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Modelling of pore water chemistry in the graphite from fuel pebbles.

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Document title

Modelling of pore water chemistry in the graphite from fuel pebbles.

Executive summary

Waste containers are expected to last for at least thousand years. Thereafter groundwater will penetrate the container. The pores of graphite matrix of the pebbles in the container are initially filled by gas but it takes only few years until the gas phase is replaced by infiltrating water, even though the graphite surface is rather hydrophobic. The pores are characterized by a very high ratio of surface area to solution volume. Under these conditions, even slow chemical reactions between water and the graphite surface may significantly modify the solution chemistry. A radiolytic graphite dissolution model has been developed considering H_2O_2 as principal reactant. The model has partly been calibrated with published experimental data but a more extensive calibration of a variety of environmental conditions (presence or absence of gas phase, pH, varying surface to volume ratio etc.) would be necessary.

Revisions

Rev.	Date	Short description	Author	WP Leader	SP Leader	Coordinator
00	05/10/2007	First issue	B. Grambow	Grambow *Signature*	W.v. Lensa *Signature*	Name, Organisation *Signature*
01	15/01/2008	Final			W. von Lensa FZJ	

1 Introduction

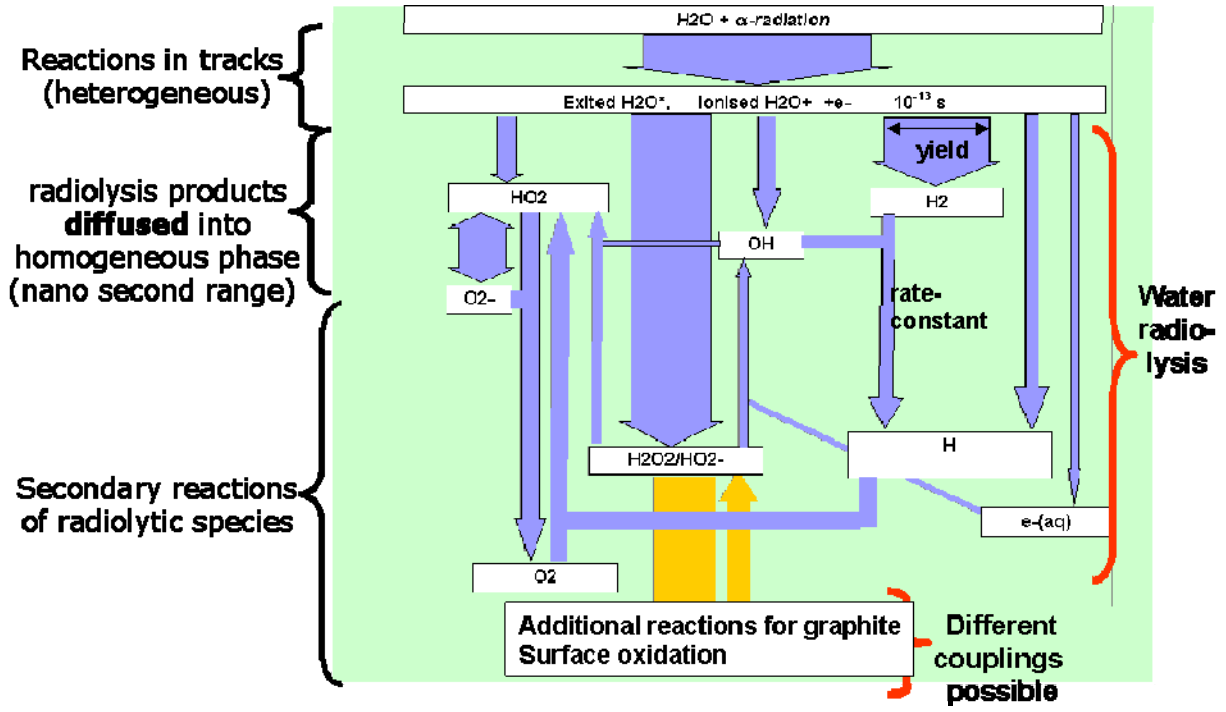
The fuel pebbles can be stored in tight iron based containers for thousands of years. Corrosion of the container by groundwater will lead sooner or later to mechanical failure of the container, caused by the rock pressure in a final repository. Today, containers are expected to last for at least thousand years. Thereafter groundwater will penetrate the container. The pores of graphite matrix of the pebbles in the container are initially filled by gas but it takes only few years until the gas phase is replaced by infiltrating water, even though the graphite surface is rather hydrophobic. The pores are characterized by a very high ratio of surface area to solution volume. Under these conditions, even slow chemical reactions between water and the graphite surface may significantly modify the solution chemistry.

