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Summary

To model the radiolytic processes in concentrated chloride brine published data (reactions and rate constants) of the radiation chemical reactions are collected and compiled in the annex. Furthermore a set of primary radiolytic yields (G-values) is made up from published experimental data (gamma) or derived from theoretical considerations (alpha). The reaction schemes for the potential contaminants Ni^{2+}, Fe^{2+}, Br^- and CO_3^{2-} as well as a scheme which allows to model the oxidative dissolution of solid UO_2 can be implemented.

The sensitivity of the kinetic model for the radiolysis of pure water and of 5 M NaCl solution at pH 8 against the variation of rate constants and G-values is determined. Sensitivity analyses for gamma and alpha irradiation and for systems with constant radiolysis gas release and for such with no gas release are conducted separately. For the analysis each rate constant is varied by a factor of 10 or 0.1; for the variation of G-values each G-value is decreased by 20% and substituted by an equivalent of another primary species. As a measure for sensitivity usually the calculated concentrations of the permanent (molecular) products hydrogen, oxygen, hydrogen peroxide (water) and chlorate (brine) reached after 1000 years are compared to values achieved with nominal rate constants and G-values.

Normally alpha and gamma radiolysis in an open system results in a continuous production of molecular products (except the H_2O_2 production in water). The gamma radiolysis in a closed system with no gas release however leads to steady state conditions with low level concentrations of all radiolytic species.

According to the calculations all variations which have an effect on the concentration of dissolved H_2 (rate constants of H_2 consuming reactions or change of the G-value of H_2) result in a variation of the final concentrations of molecular products. The reaction schemes for alpha radiolysis are less sensitive against changes in rate constants and G-values compared to schemes for gamma radiolysis (except the scheme for alpha radiolysis of brine in a closed system).

For alpha radiolysis of water and brine in an open system the parameter variation results only in a few cases in a variation of molecular product concentrations of usually some 10 %. The alpha radiolysis scheme for brine with no gas release however is influenced by several parameters and some variations of rate constants and G-values cause a complete change of the reaction mechanism: Under nominal conditions H_2 and O_2 are continuously formed with a reduced rate compared to an open system. Varying these sensitive parameters the concentration of both dissolved gases reach a low level steady state concentration.

The water scheme for an open system is most sensitive for parameters with H_2 involved as mentioned above. The water scheme for a closed system leads to steady state conditions for all species but the steady state concentrations vary in some cases for orders of magnitude when varying certain rate constants or G-values. The brine system under gamma irradiation with gas release is for most of the parameter variations less sensitive (some 10% of concentration variation of the molecular products). A change in the reaction mechanism however is observed in such an open system if a G-value variation causes the G-value of H_2O_2 to exceed 0.14. In such a case there is no more continuous ClO_3^- production (in the favour of O_2) but instead a low level concentration is established. The H_2 production is not affected. The brine scheme for a closed system is most affected by parameter variations in which H_2 is involved.

The calculated production of radiolysis species in brine is compared to a variety of experiments conducted under gamma and alpha irradiation. The standard deviation of gamma experimental results in an open system with respect to the formation rate of the molecular products H_2, O_2 and ClO_3^- is under most conditions (pH, concentration of Cl^- and contaminants) in the range of some 10 %. The deviation between experimental and calculated concentrations is approximately of the same size. Only for Fe^{2+} containing solutions the degree of compliance is poorer. The compliance between experimental and calculation results for the alpha radiolysis of brine with respect to H_2 and O_2 is similar to that for gamma radiolysis. But all chlorine species are underestimated in the calculation. The formation of ClO_3^- proportional to the dose (at higher dose) and the steady state formation for HClO however is simulated correctly. The gamma radiolysis mechanism in a closed system without any gas release with the formation of steady state concentrations for H_2, O2 and $ClO3^-$ as observed in experiments is correctly modeled if the reaction between H_2 and Cl_2^- is considered in the scheme and if the strong pH dependence is correctly described by the model. The experimentally observed ‘protecting‘ effect of dissolved H_2 and the effect of added Br^- acting in the opposite direction is reasonably modeled. The deviation between experiments and calculation is for H_2 and in most cases for O_2 in the range of some 10%. The already low ClO_3^- concentrations found in experiments however are orders of magnitude lower in the calculation.

Ein kinetisches Modell für die Radiolyse von Chloridlösungen, seine Sensitivität gegenüber Modellparametern und ein Vergleich mit Experimenten

Zusammenfassung

Um die Radiolyseprozesse in konzentrierter Chloridlauge mit Hilfe eines reaktionskinetischen Modells zu simulieren, wurden veröffentlichte Daten zu den strahlenchemischen Reaktionen (Reaktionsgleichungen und ihre Geschwindigkeitskonstanten) gesammelt und im Annex zusammengestellt. Darüber hinaus wurden die Primärausbeuten der strahlenchemisch gebildeten Spezies (G-Werte) für die Gammaradiolyse aus veröffentlichten experimentellen Daten zusammengetragen bzw. für die Alpharadiolyse aus theoretischen Überlegungen abgeschätzt. Das Reaktionssystem kann um Gleichungen für die potentiellen Kontaminanten Ni^{2+}, Fe^{2+}, Br^- and CO_3^{2-} erweitert werden, ebenso wie um Gleichungen, die die oxidative Auflösung von UO_2 beschreiben.

Die Sensitivität dieses kinetischen Modells gegenüber einer Variation der Reaktionsgeschwindigkeitskonstanten und der G-Werte wurde für die Radiolyse reinen Wassers und von 5 M NaCl Lösung bei pH 8 bestimmt. Die Sensitivitätsanalysen wurden sowohl für die Gamma- als auch für die Alpharadiolyse durchgeführt, wobei die Fälle ‚konstante Radiolysegasfreisetzung’ und ‚keine Gasfreisetzung’ unterschieden wurden. Für die Analyse wurde jede Reaktionsgeschwindigkeitskonstante um den Faktor 10 und 0,1 variiert; für die Variation der G-Werte wurde jeder G-Wert um 20 % vermindert und durch jeweils eine andere oxidierende bzw. reduzierende Spezies in äquivalenter Menge ersetzt. Als Maß für die Sensitivität einer solchen Parameteränderung wurden die berechneten Konzentrationen der molekularen Produkte Wasserstoff, Sauerstoff, Wasserstoffperoxid (Wasser) und Chlorat (Salzlösung) nach 1000 Jahren Radiolyse mit den unter Nominalbedingungen erreichten Konzentrationen verglichen.

Bei der Alpha- und Gammaradiolyse werden bei zugelassener Radiolysegasfreisetzung die molekularen Produkte (außer H_2O_2 bei der Wasserradiolyse) normalerweise mit einer konstanten Rate gebildet. In einem geschlossenen System hingegen führt die Gammaradiolyse zu Gleichgewichtszuständen mit niedrigen Konzentrationen an Radiolysespezies.

Die Rechnungen zeigen, dass alle Parametervariationen, die eine Auswirkung auf die aktuelle H_2 Konzentration haben (Wasserstoff verbrauchende Reaktionen, veränderter G-Wert für H_2), sich auch auf die Endkonzentrationen der molekularen Spezies auswirken. Die Reaktionssysteme für die Alpharadiolyse sind unempfindlicher für Parametervariationen als die für die Gammaradiolyse (außer Alpharadiolyse von Chloridlauge im geschlossenen System).

Bei der Alpharadiolyse von Wasser und von Chloridlösung im offenen System führt die Sensitivitätsanalyse nur in wenigen Fällen zu einer Variation der Konzentration molekularer Produkte von einigen 10 %. Das Reaktionssystem für Chloridlauge ohne Gasfreisetzung ist dagegen empfindlich für eine ganze Reihe von Parametern, von denen einige zu einem Wechsel des Reaktionsverlaufs führen: Während die Rechnungen mit nominalen Parametern zu einer kontinuierlichen Bildung von H_2 und O_2 führen, bewirken die Änderungen dieser sensitiven Parametern, dass die gelösten Gase nur Gleichgewichtskonzentrationen auf niedrigem Niveau erreichen, ähnlich den Prozessen bei der Gammaradiolyse ohne Gasfreisetzung.

Das Reaktionssystem für Wasser unter Gammabestrahlung mit Gasfreisetzung ist gegenüber allen Parametern, die die H_2 Konzentration beeinflussen, sehr empfindlich. Dasselbe System ohne Gasfreisetzung führt bei Parametervariation immer zu Gleichgewichtskonzentrationen der molekularen Produkte, deren Niveau in einigen Fällen aber um mehrere Größenordnungen von den Nominalwerten abweichen kann. Das Reaktionssystem für Chloridlauge unter Gammabestrahlung mit Gasfreisetzung führt bei vielen Parameteränderungen zu Konzentrationsänderungen der molekularen Produkte von einigen 10%. Wird bei diesen Parametervariationen ein G-Wert von 0,14 für H_2O_2 überschritten, so ändert sich der Reaktionsmechanismus: Die Chloratkonzentration erreicht nur einen niedrigen Gleichgewichtswert. Stattdessen bildet sich O_2. Die H_2 Bildungsrate wird nicht beeinflusst. Das entsprechende System ohne Gasfreisetzung ist an empfindlichsten für Parameteränderungen, die die Konzentration von gelöstem H_2 betreffen.

Die berechnete Bildung von Radiolysespezies in 5 M NaCl Lösung wurde mit den Ergebnissen von entsprechenden Radiolyseexperimenten unter Gamma- und Alphabestrahlung verglichen. Die Standardabweichung der Analysen bei den gamma-Experimenten im offenen System im Hinblick auf die Bildungsrate der molekularen Produkte H_2, O_2 und ClO_3^- betrug unter den meisten Bedingungen (pH, Konzentration von Cl^- und von Kontaminanten) einige 10 %. Die Abweichungen zwischen experimentell ermittelten und berechneten Werten liegen in der gleichen Größenordnung. Lediglich in Gegenwart von Fe^{2+} ist die Übereinstimmung schlechter. Der Vergleich zwischen Experimenten und Rechnung für die Alpharadiolyse im offenen System fällt im Hinblick auf H_2 und O_2 ähnlich dem für die Gammaradiolyse aus. Die Konzentrationen aller Chlorspezies werden bei der Modellierung der alpha-Radiolyse allerdings deutlich unterschätzt. Die ClO_3^- Bildung proportional zur Dosis (bei hoher Dosis) und die Bildung von HClO bis zu einer Gleichgewichtskonzentration wird vom Modell qualitativ richtig wiedergegeben. Der Gammaradiolysemechanismus im geschlossenen System ohne Gasfreisetzung (Erreichen von Gleichgewichtskonzentrationen für H_2, O_2 und ClO_3^-), wie er in den Experimenten beobachtet wurde, wird bei der Simulation richtig wiedergegeben, wenn eine Reaktion zwischen H_2 und Cl_2^- -Radikal im Reaktionssystem berücksichtigt wird und wenn die starke pH Abhängigkeit durch das Reaktionsmodell richtig beschrieben wird. Der experimentell beobachtete ‚Schutzeffekt' von gelöstem Wasserstoff und der gegenläufige Effekt durch gelöstes Br^- wird mit dem Modell ebenfalls richtig beschrieben. Die Abweichungen zwischen Experimenten und Rechnung betragen für H_2 und in den meisten Fällen auch für O_2 einige 10 %. Die bei den Experimenten ohne Gasphase gefundenen niedrigen Konzentrationen für ClO_3^- liegen bei der Modellierung noch um einige Größenordnungen tiefer.

Content

1. Introduction

Spent nuclear fuel is supposed to be buried in the deep underground in a final disposal. If rock salt as host formation is chosen chloride brine intrusion is considered as an accident scenario. When the container fails by corrosion the geological surrounding and metals from the container material etc. will have established reducing conditions even close to the fuel. As the solubility of four-valent 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 better soluble hexavalent Uranium and thus promote the radionuclide release. Many works about the radiolytical decomposition of ground waters from final disposal sites and about the radiolytically conveyed UO_2 corrosion were published in the past (review and final reports from previous EU programs: [1-3]).

To predict the long term performance of spent fuel in a final disposal the mechanism of the radiolytical processes involved must be understood. This includes not only the processes in pure systems but also the influence of possible contaminants and of long lived radiolysis products on the radiolysis (e.g [4]). Furthermore one has to distinguish between the effect of low LET (β, γ) and high LET radiation (α).

To describe the radiolysis processes in chloride brine published kinetic data for the reactions involved are collected and fed into the kinetic code MACKSIMA CHEMIST [5]. The model calculations are compared to experiments conducted under various conditions to verify the model and find sensitive points within the model from which one could derive future experiments for model improvement. As any radiolytic decomposition of aqueous solutions is inevitably accompanied by the formation of H_2 and O_2 and these gases could remain dissolved in a final disposal site in a depth of up to 1000 m until the partial pressure exceeds 300 bar at maximum, appropriate experiments are included in the comparison. From reactor chemistry it is well known that radiolysis gases and especially hydrogen develop a protective action against further progress of radiolysis [6, 7]. The question came up if one could take advantage from such processes in a final disposal too, because similar effects are observed in experiments with spent fuel [8].

As the UO_2 matrix corrosion under irradiation is in the focus of interest an approach is added to integrate the heterogeneous UO_2 dissolution into the model for reactions in homogeneous solution.

2. Overview over experiments

2.1 Gamma radiolysis in an open system

A.R. grade NaCl (Merck) is annealed at 500°C for a few hours to burn all organic matter. For purification it is once recrystallized. The salt is then dissolved in water from a MilliQ-185 Plus (Millipore) purification system in concentrations between about 1 and 5.3 Mol/L. To achieve pH 2 and pH 12 in the solution calculated amounts of 1 Mol/L NaOH or HCl standard solution (Merck) is added. Contaminants are admixed as A.R. grade compounds in chloride or sodium form: In different experiments 10^{-4} Mol/L Ni^{2+}, $2.3*10^{-3}$ Mol/L Br^- and $1.1*10^{-3}$ Mol/L Fe^{2+} are added.

The solutions are deaerated in glass ampoules with a headspace of about 10 times the solution volume by freeze and pump technique and are then sealed under vacuum (as radiolysis gases can escape from the solution this assembly is treated as an open system). Gamma doses of up to 10 MGy are applied at ambient temperature at dose rates between 0.2 and 1.2 kGy/h. The irradiation positions are calibrated using Fricke solution. After irradiation the ampoules are opened to an evacuated apparatus where a known amount of Ne is added. The composition of the radiolytic gases is then determined by mass spectrometry using the Neon as internal standard. The radiolytic products HClO, ClO_2^- and ClO_3^- are determined in the solution as described elsewhere [9]; ClO_2^- and ClO_3^- are analysed in parallel by ion chromatography [10, 11].

2.2 Alpha radiolysis in an open system

To conduct alpha irradiation experiments chloride solutions are prepared as described above and are then mixed in a glove box operated under inert gas with a stock solution of ^{238}Pu. For that purpose $^{238}PuO_2$ is dissolved in HNO_3 and then heated with a few drops of $HClO_4$ until fuming. After dilution with water aliquots of the plutonium solution are added to 20 ml of chloride brine to give activity concentrations of 15 – 380 GBq/L, which corresponds to a dose rate of 40 – 1000 Gy/h assuming that all alpha energy is homogeneously dissipated in the brine. Air is removed by purging with Ar. The irradiation vessel with brine of about 50 ml total volume is connected to an evacuated gas sampling cylinder (about 50 ml). The cylinder valve is then opened to establish reduced pressure in the apparatus. As there is sufficient head space above the solution the system is treated as open. The solutions are kept at ambient temperature and are stirred from time to time as Pu precipitates (partially) from the solution. In certain time intervals gas samples are taken and analyzed for H_2 and O_2. 3 ml samples are taken from the solution and analyzed for ClO_3^-, ClO_2^- and ClO^-. The gas space in the irradiation vessel with the remaining solution is then flushed with Ar and a new gas sampling cylinder is mounted for another irradiation cycle. [12]

2.3 Gamma radiolysis in a closed system

The γ-irradiation experiments in which no gas phase formation is allowed are performed in autoclaves 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 up to 300 bar with Ar. The bellow transfers the pressure onto the solution thus forcing radiolysis gases 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) and bubbled with Ar for >30 minutes. One experiment is conducted with 2.3 mM Br^-, another with 2.8 mM H_2 additionally added prior to irradiation. The irradiation takes place in a panoramic gamma source under a pressure of about 250 bar. The mean dose rate in the autoclaves measured with a Fricke dosimeter is 345 or 912 Gy/h. The autoclaves are thermostated at 35°C.

