

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

Hakan Alkan, Müller Wolfgang, Guido Bracke

ISTec, Institute for Safety Technology
Schwertnergasse 1
50667 Köln, Germany
Hakan.Alkan@grs.de

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. The ability of TOUGHREACT for more detailed applications of reactive transport under repository conditions is investigated.

A 2-dimensional grid model is created with refinements in the regions of interests (waste chamber and drift). 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 (so called protection fluid). The initial conditions are determined by the local hydrostatic and geothermal gradients for the simulated area. The gas generation rates are derived from realistic scenarios reported earlier. The compositions of mineral phases and of the aqueous phase (MgCl₂ rich brine) require a modification 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 drifts over a long period. The natural and engineered barriers are supposed to 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 may affect the safe enclosure and

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 rooms are located at a depth of approx. 750 m below the surface. Experimental and modelling studies were conducted on the mechanical and geochemical stability resp. hydraulics 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 will 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 room 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 room 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 room at approximately 750 m deep is modelled with dimensions of 25 x 8 m. A total volume of 200 m³ 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 m³ 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).

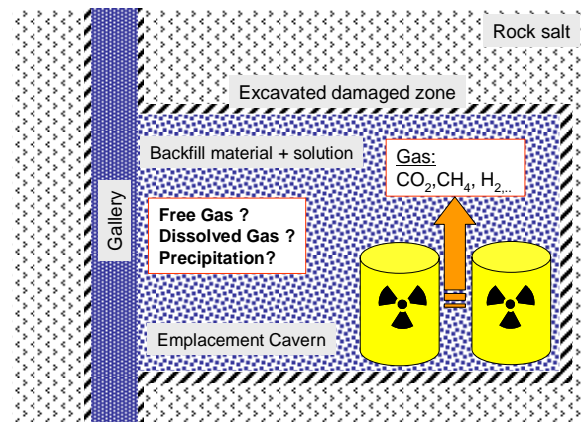


Figure 1. Schematic of the gas generation process in an emplacement room

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 rooms 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 room 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.

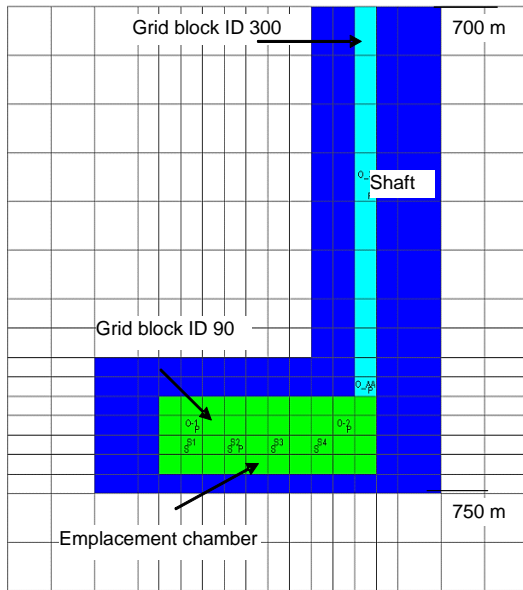


Figure 2. Schematic of the model

Table 1. Mineral compositions used in the model g/g

| 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 (Trotignon 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. (Xu et al., 2004). 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 compositions of the brines used in modelling, mg/l

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

The permeability depends on porosity and was modelled using the cubic law provided in TOUGHREACT. The convergence of salt rock is not modelled although it is very important for a repository in rock salt. Obviously the squeezing effect of the rock convergence adds pressure to the system and should therefore modelled 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 time period of 5000 years. A first modelling was made for Solution N with standard backfill material, backfill C. No gas saturation is calculated for the whole system. After 5000 years the pH in the emplacement room fell to 5.2 and the pressure increased approximately to 100 MPa. The CO₂ mass ratio in solution in the emplacement chamber was between 0.060 and 0.071. The gas in solution in the gallery (Block 300 at the upper end of the model) is even lower at 0.041. Because of applying a undersaturated brine a high rate of dissolution is apparent in the emplacement chamber. The volume of halite was 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 reached 0.323 at the end

of 1500 year and stayed at this value apparently because of a quasi-equilibrium state. The minerals calcite and magnesite were precipitating mainly. A small amount of portlandite and quartz was precipitating. The dissolution (oxidation) of iron was apparent with a reduction of approximately 0.05% of the free volume. The porosity of the vertical gallery on the other hand was reduced 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.

