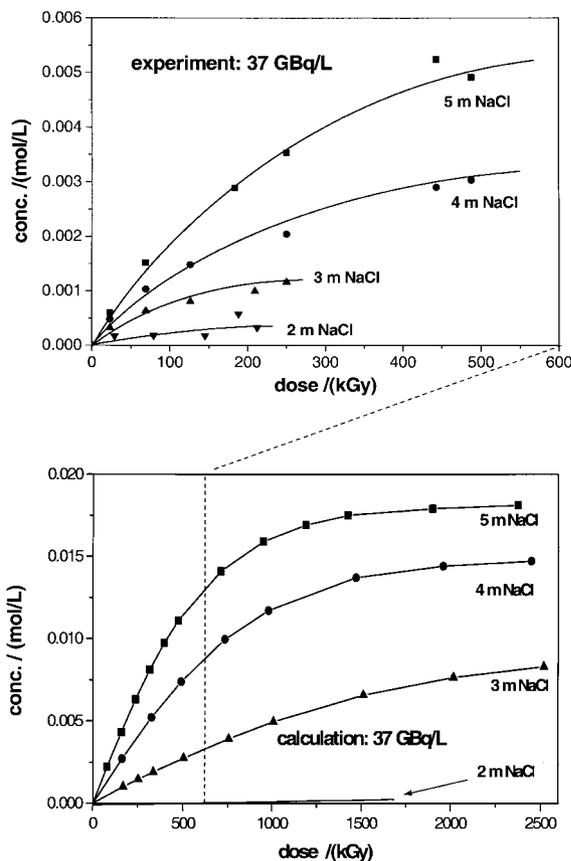


Fig. 1. Hypochlorite formed radiolytically in solutions of various NaCl concentrations at a constant alpha activity concentration of 37 GBq/l.

form stable complexes with Pu(VI). The hypochlorite complexes of Pu(VI), e.g. $\text{PuO}_2(\text{OH})\text{OCl}$ and $\text{PuO}_2(\text{OCl})_2$ are very stable ($\log\beta_{111}=14.3$ and $\log\beta_{102}=10.1$) and control the solubility of plutonium in nearly neutral saline solutions (Pashalidis and Kim, 1992; Pashalidis et al., 1993). Since hypochlorite determines the redox potential and forms complexes with Pu(VI), the knowledge about the parameters which govern its formation is of particular importance for understanding the chemical behaviour of actinides in saline solutions.

This work describes spectroscopic studies to determine quantitatively the influence of the chloride and the alpha activity concentration on the hypochlorite formation in saline solutions and gives an interpretation of the results on the basis of a kinetic reaction model.

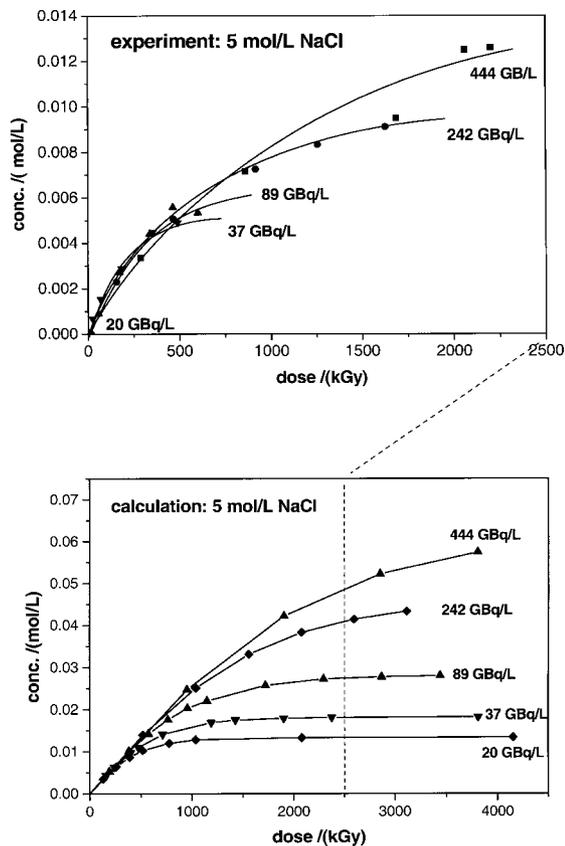


Fig. 2. Hypochlorite formed radiolytically in 5 mol/l NaCl solutions containing various alpha activity concentrations.