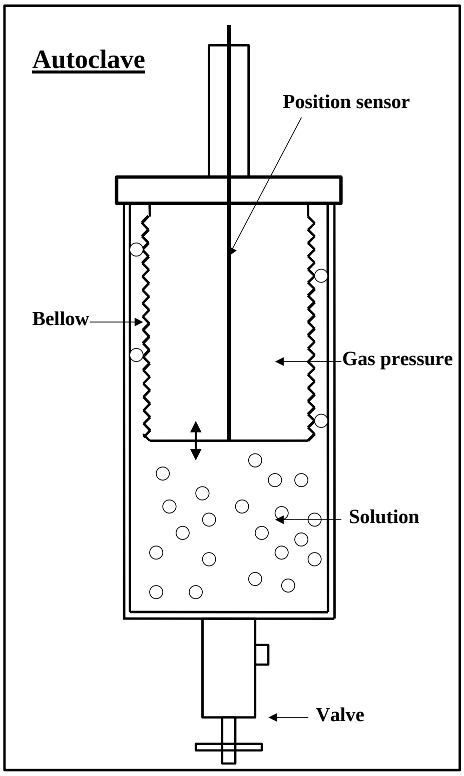

Fig. 1 : Outline drawing of autoclave in which experiments without gas phase are conducted

From time to time the irradiation is interrupted and the pressure on the bellow is released stepwise while recording its position without opening the autoclave. From the position reading the gas volume can be calculated and also the total amount of gases considering

Henry's law. At the end of the experiment gas and liquid samples are taken and analyzed as described above [10].

3. Radiolysis model

To simulate radiation chemical processes by means of a kinetic model a set of all relevant reactions and their rate constants, a set of primary yields (G- values), the prevailing dose rate and the time frame are necessary as well as a mathematical code which can cope with the requirements of very fast reactions.

3.1 Equations

The equations to simulate the processes in chloride brine are collected from published data. The majority are elementary reactions of first or second order determined by pulse radiolysis. In some cases however reactions of higher order and reactions to cover long periods of time (slow reactions like the natural decay of HClO) have to be integrated into the scheme. The desorption of radiolysis gases (H_2 and O_2) in systems with a gas phase are formulated as first order reactions (open system) under formation of the desorbed species H_2D and O_2D which do not further participate in the radiation chemical reactions, or as equilibrium reactions (quasi-open). Systems where no gas formation is allowed are called closed. Details are given in the annex together with references. To maintain compatibility with the applied mathematical code in a few cases dummy species (like O_4) with no chemical meaning have to be used but care is taken that such species cannot accumulate. The basic rate constants are taken (or converted) for zero ionic strength and for room temperature. In that form they are compiled in the annex together with the appropriate references. For the application on brine (high ionic strength) the rate constants for reactions between charged species have to be corrected according to:

$$\lg k = \lg k_0 + 1.02 * z_A * z_B * \frac{\sqrt{S}}{1+\sqrt{S}}$$

with:

k = rate constant (L/(Mol*s))

k_0 = rate constant at zero ionic strength (L/(Mol*s))

z_A and z_B = charge number of the ions involved

S = ionic strength (Mol/L)

3.2 Concentrations at start, dose, dose rate, time

For modeling radiolytic processes the concentrations of all reacting compounds which are present at start have to be defined: Concentrations of water, H^+ or OH^- (pH), Cl^- and other compounds (e.g. contaminants). The water concentrations in chloride brines are given in Table 1. In some cases it can be useful to set certain concentrations constant to avoid artefacts. In most of our calculations we set the concentrations of H_2O, pH and Cl^- constant. This allows long term calculations without consumption of water and chloride and avoids complications from HClO formation: The radiation chemistry of HClO and ClO^- are different but the reaction scheme contains only reactions of HClO (because lack of data) and therefore does not consider the dissociation of HClO. As a result any HClO formation in a calculation with pH allowed to float would give rise to an unrealistic pH increase.

Table 1: Henry's constants and the molarity of water (for pure water and 5 Mol/L NaCl)

Solution	KH_{H2} (Mol/(L*MPa))	KH_{O2} (Mol/(L*MPa))	Water molarity (Mol/L)
Water	0.007	0.0116	55.5
5M NaCl	0.00268	0.00221	49.5

Besides the start concentrations data are required for dose rate and time or others, depending on the code. The model treats the dose rate as to be effective and uniform in the bulk of the solution. This is appropriate for gamma irradiation. For beta and especially for alpha radiation of short range however these requirements are only met when the respective emitter is homogeneously distributed in the solution.

3.3 Primary radiolytic yield (G – value)

The formation rate of primary radiolytic species (G-value = number of species formed per 100 eV absorbed energy) is proportional to the dose and depends strongly on the linear energy transfer (LET) of the radiation. The primary G-value is the yield of species which is available for reactants in homogeneous solution after energy absorption and homogenization of species concentration by diffusion out of the spurs and tracks. This definition indicates that the term ‘primary yield’ is not very precise but for diluted near neutral solutions at room temperature the primary G-values for β/γ and for α radiation are well established [13]. In such solutions the energy absorption is 100 % at water molecules (indirect radiation effect). This is different for 5 molar NaCl solution. While Na^+ behaves radiation chemically inert the Cl^- reacts very efficiently with oxidizing radicals. Because of the high Cl^- concentration such reactions take place already in the tracks and spurs. In this way -with less radical recombination in the tracks and spurs- not only the total yield of species diffusing out of the tracks and spurs increases (Fig. 2) but also the species spectrum reaching a homogeneous distribution and becoming available for other reactants changes (Fig. 3). Furthermore one has to consider a direct radiation effect on the dissolved NaCl. From the concentration of electrons attached to Cl^- this effect is estimated to be about 15 % for 5 M NaCl solution.

For gamma radiolysis experimental values for the primary yields are published or can be derived from other experimental data (see references in [10] and [11]). As no experimental data are available for alpha radiolysis one has to rely on the very general deduction for the interaction of scavengers with short lived species in the tracks and spurs and its effect on the primary yield [14]. The G-values for water and 5 Mol/L NaCl solution are listed in Table 2.

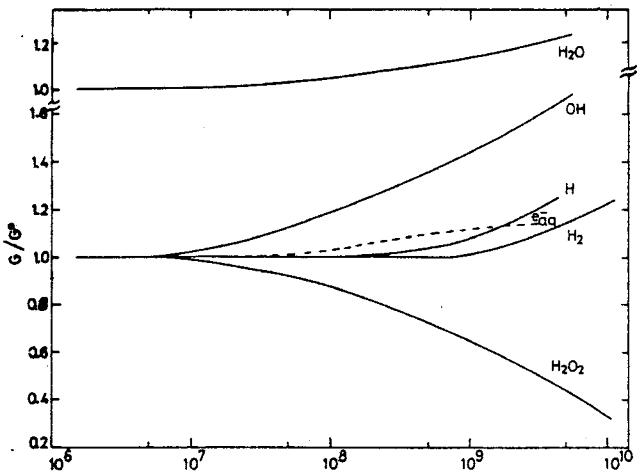

Figure 10. Fractional yield (G/G^0) dependence of primary products of water radiolysis on the reactivity toward hydroxyl radical. Best lines through the experimentally derived values: OH and e_{aq}^-, Figure 8 this work; H atom, ref 16 Figure 2; H_2, ref 18 Figure 6; H_2O_2, ref 18 Figure 5 and ref 17 Figure 1.

Fig.2 Yield of primary radiolytic species from reference [17].

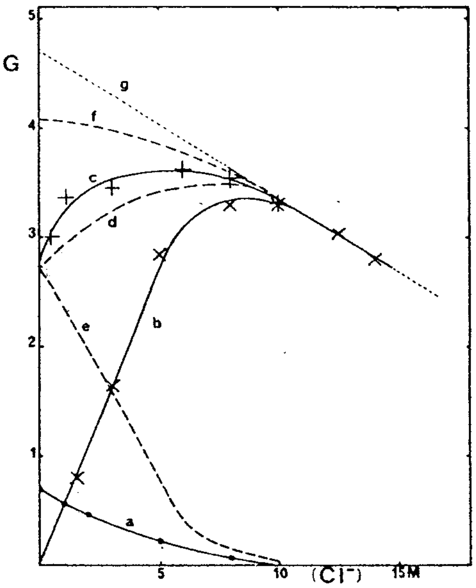

Figure 6. Yields of oxidizing species in presence of Cl^-: (a) $G_{H_2O_2}$, (b) $G_{Cl_2^-}$, (c) $G(Cl_2^-)$, pH 1, (d) $G_{OH} + G_{Cl_2^-}$, (e) G_{OH}, (f) $G_{ox} = 2G_{H_2O} + G_{OH} + G_{Cl_2^-}$ (g) $G = 4.7(1 - f_{Cl^-})$.

Fig. 3: Primary yields of chlorine and other species from reference [18].

Table 2: Radiation chemical primary yields (species per 100eV)

	Gamma		Alpha	
Species	Water	5 M NaCl	Water	5 M NaCl
H_2O_2	0.70	0.09	0.98	0.23
HO_2	0	0	0.22	0.05
H_2	0.45	0.60	1.30	1.52
H	0.55	0.03	0.21	0.26
e^-_{aq}	2.65	3.89	0.06	0.06
OH	2.70	0.09	0.25	0.06
OH^-	0.00	0	0	1.01
H^+	2.65	0.44	0.06	0
Cl^-	0.00	-6.26	0	-1.62
Cl_2^-	0.00	2.43	0	0
ClOH-	0.00	0.38	0	0.55
HClO	0.00	1.02	0	1.07
H_2O	-4.10	-1.67	-2.65	-3.25

The yield $(100\ eV)^{-1}$ is equivalent to 104 nMol/(L*Gy) in water or 123 nMol/(L*Gy) in 5 M NaCl.

3.4 Model extension for contaminants and for dissolution of UO_2

To model the interference of contaminants additional sets of equations with rate constants are needed in the reaction scheme. Questionable in that context is the availability of data from all relevant reactions. Scheme extensions are provided in the annex for Fe^{2+}, Ni^{2+},Br^- and CO_3^{2-}. These constituents seem to be important for modeling reactions in a final disposal and for simulating lab experiments: Fe^{2+} is a product from container (final disposal) or autoclave (experiments) corrosion; Ni^{2+} results from autoclave corrosion and might be an example for a not redox active component; Br^- is considered as a natural impurity of rock salt, CO_3^{2-} as a natural component in the deep underground. The four components mentioned are by far not sufficient to model the complex system expected in a final disposal with contributions from the natural surrounding, backfill material, container corrosion and dissolution of the spent fuel with all fission products etc. but their introduction into the scheme might disclose how effective contaminants can influence the radiation chemical processes and by that give guidelines for a conservative modeling.

Additional assumptions have to be made to integrate the heterogeneous dissolution of solid UO_2 into the reaction scheme which is valid for homogeneous kinetics. Further complications arise for the case of emitted alpha or beta radiation from a solid as the irradiated volume is usually different from the bulk volume and the dose rate decreases within the radiation range with the distance from the solid surface. Such facts might be adequately modeled by calculating radiolysis processes stepwise (time) in compartments (location) in homogeneous solution and combining it with transport of radiolysis products between the compartments. (TraRaMo [15])

A simple approach to describe the dissolution of solid UO_2 under alpha radiation is to calculate the radiolytic processes only near the solid surface, to use a constant dose rate within the layer of a thickness equal to the range of alpha radiation, to assume that UO_2 is 'dissolved' by oxidizing species proportional to their concentration (pseudo first order reactions) and to implement measures that avoid an accumulation of products in the layer (by formation of dummy species or by diffusion processes). Two schemes for this approach are listed in the annex.

3.5 Calculation code

Two different codes with slightly different capabilities are used in the SFS project: MACKSIMA CHEMIST [5] and Chemsimul [16]. In the D12 report of this project it is worked out that calculations with both codes deviate from each other by less than 1 %.

3.6 Sensitivity analysis

The results of modeling with respect to long lived products are mainly influenced by the kinetic rate constants and the G-values and less by the dose rate. To determine which rate constant or G-value has a strong impact on the calculated concentrations the numerical values of both are varied and the output is compared to calculations with nominal values. Each constant is varied one by one by a factor 10 and 0.1. For varying the G-values the oxidizing and reducing species are varied separately: Per calculation run each G-value is lowered by 20%. For compensation other oxidants or reductants are added one by one. In the tables with the results all equations are listed, for which the variation of the rate constant by a factor 10 and/or 0.1 from nominal leads to a variation of the concentration of a molecular product (H_2O_2, H_2D, H_2, O_2 or O_2D in water and H_2D, H_2, O_2D, O_2 or ClO_3^- in chloride brine) by more than a factor 1.1 or 0.9 (10% variation).

The concentrations of water and Cl^- and the pH (at pH 8) are kept constant. The dose rate for gamma irradiation is 8000 Gy/h that for alpha irradiation 1400Gy/h. The concentrations after 1000a of irradiation are compared. In the case of very low net turnover however (gamma radiolysis of closed water or chloride brine system) the calculation errors over a time period of 1000 years seem to produce unreasonable results. In such a case the sum of reducing species concentrations exceeds that of oxidizing species by orders of magnitude. The species concentrations created in a closed system under gamma irradiation are therefore compared after 0.1 years of irradiation. After that time span the reducing and oxidizing species are still almost equivalent.

3.6.1 Water, gamma radiolysis, open system, constant gas release (Table 3)

The modeling of pure water gamma radiolysis results in steady state concentrations of all species after a short period of time, except that for released H_2 and O_2 (i.e. H_2D and O_2D). Table 3 contains the results of the sensitivity analysis. A remarkable fact is that for pure systems without any scavenger for the reducing radicals the H_2O_2 concentration is kept at a low level and only H_2D and O_2D are produced proportional to the dose.

The H_2O_2 steady state concentration is mainly controlled by the reaction with e^-_{aq}. If the appropriate rate constant decreases (reaction 15, annex) the H_2O_2 concentration increases and vice versa. If e^-_{aq} is more efficiently scavenged by O_2 (by accelerating reaction 16) the concentration of H_2O_2 increases. The same effect has a slower desorption of O_2 (decrease of rate constant of reaction 35) and thus a higher steady state concentration of dissolved O_2. The opposite effect is observed if the desorption rate of H_2 (reaction 36) is varied. A decrease of the rate constant of reaction 36 results in lower H_2 and O_2 steady state concentrations and thus to a lower H_2O_2 concentration.

The production rate of the desorbed species H_2D and O_2D is mainly controlled by reactions of the radicals OH, E^- and H with molecular species (reactions 6, 7, 15, 16) and by the rate of desorption (reaction 35, 36).

Table 3 : Sensitivity analysis. Gamma radiolysis of water in an open system.
(Upper part: variation of rate constants; lower part: variation of primary yield = G-value)

- Eq. No gives the number of the equation in the annex.
- up/down refers to the calculation with the appropriate rate constant multiplied by 10 or 0.1
- Numbers in the table give factors with which calculated concentrations with nominal values (given in the upper line) have to be multiplied. Only deviations > 10 % from ‘normal’ are noted. The comparison is usually made for an irradiation time of 1000 years.
- Replacement: The first column shows the primary species from which 20% compared to nominal is substituted by the species in the second column.