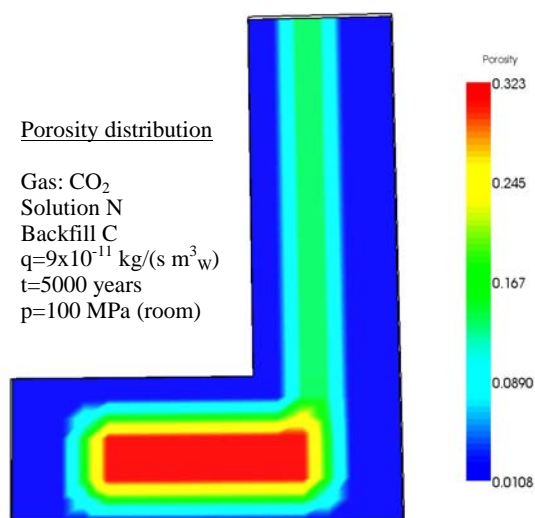


Figure 3. The porosity distribution after 5000 years, Case 1

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 modeling time. The pH value fell to 4.47 in the emplacement chamber. This result is not desirable because of the increasing solubility of the radioactive elements. After 5000 years the CO₂ concentrations in emplacement chamber in the aqueous phase is 0.077. By this date, no free gas is present in the system. The porosity remains approximately unchanged in the emplacement chamber indicating that considerable changes in solids did not occur.

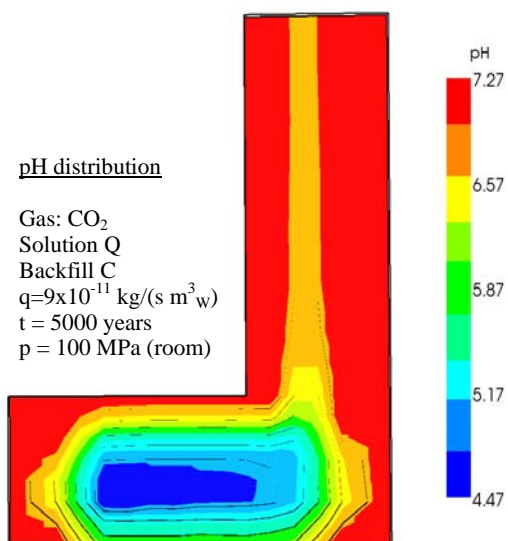


Figure 4. The pH distribution after 5000 years, Case 2

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 was 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 reached 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 was increasing 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 decreased from app. 7.8 to app. 6.8 in the beginning and remained approximately unchanged during the remaining time frame. The precipitation of carbonates such as calcite, brucite, magnesite was significant. Figure 6 shows the changes in pH value as well as the changes in volume fractions of some relevant minerals versus time. Quartz precipitated 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.

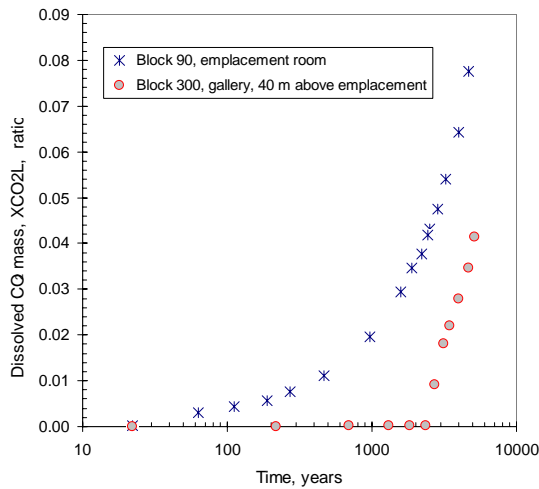


Figure 5. The calculated CO₂ mass ratio in solution, Case 3

When the material balance is checked, no considerable changes in the total solid volume were observed. The pore volume in the emplacement chamber remained 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, had a significant effect on the porosity and thus on the permeability. The permeability at the gallery was lowered to values less than $1 \times 10^{-13} \text{ m}^2$ which is an important contribution for modelling of hydraulic properties.

