

TOUGHREACT/ECO2 ON REACTIVE TRANSPORT MODELING OF CO₂ IN A GEOLOGICAL REPOSITORY

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ABSTRACT

This study reports a numerical investigation of the transport/retention mechanisms and rates of generated CO₂ in a radioactive waste repository in rock salt using TOUGHREACT. The ECO2 module is applied for equation of state. A 2-dimensional grid model is created with refinements in the regions of interests (waste and backfill). All cavities in the modelled repository area are backfilled with a Mg(OH)₂ based material. The pore volume is saturated with MgCl₂ rich brine. Hydrostatic and local geothermal gradients determine the initial conditions for the simulated area. The gas generation rates are derived from realistic scenarios reported earlier.

The ability of TOUGHREACT for more detailed applications of reactive transport under given repository conditions is investigated. The compositions of mineral phases and of the aqueous phase require an adaptation of the thermodynamic database.

The geochemical stability of a backfill based on Mg(OH)₂ under repository conditions is re-evaluated in further runs using TOUGHREACT. The impact of transport and retention of CO₂ dissolved in brine as well as the precipitation of carbonates as magnesite and calcite mainly on long term safety are analysed successfully using TOUGHREACT.

INTRODUCTION

The studies on deep geological disposal of radioactive waste are concerned mainly with conditions for safe enclosure in underground caverns and tunnels over a long period. The natural and engineered barriers should ensure the necessary conditions to avoid or to delay the migration of radioactive nuclides and contaminants to the biosphere. Gas generation due to corrosion (mainly H₂) and microbial degradation (mainly CO₂ or CH₄) of the stored wastes and their transport/retention is therefore of high relevance in assessing the performance of a repository.

The Asse research salt mine is one example of the German repositories used for the disposal of radioactive wastes. The mine is situated in a diapir of Zechstein salt in Germany. It is characterized by large excavated volumes of 4x10⁶ m³ due to the halite and potash production between the years 1906 and 1964. It has a large network of galleries and shafts. After the termination of halite/potash mining, the mine was used as a research and development site for radioactive waste disposal between the years 1967 and 1978. Low- and intermediate level waste was emplaced with a total radioactive inventory of approx. 3x10¹⁵ Bq. The excavated chambers are located at depths between 750 m and 511 m below the surface ground. Experimental and modelling studies were conducted on the mechanical, chemical and hydraulic stability of the ASSE rock salt (Pusch et al., 2002, Alkan et al., 2002). Most parts of the Asse salt mine were back-filled with crushed rock salt for geomechanical reasons. Research is going on for the selection of the suitable backfill materials in the near field of the chambers with radioactive waste. Site specific requirements for the backfill material are given by waste characteristics, geometrical limitations and geochemical modelling (Metz et al., 2004).

The backfill materials have to fulfil some requirements concerning the stability of geochemical environment and hydraulics. It is preferred that the backfill provide well-defined geochemical conditions in the emplacement chambers such as buffering of pH and sorption of radionuclides. On the other hand, the backfill material should have a sufficient hydraulic blocking effect with minimum permeability and suitable capillary characteristics. All desired properties could not be fulfilled at the same time. The geochemical or hydraulic requirements will play important roles for the selection of a suitable combination of backfill materials and additional measures.

The selection of backfill material is based on relevant radionuclides and their solubility in an expected geochemical environment. One of the most relevant factors for selection of backfill materials is the potential influence of dissolved carbonate species on the solubility of radionuclides. The microbial

degradation of the organic components of the disposed waste to inorganic carbon may increase the dissolved carbonate (CO_3^-) concentration of the solution. High concentration of CO_3^- results in an higher solubility of the radionuclides namely the actinides. This is obviously not desirable in terms of safety requirements and precautions have to be taken. A backfill material consisting mainly of brucite ($\text{Mg}(\text{OH})_2$) is found to be suitable for a robust long term geochemical environment. Experimental as well as modelling studies support the performance of brucite as backfill material by limiting/decreasing the dissolved carbonate content. These results should also be confirmed based on dynamic modelling studies. This enables to evaluate the resulting hydraulic and mechanical changes in the emplacement chambers as well as in the galleries of the underground repository system.