It is well known that the reactivity of graphite with groundwater will essentially depend on the oxidant content of the groundwater. In European repository projects almost oxygen free reducing conditions are expected in deep groundwaters. Under these conditions radiolytic decomposition of groundwater may be a key source for oxidants. One of the principal oxidizing radiolysis products is hydrogen peroxide. Indeed, previous work in the HTR-N project by FZ Jülich has shown that the corrosion rate of graphite increases strongly with the concentration of hydrogen peroxide. The present contribution assesses the evolution of pore water chemistry in fuel pebbles as a function of irradiation conditions and reaction with graphite.

2 Radiolysis model for oxidation of graphite surfaces

In order to know how much oxidants are available for graphite oxidation/dissolution, one needs first to ass water radiolysis. A water radiolysis scheme used in the present calculations is given in figure 1. The model calculates a steady state concentration of hydrogen peroxide as a function of apha, beta and gamma dose rate. The rate constants for interaction of H2O2 with the graphite surface are than obtained by calibration with experimental data from FZ Jülich on H2O2 dependency of graphite dissolution rates. For the calculations the radiolysis code MAKSIMA chemist has been used.

Figure 1: Coupling of water radiolysis model to fuel dissolution model. Different thickness of reaction arrows indicate relative importance of a given rate



The reaction of the graphite surface S with H_2O_2 is described by a two step process. In a first step, sorption of initially dissolved H_2O_2 occurs at the surface leading to a partial or complete surface coverage by oxydants (H_2O_2). This is described by the equations 1 and 2 describing both sorption and desorption. For a given H_2O_2 concentration an equilibrium between sorption and desorption in rapidly established. Surface coverage will then depend on the H_2O_2 concentration in the water.

$S + H_2O_2 = S\text{-}H_2O_2$ K1 = 1.000E+08 (1)

$S\text{-}H_2O_2 = S + H_2O_2$ K2 = 1.000E+06 (2)

Surface sorbed H_2O_2 may than lead to a chemical reaction between the carbon from the graphite leading to CO2 and H2 formation. Thermodynamically, this reaction is favored. The detachement of carbon dioxide and hydrogen from the graphite surface is then described by equation 3.

$S\text{-}H_2O_2 = S + CO2 + H2$ K3 = 1.300E-04 (3)

The rate constants K1 to K3 are obtained by calibration with data of short term experiments of reacting 1g of graphite powder (particle size < 50 µm) with 20 mL of water of different concentrations of H_2O_2 in a closed argon filled glass vessel of a total volume of 36 mL (Podruzhina 2004). The MAKSIMA code was used to simulate the reaction network with experimental H_2O_2 concentrations as input and fixing the dose rate at zero. An average spherical pore diameter of 160 nm was obtained for the calculations, leading in the pores to a surface to volume ratio S/V of 3.7E6 dm^{-1}. With the reported specific surface area of 4.8 m^2/g one obtains 6E13 pores per gram and with a density of 1.6 one obtains a total porosity of

20.5%. This corresponds to the reported porosity (see figure 2) indicating that the assumed average pore diameter of 160 nm is a representative choice. The extent of graphite corrosion in units of g(corroded) / g(graphite) has been determined from the calculated pore water concentration of produced bicarbonate ions. Bicarbonate ions are formed in equilibrium from initially produced CO2 (the latter is formed via reaction 3). The assumption was made that all internal pore surfaces of the graphite particles would be water accessible during the experiments. If diffusion resistance would have slow down the transfer of H_2O_2 from the bulk water to the pores or of dissolved HCO_3^- from the pores to the bulk water, then the calculated rate constants would be underestimated. The results of this calibration are given in the figure 3 showing that the model describes sufficiently well the experimental observations.

