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Gamma radiolysis of NaCl brine: Effect of dissolved radiolysis gases on the radiolytic yield of long-lived products

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Abstract

Five moles per litre NaCl solution is γ-irradiated in autoclaves at 35 °C and 90 °C. H_2, O_2 and ClO_3^- are formed as long-lived products and reach equilibrium concentrations at a gas partial pressure of some 10 bar. Since formation of a gas phase is completely suppressed, H_2 and O_2 are kept dissolved. The equilibrium concentration level depends on dose rate and pH. Experiments at 90 °C and with added H_2 show no gas production at all. From the kinetic simulation of the experiments we deduce that the reaction of OH and Cl_2^- radicals with H_2 limits or inhibits sustaining solution decomposition. If species are present which compete with the radicals for H_2, (such as Br^-) the decomposition is promoted. In such a case the gas partial pressure exceeds 100 bar.

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1. Introduction

If spent nuclear fuel is buried in a final disposal in rock salt in the deep underground one considers the intrusion of brine to the waste as an accident scenario. Upon initial container failure by corrosion, the geological surrounding and metals from the container material will establish reducing condition even in close proximity to the fuel. As the solubility of tetravalent uranium is low, the UO_2 matrix of spent fuel is very resistant against corrosion and thus against the release of fission products. Brine in contact with fuel, however, could radiolytically produce sufficient oxidants to convert UO_2 into the much more soluble hexavalent uranium and thus promote radionuclide release. Much work on the radiolytical decomposition of ground water from final disposal sites and radiolytically assisted UO_2 corrosion has been published in the past (review in [1, 2–7]).

Radiolytic decomposition of aqueous solutions is often accompanied by the formation of H_2 and O_2. These gases may remain dissolved in a final disposal site in a depth of up to 1000 m until the partial pressure exceeds a maximum of about 100 bar. From reactor chemistry it is well known that H_2 protects against further progress of net radiolysis. Similar effects are observed in experiments with spent fuel [8,9]. The question arises if one could take advantage from such processes in nuclear waste disposal, too. In the waste disposal case such a protective process must be sustained over thousands of years. Therefore, the mechanism of the radiolysis inhibition by H_2 must be fully understood. In our approach presented below, the radiolytic decomposition of

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5 mol/L NaCl solution under γ-irradiation, without any gas phase formation, is investigated. Br^- and an excess of H_2 are used as solution additives. Both compounds can be expected to be brine components in a final disposal site, Br^- as a minor constituent of natural rock salt and H_2 as a result of container corrosion.

2. Experimental

The γ-irradiation experiments without gas phase formation are performed in autoclaves in which all components in contact with the solution are manufactured from nickel-base alloy Hastelloy 276. The autoclave volume is about 350 ml, from which about half is occupied by a bellow, which can be pressurized with Ar up to 300 bar. The bellow transfers the pressure onto the solution, thereby forcing radiolysis gases to remain dissolved (Fig. 1). The autoclave filling is 5 mol/L NaCl solution prepared from recrystallized NaCl (Merck, p.a.) and purified water (Milli-Q 185, Millipore), bubbled with Ar for >30 min. The solution pH is not adjusted and is therefore close to neutral. One experiment is conducted with 2.3 mmol/L Br^-, another with 2.8 mmol/L H_2 added to the brine prior to irradiation. The irradiation takes place in a panoramic γ-source under a pressure of about 250 bar. The mean dose rate in the autoclaves measured with a Fricke dosimeter is 912 Gy/h (exp. 3–6, Table 1) and in other experiments 345 Gy/h (exp. 1 and 2, Table 1). The autoclaves are usually thermostated at 35 °C but in one experiment at 90 °C.

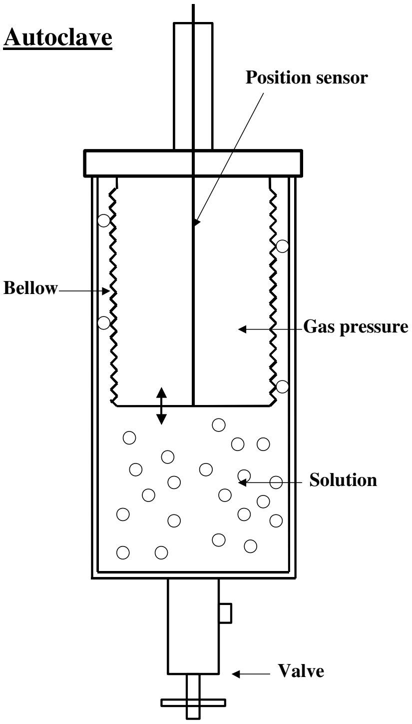

Fig. 1. Outline of the autoclave.

At varying time intervals the irradiation is interrupted and the pressure on the bellow is released stepwise so that a gas phase is formed. The bellow position where this occurs is recorded without opening the autoclave. From the position readings, the volume of the radioysis gases released from the brine can be calculated as well as the total amount of gases formed during the irradiation considering pressure, temperature and the gas solubility according to Henry's law. Gas and liquid samples are taken only at the end of each experiment. The gas composition is determined by mass spectroscopy. The solution is analyzed for HClO, ClO_2^-, ClO_3^- as described elsewhere and by ICP-MS for corrosion products from the autoclave [10].