MODELLING CONCEPT

A schematic of the gas generation process in the emplacement chamber is presented in Figure 1. The radioactive waste is disposed in the excavated volumes. The remaining volume is filled with a backfill material and the pore volume is saturated with a suitable solution depending on the backfill concept. The gallery is also backfilled to delay the transport of potential contaminants to the far field and/or directly to the biosphere. As a result of microbial degradation of the organic components and/or corrosion gas (mainly CO_2 , CH_4 , H_2) is generated. The gas may be dissolved in solution or available as a free gas phase. The pressure increases in the emplacement chamber because of the gas generation and additional rock convergence. The increased pressure may squeeze the gas and/or solution to the upper parts of the mine. The damaged zone in the near vicinity of the walls due to the excavation (excavated damaged zone) or natural pathways as well as the galleries and drifts provide potential ways for the contaminant transport with gas and solution (Alkan et al. 2002).

For the mathematical modeling of the gas generation and its contribution to the contaminant transport in a repository system TOUGHREACT/ECO2 was used. A simple irregular 2D grid model was built using the mesh maker facility of TOUGHREACT (Figure 2). An emplacement chamber at approximately 750 m deep is modelled with dimensions of 25 x 8 m. A total volume of 200 m^3 was taken for backfill material and four source terms were located in the model chamber. For the determination of the source term a waste volume of 400 m^3 was assumed based on a volume ratio of 0.66 of waste to total excavated volume. The gas generation rate was taken from previous studies as $9 \times 10^{-11} \text{ kg}/(\text{s} \cdot \text{m}^3_{\text{waste}})$ (Bracke et al., 2004).

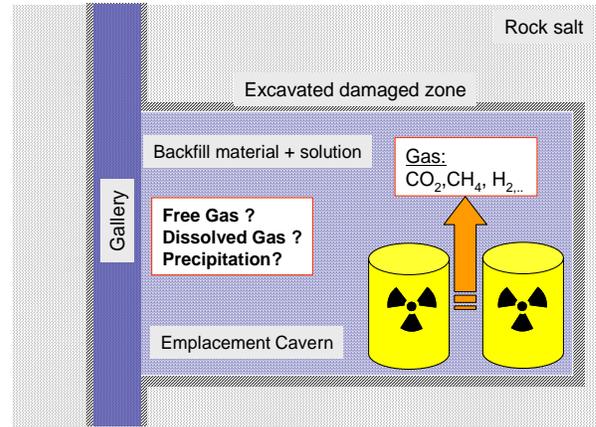


Figure 1. Schematic of the gas generation process in an emplacement chamber

The porosity and permeability of the surrounding rock salt was assumed as 0.001 and $1 \times 10^{-21} \text{ m}^2$, respectively. The porosity of the backfill was given as 0.30 and the permeability as $5 \times 10^{-13} \text{ m}^2$. A vertical gallery with porosity of 0.25 and permeability of $1 \times 10^{-13} \text{ m}^2$ connecting the emplacement chamber to the above situated chambers was also modelled with a width of 4 m. The relative permeability and capillary pressure data were collected from the similar studies and introduced by using the van Genuechten-Mualem model. The initial conditions of the model were calculated based on hydrostatic and geothermal gradients. The pressure and temperature on the emplacement chamber was set to 9.2 MPa and 40°C, respectively. Free or dissolved amounts of gas were set zero at start of modelling.

The composition of the rock salt was set to 99% halite and 1% anhydrite. Two different compositions of backfill materials were used for modelling. The first one represented standard backfill material used with waste disposal in rock salt (Backfill C). The second one is brucite based backfill material which is also called Mg-Depot (Backfill B). In previous studies it was concluded that this backfill material has advantages for setting up a robust geochemical environment and hydraulics. The compositions of both backfill materials are given in the Table 1. A small amount of iron was included in the composition in both cases to simulate steel waste drums. Secondary phases, which are likely to exist in the backfill, were added to the composition.