2. Experiments

For all experiments ^{238}Pu with its specific alpha activity of 635 GBq/g is used. Samples are prepared by contacting Pu(VI)-hydroxide of known activity with NaCl solutions of various concentrations in closed silica vessels. The investigated samples are:

1. four solutions with a constant activity concentration of 37 GBq/l and NaCl concentrations of 2, 3, 4, and 5 mol/l and
2. five solutions of 5 mol/l NaCl with activity concentrations of 20, 37, 89, 241 and 444 GBq/l.

The pH of all solutions is adjusted to approx. 12 by adding saturated NaOH solution. The particle size of the Pu species is assumed to remain small over the duration of all experiments, so that the α -decay energy is completely transferred into the solution and the dose rate can be given by the activity concentration.

Over a period of up to 200 days the concentration of hypochlorite in solutions is monitored by UV/VIS spectroscopy using its molar extinction coefficient of

(350 ± 15) l/(mol·cm) at 290 nm (Pashalidis and Kim, 1992).

3. Results of the experiments

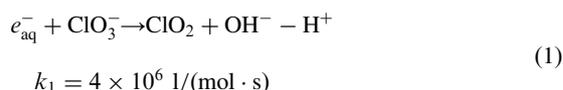
Fig. 1 shows the radiolytic formation of hypochlorite in saline solutions within 200 days after mixing the NaCl solution with ²³⁸Pu. The hypochlorite concentration increases with time and appears to approach a maximum. The value of [OCl⁻]_{max.} depends on the chloride concentration. Below a chloride ion concentration of 2 mol/l no hypochlorite can be observed.

The influence of different α-activity concentrations on the formation of hypochlorite is shown in Fig. 2. After 100 days an equilibrium concentration of hypochlorite is not yet established. From the slopes of the experimental curves in Fig. 2 one can estimate that the activity concentration has only a minor effect on [ClO⁻]_{max.}

4. Modelling of the reactions

The radiation chemical reaction occurring in concentrated NaCl solutions in the presence of the α-radiation of ²³⁸Pu is simulated by a system of parallel second order elementary reactions. The 82 reaction equations for 31 species published by Sunder and Christensen (1993) are used as a basis without correcting the concentrations and rate constants for high ionic strength. However, some minor changes and necessary completions are introduced to the reaction scheme:

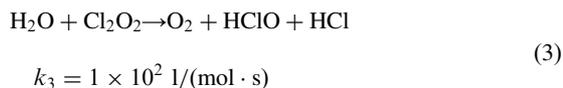
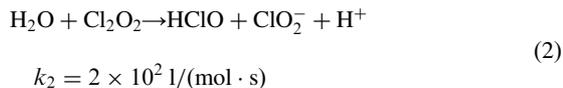
- Instead of the undissociated acids HClO₂ and HClO₃, their anions are used for which the rate constants are considered to be unchanged.
- The bimolecular rate constant k_1 for the chlorate reduction¹ given by:



is set to zero, because γ-radiolysis experiments show that chlorate is formed proportional to the dose and this equation would limit the increase in chlorate concentration (Kelm and Bohnert, 1997). Furthermore Buxton et al. (1988) give a value for k_1 of $< 1 \times 10^6 \text{ l}/(\text{mol} \cdot \text{s})$.

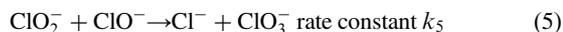
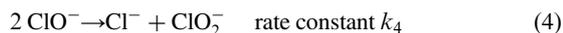
- The original reaction scheme given by Sunder and

Christensen (1993) contains two different hydrolysis equations for Cl₂O₂ of which Eqs. (2) and (3) result in the formation of chlorine species and oxygen, respectively:



For the simulation of γ-experiments (Kelm and Bohnert, 1997), Eq. (3) is eliminated to give a better agreement with the experimental results. The same modification of the scheme is applied for the α-radiolysis.