Eq.	Reaction		H2O2	O2D	H2D
No	Conc. (Mol/L) using nominal k		2,75E-6	6,51E2	1,30E3
5	OH + O2- = O2 + OH-	down	1	0,3	0,3
5		up	1	1,26	1,26
6	OH + H2O2 = HO2 + H2O	down	1	0,23	0,23
6		up	1	1,95	1,95
7	OH + H2 = H + H2O	down	1	2,21	2,21
7		up	1	0,014	0,014
9	OH + HO2- = HO2 + OH-	up	1	1,18	1,18
13	E- + O2- = HO2- + OH-	down	1	1,12	1,07
13		up	1	0,46	0,46
15	E- + H2O2 = OH + OH-	down	15	1,92	1,92
15		up	0,04	0,19	0,19
16	E- + O2 = O2-	down	0,08	0,17	0,17
16		up	12,5	2,0	2,0
22	H + O2- = HO2-	up	1	0,53	0,53
25	H + O2 = HO2	down	1	0,53	0,53
25		up	1	1,07	1,07
28	HO2 + O2- = O2 + HO2-	up	1	0,87	0,87
29	HO2 = H+ +O2-	down	1	0,87	0,87
30	H+ + O2- = HO2	up	1	0,87	0,87
31	H2O2 = H+ + HO2-	up	1	1,18	1,18
32	H+ + HO2- = H2O2	down	1	1,19	1,19
35	O2 = O2D	down	13	2	2
35		up	0,1	0,13	0,13
36	H2 = H2D	down	0,1	0,014	0,014
36		up	1,68	2,2	2,2
40	H2O2 = H2O + O	up	1	1,12	1,12

20 % of primary yield of	replaced by			
E-	H	1,454	1,149	1,146
E-	H_2	2,072	1,981	2,153
H	E-	0,909	0,973	0,969
H	H_2	1,130	1,184	1,153
H_2	E-	0,654	0,676	0,669
H_2	H	0,727	0,707	0,624
H_2O_2	HO_2	1,055	1,261	0,715
H_2O_2	OH	0,614	0,800	0,800
OH	H_2O_2	2,036	1,323	1,307
OH	HO_2	2,109	1,692	1,692

3.6.2 Water, gamma radiolysis, closed system, no gas phase formation (Table 4)

Gamma radiolysis of water in a closed system results in a very low net turnover and leads to low steady state concentrations of molecular products in the μ-molar range (Table 4). If the rate constants of equations in which the OH radical is involved (i.e. consumed) are increased (reaction 1, 2, 5, 6 and 9) the equilibrium concentrations of H_2, O_2 and H_2O_2 increase (for equation 5 and 6 more than two orders or magnitude) as less OH radicals will be able to react with H_2 (reaction 7). With a higher rate of reaction 7 however H_2 consumption is increased and thus the steady state concentrations of molecular products decrease.

Furthermore the acidic dissociation of H_2O_2 (equation 31/32) has a strong influence on the equilibrium concentrations of molecular species: The more H_2O_2 is dissociated the higher are the concentrations.

The effect of the reducing species H and E^- towards O_2 and O_2^- are similar: An increase in the rate constant of the equations with O_2 involved (equation 16 and 25) by a factor 10 increases the steady state concentrations of H_2 and O_2 by more than one order of magnitude. An opposite effect is calculated for the reactions with the O_2^- radical (equations 13 and 22).

With respect to the variation of the G-values on the reducing side the calculation shows that the equilibrium concentrations of the molecular products follow the primary yield of H_2. On the oxidizing side a higher yield of HO_2 on the expense of OH or H_2O_2 gives higher equilibrium concentrations. A similar effect is calculated for an increased primary yield of H_2O_2 on the expense of OH radicals.

In general the equilibrium concentrations achieved in a closed system mainly depend on the rate constants of the reactions with OH, E^- and H radicals involved and the actual primary yields of H_2, H_2O_2 and HO_2.

Table 4 : Sensitivity analysis. Gamma radiolysis of water in a closed system.
(see remarks in Table 3; deviating from the conditions given there the comparison is made for an irradiation time of 0.1 years; see chapter 3.6)

Eq. No	Reaction		H2O2	O2	H2
	Conc. (Mol/L) using nominal k		3,72E-7	3,56E-7	1,14E-6
1	$OH + OH = H_2O_2$	down	0,478	0,477	0,492
1		up	2,849	2,865	2,798
2	$OH + O = H_2O$	up	1,161	1,250	1,219
5	$OH + O_2^- = O_2 + OH^-$	down	1,166	0,0025	0,412
5		up	216,1	528,1	400,9
6	$OH + H_2O_2 = HO_2 + H_2O$	down	1,285	0,0023	4,438
6		up	62,09	112,4	92,98
7	$OH + H_2 = H + H_2O$	down	379,0	1303,4	938,6
7		up	0,32	0,00044	0,125
9	$OH + HO_2^- = HO_2 + OH^-$	down	0,913	0,738	0,804
9		up	6,908	11,09	9,473
13	$E^- + O_2^- = HO_2^- + OH^-$	down	1,011	17,05	14,47
13		up	1,069	0,055	0,411
15	$E^- + H_2O_2 = OH + OH^-$	down	2,228	0,0092	0,759
15		up	0,187	0,564	0,446
16	$E^- + O_2 = O_2^-$	down	0,511	0,472	0,493
16		up	0,814	15,76	37,54
17	$E^- + H^+ = H$	down	1	1	1
17		up	1,207	1,025	1,087
18	$E^- + H_2O = H + OH^-$	down	1	1	1
18		up	1,919	1	0,659
22	$H + O_2^- = HO_2^-$	down	6,989	11,26	9,649
22		up	1,172	0,0027	0,408
25	$H + O_2 = HO_2$	down	1	0,141	0,452
25		up	7,043	11,35	9,736
31	$H_2O_2 = H^+ + HO_2^-$	down	1	1	1
31		up	3,978	6,264	4,894
32	$H^+ + HO_2^- = H_2O_2$	down	6,855	9,269	9,473
32		up	0,916	0,750	0,805
40	$H_2O_2 = H_2O + O$	down	1	1	1
40		up	1,051	1,160	1,122

20 % of primary yield of	replaced by			
E-	H	1,623	1,438	1,482
E-	H_2	46,77	60,95	54,29
H	E-	1,05	1,211	1,114
H	H_2	2,45	3,792	3,307
H_2	E-	0,72	0,418	0,498
H_2	H	0,82	0,044	0,342
H_2O_2	HO_2	12,61	22,95	19,04
H_2O_2	OH	0,77	0,778	0,777
OH	H_2O_2	10,06	10,64	10,43
OH	HO_2	37,40	46,07	42,11

3.6.3 Water, alpha radiolysis, open system, constant gas release (Table 5)

The simulation of the alpha radiolysis of water in an open system discloses that the reaction scheme is completely insensitive against variation of rate constants (Table 5). The concentrations of all molecular products change by less than 10% as a result of rate constant variation by a factor of 10 and 0.1 respectively. The exception is the H_2O_2 concentration when varying the rate constant of equation 40.

If 20% of primary H_2 is replaced by E- or H radicals the final H_2D concentration decreases by roughly 20% and such variation has an even more pronounced effect on the H_2O_2 concentration (about 50 % decrease of H_2O_2 concentration if primary H_2 is replaced by E^-, about 30% increase if it is replaced by H). The substitution of primary H_2O_2 by HO_2 or OH radicals results in a decrease of final H_2O_2 concentration but has no effect on the concentrations of H_2D and O_2D.

Summarizing the results one can say that water is decomposed by alpha radiation into H_2D and O_2D in equivalent amounts (the yield of H_2O_2 is orders of magnitude smaller) and that the final yield of H_2D follows its primary yield. The rate constants and the G-values (except that for H_2) have practically no influence (if varied in the extent of our analysis).

Table 5: Sensitivity analysis. Alpha radiolysis of water in an open system.
Remarks: See Table 3

Eq. No	Reactions	H2O2	O2D	H2D
	Conc. (Mol/L) using nominal k	4,09E-5	8,19E2	1,64E3
40	$H_2O_2 = H_2O + O$ down	9,315	1,004	1
40	up	0,106	0,996	0,993

20 % of primary yield of	replaced by			
H_2	E^-	0,550	0,785	0,780
H_2	H	1,344	0,800	0,798
H_2O_2	HO_2	0,863	1	1
H_2O_2	OH	0,635	0,976	0,975

3.6.4 Water, alpha radiolysis, closed system, no gas phase formation (Table 6)

The closed system yields practically similar results with respect to the variation of rate constants as the open system even though the net production rate of the molecular products is reduced by about 20%. The replacement of oxidizing species by OH radicals results in a decrease of H_2 and O_2 yield as OH reacts more efficiently with H_2.

Table 6: Sensitivity analysis. Alpha radiolysis of water in a closed system.
Remarks: See Table 3

Eq. No	Reactions Conc. (Mol/L) using nominal k	H2O2 5,45E-5	O2 6,67E2	H2 1,33E3
40	$H_2O_2 = H_2O + O$ down	10	1	1
40	up	0,1	1	1

20 % of primary yield of	replaced by			
H_2	E^-	1,192	0,749	0,752
H_2	H	1,192	0,749	0,752
H_2O_2	OH	1	0,615	0,616
HO_2	OH	1,027	0,884	0,887

3.6.5 5 Mol/L NaCl solution, gamma radiolysis, open system, constant gas release (Table 7)

In 5 M chloride solution all species involved reach only low level concentrations, except H_2D, O_2D and ClO_3^- which are formed linearly with the dose and are addressed as final stable products. Even though the chloride system is more complex than the pure water system there are only two reaction rate constants which remarkably influence the production rate of H_2D and thus the total radiolytic effect: The reaction of H_2 with Cl_2^- (eq. 154) and the H_2 desorption reaction (eq. 36). Reaction 154 is responsible for the 'protective' action of H_2. The turnover via reaction 154 depends on the steady state concentration of dissolved H_2 in the solution which on the other hand is determined by the desorption rate of H_2 (reaction 36). If the rate constant 154 is decreased or the rate constant 36 is increased there is only little increase of the H_2D formation rate (and that is the reason why the integration of reaction 154 into the scheme is not really needed for an open system), but the opposite variation of the rate constants halves the formation rate of H_2D. This fact indicates the sensitivity of the system against dissolved H_2 which is in the 10 μ-molar range at nominal conditions and which seems to be close to the threshold concentration from which a 'protective' action takes place. In parallel to the H_2D yield the yields of O_2D and ClO_3^- vary. But the distribution of the equivalent oxidizing long-lived products between O_2D and ClO_3^- depends on a few more rate constants. If the rate constant of the reaction describing the further oxidation of HClO (eq. 101) is increased or that describing the further oxidation of ClO_2^- (eq. 102) is decreased, the yield of ClO_3^- increases on the expense of O_2D. The same effect is achieved if the rate constant describing the reduction of HClO (eq.106) is decreased or that describing the reduction of ClO_2^- is increased (eq. 109). Furthermore the hydrolysis reactions of Cl_2O_4 influence the yield ratio of ClO_3^- and O_2D. If reaction 132 which produces ClO_2^- and ClO_3^- is accelerated the final yield of ClO_3^- increases while the yield decreases if hydrolysis reaction 133 which produces HClO is accelerated.

The variation of G-values influences the production rate of H_2D only if its primary yield is directly affected (H_2 replaced by other reductants or vice versa). The decrease of the H_2D formation rate is accompanied by a slight decrease of ClO_3^- yield in favour of O_2D. A stronger decrease of the formation rate of ClO_3^- is given if the G-value of H_2O_2 or HO_2 is increased on the expense of other oxidizing species (Cl_2^-, $ClOH^-$, HClO). If the G-value of H_2O_2 exceeds a threshold of 0.14 (by substituting oxidants by H_2O_2), the formation of all final chlorine compounds drops practically to zero; H_2D and O_2D become the only radiolysis products. This is the case if 20 % of the G-value for Cl_2^- or HClO is substituted by H_2O_2.

Table 7: Sensitivity analysis. Gamma radiolysis of 5 M NaCl solution in an open system. Remarks: See Table 3

Eq. No	Reactions Conc. (Mol/L) using nominal k		ClO3- 3,84E2	O2D 1,42E3	H2D 3,99E3
33	H2O = H+ +OH-	down	0,966	0,788	0,975
33		up	1,096	1,049	1,060
34	H+ +OH = H2O	down	1,096	1,049	1,060
34		up	0,966	0,788	0,975
36	H2 = H2D	down	0,297	0,621	0,529
36		up	1,122	1,070	1,083
101	OH +HClO = ClO+H2O	down	0,958	0,979	0,975
101		up	1,723	0,725	1,012
102	OH +ClO2-= ClO2+H2O-H+	down	1,729	0,718	1,012
102		up	1	1	1
106	E- +HClO = ClOH-	down	1,781	0,697	1,010
106		up	0,958	0,979	0,972
109	E- +ClO2-= ClO+OH- -H+	down	1	1	1
109		up	1,705	0,732	1,003
126	OH- +Cl2- =ClOH- +Cl-	down	0,966	0,978	0,975
126		up	1,096	1,049	1,060
132	H2O+Cl2O4=ClO2-+ClO3-+2H+	down	0,158	1,331	0,982
132		up	2,070	0,573	1,005
133	H2O +Cl2O4 =HClO +HCl +O4	down	2,070	0,573	1,005
133		up	0,158	1,331	0,982
141	Cl2- +Cl2- = Cl3- +Cl-	down	0,880	0,937	0,922
141		up	1,083	1,042	1,055
154	Cl2- +H2 =H+HCl +Cl-	down	1,122	1,071	1,083
154		up	0,297	0,622	0,529

20 % of primary yield of	replaced by			
Cl2-	H2O2	6,7E-6	1,47	1,050
Cl2-	HO2	0,100	1,331	0,977
ClOH-	H2O2	0,779	1,085	1
ClOH-	HO2	0,833	1,063	1
E-	H2	1,997	1,52	1,664
H2	E-	0,695	0,838	0,797
H2	H	0,695	0,838	0,797
H2O2	Cl2-	1,106	0,951	1
H2O2	ClOH-	1,106	0,957	1
H2O2	HClO	1,106	0,857	1
H2O2	OH	1,106	0,957	1
HClO	H2O2	5,3E-5	1,394	1
HClO	HO2	0,328	1,253	1

3.6.6 5 Mol/L NaCl solution, gamma radiolysis, closed system, no gas phase formation (Table 8)

Similar as in pure water the radiolysis in chloride brine in a closed system results in practically steady state concentrations for the molecular products H_2 and O_2. After 0.1 years the concentration level however is in the 10 m-molar range for H_2 and O_2 (μ-molar level in water) and 3 to 4 orders of magnitude lower for H_2O_2 and ClO_3^-. The ClO_3^- concentration is the only species concentration which slowly increases with time and reaches the m-molar level after 1000 years. In the sensitivity analysis conducted for 0.1 years the concentrations of H_2 and O_2 remain practically equivalent even though the concentrations of H_2O_2 or ClO_3^- changes as a result of rate constant variation. The largest effect on the H_2/O_2 concentration level has the variation of the rate constant of reaction 154 which describes the scavenging of H_2 against Cl_2^- radicals. A decrease of the rate constant increases the concentrations of the radiolysis gases and vice versa. A somewhat smaller effect has the variation of the rate constant of reaction 7 between H_2 and the OH radical. Furthermore the production/ consumption of O_2^- radicals seem to influence the concentration level of H_2 and O_2. An acceleration of reactions which produce O_2^- (eq. 16, 29) (or influencing the equilibrium reactions 29 and 30) increase the H_2 and O_2 concentration while an acceleration of reactions which consume O_2^- (eq. 28, 30 and 122) leads to lower H_2 and O_2 concentrations. Actually the reactions 16, 28, 29, 30 and 122 determine the availability of O_2^- radicals (which acts as a competitor for H_2) for their reaction with Cl_2^- (eq. 121). As a consequence an increase of the rate constant of reaction 136 which generates Cl_2^- as reaction partner of O_2^- in eq. 121 increases also the H_2/O_2 concentrations. An acceleration of the elimination reaction between the radiolysis products H_2O_2 and HClO (eq. 125) results also in an increase of the H_2/O_2 concentration. The concentration of ClO_3^- varies in the sensitivity analysis in some cases by more than a factor of 10 or 0.1 i.e. more than the variation of a rate constant (eq. 100, 136, 139 and 154) and its variation is not related to the yield of H_2/O_2.

The steady state concentrations of H_2 and O_2 depend on various G-values. The largest increase in H_2/O_2 yield is observed if the primary chlorine species Cl_2^- and HClO are substituted by primary radiolysis products of water (H_2O_2, HO_2) or if E^- is substituted by H_2. A substitution of H_2 by radical species (E^- or H) results in a decrease of the H_2/O_2 steady state concentration. Other G-value replacements cause minor changes in H_2/O_2 concentration. In most of the cases an increase of H_2/O_2 yield gives rise to a decrease of the ClO_3^- concentration and vice versa.