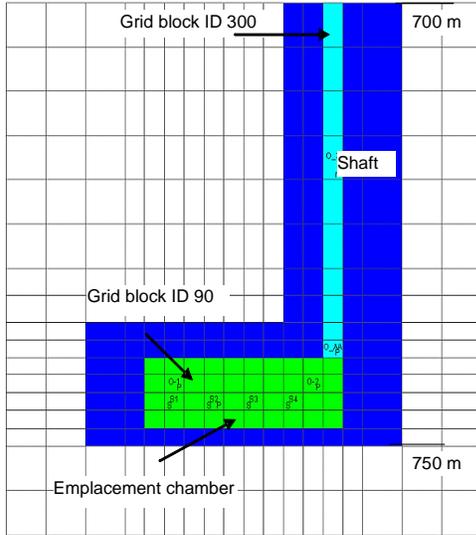


Figure 2. Schematic of the model

Table 1. Mineral compositions used in the model

Minerals	Salt	Backfill C	Backfill B
Halite	0.99	0.40	0.25
Portlandite	-	0.50	-
Quartz	-	0.08	0.03
Iron	-	0.01	0.01
Brucite	-	-	0.70
Dolomite	-	0.01	-
Anhydrite	0.01	-	-
Fayalite	-	-	0.005
Fosterite	-	-	0.005

As the provided thermodynamic database does not include portlandite and brucite, their published properties (chemical formula, molar volume, stoichiometric coefficients and dissociations constants) were added to the database. The kinetic parameters (kinetic constants at 25 °C and activation energies for neutral, acid and alkaline reactions) for all minerals were taken from previous studies, the kinetic parameters for modelling portlandite and brucite were approximated as a first estimation based on the properties of the similar compositions (Tritignant et al., 2005, Pruess et al., 2005).

A limitation of TOUGHREACT has been faced when modelling the composition of the MgCl₂ based brines. It is reported that the activity coefficients of the aqueous species is calculated according to Debye-Hückel rules with parameters derived by Helgeson et al. (Pruess et al., 2005). A major assumption is that the dominant cation and anion in solution are sodium and chloride, respectively. This means that the applicability of this method depend strongly on the

dominant presence of NaCl. Therefore the use of a MgCl₂ based brine as aqueous phase in TOUGHREACT is somewhat restricted. As a ionic strength smaller than 3-4 is proposed as a practical limit for application of Debye-Hückel rules the concentration of the MgCl₂ was limited to 2 M in the modelling.

Table 2. Initial solution compositions used in the model, mg/l

Species	Solution N	Solution Q
NaCl	200	-
MgCl ₂	-	190
MgSO ₄	-	20
KCl	-	10
CaSO ₄	10	1

The dependence of the permeability on the porosity was considered based on the cubic law provided in TOUGHREACT. A very important assumption of the model is the negligence of the physical convergence which can be very important for the repository considerations in rock salt. Obviously the squeezing effect of the rock convergence is an additional pressure to the system should therefore be taken into account in the next steps of the study.

As depicted in Figure 2, the non coloured grid blocks were set inactive in order to save computing time. Two blocks with ID number of 90 and 300 were selected for monitoring. Block 300 is situated 40 m above the emplacement chamber. Prior to each run a period of 10 years was allowed for a chemical equilibrium of the phases.

MODELLING RESULTS

Case 1: Solution N, Backfill C

The runs were performed for a 5000 years time period. A first modelling attempt was made for Solution N with conventional backfill material, Backfill C. No gas saturation is calculated for the whole system. After 5000 years the pH in the emplacement chamber is reduced down to 5.2 and the pressure reaches approximately to 100 MPa. The CO₂ mass ratio in solution in the emplacement chamber is estimated to be between 0.060 and 0.071. The gas in solution reduces to 0.041 at the upper end of the model, in the gallery, Block 300. Because of applying an undersaturated solution a high rate of dissolution is apparent in the emplacement chamber. The volume of halite is reduced app. 2.5% after 5000 year and this resulted in considerably increased porosity as seen in Figure 3. The porosity of the emplacement chamber reaches 0.323 at the end of 1500 year and stays app. at this value because of a quasi-equilibrium state. The precipitated minerals are mainly calcite

and magnesite. Some small amount of precipitation of portlandite and quartz is observed. On the other hand the dissolution (oxidation) of iron is apparent with a reduction of approximately 0.05% of the total volume. The porosity of the vertical gallery (shaft) on the other hand reduces from 0.25 up to 0.15 indicating a stronger precipitation of calcite, magnesite and portlandite mainly. This also implies a decrease in permeability in this region causing a lower conductivity for the CO₂ containing fluid to the upper parts of the repository.