The reaction progress in the brine is simulated using a kinetic reaction model and the code MACKSIMA-CHEMIST [11]. The calculation results are compared to the experimental findings.

3. Results and discussion

In experiments with and without gas release the main final radiolysis products are H_2, O_2 and ClO_3^- [12,13]. The difference between both cases is that in an open system these products are formed proportional to the dose, while in pressurized systems, where all gases remain dissolved, the product concentrations reach equilibrium values; in certain cases practically no gas formation is observed at all. HClO and ClO_2^- are found in concentrations below 10 μmol/L, near the detection limit. H_2O_2 is not a final product in the radiolysis of concentrated chloride solutions.

The total amount of dissolved gases ($H_2 + O_2$) found in our autoclave experiments after the application of different doses is shown in Fig. 2, together with the corresponding final gas pressures. In most cases (except for the bromide containing solution) the total gas concentration levels off and reaches a plateau value. Surprisingly three different results for the final gas content are obtained in three nominally similar experiments (no. 1–3) conducted at 35 °C. At 90 °C no radiolysis gas is formed (no. 4). In the experiment with added H_2 prior to irradiation (no. 5) no further H_2 and practically no O_2 is produced (Table 1). The bromide containing solution evolves radiolysis gases nearly proportional to the dose (no. 6). Such strong influence of bromide on the gas production is well known and understood from the radiolysis of pure water [14] but is also described for brines [15]. While in open systems about 0.01 mol/L chlorate is formed per MGy, in the pressurized system the chlorate concentration reaches only about

Table 1
Experimental conditions and radiolysis product concentrations at the end of the experiments

Exp. no.	Conditions	Dose (kGy)	Time (d)	H_2 (mol/L)	O_2 (mol/L)	ClO_3^- (mol/L)
1	35 °C	3335	403	9.61E−03	3.32E−03	8.10E−05
2	35 °C	5350	645	4.10E−02	8.08E−03	8.60E−05
3	35 °C	9094	415	6.32E−03	1.09E−03	1.89E−04
4	90 °C	9094	415	No	No	1.63E−05
5	H_2 added	2014	92	2.76E−03/no	3.52E−06	1.56E−05
6	Br^- added	2014	92	6.44E−02	2.82E−02	1.98E−04

In experiment 5 the initial and final H_2 concentrations are equal.

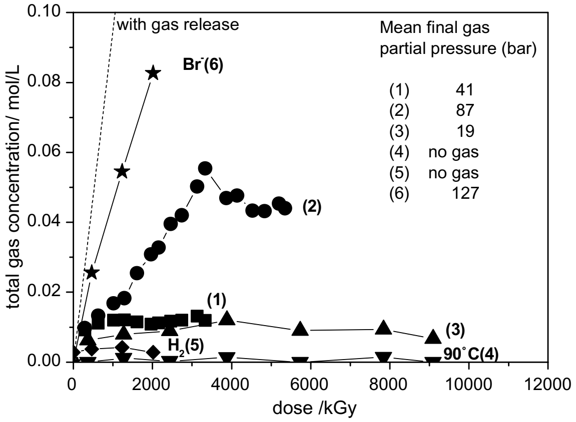

Fig. 2. Experimental results: radiolysis gas concentrations ($H_2 + O_2$) and final partial pressures (numbers correspond to experiment no.).

10^{-4} mol/L. In the experiments at 90 °C and in the experiments with added H_2 the concentration is one order of magnitude lower. The final radiolysis product concentrations resulting from doses of >2 MGy per run are summarized in Table 1.

The data show that the balance between reducing (H_2) and oxidizing radiolysis species ($O_2 + ClO_3^-$) is in all experiments in the favour of H_2. The reason could be a corrosion of the autoclave material. At the end of the experiments, however, the brines contained a maximum of 10^{-4} mol/L dissolved Ni^{2+} as the main Hastelloy component and much less of the other components. Such amounts do not remarkably influence the stoichiometric balance. A precipitation of Hastelloy corrosion products on the autoclave walls and bellow cannot be excluded, but was never observed, so that a conclusive explanation for the imbalance cannot be given.

The pressure relief data allow not only the determination of the amount of the radiolysis gas mixture ($O_2 + H_2$) formed in the autoclave but also to calculate Henry's constant for its solubility in the brine. Using a mean Henry constant for the gas mixture seems reasonable as the solubilities of H_2 and O_2 are similar and the gas composition is similar in all cases, except in experiment no. 5. The mean Henry constant averaged over all measurements from experiment no. 1, 2, 3 and 6 (in concentrated NaCl solution at 35 °C) is 0.0047 mol/(L MPa) with a standard deviation of 50% . The mean constant is about 80% higher than published solubilities for hydrogen in 5 mol/L NaCl solution at room temperature. The high standard deviation could be a result of uncertainties in the determination of the absolute gas pressure from the position reading of the bellow if only little gas is produced. In such a case, low pressures have to be adjusted in the pressure relief steps and then the relative error of the pressure gauge is at maximum. Furthermore the pressure is mainly determined by the spring forces of the bellow thus contributing errors of the bellow spring constant and that of the bellow position calibration to the total error. As the gas pressure is directly related to the total amount of gases, the standard deviation of the Henry constant applies also to the gas concentrations in Table 1.