Table 8: Sensitivity analysis. Gamma radiolysis of 5 M NaCl solution in a closed system. (see remarks in Table 3; deviating from the conditions given there the comparison is made for an irradiation time of 0.1 years; see chapter 3.6)

Eq. No	Reactions Conc. (Mol/L) using nominal k		ClO3- 7,86E-7	O2 2,31E-2	H2 4,62E-2
7	OH +H2 = H +H2O	down	1,400	1,340	1,335
7		up	0,360	0,312	0,314
15	E-+ H2O2 = OH +OH-	own	0,975	1,013	1,013
15		up	1,190	0,892	0,905
16	E-+O2 = O2-	down	1,190	0,892	0,880
16		up	0,975	1,013	1,013
28	HO2 +O2- = O2 + HO2-	down	0,903	1,470	1,470
28		up	0,916	0,550	0,550
29	HO2 = H+ +O2-	down	0,916	0,550	0,550
29		up	0,903	1,470	1,470
30	H+ +O2- = HO2	down	0,903	1,470	1,470
30		up	0,916	0,550	0,550
40	H2O2 = H2O + O	down	0,623	1,530	1,536
40		up	1,616	0,666	0,670
100	OH +Cl- = ClOH-	down	15,90	0,319	0,320
100		up	0,017	1,342	1,470
101	OH +HClO = ClO+H2O	down	0,098	1	1
101		up	9,410	1	1
102	OH +ClO2-= ClO2+H2O-H+	down	0,125	1	1
102		up	3,944	1	1
109	E- +ClO2-= ClO+OH- -H+	down	3,820	1	1
109		up	0,125	1	1
121	O2- +Cl2- =Cl-+Cl-+O2	down	0,344	0,129	0,132
121		up	5,150	2,294	2,165
122	O2- +HClO= ClOH- +O2	down	4,400	1,628	1,623
122		up	0,290	0,650	0,650
125	H2O2+HClO=HCl+H2O+O2	down	1,650	0,650	0,650
125		up	0,581	1,628	1,623
132	H2O+Cl2O4=ClO2-+ClO3-+2H+	down	0,170	1	1
132		up	1,950	1	1
133	H2O +Cl2O4 =HClO +HCl +O4	down	1,950	1	1
133		up	0,170	1	1
136	Cl- +ClOH- =Cl2- +OH-	down	15,90	0,319	0,320
136		up	0,017	1,342	1,340
139	ClOH- = OH + Cl-	down	0,017	1,342	1,340
139		up	15,90	0,319	0,320
154	Cl2- +H2 =H+HCl +Cl-	down	38,93	2,280	2,273
154		up	0,185	0,132	0,132

20 % of primary yield of	replaced by			
Cl2-	ClOH-	1,526	0,883	0,883
Cl2-	H2O2	0,247	1,690	1,690
Cl2-	HClO	1,526	1	1
Cl2-	HO2	0,331	1,600	1,60
Cl2-	OH	1,526	0,883	0,883

ClOH-	H2O2	0,598	1,169	1,169
ClOH-	HClO	1,526	1,040	1,04
ClOH-	HO2	0,662	1,169	1,017
E-	H	1,183	1	1
E-	H2	0,331	1,710	1,710
H2	E-	1,250	0,780	0,780
H2	H	0,712	0,780	0,780
H2O2	Cl2-	1,272	0,91	0,910
H2O2	ClOH-	1,272	0,91	0,91
H2O2	HClO	1,272	0,92	0,92
H2O2	HO2	1,145	0,98	0,98
H2O2	OH	1,272	0,909	0,909
HClO	Cl2-	0,674	0,950	0,950
HClO	ClOH-	1	0,857	0,860
HClO	H2O2	0,191	1,490	1,490
HClO	HO2	0,267	1,420	1,420
HClO	OH	1	0,86	0,86
OH	H2O2	0,865	1,040	1,040
OH	HO2	0,865	1,040	1,040

3.6.7 5 Mol/L NaCl solution, alpha radiolysis, open system, constant gas release (Table 9)

Alpha radiolysis of chloride brine yields H_2D, O_2D and ClO_3^- as products linearly formed with dose. Similar to water the reaction system is insensitive against variation of rate constants. A little effect on the distribution of oxidizing species between O_2D and ClO_3^- is seen if the rate constants of the Cl_2O_4 hydrolysis reactions (eq. 132 and 133) are varied. An increase of the rate constant of reaction 132 or a decrease of that of reaction 133 results in a higher yield of ClO_3^- on the expense of O_2D.

Varying the G-values an effect on the H_2D production rate is observed only in cases in which the primary yield of H_2 is directly affected. A substitution of reducing (H_2) or oxidizing molecular species (HClO) by radicals results in a decrease of the ClO_3^- formation rate in favour of O_2D.

Table 9: Sensitivity analysis. Alpha radiolysis of 5 M NaCl solution in an open system.
Remarks: See Table 3

Eq. No	Reactions Conc. (Mol/L) using nominal k	ClO3- 3,2E2	O2D 4,86E2	H2D 1,93E3
132	H2O+Cl2O4=ClO2-+ClO3-+2H+ down	0,850	1,148	1
132	up	1,209	0,790	1
133	H2O+Cl2O4=HClO+HCl+O4 down	1,209	0,790	1
133	up	0,850	1,148	1

20 % of primary yield of	replaced by			
ClOH-	H2O2	1	1,111	1
H	H2	1,106	0,941	1,021
H2	E-	0,556	1,047	0,803
H2	H	0,359	1,121	0,782
H2O2	Cl2-	1,093	0,901	1
H2O2	ClOH-	1,093	0,901	1
H2O2	HClO	1,180	0,817	1
H2O2	OH	1,093	0,901	1
HClO	Cl2-	0,616	1,370	1
HClO	ClOH-	0,609	1,385	1
HClO	H2O2	0,296	1,671	0,984
HClO	HO2	0,378	1,597	0,995
HClO	OH	0,609	1,385	1
HO2	HClO	1,091	0,909	1

3.6.8 5 Mol/L NaCl solution, alpha radiolysis, closed system, no gas phase formation (Table 10)

With no gas phase formation allowed the alpha radiolysis yields practically H_2 and O_2 only. Over a period of 1000 years their net formation rate does not come to an end, but the yield is smaller compared to an open system and compared to the alpha radiolysis of pure water in a closed system. The other molecular species like H_2O_2 and ClO_3^- reach a steady state concentration but on a several orders of magnitude lower level. Similar to gamma irradiation in a closed system the formation rate of H_2/O_2 is mainly influenced by reactions with O_2-involved (eq. 28, 29, 30 and 122). However the effect of rate constant variation is opposite to that under gamma irradiation. As there is very little primary formation of OH, E^- and Cl_2^- the respective equations 7, 16 and 63 play no role for the formation rate of H_2/O_2 (as under gamma irradiation). The increase of the rate constant of reaction 29 or 122 or the decrease of the rate constant of reaction 28, 30 or 125 leads to a dramatic decrease of the concentrations of H_2 and O_2 for 2 to 3 orders of magnitude and more important to a steady state concentration of the dissolved gases (but not to a complete stop of ClO_3^- net production). The ClO_3^- concentration is influenced by variation of several rate constants. An effect larger than proportional to the rate constant variation is observed in two cases, reaction 40 and 125.

The variation of G-values has in some cases also a large effect. The substitution of molecular species (on the reducing side H_2 or on the oxidizing side H_2O_2 or HClO) by radicals can lower the H_2/O_2 concentration for nearly three orders of magnitude. This is accompanied by formation of a steady state concentration for H_2 and O_2 (no further net decomposition of the solution). With the sharp drop of the H_2 and O_2 concentration an increase of the ClO_3^- concentration by a factor of 10 – 20 occurs.

Table 10: Sensitivity analysis. Alpha radiolysis of 5 M NaCl solution in a closed system.
Remarks: See Table 3

Eq.	Reactions		ClO3-	O2	H2
No	Conc. (Mol/L) using nominal k		1,85E-5	6,56E1	1,31E2
7	OH +H2 = H +H2O	down	4,481	1	1
7		up	0,39	1	1
16	E-+O2 = O2-	down	1	1	1
16		up	1,145	1	1
28	HO2 +O2- = O2 + HO2-	down	3,173	0,016	0,016
28		up	1,070	2,576	2,580
29	HO2 = H+ +O2-	down	1,070	2,576	2,580
29		up	3,173	0,016	0,016
30	H+ + O2- = HO2	down	3,173	0,016	0,016
30		up	1,070	2,576	2,580
33	H2O = H+ +OH-	down	0,843	1	1
33		up	1,800	1	1
34	H+ +OH- = H2O	down	1,800	1	1
34		up	0,843	1	1
40	H2O2 = H2O + O	down	0,505	3,917	3,917
40		up	31,35	0,412	0,414
100	OH +Cl- = ClOH-	down	2,886	1	1
100		up	0,422	1	1
101	OH +HClO = ClO+H2O	down	0,108	1	1
101		up	8,378	1	1
102	OH +ClO2-= ClO2+H2O	down	0,729	1	1
102		up	1,151	1	1
109	E- +ClO2-= ClO+OH- -H+	down	1,151	1	1
109		up	0,805	1	1
121	O2- +Cl2- =Cl-+Cl-+O2	down	0,843	1	1
121		up	2,535	1	1
122	O2- +HClO= ClOH- +O2	down	3,032	3,912	3,912
122		up	3,297	0,0041	0,0041
125	H2O2+HClO=HCl+H2O+O2	down	31,35	0,0041	0,0041
125		up	0,505	3,912	3,912
126	OH- +Cl2- =ClOH- +Cl-	down	0,843	1	1
126		up	1,800	1	1
132	H2O+Cl2O4=ClO2-+ClO3-+2H+	down	0,147	1	1
132		up	2,389	1	1
133	H2O +Cl2O4 =HClO +HCl +O4	down	2,389	1	1
133		up	0,147	1	1
136	Cl- +ClOH- =Cl2- +OH-	down	2,880	1	1
136		up	0,422	1	1
139	ClOH- = OH + Cl-	down	0,422	1	1
139		up	2,880	1	1
141	Cl2- +Cl2- = Cl3- +Cl-	down	0,875	1	1
141		up	1,740	1	1
154	Cl2- +H2 =H+HCl +Cl-	down	9,297	1	1
154		up	0,665	1	1

20 % of primary yield of	replaced by			
ClOH-	H2O2	0,572	2,165	2,251
ClOH-	HClO	0,924	1,570	1,580
ClOH-	HO2	0,638	2,103	2,099
H	H2	0,978	1,242	1,244
H2	E-	18,702	0,00298	0,00301
H2	H	19,891	0,00298	0,00301
H2O2	Cl2-	4,119	0,0395	0,0395
H2O2	ClOH-	5,459	0,0265	0,0266
H2O2	HClO	1,784	0,448	0,448
H2O2	HO2	1,145	0,856	0,855
H2O2	OH	5,459	0,0265	0,0266
HClO	Cl2-	9,027	0,00613	0,00614
HClO	ClOH-	16,162	0,00405	0,00407
HClO	H2O2	0,198	3,140	3,137
HClO	HO2	0,276	2,896	2,740
HClO	OH	16,162	0,00405	0,00407
HO2	Cl2-	1,156	0,727	0,729
HO2	ClOH-	1,183	0,725	0,727
HO2	HClO	1,270	0,743	0,744
HO2	OH	1,184	0,725	0,727
OH	H2O2	0,892	1,205	1,206
OH	HO2	0,870	1,274	1,274

3.6.9 Nominal reaction behaviour

In table 11 the general behaviour of the different systems under investigation is summarized. From the table one can distinguish easily between conditions that lead to continuous formation of molecular species proportional to the dose and conditions which result in low level steady state concentrations. Furthermore those systems are marked which are influenced by only a few parameters in the sensitivity analysis.

Table 11: Calculated behaviour of different radiolysis system:
x= formation proportional to dose; o = establishment of steady state conditions; bold and underlined symbols mark species concentrations which are influenced only by a few parameters in the sensitivity analysis.

System	H2O			5 M NaCl solution		
	H_2	O_2	H_2O_2	H_2	O_2	ClO_3^-
gamma-open	x	x	o	x	x	x
gamma-closed	o	o	o	o	o	o
alpha-open	**x**	**x**	**o**	**x**	**x**	**x**
alpha-closed	**x**	**x**	**o**	x	x	o

4. Comparison of experimental and modeling results

The experiments described in chapter 2 (experimental procedure and range of parameters) are compared with modeling results as explained in chapter 3 using the data from the annex, Table 1 and Table 2. When comparing experimental and modeling results the experiments are always taken as reference.

4.1 Gamma radiolysis in an open system

Gamma radiolysis in an open system generates H_2, O_2 and ClO_3^- as long lived products proportional to the dose. HClO and ClO_2^- are formed only in minor amounts, usually in concentrations near the detection limit of some 10^{-5} Mol/L. For 5 Mol/L NaCl solution the calculations however give steady state concentrations for HClO of some 10^{-3} Mol/L and for ClO_2^- of some 10^{-4} Mol/L. It seems that the conversion of both compounds to ClO_3^- and O_2 is not adequately modeled. This is supported by the fact that the chlorate concentrations are mostly underestimated by the calculation (Table 12). But with increasing dose the portion of HClO and ClO_2^- from all oxidizing species becomes negligible.

As all experiments are carried out independently one can calculate radiolytic yields for the three compounds and compare them with each other as far as pH and Cl^- concentrations are equal. From that comparison standard deviations for the experiments are calculated. Such standard deviations comprise all experimental errors including those from analyses, gas volume and pressure determination as well as dose rate calibration etc. The modeling is carried out for chloride solutions assuming constant gas release and with concentrations of H_2O, Cl^- and pH set constant. The comparison is summarized in Table 12 and illustrated for certain conditions in Fig. 4, 5 and 6. In the upper part of Table 12 the experimental mean yields for the long lived species H_2, O_2 and ClO_3^- are given (as G-values). The standard deviation for all conditions and all compounds is in most cases less than 50 % with two exceptions for chlorate. The agreement between individual experiments and their direct modeling (given in the lower part of Table 12) is better in most cases. No comparison is made for chlorate in solutions with less than 4 Mol/L NaCl as the chlorate formation is too little in experiments and in modeling. We conclude that the model satisfactorily describes the gamma experiments with respect to H_2, O_2 and ClO_3^- even though the steady state concentrations of HClO and ClO_2^- are overestimated in the model.

Table 12: Gamma radiolysis in an open system: Comparison of experimental and modeling results for long lived products.
Upper part: Experimental errors of radiation yields (G-values) at different conditions.
Lower part: Individual comparison of experiments with simulation.