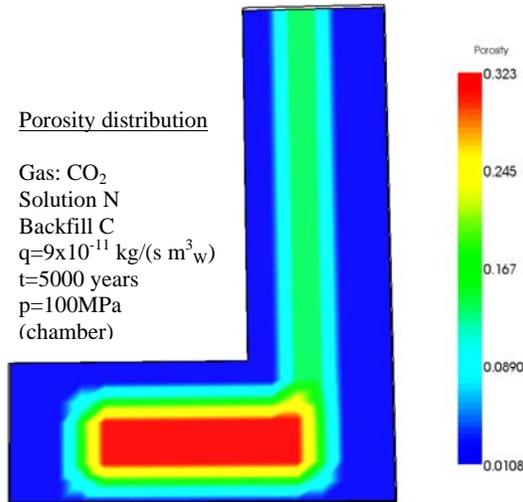


Figure 3. The porosity distribution after 5000 years, Case 1

Case 2: Solution Q, Backfill C

In a second case the modelling was carried out using the solution Q with backfill C. Due to the limitation of the Debye-Hückel rules for the calculation of the activity coefficients of aqueous species, a representative case was performed using 2 M MgCl₂ brine as solution. The material compositions were identical with the previous case.

Figure 4 shows the pH values at 5000 years simulation time. The pH value is decreased down to 4.47 in the emplacement chamber. This result is not desirable because of the increasing solubility of the radioactive elements. By this date, no free gas is present in the system and the porosity remains approximately unchanged in the emplacement chamber. This indicates that considerable changes in solid volumes did not occur.

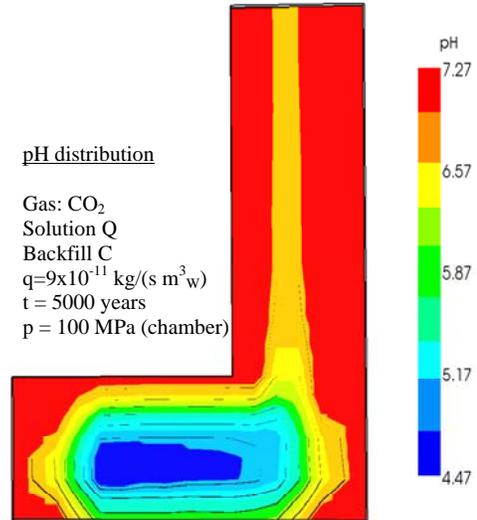


Figure 4. The pH distribution after 5000 years, Case 2

Case 3: Solution Q, Backfill B

The composition of backfill B was introduced to investigate the effect of the so called Mg-Depot on the geochemical environment of the system and its stability. After 5000 years no free gas is present in the system. Figure 5 shows the CO₂ concentration in the solution as mass ratio at the blocks 90 and 300 versus time. As expected, (see e.g. block 90 situated in the emplacement chamber) the dissolved gas concentration increased with cumulating gas generation and approached a value of 0.08 after 5000 years. It is obvious that this increase would end with outgassing of CO₂ when saturation is reached depending on pressure, temperature and composition. The solution with dissolved gas reaches the block 300 situated 40 m above the emplacement room after app. 2500 years in the modelling. After this time the concentration of the dissolved CO₂ increases steadily.

A very important aspect of this case is the expected pH value and its stability at the end of the modelled time frame. The pH value decreases from app. 7.8 to app. 6.8 in the beginning and remains approximately unchanged during the remaining time frame. The precipitation of carbonates such as calcite, brucite, magnesite is significant. Figure 6 shows the changes in pH value as well as the changes in volume fractions of some relevant minerals versus time. Quarz precipitates also in a small amount. In Figure 6 the changes in pH of the simulation case performed using backfill C without brucite is also given for comparison. The precipitation of minerals is linked with positive volume changes.