Figure 2 Relation between pore diameter and porosity of A3 graphite (Reference?)

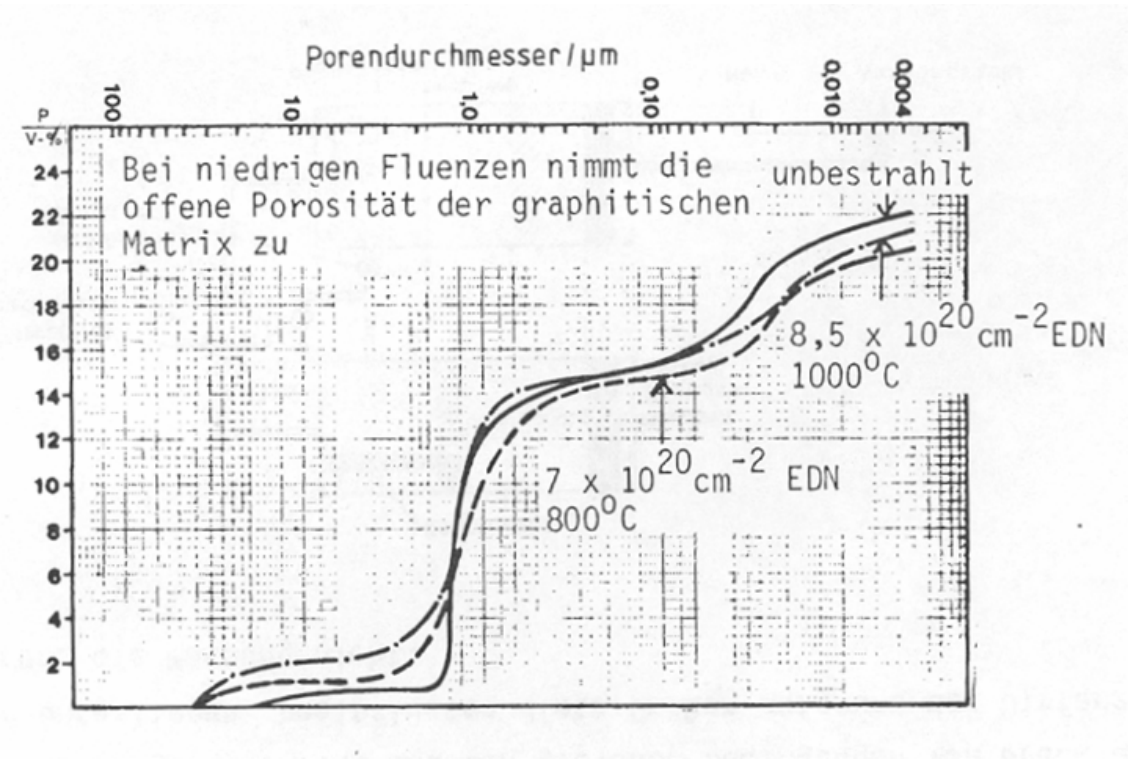
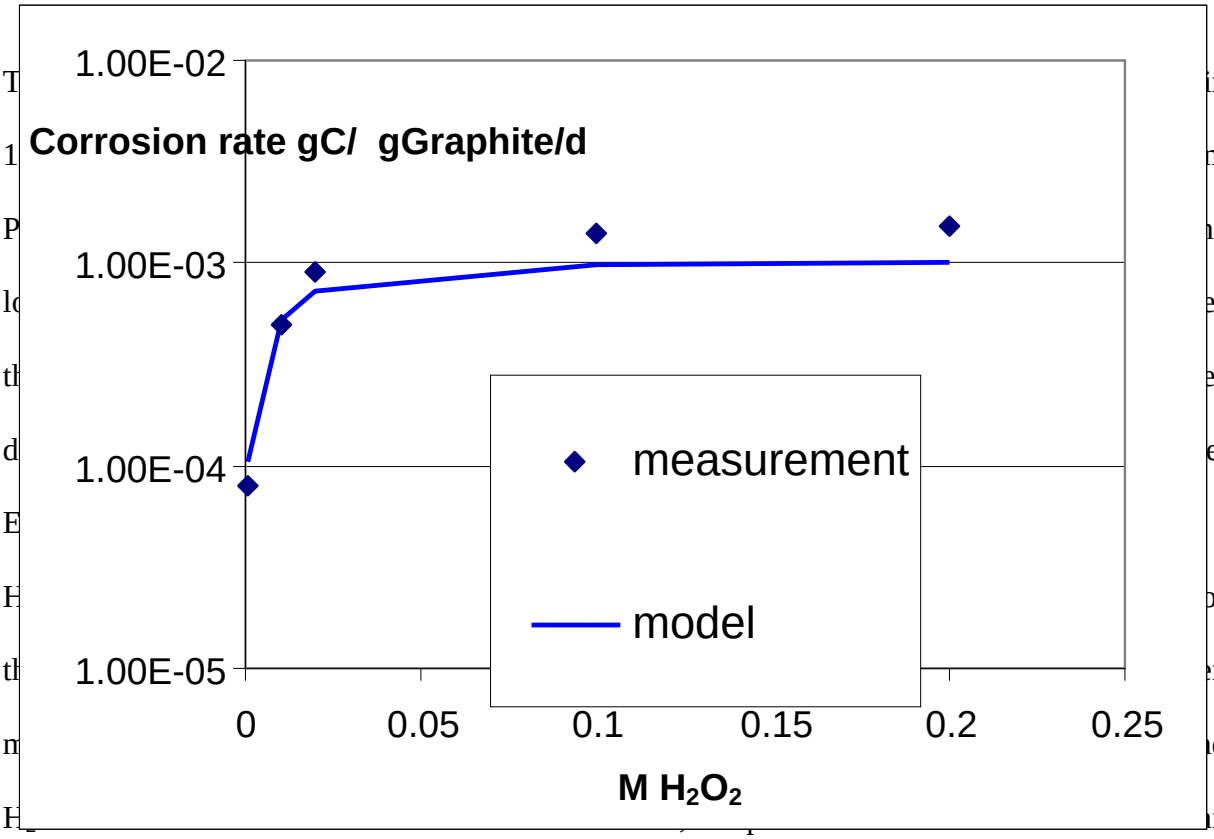