Conc. Mol/L	pH	H_2		O_2		ClO_3^-	
		Mean G-Value	Standard dev. (%)	Mean G-Value	Standard dev. (%)	Mean G-Value	Standard dev. (%)
5.3	7	0.59	33.9	0.18	19.9	0.072	12.9
5.3	12	0.49	18.7	0.20	20.9	0.027	51
5.3	2	0.37	2.4	0.17	37.1	0.005	123.4
4	7	0.76	47.2	0.26	46.5	0.042	47.3
3	7	0.56	20.3	0.24	21.8	0.016	71.5
2	7	0.54	31.1	0.26	30.7	-	-
1	7	0.48	20.2	0.25	11.8	-	-

No	Conc. Mol/L pH	H2 conc. (Mol/L)			O2 conc. (Mol/L)			ClO3- conc. (Mol/L)		
		Exp.	Calc.	Dev. %	Exp.	Calc.	Dev. %	Exp.	Calc.	Dev. %
1	5.3 M pH 7	0,0131	0,0138	5,4	0,0044	0,0044	-0,5	0,00157	0,00115	-26,7
2		0,0294	0,0266	-9,7	0,0081	0,0089	9,5	0,00266	0,00243	-8,7
3		0,0401	0,0385	-3,9	0,0120	0,0130	8,0	0,00545	0,00360	-34,0
4		0,0439	0,0417	-4,9	0,0127	0,0161	26,3	0,00611	0,00446	-27,0
5		0,0271	0,0611	125,7	0,0151	0,0210	38,9	0,00844	0,00586	-30,6
6		0,0606	0,0703	16,1	0,0193	0,0242	25,2	0,00793	0,00677	-14,6
7		0,1723	0,1110	-35,6	0,0481	0,0384	-20,1	0,01236	0,01080	-12,6
8	5.3 M pH12	0,0120	0,0116	-3,7	0,0053	0,0037	-29,9	0,00087	0,00137	57,5
9		0,0251	0,0324	28,9	0,0113	0,0105	-6,7	0,00108	0,00380	250,4
10		0,0304	0,0445	46,3	0,0121	0,0145	19,5	0,00096	0,00520	439,8
11		0,0780	0,0822	5,3	0,0301	0,0268	-10,8	0,00491	0,00949	93,4
12	5.3 M pH 2	0,0110	0,0174	58,4	0,0037	0,0027	-27,3	0,00002	0,00000	-99,3
13		0,0284	0,0466	64,1	0,0169	0,0071	-57,7	0,00070	0,00000	-99,7
14	4 M pH 7	0,0058	0,0061	4,1	0,0020	0,0024	21,8	0,00065	0,00031	-51,9
15		0,1749	0,0917	-47,6	0,0593	0,0378	-36,3	0,00484	0,00526	8,6
16	3 M pH 7	0,0050	0,0054	7,8	0,0021	0,0025	19,9			
17		0,0949	0,0880	-7,3	0,0417	0,0415	-0,6			
18		0,1204	0,0879	-27,0	0,0526	0,0414	-21,4			
19	2 M pH 7	0,0046	0,0050	8,8	0,0023	0,0024	7,6			
20		0,0073	0,0080	9,1	0,0036	0,0039	8,2			
21		0,1187	0,0787	-33,7	0,0577	0,0380	-34,2			
22	1 M pH 7	0,0065	0,0074	14,5	0,0036	0,0037	2,9			
23		0,0759	0,0655	-13,7	0,0375	0,0328	-12,6			

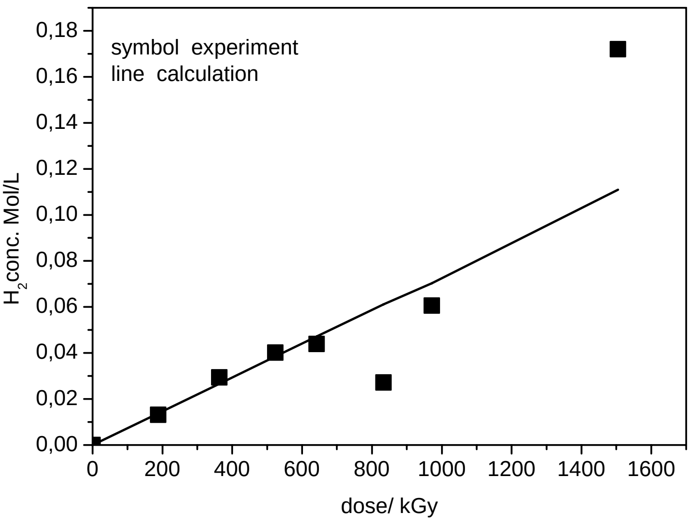

Fig. 4: Hydrogen formation under gamma irradiation: Open system, 5.3 M NaCl, pH 7

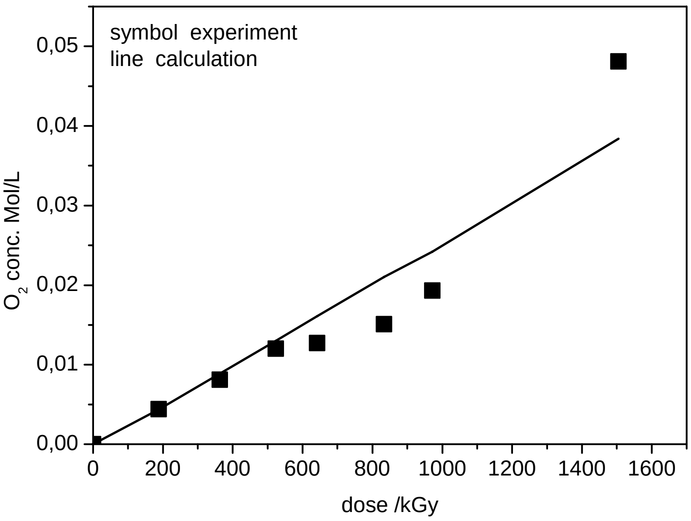

Fig. 5: Oxygen formation under gamma irradiation: Open system, 5.3 M NaCl, pH7

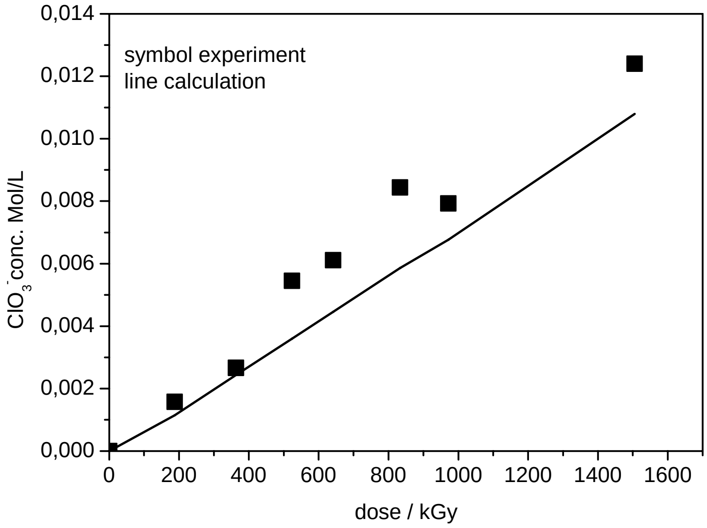

Fig. 6: Chlorate formation under gamma irradiation: Open system, 5.3 M NaCl, pH7

4.2 Gamma radiolysis in an open system with contaminants added

Similar to the experiments with pure brines experiments with 5 Mol/L NaCl solutions at neutral pH and containing Ni^{2+}, Br^- and Fe^{2+} are evaluated. No experiments with carbonate containing brine where conducted. As in pure solutions the HClO steady state concentrations are strongly overestimated from the calculations. Table 13 summarizes in the upper part the radiolytic yields (G-values) for H_2 ,O_2 and ClO_3^- and the standard deviations. In the lower part the individual experiments are compared with simulations. For the Nickel containing solutions the standard deviation of the experimental results and the differences between experiments and calculations are less than 30% for all three long lived products. For the bromide containing solutions this is true only for H_2 and O_2. A comparison of the chlorate concentrations for this solutions cannot be conducted as the analytics of chlorine species in the presence of Br^- is not yet reliable. The standard deviations of the experimental results for H_2, O_2 and ClO_3^- formation in Fe^{2+} containing solutions are about 70%. The differences between experiments and calculations for H_2 and O_2 in experiment 11 and 12 (Table 13) are lower than the standard deviation of the experiments. The chlorate concentrations for these two experiments are overestimated by the calculation by about 150%. No 13 and 14 are high dose experiments and the calculation overestimates the experiments remarkably with respect to all three species. It is assumed that because of the high gas evolution the system cannot be treated as open.

We conclude that modeling of the radiolysis of solutions with contaminants is satisfactorily with respect to H_2 and O_2 formation. The chlorate formation is calculated with fair agreement to the experiments in Ni^{2+} containing solutions; the deviation is larger in solutions with Fe^{2+}.

Table 13: Gamma radiolysis in an open system with contaminants added: Comparison of experimental and modeling results for long lived products.
Upper part: Experimental errors of radiation yields (G-values) at different conditions.
Lower part: Individual comparison of experiments with simulation.

Contaminant Mol/L	H_2 Mean G-Value	H_2 Standard dev. (%)	O_2 Mean G-Value	O_2 Standard dev. (%)	ClO_3^- Mean G-Value	ClO_3^- Standard dev. (%)
10^{-4} Ni^{2+}	5,86E-01	7,3	3,47E-01	5,2	1,77E-01	20,9
$2.3*10^{-3}$ Br^-	5,47E-01	19,6	4,86E-01	16,5		
$1.1*10^{-3}$ Fe^{2+}	3,34E-01	62,5	2,53E-01	41,3	5,08E-02	60,7

No	Conta-minant	H2 conc. (Mol/L)			O2 conc. (Mol/L)			ClO3- conc. (Mol/L)		
		Exp.	Calc.	Dev. %	Exp.	Calc.	Dev. %	Exp.	Calc.	Dev. %
1	Ni^{2+}	0,0149	0,0165	10,4	0,0049	0,0054	10,3	1,88E-03	1,44E-03	-23,6
2		0,0225	0,0209	-7,1	0,0062	0,0070	12,8	1,47E-03	1,88E-03	27,5
3		0,2162	0,2320	7,3	0,0612	0,0811	32,6	1,92E-02	2,28E-02	18,5
4		0,0871	0,0859	-1,4	0,0261	0,0297	13,8	9,23E-03	8,35E-03	-9,5
5		0,0860	0,0859	-0,2	0,0259	0,0297	14,5	1,03E-02	8,35E-03	-19,1
6	Br^-	0,0292	0,0284	-2,7	0,0120	0,0085	-28,7			
7		0,0430	0,0539	25,4	0,0195	0,0174	-10,8			
6		0,1600	0,2450	53,2	0,0757	0,0845	11,7			
9		0,0949	0,1010	6,4	0,0440	0,0338	-23,2			
10		0,1248	0,1170	-6,3	0,0548	0,0395	-27,9			
11	Fe^{2+}	0,0200	0,0210	5,3	0,0051	0,0068	31,7	7,37E-04	1,79E-03	142,8
12		0,1670	0,2260	35,3	0,0565	0,0787	39,3	9,08E-03	2,21E-02	143,3
13		0,1354	0,6530	382,4	0,0534	0,2290	329,2	1,80E-03	6,43E-02	3468,6
14		0,1046	0,3100	196,4	0,0848	0,1080	27,3	1,10E-02	3,02E-02	174,1

4.3 Alpha radiolysis in an open system

As in alpha experiments individual samples are taken consecutively from one start solution the results are not independent from each other. Only a few experiments at similar conditions are conducted truly in parallel. For that reason we did not determine the experimental error as we did for gamma radiolysis but limit ourselves to compare the experimental and modeling results of individual samples. According to experiments alpha radiolysis produces H_2, O_2 and (at least for high dose) ClO_3^- proportional to the dose. But different from gamma radiolysis remarkable amounts of HClO are additionally formed. The comparison is summarized in Table 14 for H_2 and O_2 and in Table 15 for HClO and ClO_3. Fig.7, 8 and 9 illustrate the comparison for certain conditions. The deviation of the calculated concentrations from the experimental results is for H_2 and O_2 in most cases less than 30% with a maximal difference of less than 50 %. Similar as for gamma radiolysis the match between calculation and experiments is worse for the chlorine species. The calculation overestimates the chlorate formation by a factor of about 2 – 3, the hypochlorite formation even by a factor 10 to 20. As we use dissolved / precipitated Pu as alpha source we cannot exclude that there is some interaction of Pu compounds in the radiolysis and in decay processes of HClO which are not included in the modeling. We conclude that the H_2 and O_2 formation in alpha radiolysis can be modeled satisfactorily, but that the formation of chlorine species is modeled only qualitatively correct: Linear formation of ClO_3^- with dose, limited formation of HClO.

Table 14: Alpha radiolysis in an open system: Comparison of experimental and modeling results for H2 and O2.

No	Conc. Mol/L pH	H2 conc. (Mol/L)			O2 conc. (Mol/L)		
		Exp.	Calc.	Dev. %	Exp.	Calc.	Dev. %
0-1	5 M pH 12	0,087	0,095	10,3	0,0310	0,0253	-18,4
0-2		0,187	0,200	7,0	0,0705	0,0532	-24,5
0-3		0,352	0,384	9,1	0,1320	0,1010	-23,5
0-4		0,647	0,604	-6,6	0,2490	0,1580	-36,5
0-5		1,210	0,901	-25,5	0,4660	0,2340	-49,8
0-6		1,410	1,150	-18,4	0,5480	0,2980	-45,6
0-7		1,720	1,670	-2,9	0,6910	0,4280	-38,1
1-1	5 M pH 12	0,017	0,018	5,4	0,0048	0,0046	-3,5
1-2		0,032	0,035	8,0	0,0100	0,0092	-7,4
1-3		0,065	0,070	8,0	0,0208	0,0185	-11,1
1-4		0,116	0,108	-6,9	0,0392	0,0284	-27,6
1-5		0,158	0,161	1,9	0,0549	0,0423	-23,0
1-6		0,197	0,206	4,6	0,0692	0,0540	-22,0
1-7		0,267	0,295	10,5	0,0971	0,0770	-20,7
2-1	5 M pH 12	0,014	0,016	15,9	0,0040	0,0042	5,8
2-2		0,042	0,051	22,8	0,0132	0,0135	2,3
2-3		0,087	0,095	9,7	0,0312	0,0250	-19,9
2-4		0,143	0,136	-4,9	0,0513	0,0356	-30,6
2-5		0,228	0,181	-20,6	0,0874	0,0471	-46,1
2-6		0,276	0,234	-15,2	0,1070	0,0607	-43,3
3-1	4 M pH 12	0,010	0,015	47,1	0,0045	0,0046	2,0
3-2		0,042	0,049	15,4	0,0150	0,0149	-0,7
3-3		0,075	0,093	23,6	0,0332	0,0283	-14,8
3-4		0,134	0,134	0,0	0,0550	0,0411	-25,3
3-5		0,227	0,176	-22,5	0,1020	0,0537	-47,4
3-6		0,280	0,228	-18,6	0,1230	0,0693	-43,7
4-1	3 M pH 12	0,0139	0,0147	5,8	0,0052	0,0053	1,0
4-2		0,0432	0,0470	8,8	0,0173	0,0170	-1,7
4-3		0,0678	0,0776	14,5	0,0269	0,0283	5,2
4-4		0,1140	0,1290	13,2	0,0450	0,0471	4,7
4-5		0,1700	0,1700	0,0	0,0754	0,0621	-17,6
4-6		0,2150	0,2200	2,3	0,0947	0,0805	-15,0
5-1	5 M pH 7	0,0142	0,0154	8,5	0,0041	0,0038	-8,0
5-2		0,0360	0,0503	39,7	0,0207	0,0131	-36,7
5-3		0,0726	0,0833	14,7	0,0317	0,0217	-31,5
5-4		0,1250	0,1380	10,4	0,0480	0,0359	-25,2
5-5		0,1820	0,1810	-0,5	0,0667	0,0471	-29,4
5-6		0,2290	0,2340	2,2	0,0832	0,0605	-27,3

No	Conc. Mol/L pH	H2 conc. (Mol/L)			O2 conc. (Mol/L)		
		Exp.	Calc.	Dev. %	Exp.	Calc.	Dev. %
6-1	5 M pH 7	0,0133	0,0138	3,8	0,0039	0,0034	-12,1
6-2		0,0464	0,0503	8,4	0,0148	0,0131	-11,5
6-3		0,0892	0,0837	-6,2	0,0276	0,0219	-20,7
6-4		0,1550	0,1380	-11,0	0,0516	0,0359	-30,4
6-5		0,2200	0,1840	-16,4	0,0736	0,0479	-34,9
7-1	5 M pH 2	0,0066	0,0074	11,7	0,0013	0,0014	4,6
8-1		0,0057	0,0067	17,7	0,0006	0,0012	112,3
9-1	5 M pH 7	0,0134	0,0152	13,4	0,0028	0,0226	712,9
9-2		0,0328	0,0368	12,2	0,0130	0,0343	163,8
9-3		0,0920	0,0670	-27,2	0,0306	0,0596	94,8
9-4		0,1270	0,0884	-30,4	0,0422	0,0853	102,1

Table 15: Alpha radiolysis in an open system: Comparison of experimental and modeling results for HClO and ClO3-.