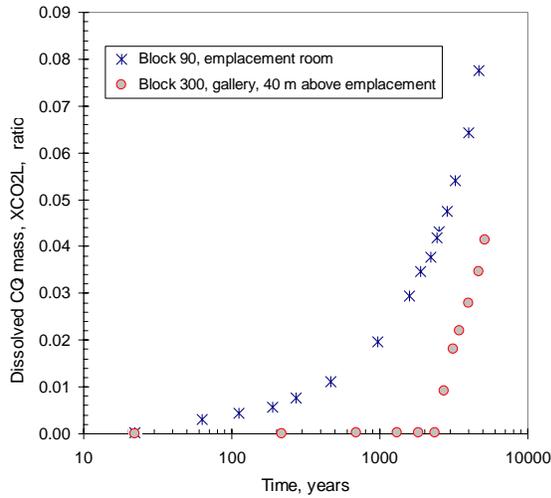


Figure 5. The calculated CO₂ mass ratio in solution, Case 3

When the material balance is checked, no considerable changes in the total solid volume are observed. The pore volume in the emplacement chamber remains approximately unchanged. This is due to the dissolution process taking place at the same time. The precipitation occurring at the gallery on the other hand, has a significant effect on the porosity and thus on the permeability. The permeability at the gallery is lowered to the values less than $1 \times 10^{-13} \text{ m}^2$ which is an important contribution to the prediction of hydraulic properties.

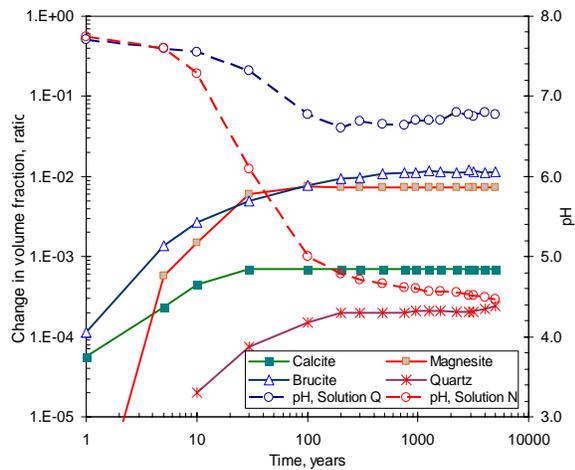


Figure 6. The volume change of some minerals and pH values, Case 3

The comparison of the dissolved CO₂ amounts of the two last simulation cases, in other words cases 2 and 3 (with and without brucite) shows smaller dissolved CO₂ values for the brucite cases. The gas generation rates are in both cases identical. The difference is mainly at the initial time period up to the 1000 years. No free gas is present in the system.

The difference is likely to be explained by the stoichiometric precipitation of additional amounts of CO₂ due to brucite. The initial Mg amount although is not sufficient for further stabilization of the geochemical environment. However; the advantages of the backfill system B can be concluded.

The effects of some parameters are investigated in more detail in order to prove the conservative approach. Three main parameters, the gas generation rate, the dissolution mechanisms and the gas type are found to be critical for their effects on reactive transport modelling.

Effects of the selected parameters

Gas generation rate

The gas generation rate was applied according to previous studies with realistic rather than conservative values. However, as concluded in previous chapters this is a critical parameter concerning thermodynamic behavior of the phases present. The dissolved CO₂ after 5000 years is approximately at the solubility limit and gas can outgas. If gas is present as free phase the chemical and hydraulic parameters change considerably. In order to investigate the effect of the likely presence of free gas phase in the system, the gas generation rate is augmented four fold and a total rate of $3,6 \times 10^{10} \text{ kg}/(\text{s m}^3_{\text{waste}})$ was inserted in the model.

The system passes to the two-phase regime after approximately 500 years. The dissolved amount of gas increases rapidly in the emplacement chamber. Figure 7 shows the gas saturation of the model after 555 years. Because of the time required for the diffusion in the solution, gas saturation is built up in the near field of the waste. The dispersion is limited. The pressure in the emplacement chamber increases. The outgassing of the gas will affect the solubility of the minerals thus changes in precipitation behavior should be expected.

Dissolution rate

Three mechanisms contribute to the process of dissolution of the gas in the solution when gas is generated in an emplacement chamber.

Firstly molecular diffusion of the CO₂ within the aqueous phase allows further dissolution.

Second, reactions between the dissolved gas and the host mineralogy, dissolving or precipitating carbonate minerals may change the dissolution capacity of the aqueous phase.