- As the observation of the radiolytic hypochlorite formation covers a time period of up to 200 days, the slow spontaneous decay of that compound has to be considered. The decay reaction mechanism has been investigated in the past (Lister, 1956a; Lister and Petterson, 1962) and is usually described as a set of consecutive reactions. In the alkaline region the following reactions have to be introduced into the scheme:



This mechanism was verified for alkaline pH only recently (Church, 1994; Adam, 1994) but it changes towards the neutral region where the free hypochlorous acid and hypochlorite anions coexist (Adam et al., 1992; D'Ans and Freund, 1957). These decay reactions are furthermore superimposed by a catalyzed decay which is caused by traces of heavy metal oxides (Lister, 1956b; Church, 1994). As the catalytic activity of Pu compounds on the decay of hypochlorite is not yet investigated, such effect is not introduced into the scheme. The rate constants of reactions (4)–(6) depend mainly on the temperature and ionic strength; the respective data are published (Lister, 1956a). Unfortunately, the fastest and therefore most relevant reaction (5) for the limiting of build-up of hypochlorite is investigated in less detail than the reactions (4) and (6). In pure hypochlorite solution the exact rate of reaction (5) is unimportant because the reaction (4) is rate determining and the concentration of chlorite is always very low. For calculations, all rate constants are taken from Lister

¹ As the kinetic code used for the calculation is designed for mono- and bimolecular reactions only, a third component on the left-hand side of the equation is introduced with a minus sign on the product side.

Table 1

Reaction rate constants for the decay of hypochlorite calculated for 23°C and different ionic strengths taken from Lister (1956a) and Lister and Petterson (1962)

| Cl ⁻ conc. (mol/l) | k_4 [l/(mol.s)] | k_5 [l/(mol.s)] | k_6 [l/(mol.s)] |
|-------------------------------|-----------------------|-----------------------|------------------------|
| 5 | 3.43×10^{-8} | 4.10×10^{-6} | 2.10×10^{-9} |
| 4 | 2.40×10^{-8} | 3.10×10^{-6} | 1.73×10^{-9} |
| 3 | 1.72×10^{-8} | 2.20×10^{-6} | 1.32×10^{-9} |
| 2 | 1.25×10^{-8} | 1.70×10^{-6} | 9.68×10^{-10} |

(1956a) and Lister and Petterson (1962) for 23°C at appropriate ionic strength (Table 1).

All 85 equations [82 published by Sunder and Christensen (1993) plus Eqs. (4)–(6)] are fed into the kinetic code MACKSIMA-CHEMIST (Carver et al., 1986/87) to calculate the concentrations of all species over the time. For further input data the code needs the G -values (radiolytic yield in molecules per 100 eV absorbed energy) of all primarily formed species. These G -values for α -radiation in concentrated brines are not yet determined experimentally and they are different from the G -values in diluted solutions. Therefore, they are calculated as follows and summarized in Table 2.

A direct radiation effect on the Cl⁻ ion with a G -value of 6.2 (Grigor'eva et al., 1991) is assumed according to their electron fraction. For the indirect radiation effect the yield of chlorine species formed in the scavenging reaction between OH radicals and chloride ions within the tracks is calculated according to the theory of Ganguly and Magee (1956). The G -value for 100% yield is taken from published data of the radiolysis of water (Eriksen et al., 1986). The yield of the reducing species are believed to be not changed by the scavenger. The oxidizing chlorine species formed in the tracks of α -radiation are assumed to be 20% ClOH⁻ and 80% Cl₃⁻. The high percentage of Cl₃⁻ reflects the high primary yield of molecular products related to high LET radiation. In the reaction model it causes the parallel formation of O₂, chlorate, chlorite and hypochlorite on the oxidizing side in comparable amounts, while a lower percentage of Cl₃⁻

(<60%) would keep the concentrations of chlorite and hypochlorite in the μ mol/l region, thus contradicting the experimental results.