Figure 3: Calibration of model for radiolytic graphite dissolution with experimental data from FZ Jülich (Podruzhina 2004)



order of magnitude lower than the values predicted in table 2, coming closer to the experimentally measured values.

Table 2 comparison of calculated and measured dissolution rates of graphite under gamma radiation

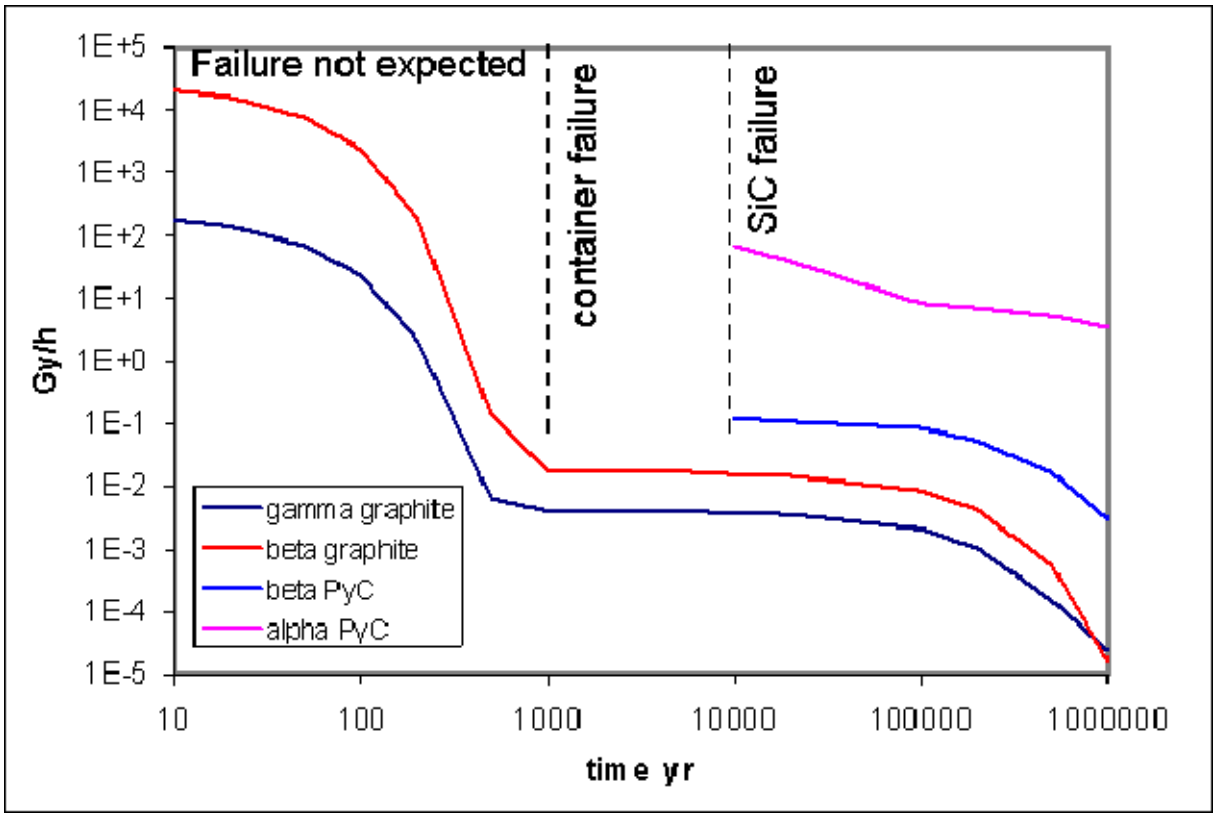
MGy	Rate meas. gC/g/d	Rate calcul gC/g/d	HCO_3 M	H_2O_2 M
2.2	2E-6	2E-6	1.1^{E}-3	4^{e}-5
4.3	3E-7	5E-6	4.8^{E}-3	1^{e}-4
5.3	2E-7	7E-6	0.01	1.5^{e}-4

It shall be mentioned that the above presented calibration of the model for radiolytic graphite dissolution is only of preliminary character. The experimental data used are not entirely consistent with the model. In particular the gas phase present in the experiments plays a large role in the calculations. Experimentally it has been observed that a large quantity of O2 accumulates in the gas phase of experiments with H_2O_2. This is not calculated in the model. It seems to indicate strong instability of H_2O_2 even in blank tests. A confirmation of the experimental observation and in particular of H_2O_2 stability during the experiment would be necessary (outside of the scope of the Raphael project).

3 Relevant dose rates

Calculation of the dose rates for alpha, beta and gamma radiation both for the graphite pore space and the inner pyrocarbon coatings are calculated in deliverable D2.3 and the results are reproduced here, to identify the reference dose to be used for the calculation of radiolytic decomposition of pore water.

Figure 4: dose rates in the fuel pebble as a function of time. Calculations are from deliverable D2.3.



After container failure and prior to water access to the fuel kernel (SiC failure) dose rates are governed by high energy beta radiation. An average dose rate is 0.017 Gy/h.