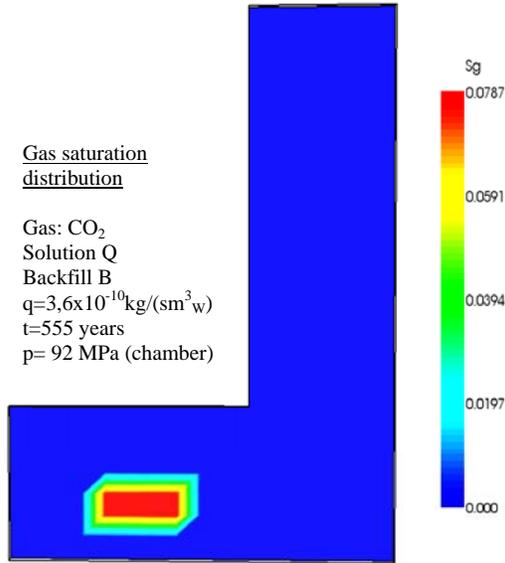


Figure 7. Effect of the free gas evaluation

Third, there is convective mixing that occurs because the density of the brine saturated with CO₂ is approx. 1% greater than unsaturated brine. CO₂ becomes saturated with dissolved gas, a density inversion is created. When the layer of saturated brine becomes thick enough instability occurs and plumes of brine saturated with CO₂ migrate downwards, slowly diluting as they go.

To investigate the effect of the molecular diffusion process on the dissolution rate of CO₂ a run neglecting the diffusion was performed. Note that the diffusion coefficient of CO₂ in aqueous phase was introduced in the previous runs as $3 \times 10^{-9} \text{ m}^2/\text{s}$.

The effect of neglecting the molecular diffusion between gas-aqueous phase is determined firstly as a delay in the diffusion of the CO₂ concentration in the liquid phase. The dissolved CO₂ amount increases first in the vicinity of the source term blocks. The local increase of the dissolved gas results in the saturation of the solution to CO₂ and CO₂ passes to free phase earlier. With the assumed modelling conditions the formation of two phases in the emplacement chamber is calculated to take approximately 2100 years.

Effect of the gas type

The microbial degradation of the organic components of the waste to inorganic carbon species results not only in the generation of the CO₂ but also methane, CH₄. As shown in Figure 8, the solubility of CH₄ in aqueous solutions is considerably smaller than the solubility of CO₂ in brine (Duan et al., 1992, 2003). Therefore it is expected that if CH₄ makes a part of the organic-inorganic degradation, it should move rather as free gas. To investigate this feature in a

conservative way, a run with CH₄ as gas source term is performed. The source term was kept unchanged.

The CH₄ is in free phase after approximately 300 years after the beginning of the gas generation. Figure 8 shows three successive sequences (475, 850 and 1530 years) of the formation and advance of the gas saturation in the model. First, the gas accumulates in the higher parts of the emplacement chamber (Figure 9a). Further increase of the pressure and gas saturation drives the gas towards the gallery as well as the wall of the emplacement chamber (Figure 9b). Because of the higher conductivity of the gallery, free gas passes to the gallery preferentially. In the gallery, gas moves upward rapidly due to the additional effect of the gravitation (Figure 9c). Gas reaches to block 300 approximately after 1000 years from the occurrence of the free gas in the emplacement chamber. The remaining gas saturation in the emplacement chamber is approximately equal to 0.05. The transport of the gas phase to the upper parts of the repository and thus probably to the atmosphere will take place as long as the gas generation continues. This is an important result if the impacts of the two phases flow on the transport of the contaminants are considered.

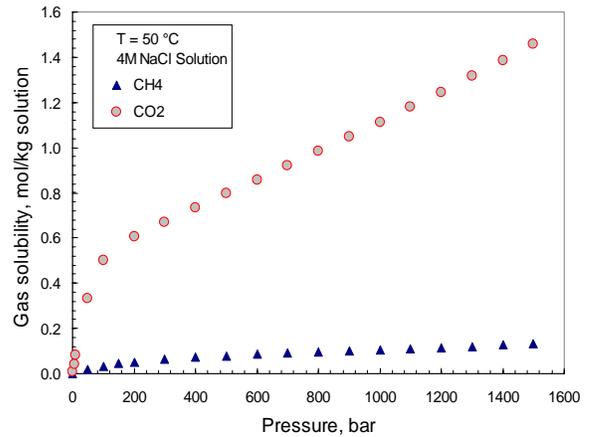


Figure 8. The comparison of the solubility of the CO₂ and CH₄ in brine (Duan et al, 1992, 2003)