No	Conc. Mol/L pH	HClO conc. (Mol/L)			ClO3- conc. (Mol/L)		
		Exp.	Calc.	Dev. %	Exp.	Calc.	Dev. %
0-1	5 M pH 12	3,84E-03	1,58E-02	311,5	2,55E-03	4,20E-03	64,7
0-2		3,20E-03	3,06E-02	856,3	8,80E-03	1,08E-02	22,7
0-3		3,17E-03	4,80E-02	1414,2	6,47E-03	2,93E-02	352,9
0-4		3,59E-03	5,81E-02	1518,4	1,72E-02	5,97E-02	247,1
0-5		4,29E-03	6,32E-02	1373,2	2,88E-02	1,06E-01	268,1
0-6		3,22E-03	6,47E-02	1909,3	3,61E-02	1,46E-01	304,4
0-7		8,10E-03	6,55E-02	708,6	3,66E-02	2,32E-01	533,9
1-1	5 M pH 12	4,35E-03	3,15E-03	-27,6	3,35E-04	6,98E-04	108,4
1-2		6,55E-03	5,97E-03	-8,9	4,86E-04	1,48E-03	204,5
1-3		8,58E-03	1,12E-02	30,5	2,42E-03	3,50E-03	44,6
1-4		8,53E-03	1,57E-02	84,1	3,39E-03	6,51E-03	92,0
1-5		8,47E-03	2,03E-02	139,7	5,28E-03	1,22E-02	131,1
1-6		4,35E-03	2,28E-02	424,1	8,12E-03	1,81E-02	122,9
1-7		3,67E-03	2,56E-02	597,5	1,36E-02	3,14E-02	130,9
2-1	5 M pH 12	3,29E-03	2,85E-03	-13,4	2,49E-04	6,36E-04	155,4
2-2		6,28E-03	8,13E-03	29,5	1,01E-03	2,63E-03	160,4
2-3		7,52E-03	1,28E-02	70,2	2,04E-03	6,68E-03	227,5
2-4		5,22E-03	1,54E-02	195,0	4,99E-03	1,18E-02	136,5
2-5		2,82E-03	1,69E-02	499,3	4,79E-03	1,83E-02	282,0
2-6		2,38E-03	1,79E-02	652,1	1,12E-02	2,66E-02	137,5
3-1	4 M pH 12	2,42E-03	2,02E-03	-16,5	2,31E-04	6,13E-04	165,4
3-2		4,38E-03	5,69E-03	29,9	9,23E-04	2,32E-03	151,4
3-3		5,46E-03	9,31E-03	70,5	1,62E-03	5,56E-03	243,2
3-4		1,89E-03	1,15E-02	508,5	4,21E-03	9,68E-03	129,9
3-5		1,10E-03	1,27E-02	1054,5	3,97E-03	1,44E-02	262,7
3-6		1,04E-03	1,35E-02	1198,1	9,52E-03	2,09E-02	119,5
4-1	3 M pH 12	1,32E-03	1,04E-03	-21,2	3,28E-04	6,16E-04	87,8
4-2		1,89E-03	2,69E-03	42,3	6,30E-04	2,19E-03	247,6
4-3		1,85E-03	3,99E-03	115,7	1,09E-03	3,87E-03	255,0
4-4		3,94E-04	5,62E-03	1326,4	3,05E-03	7,15E-03	134,4
4-5		3,93E-04	6,48E-03	1548,9	2,83E-03	1,01E-02	256,9
4-6		3,73E-04	7,15E-03	1816,9	6,02E-03	1,41E-02	134,2
5-1	5 M pH 7	1,69E-03	3,12E-03	84,6	6,77E-04	5,11E-04	-24,5
5-2		2,58E-03	8,31E-03	222,1	2,67E-03	2,52E-03	-5,6
5-3		2,42E-03	1,19E-02	391,7	4,41E-03	5,45E-03	23,6
5-4		2,40E-03	1,55E-02	545,8	6,45E-03	1,21E-02	87,6
5-5		2,09E-03	1,70E-02	713,4	5,78E-03	1,86E-02	221,8
5-6		1,84E-03	1,79E-02	872,8	1,33E-02	2,68E-02	101,5

No	Conc. Mol/L pH	HClO conc. (Mol/L)			ClO3- conc. (Mol/L)		
		Exp.	Calc.	Dev. %	Exp.	Calc.	Dev. %
6-1	5 M pH 7	1,70E-03	2,86E-03	68,2	9,24E-04	4,46E-04	-51,7
6-2		2,05E-03	8,31E-03	305,4	2,65E-03	2,52E-03	-4,9
6-3		1,17E-03	1,20E-02	925,6	4,41E-03	5,49E-03	24,5
6-4		2,30E-03	1,55E-02	573,9	6,88E-03	1,21E-02	75,9
6-5		1,85E-03	1,70E-02	818,9	6,67E-03	1,90E-02	184,9
7-1	5 M pH 2	3,46E-04	7,66E-05	-77,9	9,02E-05	2,70E-08	-100,0
8-1		2,16E-04	6,92E-05	-68,0	1,07E-04	1,91E-08	-100,0
9-1	5 M pH 7	1,03E-03	2,93E-03	184,5	2,85E-04	5,55E-04	94,7
9-2		1,43E-03	6,03E-03	321,7	1,69E-03	1,88E-03	11,2
9-3		1,48E-03	9,09E-03	514,2	3,02E-03	4,78E-03	58,3
9-4		1,22E-03	1,05E-02	760,7	3,64E-03	7,44E-03	104,4

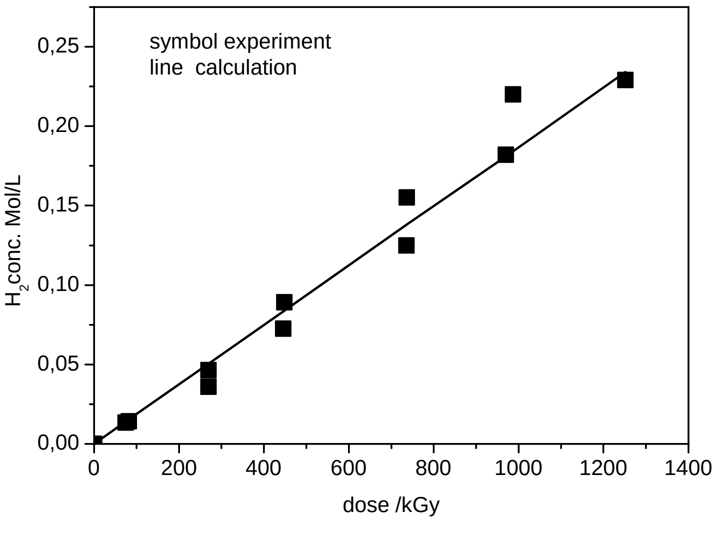

Fig. 7: Hydrogen formation under alpha irradiation: Open system, 5 M NaCl, pH7

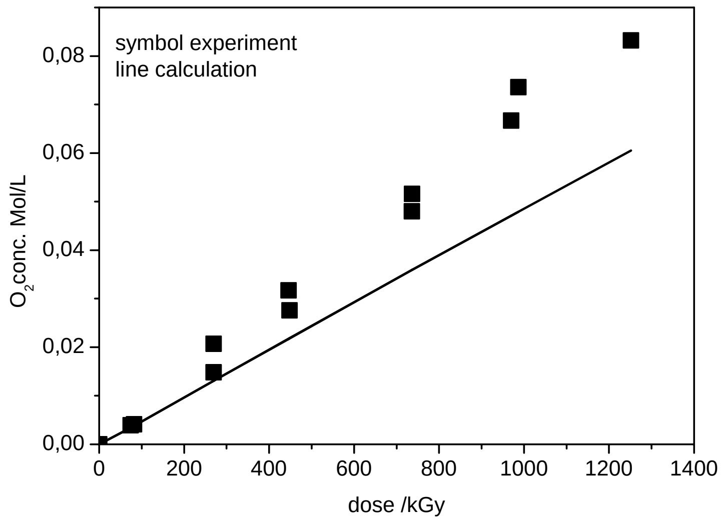

Fig. 8: Oxygen formation under alpha irradiation: Open system, 5 M NaCl, pH7

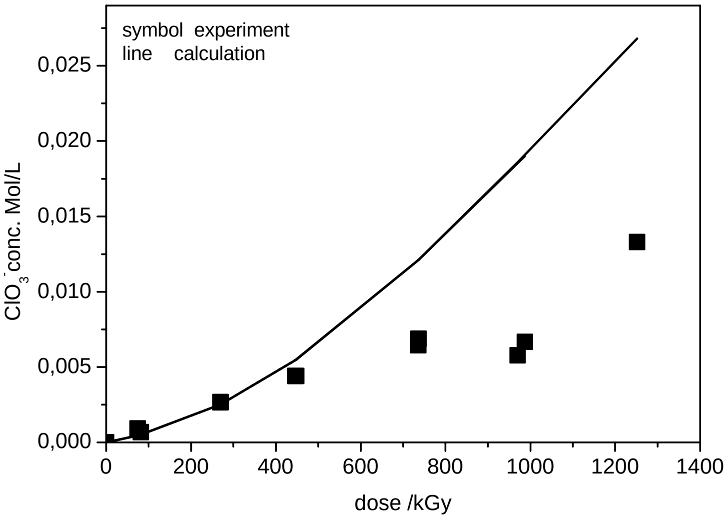

Fig. 9: Chlorate formation under alpha irradiation: Open system, 5 M NaCl, pH7

4.4 Gamma radiolysis in a closed system

The course of the radiolysis reactions in a closed system with no gas phase formation is completely different from that in an open system. In pure chloride solution all net production of long lived products comes to a stop. With H_2 added prior to irradiation there is no further gas production at all and with Br^- added a behaviour is found that is close to continuous gas production (Fig. 10). These phenomena are verified by simulation. The data scatter for nominally equal experiments (exp. 1 – 3 in Fig. 9) is explained at the time being by slight variations in pH. This interpretation is a result of calculation runs at different pH which gives within a pH range 6 – 9 a larger variation in gas concentration as experimentally observed. In all experiments with no gas phase the formation of chlorate is less than some 10^{-4} Mol/L. That is far less than observed in open systems but much larger than the modeling results. A comparison of the steady state concentrations achieved in experiments and from modeling at pH 7 is given in Table 16. We conclude that the substantial change in radiolytic decomposition is correctly modeled in all cases (limited formation of H_2, O_2 and ClO_3^- to steady state concentrations), that deviations between experiment and modeling may become smaller if the actual experimental pH is introduced into the modeling and that chlorate is still underestimated in modeling even though the concentrations in the experiments are already low.

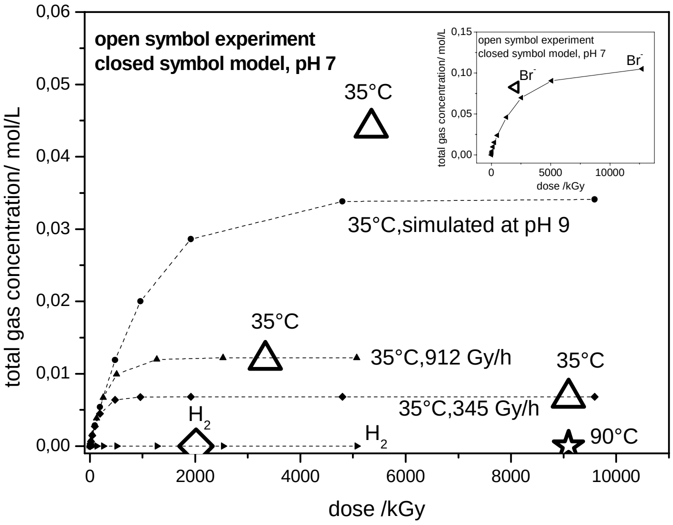

Fig. 10: Simulation results of experiments conducted in autoclaves without gas phase

Table 16: Gamma radiolysis in a closed system. Comparison of experimental and modeling results for long lived products.

No	Conc. Mol/L pH	H2 conc. (Mol/L)			O2 conc. (Mol/L)			ClO3- conc. (Mol/L)	
		Exp.	Calc.	Dev. %	Exp.	Calc.	Dev. %	Exp.	Calc.
1	5.3 M pH 7	9,61E-03	4,54E-03	-52,8	3,32E-03	2,27E-03	-31,6	8,10E-05	4,64E-08
2		4,10E-02	4,54E-03	-88,9	8,08E-03	2,27E-03	-71,9	8,60E-05	7,46E-08
3		6,32E-03	8,13E-03	28,6	1,09E-03	4,06E-03	272,5	1,89E-04	2,55E-07
4		0	0		3,52E-06	2,08E-14	-100,0	1,56E-05	2,28E-17
5		6,44E-02	4,32E-02	-32,9	2,82E-02	1,85E-02	-34,4	1,98E-04	1,49E-04

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Annex

Reactions and rate constants

The following tables contain the reaction scheme based on the publications: Sunder and Christensen (Nucl. Technology 104,403(1993)) and of Christensen, Sunder and Shoesmith (J.Alloy Compounds 213/214 (1994)93-99). They were modified and extended as far as newer or more reliable data were available. Further extensions were made for some reactive components.

Remarks for the tables

[a] Constants given for room temperature (for 1st order reactions in s^{-1}, for true and pseudo 2nd order reactions in L/(mol*s), for third order reaction (marked with *) in $L^2/(mol^2*s)$).

[b] Read this and the following constants as 5.5 * 10^9.

[c] E^- symbolizes the solvated electron

[d] As kinetic codes may accept only a maximum of 2 reactants, a third species can be introduced as a catalyst which is written with a negative sign on the right hand side of the equation. But only eq. having a * are true third order.

[e] O_2D and H_2D represent O_2 and H_2 which have desorbed from the solution and do not further participate in radiation chemical reactions.

[f] ClR-- is the radical anion ClO_3^{2-}, BrL2- is BrCl2- and Br2L- is Br2Cl-.

[g] UO2D and UO3D represent U compounds which do not further participate in radiation chemical reactions

[h] R refers to the remarks at the end of each table

Water scheme

Eq.No	Reaction	Rate Constant[a]	Ref.
1	OH +OH =H_2O_2	k(1) = 5.500E+09[b]	1
2[c]	OH +E^- =OH^-	k(2) = 3.000E+10	4
3	OH +H =H_2O	k(3) = 9.700E+09	21
4	OH +HO_2 =H_2O +O_2	k(4) = 7.000E+09	21
5	OH +O_2^- =O_2 +OH^-	k(5) = 1.000E+10	1
6	OH +H_2O_2 =HO_2 +H_2O	k(6) = 2.700E+07	1
7	OH +H_2 =H +H_2O	k(7) = 3.400E+07	1
8	OH +OH^- =H_2O +O^-	k(8) = 1.300E+10	4
9	OH +HO_2^- =HO_2 +OH^-	k(9) = 7.500E+09	1
10	O^- +H_2O =OH +OH^-	k(10) = 1.800E+06	4
11	E^- +E^- =H_2 +OH^- +OH^-	k(11) = 5.500E+09	1
12	E^- +H =H_2 +OH^-	k(12) = 2.500E+10	1
13	E^- +O_2^- =HO_2^- +OH^-	k(13) = 1.300E+10	1
14	E^- +HO_2 =HO_2^-	k(14) = 2.000E+10	1
15	E^- +H_2O_2 =OH +OH^-	k(15) = 1.100E+10	1
16	E^- +O_2 =O_2^-	k(16) = 1.900E+10	1
17	E^- +H^+ =H	k(17) = 2.300E+10	1
18	E^- +H_2O =H +OH^-	k(18) = 1.900E+01	1
19	E^- +HO_2^- =O^- +OH^-	k(19) = 3.500E+09	1
*20[d]	O_2^- +O_2^- =HO_2^- +O_2 -H^+	k(20) = 1.800E+09	29
21	H +H =H_2	k(21) = 7.800E+09	1
22	H +O_2^- =HO_2^-	k(22) = 2.000E+10	1
23	H +HO_2 =H_2O_2	k(23) = 8.500E+09	21
24	H +H_2O_2 =H_2O +OH	k(24) = 4.200E+07	21,22
25	H +O_2 =HO_2	k(25) = 2.100E+10	1
26	H +OH^- =E^- +H_2O	k(26) = 2.200E+07	1
27	HO_2 +HO_2 =H_2O_2 +O_2	k(27) = 8.400E+05	1

28	$HO_2 \quad +O_2^- \quad =O_2 \quad +HO_2^-$	k(28) = 9.600E+07	1
29	$HO_2 \quad =H^+ \quad +O_2^-$	k(29) = 8.000E+05	1
30	$H^+ \quad +O_2^- \quad =HO_2$	k(30) = 5.000E+10	1
31	$H_2O_2 \quad =H^+ \quad +HO_2^-$	k(31) = 3.560E-02	1
32	$H^+ \quad +HO_2^- \quad =H_2O_2$	k(32) = 2.000E+10	1
33	$H_2O \quad =H^+ \quad +OH^-$	k(33) = 2.599E-05	1
34	$H^+ \quad +OH^- \quad =H_2O$	k(34) = 1.430E+11	1
35[e]	$O_2 \quad =O_2D$	k(35) =	R[h]
36[e]	$H_2 \quad =H_2D$	k(36) =	R[h]
37	$H_2D \quad =H_2$	k(37)=	R[h]
38	$O_2D \quad =O_2$	k(38)=	R[h]
39	$OH \quad +O- \quad =HO_2^-$	k(49)= 1.800E+10	30
40	$H_2O_2 \quad =H_2O \quad +O$	k(40)= 1.000E-03	31
41	$O \quad +O \quad =O_2$	k(41)= 1.000E+09	31

Remark: The rate constants k(35) – k(38) describe the desorption of radiolysis gases. Their value depend on the system which is modeled: open (constant gas release), quasi-open (gas release according to Henry’s law), closed (all gas remain dissolved), Argon purged (gases are release with a high rate).