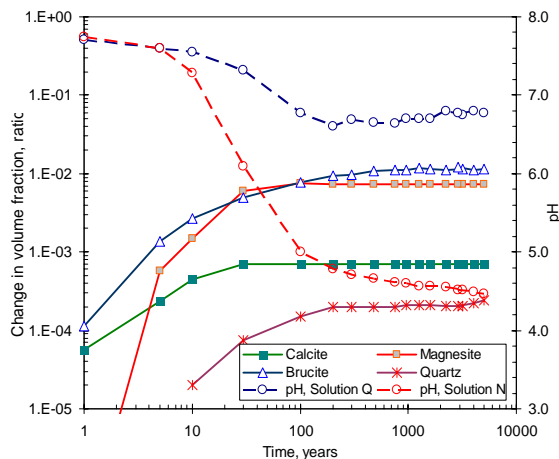


Figure 6. The volume change of some minerals and pH values, Case 3

The comparison of the amounts of dissolved CO₂ of the simulation cases 2 and 3 (with and without brucite) shows smaller amounts of dissolved CO₂ when brucite is present. The gas generation rates

were 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 was 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.

Parameter studies

Effect of the 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 was approximately at the solubility limit. Gas outgases if gas is present as free phase and the chemical and hydraulic parameters change. In order to consider 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 passed to the two-phase regime after approximately 500 years. The dissolved amount of gas increased rapidly in the emplacement chamber. Figure 7 shows the relative gas saturation of the model after 555 years. Because of the time required for the diffusion in the solution, gas saturation was built up in the near field of the waste. The dispersion was limited. The pressure in the emplacement room increased. The outgassing of the gas will affect the solubility of the minerals thus changes in precipitation behavior should be expected.

Effect of the 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.

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.

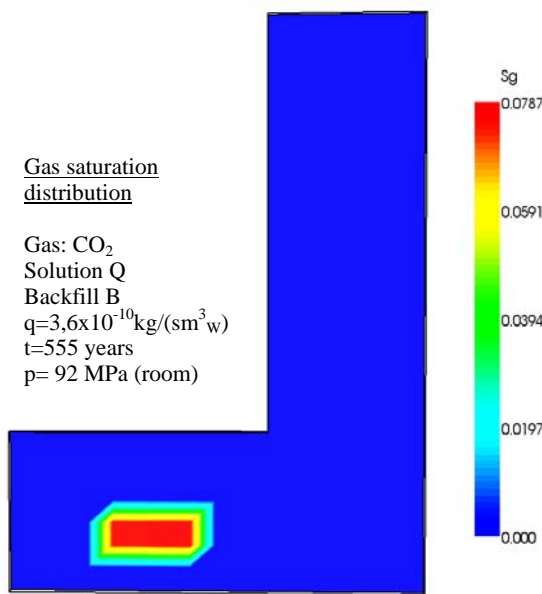


Figure 7. Effect of the free gas evaluation

A modelling run neglecting molecular diffusion was performed, to investigate the effect of molecular diffusion process on the dissolution rate of CO₂ by comparison. 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 saturation of the solution with CO₂ and CO₂ outgases earlier to free gas phase. With the assumed modelling conditions the formation of two phases in the emplacement room 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 is a part of the microbial 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 gas phase after approximately 300 years after beginning of gas generation. Figure 9 shows three successive sequences of points in time (475, 850, 1530 a) with their degree of gas saturation. First, the gas accumulated in the higher parts of the emplacement chamber (Figure 9a). Further increase of the pressure and gas saturation moved 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 passed to the gallery, preferentially. In the gallery the gas moved upward rapidly due to gravitation and hydraulics (Figure 9c) and reached to block 300 approximately after 1000 years from the first occurrence of free gas in the emplacement chamber. The remaining gas saturation in the emplacement room was approximately 0.05. The transport of the gas phase to the upper parts of the repository and thus to the atmosphere will take place as long as the gas generation continues. This is an important result on the transport of gaseous contaminants since the impacts of the two phases flow have to be considered.