4 Long term predictions

Predictions were performed using the above described radiolysis model both for a dose rate of 3000 Gy/h (not expected scenario of early container failure) and for a dose rate àf 0.1 Gy/h, a conservative choice for the expected container failure after 1000 to 10000 of years, prior to the breaching of the SiC coating. In contrast to the experiments used for model calibration, no gas phase was assumed to be present in the pore space of the graphite. In a first model step, the system pore water/graphite is described as a closed system, allowing unlimited accumulation of radiolysis products and of dissolved graphite components. The predicted results are shown in figure 5 and 6.

In case of early container failure, after saturation of the graphite pore space by infiltrating groundwater radiolytic H_2 gas will form and oxalate ions and bicarbonate (HCO_3^-) ions form upon reaction of formed H_2O_2 with graphite. The bicarbonate concentrations expected with the hypothesis of a closed systems are similar to those in typical groundwaters (10^{-3} – 10^{-2} M), but expected oxalate concentrations are much higher. Oxalate is a strong complexing agent for actinide ions indicating increased actinide and UO_2 solubility in the pore space once the SiC cladding would have failed. However, in reality the pore space of graphite is not a closed system. A diffusion coefficient of about $2 \cdot 10^{-12}$ m^2/s has been measured by FZJ.

Figure 5: Results of predicting pore water composition in A3 graphite as a function of time for the not expected early canister failure scenario at a constant dose rate of 3000 Gy/h.

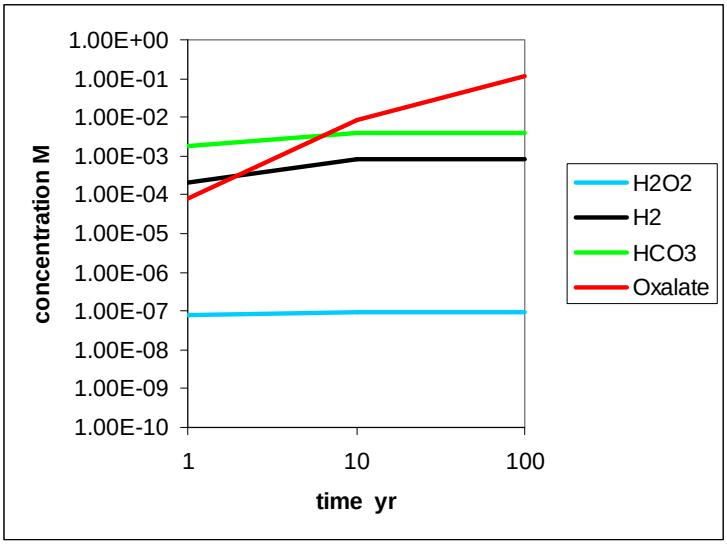
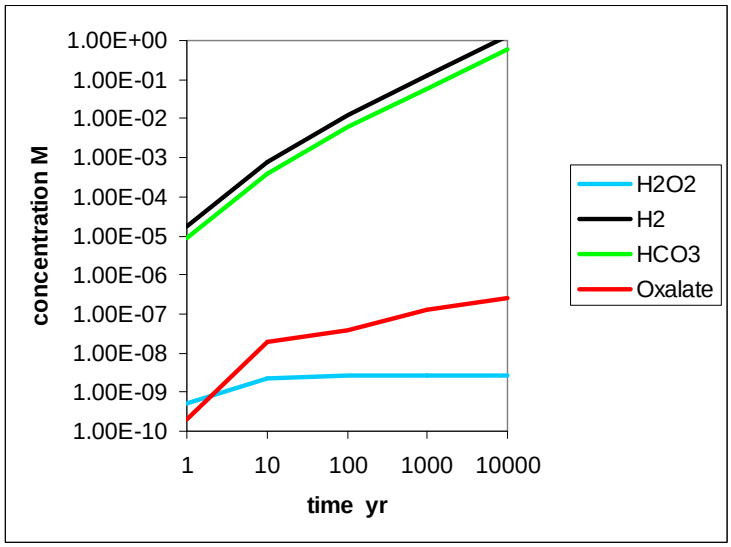


Figure 6: Results of predicting pore water composition in A3 graphite as a function of time for the expected container failure after more than 1000 years at a constant dose rate of 0.1 Gy/h.