All experiments are simulated using the appropriate reaction scheme and primary yields [16]; all rate constants are in accordance to the Notre Dame data bank [17]. In an earlier paper [13] we made an attempt to interpret the strong effect of dissolved radiolysis gases found in our first experiments under pressure by introducing a set of reactions with Ni^{2+} ions (as corrosion product from the autoclave material) into the scheme. A much better match between the experimental results and the simulation is achieved if the following Eq. (1) is added to the scheme:

$$H_2 + Cl_2^- = H + H^+ + 2Cl^- \quad k1 = 4.3 \times 10^5\ \mathrm{L\,mol^{-1}\,s^{-1}}. \tag{1}$$

This reaction seems reasonable as Cl_2^- is a main intermediate of the radiolysis of 5 mol/L chloride solution and an oxidant of similar strength as the OH radical ($E_h(OH/OH^-) = 1900$ mV, $E_h(Cl_2^-/2Cl^-) = 2300$ mV) [17]. The reaction of OH with H_2 is responsible for the suppression of the decomposition of pure water [14]. As no measured rate data for reaction (1) are available, we adjusted the rate constant according to the results found in experiment 3 (experiment with the lowest plateau gas concentration). The relation between the simulated total gas evolution and the dose is shown in Fig. 3 together with the measured final gas concentrations taken from Fig. 2. To explain the differing results in gas production under formally similar conditions (experiments 1–3), we initially considered reactions of iron ions (from autoclave corrosion) with different radiolytic species. However, a thorough check of the reaction scheme showed that a pH increase from 7 to 9 (the experimental values at the end of the irradiation ranged between 6.4 and 7.9) gives rise to an increase of the plateau gas concentrations by a factor of >4 (Fig. 3). The pure dose rate effect is negligible in comparison (Fig. 3 curve (1, 2) at 345 Gy/h and curve (3) at 912 Gy/h). Therefore we propose the scatter of results for experiments 1–3 is due to slight variations of the pH. Efforts are made to measure the value of the rate constant $k1$ for reaction (1), and to verify the pH effect on the final gas concentrations. Experiment no. 4 at 90 °C is not simulated, as no complete set of high temperature rate data, especially for the chloride system, is available. The calculations show that an increase in $k1$ (that can reasonably be expected at 90 °C) results in a sharp decrease of the plateau gas concentration. Thus, a higher value for $k1$ could be the reason for the fact that no gas is found in experiment no. 4. If H_2 is added to the solution prior to irradiation (experiment no. 5) the simulation shows no further gas production in accordance with the experiments (Table 1). For the simulation of experiment no. 6 (addition of Br^-) it is necessary to integrate the complex bromide system into the reaction scheme [16,18]. The calculation shows that Br^- competes successfully with H_2 for Cl_2^- and OH radicals so that gas evolution can proceed as observed in the experiment (Fig. 3). In pure water the over-all effect of Br^- is the promotion of the recombination of oxidizing and reducing radicals [14]. As a result, OH radicals no longer oxidize H_2 to water and therefore the net radiolytic decomposition proceeds. A similar mechanism (probably with Cl_2^- involved) seems to be effective in brine.

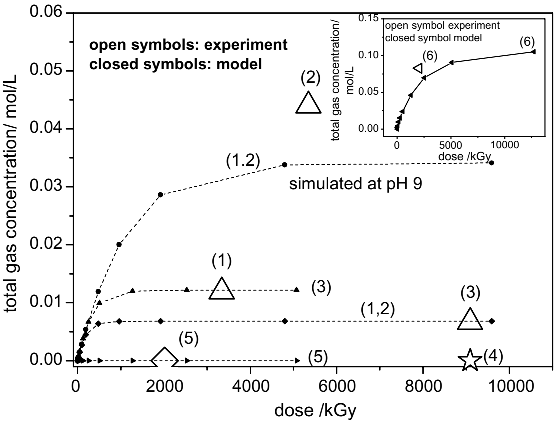

Fig. 3. Simulation results: total gas concentrations ($H_2 + O_2$) at pH 7 and final values from experiments. Experiment 1 and 2 additionally simulated at pH 9. Inset: data for experiment 6 (Br^- containing solution).

The experiments and their simulation show clearly that dissolved gases from γ-radiolysis, and an excess of H_2 to a higher degree suppress a sustaining decomposition of NaCl solution under pressure. The dose rate and traces of radiation chemically active contaminants like Br^- can shift the equilibrium gas concentrations to higher values. With sufficient Br^- present the partial pressure can exceed 100 bar so that a reliable protective action of H_2 towards solution decomposition becomes questionable.

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