The calculation results of the hypochlorite formation with the reaction model are shown in the lower parts of Figs. 1 and 2.

5. Discussion

The comparison with the experimental results shows that the calculated concentrations are up to about 6 times higher (at the highest dose rate in 5 mol/l chloride solution). Even though the calculation shows the general features of experimental data:

- At low doses the increase of the hypochlorite concentration is independent of the dose rate. The main decay reaction (5) is slow compared to the build-up of hypochlorite and chlorite. Thus, the initial formation of hypochlorite is proportional to the dose and independent of the dose rate (Fig. 2).
- At high doses Fig. 2 shows that the increase of the hypochlorite concentration depends on the dose rate. The reaction model describes this behaviour properly because the chlorite formation rate is smaller than that of hypochlorite and both are proportional to the dose rate. Therefore, the decay reactions (4)–(6) can confine the concentration increase of both compounds to a dose rate dependent level.
- Even though the range of applied dose rate varies by a factor of 22 between 1190 and 54 Gy/h the final concentration of hypochlorite varies only by a factor of about 5 in the experiment as well as in the calculation. This reflects the outline of the reaction model: The excess of hypochlorite over chlorite decays via second order reactions (4) and (6). Therefore, at constant chloride concentration the hypochlorite concentration at equilibrium becomes proportional to the square root of the applied dose rate (or activity concentration). This can be derived from the following considerations:

Table 2

Primary G -values calculated for different chloride concentrations

| Cl ⁻ conc. (mol/l) | G -value | | | | | | | | | | |
|----------------------------------|------------------|----------------|----------------|-------------------|-------------------------------|-----------------|-----------------|-----------------|-------------------|------------------------------|-----------------|
| | H ₂ O | H ₂ | H [·] | e_{aq}^- | H ₂ O ₂ | HO ₂ | OH [·] | OH ⁻ | ClOH [·] | Cl ₃ ⁻ | Cl ⁻ |
| 5 | -3.25 | 1.52 | 0.26 | 0.06 | 0.23 | 0.05 | 0.06 | 2.08 | 0.55 | 1.07 | -3.76 |
| 4 | -3.15 | 1.48 | 0.24 | 0.06 | 0.27 | 0.06 | 0.07 | 1.92 | 0.50 | 0.99 | -3.47 |
| 3 | -3.02 | 1.43 | 0.23 | 0.06 | 0.32 | 0.07 | 0.08 | 1.72 | 0.44 | 0.89 | -3.11 |
| 2 | -2.92 | 1.39 | 0.23 | 0.06 | 0.40 | 0.09 | 0.10 | 1.46 | 0.38 | 0.76 | -2.66 |

Formation of hypochlorite:

$$\frac{d}{dt}[\text{ClO}^-] = k_7 \cdot A \cdot [\text{Cl}^-]^n \quad (7)$$

Formation of chlorite:

$$\frac{d}{dt}[\text{ClO}_2^-] = R \cdot k_7 \cdot A \cdot [\text{Cl}^-]^n + k_4 \cdot [\text{ClO}^-]^2 \cdot [\text{Cl}^-]^m \quad (8)$$

Decay of hypochlorite:

$$\frac{d}{dt}[\text{ClO}^-] = k_5 \cdot [\text{ClO}^-] \cdot [\text{ClO}_2^-] \cdot [\text{Cl}^-]^m + (k_4 + k_6) \cdot [\text{ClO}^-]^2 \cdot [\text{Cl}^-]^m \quad (9)$$

Decay of chlorite:

$$\frac{d}{dt}[\text{ClO}_2^-] = k_5 \cdot [\text{ClO}^-] \cdot [\text{ClO}_2^-] \cdot [\text{Cl}^-]^m \quad (10)$$

with:

- $[\text{ClO}^-]$, $[\text{ClO}_2^-]$, $[\text{Cl}^-]$ = concentration of hypochlorite, chlorite, chloride
- k_4 – k_7 = reaction rate constant
- $[\text{Cl}^-]^n$ = term, which describes the influence of the Cl^- concentration on the hypochlorite formation rate
- $[\text{Cl}^-]^m$ = term, which describes the influence of ionic strength on the rate constants k_4 – k_6 and which is assumed to be equal for all constants
- A = activity concentration or dose rate
- t = time
- R = ratio of the formation rate constants for ClO_2^- and ClO^- (always < 1)
- index (eq.) = at equilibrium

At equilibrium, for both compounds the formation and decay rates are equal:

$$(1 - R) \cdot k_7 \cdot A \cdot [\text{Cl}^-]^n = (2 \cdot k_4 + k_6) \cdot [\text{ClO}_{\text{eq}}^-]^2 \cdot [\text{Cl}^-]^m \quad (11)$$

At constant chloride concentration:

$$[\text{ClO}^-]_{\text{eq.}} \sim (A)^{1/2} \quad (12)$$

- The formation of hypochlorite depends strongly on the chloride concentration. Both the experiment and calculation indicate that during the observation period the hypochlorite concentration develops proportional to more than the third power of the chloride concentration [the mean value from calculation is 3.6; exponent n in Eqs. (7), (8) and (11)]. But within the reaction scheme the chloride concentration has practically no influence at all. The strong dependence is solely caused by the primary G -values

(probably that of Cl_3^- and the competing product H_2O_2) which vary moderately with the chloride concentration (Table 2). The calculation further discloses that the equilibrium concentration of hypochlorite is proportional to the chloride concentration only with a power of 1.3. This can be understood as the reaction rate constants k_4 – k_6 increase with about the power of 1.1 of ionic strength or the chloride concentration [$m = 1.1$ in Eqs. (8)–(11)]. Using Eq. (11) for the equilibrium one gets the following relation at constant dose rate (i.e. activity concentration):

$$[\text{ClO}^-]_{\text{(eq.)}} \sim \left([\text{Cl}^-]^{3.6} / [\text{Cl}^-]^{1.1} \right)^{1/2} \sim [\text{Cl}^-]^{1.3} \quad (13)$$

- At 2 mol/l chloride the experimentally found hypochlorite formation is very low. This corresponds to the calculation which gives a concentration in the $\mu\text{mol/l}$ range. According to the model the reaction mechanism changes sharply when the chloride concentration is decreased towards 2 mol/l: the formation of chlorite and hypochlorite stops in favour of chlorate and oxygen.
- The reason for the differences in the hypochlorite concentration determined experimentally and by calculation could not be clarified satisfactorily. But some aspects have to be considered:
 - The reaction mechanism is very sensitive against the primary G -values which on the other hand are not well known for α -radiolysis in concentrated solutions. Therefore, discrepancies between the calculation and experiment of much less than one order of magnitude seem to be acceptable.
 - As the plutonium forms a precipitate in the alkaline solution, the primary assumption that the α energy is quantitatively transferred into the solution can be wrong. Self absorption in the precipitate would reduce the effective dose rate and reduce the calculated hypochlorite concentration.
 - Additionally, the precipitation of Pu causes a higher local dose rate. As the relationship between dose and hypochlorite concentration is non-linear at higher doses (Fig. 2) the inhomogeneous irradiation lowers the yield of hypochlorite.
 - The catalytic effect of the plutonium precipitate in respect to the decay of the hypochlorite is not known. But Pu occurs in the radiolytic solutions in an unstable oxidation state (Pu(VI)). Such a fact is believed to be necessary for a catalytic active compound (Lister, 1956b). An additional catalytic decay of hypochlorite would result in lower concentrations.

The last 3 factors mentioned cause a smaller hypochlorite yield so that the calculation probably overesti-

mates its concentration. Thus, the difference between experiment and calculation could be smaller than found. An improvement is expected from a direct measurement of the irradiation dose. For the further development of the reaction model for the chloride system the determination of all other radiolytic products besides hypochlorite is needed.

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