Under these conditions, no accumulation of radiolysis products and of graphite corrosion products is possible in the graphite pore space. Additional calculations have shown that it takes less than a year before the concentration dependent diffusion rate of dissolved components from the centre of the pebble to the groundwater in the disposal horizon will become equal to the dissolution rate of the graphite pore surfaces. Under these conditions, maximum solution concentrations of oxalate will be $<10^{-5}$ M, rather insignificant for complexation of actinides.

In the expected case for container failure only after more than 1000 years, the expected situation is quite different for closes conditions. Even under closed systems conditions, oxalate formation seems to be much less important. Instead very high bicarbonate and hydrogen concentrations are expected. Also bicarbonate is a strong complexing agent for actinides. However again, additional transport calculations have shown that it will take less than a year before diffusion rates out of the fuel pebble become equal to the dissolution rates of the graphite surface. Hence, the static systems calculation of solution concentrations in figure 6 is meaningless and rapid exchange with the groundwater will assure that maximum oxalate concentrations will not become higher than insignificant values of 10^{-9} M and **bicarbonate concentrations will become very close to concentrations already present in the groundwater.**

The calculated concentrations of about 1 M for the static system of dissolved hydrogen correspond to about 1000 bar. This pressure is higher than the hydrostatic pressure in a repository, which would indicate formation of H_2 gas bubbles in the pore space and partial desaturation. It would then be expected that gas bubbles would push pore water out of the graphite, hence, already without invoking diffusion, pressure build-up will be slower than

indicated in figure 6 and maximum pressures would become only slightly higher than hydrostatic pressure. Diffusion of H_2 will produce maximum overpressures of less of only 0.01 atm. Hence, in reality, H2 bubble formation by radiolysis is probably an insignificant process.

Finally, from the data in figures 5 and 6 a radiolytic graphite dissolution rate can be calculated. These calculations are independent on the mode of calculation (static or dynamic). In fractional units it is 4.7E-6/yr at 3000 Gy/h and it is 1.3E-7/yr at a dose rate of 0.1 Gy/h. This shows that with respect to radiolytic degradation processes, graphite will remain stable in disposal time and no significant change of pore diameters by potential dissolution of graphite pore surfaces is expected. Direct chemical dissolution of graphite will even give lower dissolution rates than the radiation assisted rates.

5 Conclusions

A radiolytic graphite dissolution model has been developed considering H_2O_2 as principal reactant. The model has partly been calibrated with published experimental data but a more extensive calibration of a variety of environmental conditions (presence or absence of gas phase, pH, varying surface to volume ratio etc.) would be necessary. The current model seems to overestimate graphite dissolution rates under gamma irradiation conditions. High carbonate and oxalate concentrations are not expected in the pore water since exchange between groundwater and the graphite pore water is fast on the scale of a year. This will lead to a situation, were radionuclide mobility in graphite pore water can be assessed from groundwater composition alone. Graphite dissolution rates will be too slow to allow dissolved HCO3 and oxalate to contribute significant pore water composition. Hence, HCO3 concentrations as well

as major element concentrations are essentially governed by external groundwater chemistry.

Radiolysis is main source for graphite oxidation/dissolution, but there is no problem for

graphite long-term stability for >> 1 Mio yr.

6 References

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J. Fachinger, M. den Exter, B. Grambow, S. Holgersson, C. Landesman, M. Titov, T. Podruhzina, „Behavior of spent HTR fuel elements in aquatic phases of repository host rock formations“, Nuclear Engineering and Design, 236, 543-554 (2006)