Open system, constant gas release

35	$O_2 \quad =O_2D$	k(35) = 4.000E-03	31
36	$H_2 \quad =H_2D$	k(36) = 1.000E-02	31
37	$H_2D \quad =H_2$	k(37)= 0.000E+00	
38	$O_2D \quad =O_2$	k(38)= 0.000E+00	

Quasi-open system, gas release according to Henry’s law

35	$O_2 \quad =O_2D$	k(35) = 1.000E+06	R[h]
36	$H_2 \quad =H_2D$	k(36) = 1.000E+06	R[h]
37	$H_2D \quad =H_2$	k(37)= A	R[h]
38	$O_2D \quad =O_2$	k(38)= B	R[h]

Remark: The desorption reactions 35 and 36 are assumed to be fast ($k=1*10^6 s^{-1}$). The back reaction rate constants are calculated as follows:

$$A = 10^6 * \frac{KH_{H2} * V_{Lq.}}{0.4036 * V_{Gas}}$$

$$B = 10^6 * \frac{KH_{O2} * V_{Lq.}}{0.4036 * V_{Gas}}$$

with: $V_{Lq.}$ = Volume of the liquid
V_{gas} = Gas phase volume

Henry's constants

Solution	**KH_{H2} (Mol/(L*MPa))**	**KH_{O2} (Mol/(L*MPa))**	**Ref.**
Water	0.007	0.0116	R[h]
5M NaCl	0.00268	0.00221	R[h]

Remark: The solubilities of H_2 and O_2 in 5 M Na Cl solution were obtained from autoclave experiments and compared to literature data [35] and [36] which contained also data for pure water.

Closed system, no gas phase

35	O_2	$=O_2D$	k(35) = 0.000E+00	
36	H_2	$=H_2D$	k(36) = 0.000E+00	
37	H_2D	$=H_2$	k(37) = 0.000E+00	
38	O_2D	$=O_2$	k(38) = 0.000E+00	

Open system, Argon purged

35	O_2	$=O_2D$	k(35) = 2.100E-01	1
36	H_2	$=H_2D$	k(36) = 3.500E-01	1
37	H_2D	$=H_2$	k(37) = 0.000E+00	
38	O_2D	$=O_2$	k(38) = 0.000E+00	

Scheme extension for chloride system

Eq.No	**Reaction**					**Rate Constant**[a]	**Ref.**
100	OH	$+Cl^-$	$=ClOH^-$			k(100) = 4.300E+09	1
101	OH	+HClO	=ClO	$+H_2O$		k(101) = 9.000E+09	1
102[d]	OH	$+ClO_2^-$	$=ClO_2$	$+H_2O$	$-H^+$	k(102) = 6.300E+09	1
103	E^-	+ Cl	$=Cl^-$	$+H_2O$		k(103) = 1.000E+10	1
104	E^-	$+ Cl_2^-$	$=Cl^-$	$+Cl^-$	$+H_2O$	k(104) = 1.000E+10	1
105	E^-	$+ClOH^-$	$= Cl^-$	$+OH^-$	$+H_2O$	k(105) = 1.000E+10	1
106	E^-	+HClO	$= ClOH^-$			k(106) = 5.300E+10	1
107	E^-	$+Cl_2$	$= Cl_2^-$			k(107) = 1.000E+10	1
108	E^-	$+Cl_3^-$	$= Cl_2^-$	$+Cl^-$		k(108) = 1.000E+10	1
109[d]	E^-	$+ClO_2^-$	= ClO	$+OH^-$	$-H^+$	k(109) = 4.500E+10	1
110[d]	E^-	$+ClO_3^-$	$= ClO_2$	$+OH^-$	$-H^+$	k(110) = 0.000E+00	
111	H	+Cl	$= Cl^-$	$+H^+$		k(111) = 1.000E+10	1
112	H	$+Cl_2^-$	$= Cl^-$	$+Cl^-$	$+H^+$	k(112) = 8.000E+09	1
113	H	$+ClOH^-$	$= Cl^-$	$+H_2O$		k(113) = 1.000E+10	1
114	H	$+Cl_2$	$= Cl_2^-$	$+H^+$		k(114) = 7.000E+09	1
115	H	+HClO	$= ClOH^-$	$+H^+$		k(115) = 1.000E+10	1
116	H	$+Cl_3^-$	$= Cl_2^-$	$+Cl^-$	$+H^+$	k(116) = 1.000E+10	1
117	HO_2	$+Cl_2^-$	$= Cl^-$	+HCl	$+O_2$	k(117) = 4.000E+09	1
118	HCl		$= Cl^-$	$+H^+$		k(118) = 5.000E+05	1
119	HO_2	$+Cl_2$	$= Cl_2^-$	$+H^+$	$+O_2$	k(119) = 1.000E+09	1
120	HO_2	$+Cl_3^-$	$= Cl_2^-$	+HCl	$+O_2$	k(120) = 1.000E+09	1
121	O_2^-	$+Cl_2^-$	$= Cl^-$	$+Cl^-$	$+O_2$	k(121) = 1.200E+10	1
122	O_2^-	+HClO	$= ClOH^-$	$+O_2$		k(122) = 7.500E+06	1
123	H_2O_2	$+Cl_2^-$	= HCl	+HCl	$+O_2^-$	k(123) = 1.400E+05	1
124	H_2O_2	$+Cl_2$	$= HO_2$	$+Cl_2^-$	$+H^+$	k(124) = 1.900E+02	1

125	H_2O_2	+HClO	= HCl	$+H_2O$	$+O_2$		k(125) = 1.700E+05	1
126	OH^-	$+Cl_2^-$	$= ClOH^-$	$+Cl^-$			k(126) = 7.300E+06	1
127	OH^-	$+Cl_2$	= HClO	$+Cl^-$			k(127) = 6.000E+08	20
128	H^+	$+ClOH^-$	= Cl	$+H_2O$			k(128) = 2.100E+10	1
129	H_2O	$+Cl_2O_2$	= HClO	$+ClO_2^-$ $+H^+$			k(129) = 2.000E+02	1
130	H_2O	$+Cl_2O_2$	$= O_2$	+HClO+HCI			k(130) = 0.000E+00	
131	H_2O	$+Cl_2O$	= HClO	+HClO			k(131) = 1.000E+02	1
132	H_2O	$+Cl_2O_4$	$= ClO_2^-$	$+ClO_3^-$ $+H^+$		$+H^+$	k(132) = 1.000E+02	1
133	H_2O	$+Cl_2O_4$	= HClO	+HCl	$+O_4$		k(133) = 1.000E+02	1
134	O_4		$= O_2$	$+O_2$			k(134) = 1.000E+05	1
135	Cl^-	+Cl	$= Cl_2^-$				k(135) = 2.100E+10	1
136	Cl^-	$+ClOH^-$	$= Cl_2^-$	$+OH^-$			k(136) = 9.000E+04	1
137	Cl^-	+HClO	$= Cl_2$	$+OH^-$			k(137) = 3.600E-03	R[h]
138	Cl^-	$+Cl_2$	$= Cl_3^-$				k(138) = 1.000E+04	1
139	$ClOH^-$		= OH	$+Cl^-$			k(139) = 6.100E+09	1
140	Cl_2^-		= Cl	$+Cl^-$			k(140) = 1.100E+05	1
141	Cl_2^-	$+Cl_2^-$	$= Cl_3^-$	$+Cl^-$			k(141) = 7.000E+09	1
142	Cl_3^-		$= Cl_2$	$+Cl^-$			k(142) = 5.000E+04	1
143	ClO	+ClO	$= Cl_2O_2$				k(143) = 1.500E+10	1
144	ClO_2	$+ClO_2$	$= Cl_2O_4$				k(144) = 1.000E+02	1
145	Cl_2O_2	$+ClO_2^-$	$= ClO_3^-$	$+Cl_2O$			k(145) = 1.000E+02	1
146[f]	E^-	$+ClO_3^-$	$= ClR^{--}$				k(146) = 1.600E+05	3
147[f]	ClR^{--}	+OH	$=OH^-$	$+ClO_3^-$			k(147) = 1.000E+10	3
148[f]	ClR^{--}	$+O^-$	$=OH^-$	$+ ClO_3^-$	$-H^+$		k(148) = 1.200E+09	3
149	HClO	+HClO	$=Cl^-$	$+ ClO_2^-$	$+H^+$	$+H^+$	k(149) = 6.000E-09	32,33
150	ClO_2^-	+HClO	$=Cl^-$	$+ClO_3^-$	$+H^+$		k(150) = 9.000E-07	32,33
151	HClO	+HClO	$=O_2$	+HCl	+HCl		k(151) = 3.000E-10	34
*152[d]	HClO	+Cl-	=Cl2	+H2O	$-H^+$		k(152)=9.000E+03	7
153	Cl_2		=HClO	$+Cl^-$	$+H^+$	-H2O	k(153)=1.500E+01	7
154	Cl_2^-	$+H_2$	=H	+HCl	$+Cl^-$		k(154)=4.300E+05	fit

Remark : k(137)= k(127) * k(152)* 10^{-14} /k(153)
Fit : k(154) fitted to match results from autoclave experiments

According to reference [32, 33, 34] the rate constants of the reactions 149, 150 and 151 in 5 Mol/L ionic strength are: k(149) = 3.43E-08 , k(150) = 4.10E-06 and k(151) = 2.10E-09

Scheme extension for Ni containing solutions

Eq. No.	Reaction	Rate constant[a]	Ref.
200	Ni^{++} $+E^-$ $=Ni^+$	k(200)=2.900E+10	4
201	Ni^+ +OH $=Ni^{++}$ $+OH^-$	k(201)=2.200E+10	4
202	Ni^+ $+H_2O_2$ $=Ni^{++}$ +OH $+OH^-$	k(202)=4.300E+07	4
203	Ni^+ +Cl2- $=Ni^{++}$ +Cl- +Cl-	k(203)=3.000E+09	4
204	Ni^+ $+O_2$ $=NiO_2^+$	k(204)=1.700E+09	4
205	NiO_2^+ $=Ni^{++}$ $+O_2^-$	k(205)=7.800E+02	4

Scheme extension for Fe containing solutions

Eq. No.	Reaction	Rate constant[a]	Ref.
300	Fe^{+2} +OH $=Fe^{+3}$ $+OH^-$	k(300)=4.300E+08	4
301	Fe^{+2} $+HO_2$ $=H_2O_2$ $+Fe^{+3}$ $-H^+$	k(301)=1.200E+06	4
302	Fe^{+2} $+O^-$ $=Fe^{+3}$ $+OH^-$ $-H^+$	k(302)=3.800E+09	4
303	Fe^{+2} $+O_2^-$ $=H_2O_2$ $+Fe^{+3}$ $-H^+$ $-H^+$	k(303)=1.000E+07	4
304	Fe^{+2} +Cl $=Fe^{+3}$ $+Cl^-$	k(304)=1.300E+10	4
305	Fe^{+2} $+Cl_2^-$ $=Fe^{+3}$ $+Cl^-$ $+Cl^-$	k(305)=3.100E+07	4
306	Fe^{+2} $+ClO_2$ $=ClO_2^-$ $+Fe^{+3}$	k(306)=3.000E+03	4
307	Fe^{+3} $+HO_2$ $=Fe^{+2}$ $+H^+$ $+O_2$	k(307)=3.100E+05	4
308	Fe^{+3} $+E^-$ $=Fe^{+2}$	k(308)=6.000E+10	4
309	Fe^{+3} +H $=Fe^{+2}$ $+H^+$	k(309)=1.200E+09	4
310	Fe^{+2} $+H_2O_2$ $=Fe^{+3}$ +OH $+OH^-$	k(310)=7.000E+01	5

Scheme extension for carbonate containing solutions

Eq. No.	Reaction	Rate constant	Ref.
400	H^{+} $+CO_3^{-2}$ $=HCO_3^{-}$	k(400)=5.000E10	6
401	CO_2 $+H_2O$ $=H^{+}$ $+HCO_3^{-}$	k(401)=2.000E04	6
402	H^{+} $+HCO_3^{-}$ $=CO_2$ $+H_2O$	k(402)=5.000E10	6
403	HCO_3^{-} $=CO_3^{-2}$ $+H^{+}$	k(403)=2.000E00	6
404	CO_2 $+E^{-}$ $=CO_2^{-}$	k(404)=7.700E09	6
405	HCO_3^{-} $+OH$ $=CO_3^{-}$ $+H_2O$	k(405)=8.500E06	6
406	CO_3^{-2} $+OH$ $=CO_3^{-}$ $+OH^{-}$	k(406)=3.900E08	6
407	HCO_3^{-} $+H$ $=H_2$ $+CO_3^{-}$	k(407)=4.400E04	6
408	CO_3^{-2} $+E^{-}$ $=CO_2^{-}$ $+OH^{-}$ $+OH^{-}$ $-H_2O$	k(408)=3.900E05	6
409	CO_3^{-} $+CO_3^{-}$ $=C_2O_6^{-2}$	k(409)=1.400E07	6
410	CO_3^{-} $+H_2O_2$ $=CO_3^{-2}$ $+ O_2^{-}$ $+H^{+}$ $+H^{+}$	k(410)=9.800E05	6
411	CO_3^{-} $+HO_2^{-}$ $=CO_3^{-2}$ $+O_2^{-}$ $+H^{+}$	k(411)=1.000E07	6
412	CO_3- $+O_2^{-}$ $=CO_3^{-2}$ $+O_2$	k(412)=4.000E08	6
413	CO_3^{-} $+CO_2^{-}$ $=CO_3^{-2}$ $+CO_2$	k(413)=3.000E08	6
414	CO_2^{-} $+E^{-}$ $=HCOO^{-}$ $+OH^{-}$ $-H_2O$	k(414)=1.000E09	6
415	CO_2^{-} $+CO_2^{-}$ $=C_2O_4^{-2}$	k(415)=6.500E08	6
416	CO_2^{-} $+O_2$ $=CO_2$ $+O_2^{-}$	k(416)=2.000E09	6
417	CO_2^{-} $+H_2O_2$ $=CO_2$ $+OH^{-}$ $+OH$	k(417)=7.300E05	6
418	CO_2^{-} $+HCO_3^{-}$ $=HCOO^{-}$ $+CO_3^{-}$	k(418)=1.000E03	6
419	$C_2O_6^{-2}$ $= C_2O_4^{-2}$ $+O_2$	k(419)=1.000E00	6
420	$C_2O_6^{-2}$ $=HO_2^{-}$ $+OH^{-}$ $+CO_2$ $+CO_2$ $-H_2O$	k(420)=2.000E02	6
421	CO_3^{-} $+C_2O_4^{-2}$ $=C_2O_4^{-}$ $+CO_3^{-2}$	k(421)=3.000E03	6
422	$C_2O_4^{-2}$ $+E^{-}$ $=C_2O_4^{-3}$	k(422)=3.100E07	6
423	$C_2O_4^{-2}$ $+OH$ $=C_2O_4^{-}$ $+OH^{-}$	k(423)=7.700E06	6
424	CO_3^{-} $+HCOO^{-}$ $=HCO_3^{-}$ $+CO_2^{-}$	k(424)=1.500E05	6
425	HCOO-+OH $=H_2O$ $+CO_2^{-}$	k(425)=3.200E09	6
426	HCOO-+H $=H_2$ $+CO_2^{-}$	k(426)=2.100E08	6
427	HCOO-+E^{-} $=H_2$ $+CO_2^{-}$ $-H^{+}$	k(427)=8.000E03	6