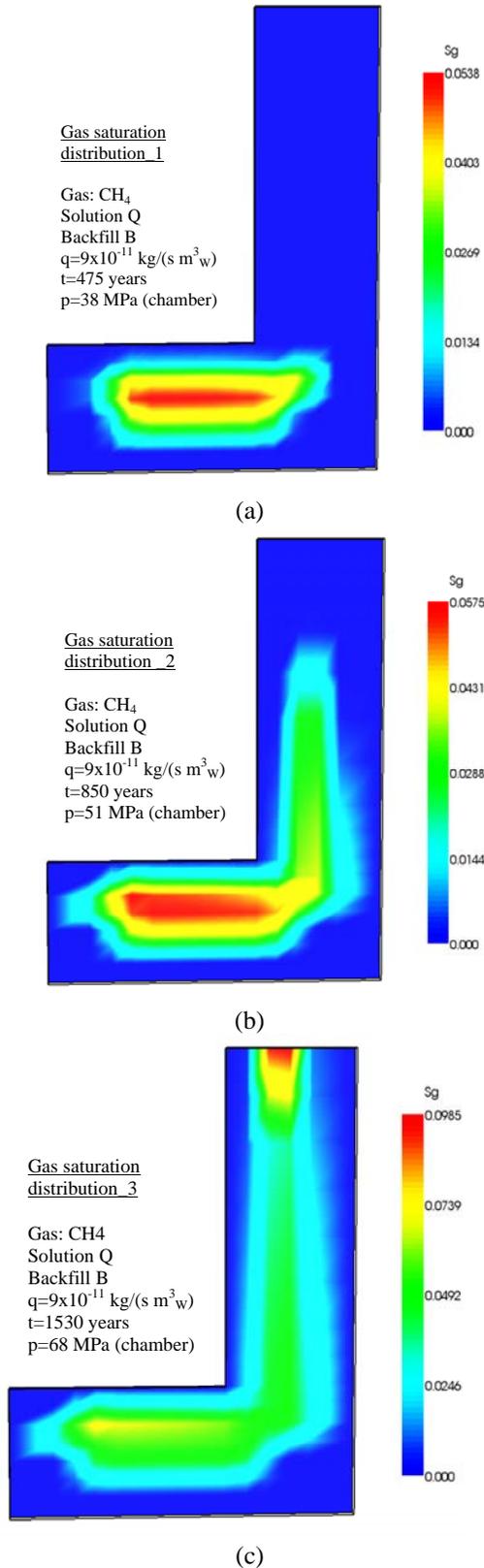


Figure 9. The advance of the free gas front in the emplacement chamber and in the gallery, three time steps.

CONCLUSIONS AND OUTLOOK

A preliminary modeling study of reactive transport for a salt mine has been performed. The backfill of an emplacement chamber with conventional and unconventional materials was considered. The gas generation rates were determined based on realistic scenarios. The principal aim was the evaluation and estimation of the solubility of the inorganic carbon as CO₂ and CH₄ for predicting the transport of radioactive elements in the system.

The backfill concept of the salt mine used as a repository can consider some special precautions; This may be a backfill material based on Mg(OH)₂ and a fluid as a MgCl₂ based brine. This means that the database and some numerical considerations of TOUGHREACT have to be properly modified. The calculation of the activity coefficients of the aqueous phase, the solubility data and the kinetic parameters for the mineral phases needs be reconsidered in some details. This may improve the modeling results. Nevertheless TOUGHREACT showed in a first attempt the capacity to model this unique backfill concept for a safety analysis considering two-phase and reactive transport.

The detailed investigation of the effect of the geochemical and hydraulic behavior of the gas generation on the solubility of the radioactive elements such as actinides was not the aim of the present study. However the capacity of TOUGHREACT should give the possibility to extend the project to include this part.

TOUGHREACT is therefore a useful tool for the assessment of the reactive flow and its impacts on the safety analysis for underground waste repositories.

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