Scheme extension for bromide containing solutions

Eq. No.	Reaction	Rate constant	Ref.
500	$Br^- + OH = BrOH^-$	k(500)=1.100E+10	4
501	$Br^- + Br = Br_2^-$	k(501)=1.000E+10	4
502	$Br^- + H = HBr^-$	k(502)=0.000E+06	4
503	$Br^- + O^- = Br + OH^- + \; - H^+$	k(503)=2.200E+08	4
504	$Br + BrO^- = Br^- + BrO$	k(504)=4.100E+09	4
505	$Br = BrOH^- + H^+$ -H2O	k(505)=1.400E+00	4
506	$Br + HO_2 = H^+ + Br^- + O_2$	k(506)=1.600E+08	4
507	$Br + OH^- = BrOH^-$	k(507)=1.300E+10	4
508	$Br + H_2O_2 = Br^- + O_2^- + H^+ + H^+$	k(508)=2.500E+09	4
509	$Br_2^- = Br + Br^-$	k(509)=1.900E+04	4
510	$Br_2^- + Br_2^- = Br^- + Br_3^-$	k(510)=3.400E+09	23
511	$Br_2^- + BrO_2^- = BrO_2 + Br^- + Br^-$	k(511)=8.000E+07	4
512	$Br_2^- + BrO^- = BrO + Br^- + Br^-$	k(512)=6.200E+07	4
513	$Br_2^- + ClO_2^- = Br^- + ClO_2 + Br^-$	k(513)=2.000E+07	4
514	$Br_2^- + H = H^+ + Br^- + Br^-$	k(514)=1.400E+10	4
515	$Br_2^- + HO_2 = H^+ + Br^- + Br^- + O_2$	k(515)=1.000E+08	4
516	$Br_2^- + O_2^- = Br^- + Br^- + O_2$	k(516)=1.700E+08	4
517	$Br_2^- + E^- = Br^- + Br^-$	k(517)=1.100E+10	4
518	$Br_2^- + H_2O_2 = Br^- + Br^- + HO_2 + H^+$	k(518)=1.900E+06	4
519	$BrO^- + OH = BrO + OH^-$	k(519)=4.200E+09	4
520	$BrO^- + O^- = BrO + OH^- - H^+$	k(520)=3.500E+09	4
521	$BrO^- + E^- = Br^- + O^-$	k(521)=1.500E+10	4
522	$BrO_2^- + OH = BrO_2 + OH^-$	k(522)=2.300E+09	4
523	$BrO_2^- + BrO = BrO^- + BrO_2$	k(523)=4.000E+08	4
524	$BrO_2^- + O^- = BrO_2 + OH^- - H^+$	k(524)=1.600E+09	4
525	$BrO_2^- + E^- = BrO + H_2O - H^+ - H^+$	k(525)=1.100E+10	4
526	$BrO_3^- + OH = BrO_3 + OH^-$	k(526)=0.000E+06	4
527	$BrO_3^- + H = BrO_2 + OH^-$	k(527)=2.000E+07	4
528	$BrO_3^- + O^- = BrO_3 + OH^- - H^+$	k(528)=0.000E+06	4
529	$BrO_3^- + E^- = BrO_2 + OH^- + OH^- - H_2O$	k(529)=3.400E+09	4
530	$Br_2 + H = Br_2^- + H^+$	k(530)=1.000E+10	4
531	$Br_2 + HO_2 = H^+ + O_2 + Br_2^-$	k(531)=1.300E+08	4
532	$Br_2 + O_2^- = O_2 + Br_2^-$	k(532)=5.000E+09	4
533	$Br_2 + Br^- = Br_3^-$	k(533)=9.600E+08	24
534	$Br_2 + E^- = Br_2^-$	k(534)=5.300E+10	4
535	$HOBr + OH = BrO + H_2O$	k(535)=2.000E+09	4
536	$HOBr + O_2^- = O_2 + Br + OH^-$	k(536)=3.500E+09	4
537	$BrO_2 + OH = BrO_3^- + H^+$	k(537)=2.000E+09	4
538	$BrO_2 + BrO_2 = BrO_3^- + BrO_2^- + H^+ + H^+ - H_2O$	k(538)=4.000E+07	4
539	$BrO_2 + ClO_2^- = BrO_2^- + ClO_2$	k(539)=3.600E+07	4
540	$Br_3^- + H = H^+ + Br_2^- + Br^-$	k(540)=1.200E+10	4
541	$Br_3^- + O_2^- = O_2 + Br_2^- + Br^-$	k(541)=1.500E+09	4
542	$Br_3^- = Br_2 + Br^-$	k(542)=5.500E+07	24
543	$Br_3^- + E^- = Br_2^- + Br^-$	k(543)=2.700E+10	4
544	$BrOH^- = Br^- + OH$	k(544)=3.000E+07	14
545	$BrOH^- = Br + OH^-$	k(545)=4.200E+06	14
546	$BrOH^- + H^+ = Br + H_2O$	k(546)=1.300E+10	14
547	$BrOH^- + Br^- = Br_2^- + OH^-$	k(547)=1.900E+08	14
548	$BrO + BrO = BrO^- + BrO_2^- + H^+ + H^+ - H_2O$	k(548)=2.800E+09	4

549	$BrO +BrO_2^-$	$=BrO^- + BrO_2$	k(549)=4.000E+08	4
550	$HOBr$	$=H^+ +BrO^-$	k(550)=1.580E+01	18
551	$BrO^- +H^+$	$=HOBr$	k(551)=1.000E+10	18
552	$Br^- +Cl_2^-$	$=BrCl^- +Cl^-$	k(552)=4.00E+09	23
553	$BrCl^- +Cl^-$	$=Cl_2^- +Br^-$	k(553)=1.10E+02	23
554	$BrCl^-$	$=Cl^- +Br$	k(554)=8.50E+07	23
555	$Br +Cl^-$	$=BrCl^-$	k(555)=1.00E+10	23
556	$BrCl^- +Br^-$	$=Br_2^- +Cl^-$	k(556)=8.00E+09	23
557	$Br_2^- +Cl^-$	$=BrCl^- +Br^-$	k(557)=4.30E+06	23
558[f]	$Br^- +Cl_2$	$=BrL2^-$	k(558)=6.00E+09	24
559[f]	$BrL2^-$	$=Cl_2 +Br^-$	k(559)=9.00E+03	24
560[f]	$BrL2^-$	$=BrCl +Cl^-$	k(560)=1.70E+05	24
561[f]	$BrCl +Cl^-$	$=BrL2^-$	k(561)=1.00E+06	24
562[f]	$BrL2^- +Br^-$	$=Br2L^- +Cl^-$	k(562)=3.00E+08	24
563	$BrCl$	$=HOBr +H^+ +Cl^- -H_2O$	k(563)=3.00E+06	25
*564[d]	$HOBr +Cl^-$	$=BrCl +H_2O -H^+$	k(564)=2.30E+10	25
565	$BrCl$	$=HOCl+H^+ +Br^- -H_2O$	k(565)=1.15E-03	25
*566[d]	$HOCl +Br^-$	$=BrCl +H_2O -H^+$	k(566)=1.32E+06	25
*567[d]	$Br^- +HOBr$	$=Br_2 +H_2O -H^+$	k(567)=3.00E+09	26
568	Br_2	$=Br^- +HOBr +H^+ -H_2O$	k(568)=2.00E+00	26
*569[d]	$Br^- +HBrO_2$	$=HOBr +HOBr -H^+$	k(569)=3.00E+06	26
570	$HOBr +HOBr$	$=Br^- +HBrO_2 +H^+$	k(570)=2.00E-05	26
*571[d]	$Br^- +BrO_3^-$	$=HOBr +BrO_2^- -H^+$	k(571)=2.500E-7	26
572	$HOBr +HBrO_2$	$=Br^- +BrO_3^- +H^+ +H^+$	k(572)=3.20E+00	26
573	$HBrO_2 +HBrO_2$	$=HOBr +BrO_3^- +H^+$	k(573)=3.00E+03	26
*574[d]	$HOBr +BrO_3^-$	$=HBrO_2 +HBrO_2 -H^+$	k(574)=1.00E-08	26
*575[d]	$HBrO_2 +BrO_3^-$	$=BrO_2 +BrO_2 +H_2O -H^+$	k(575)=4.20E+01	26
576	$BrO_2 +BrO_2$	$=HBrO_2 +BrO_3^- +H^+ -H_2O$	k(576)=4.20E+07	26
577	$HBrO_2$	$=BrO_2^- +H^+$	k(577)=5.00E+05	27, R1
578	$BrO_2^- +H^+$	$=HBrO_2$	k(578)=1.35E+09	27
579	$BrCl^- +BrCl^-$	$=BrCl +Br^- +Cl^-$	k(579)=1.20E+09	R[h] 2
580[f]	$Br_2 +Cl^-$	$=Br2L^-$	k(580)=1.00E+07	R[h] 3,4
581[f]	$Br2L^-$	$=Br_2 +Cl^-$	k(581)=7.69E+06	24
582[f]	$BrCl +Br^-$	$=Br2L^-$	k(582)=1.00E+07	R[h] 3,4
583[f]	$Br2L^-$	$=BrCl +Br^-$	k(583)=5.56E+02	24

Remarks:

1. Reaction 577 is described as ‘fast’. Therefore a rate constant for the dissociation is assumed to be 5.0E+5 s^{-1}.
2. No measured data are available for reaction 579. It is assumed that the rate constant is about the same as those for Cl2- and Br2-.
3. No measured data are available for the formation rate of the trihalide ions. A mean value of the similar reactions 138, 533 und 561 is used.
4. The establishment of the equilibria eq. 580/581 and 582/583 is assumed to be fast.
5. As no reaction data for the consumption of the formed species are available the reactions 502, 526 and 528 are not considered.

For the oxidation/dissolution of UO_2 and the integration into the homogeneous kinetic model two approaches are given:

1. Scheme extension for describing the oxidation/dissolution of solid UO_2

Eq.No	Reaction					Rate Constant[a]	Ref.
600	UO_2	$+OH$	$=UO_3H$			k(600)= 4.000E+08	28
601	UO_2	$+H_2O_2$	$=UO_3H$	$+OH$		k(601)= 2.000E-02	28
602[d]	UO_2	$+HO_2$	$=UO_3H$	$+H_2O_2$	$-H_2O$	k(602)= 2.000E+08	28
603[d]	UO_2	$+O_2^-$	$=UO_3H$	$+HO_2^-$	$-H_2O$	k(603)= 2.000E+08	28
604	UO_3H	$+UO_3H$	$=UO_3$	$+UO_2$	$+H_2O$	k(604)= 3.000E+00	28
605	UO_3H	$+OH$	$=UO_3$	$+H_2O$		k(605)= 8.000E+08	28
606	UO_3H	$+E^-$	$=UO_2$	$+OH^-$		k(606)= 5.000E+08	28
607	UO_3H	$+H_2O_2$	$=UO_3$	$+H_2O$	$+OH$	k(607)= 2.000E-02	28
608	UO_3H	$+O_2^-$	$=UO_3$	$+HO_2^-$		k(608)= 2.000E+08	28
609	UO_3H	$+O_2^-$	$=UO_2$	$+OH^-$	$+O_2$	k(609)= 4.000E+08	28
610	UO_3H	$+HO_2$	$=UO_3$	$+H_2O_2$		k(610) = 4.000E+08	28
611[d]	UO_3	$+E^-$	$=UO_3H$	$+OH^-$	$-H_2O$	k(611)= 5.000E+07	28
612	UO_3	$+O_2^-$	$=UO_3^-$	$+O_2$		k(612)= 4.000E+06	28
613	UO_3^-	$+H_2O$	$=UO_3H$	$+OH^-$		k(613)= 1.000E+01	28
614	UO_3H	$+H$	$=UO_2$	$+H_2O$		k(614)= 4.500E+06	28
615	UO_3	$+H$	$=UO_3H$			k(615)= 4.500E+05	28
616	UO_3	$+HO_2$	$=UO_3H$	$+O_2$		k(616)= 4.000E+06	28
617[g]	UO_3		$=UO_3D$			k(617)= 4.000E-05	28
618[d]	UO_2	$+O_2$	$=UO_3H$	$+HO_2$	$-H_2O$	k(618)= 1.000E-04	28
619	UO_3H	$+O_2$	$=UO_3$	$+HO_2$		k(619)= 1.000E-04	28
620[g]	UO_2		$=UO_2D$			k(620) = 7.000E-02	28
621[g]	UO_2D		$=UO_2$			k(621) = 7.000E-09	28
622[d]	UO_2	$+Cl_2^-$	$=UO_3H$	$+HCl$ $+Cl^-$	$-H_2O$	k(622)= 1.500E+05	37
623	UO_2	$+HClO$	$=UO_3H$	$+Cl$		k(623)= 4.000E-03	28
624	UO_3H	$+Cl_2^-$	$=UO_3$	$+HCl$	$+Cl^-$	k(624)= 3.000E+05	37
625	UO_3H	$+HClO$	$=UO_3$	$+Cl$	$+H_2O$	k(625)= 4.000E-03	28

626	H_2O_2	$=H_2O_2D$	k(626)=3.000E-03	31

Remarks:

This system is applicable for the 'active' layer only. In a first approach the layer thickness adjacent to the solid is assumed to be equal to the range of alpha radiation (about 45 μm). The species UO_2 is defined to represent the solid four-valent U which acts as reaction partner for all possible oxidants and which occurs only in the reactive layer. Its concentration in the layer is kept constant by the equilibrium according to eq. 620 and eq. 621. With starting concentrations [UO2]= $5*10^{-4}$ mol/L and [UO2D]= 1000 mol/L a steady state concentration of [UO2]= $1*10^{-4}$ is achieved very rapidly.

When using this scheme care has to be taken that at least no long lived products accumulate in the layer. This can be established by addition of diffusion equations to the scheme (e.g. eq. 626 for H_2O_2) or by applying TRARAMO.

2. Scheme extension for describing the oxidation/dissolution of solid UO_2

Eq.No	**Reaction**				**Rate Constant**[a]	**Ref.**
700	$>UO_2$	$+H_2O_2$	$=>UO_3$	$+H_2O$	k(700)= 3.600E-02	R[h]
701	$>UO_2$	$+O_2$	$=>UO_2\text{-}O_2$		k(701)= 1.300E-03	R[h]
702	$>UO_2\text{-}O_2$	$+ >UO_2$	$=>UO_3$	$+>UO_3$	k(702)= 1.000E+16	R[h]
703	$>UO_3$	$+H^+$	$=UO_2OH^+$		k(703)= 5.000E+00	R[h]
704	$>UO_3$	$+H_2O$	$=UO_2(OH)_2$		k(704)= 5.000E-02	R[h]
705	$>UO_3$	$+HCO_3^-$	$=UO_2CO_3$	$+OH^-$	k(705)= 1.000E+11	R[h]
706	UO_2CO_3	$+HCO_3^-$	$=UO_2(CO_3)_2^{2-}$	$+H^+$	k(706)= 1.000E+11	R[h]

Remark: The complete reaction scheme is obtained from the D12 report of this project. For its application additional assumptions have to be made e.g. for the ‘active’ layer and the concentrations of $>UO_2$ at start.

As both reaction schemes for the UO_2 oxidation/dissolution describe the rate determining step as a pseudo first order reaction of the solid UO_2 with different oxidants one could avoid the formulation of equations in which concentrations of ‘dissolved solid UO_2’ or ‘reactive sites’ occur by writing them as first order reactions but this seems to be less descriptive.

Equation 600 would become: $OH = UO_3H$ $k = 4*10^8 * [UO_2] = 10^4\ s^{-1}$

Equation 700 would become: $H_2O_2 = >UO_3$ $k = 3.6*10\text{-}2 * [>UO2]\ s^{-1}$ etc.

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