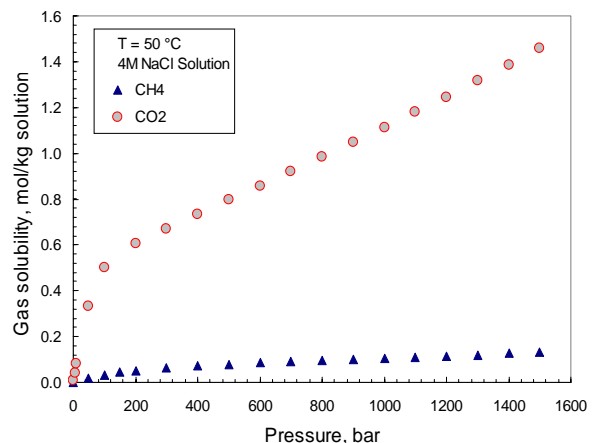


Figure 8. The comparison of the solubility of the CO₂ and CH₄ in brine (Duan et al, 1992, 2003)

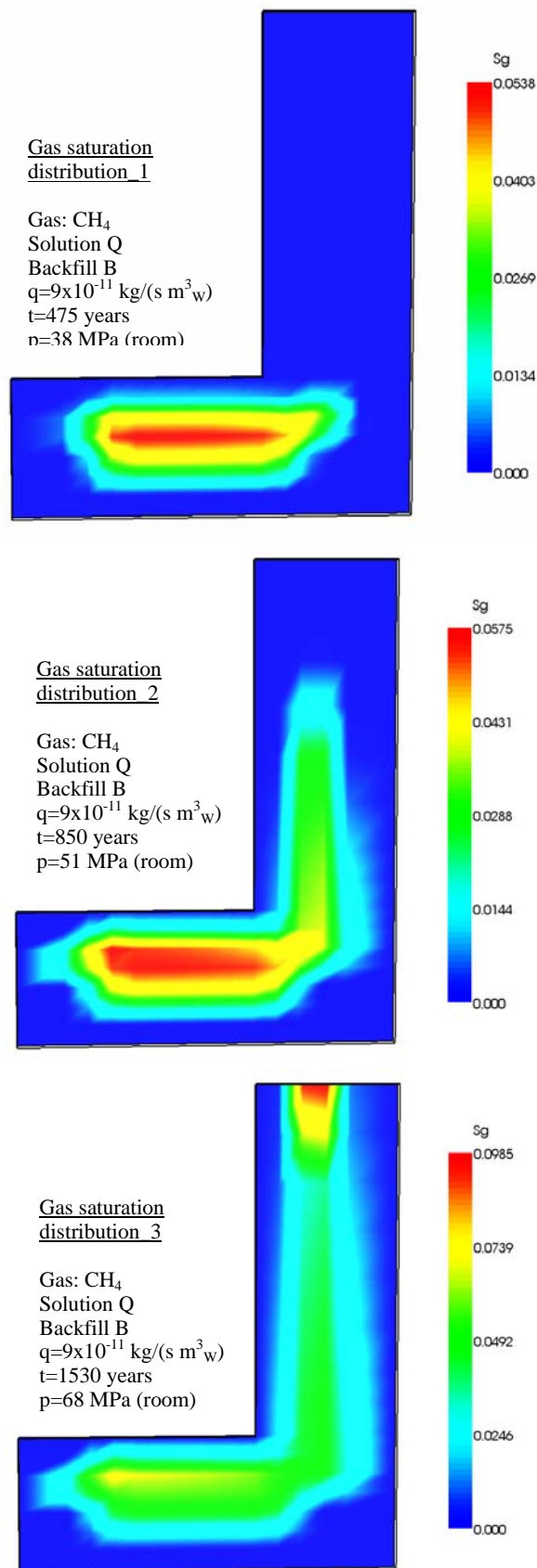


Figure 9. advance of the free gas front in the emplacement room and in the gallery, three time steps.

CONCLUSIONS AND OUTLOOK

A preliminary modeling study of reactive transport for a salt mine has been performed. The backfill with the standard and Mg(OH)₂-based materials of an emplacement chamber was considered. The gas generation rates were applied 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 using two-phase flow 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 an useful tool for the assessment of the reactive flow and its impacts on the safety analysis for underground waste repositories.

REFERENCES

Alkan H., Pusch G., Definition of the dilatancy boundary based on hydro-mechanical experiments and acoustic detection, SMRI Fall 2002 Meeting, Bad Ischl, Oct. 2002.

Bracke G., Müller W., Kugel K., Derivation of Gas Generation Rates for the Morsleben Radioactive Waste Repository (ERAM), International Conference on Radioactive Waste Disposal, April 26-28, Proceedings, 322-328, 2004.

Duan Z., Moller N., Greenberg J., Weare J H., The Prediction of methane solubility in natural waters to high ionic strength from 0 to 250°C and from 0 to 1600 bar, *Geochimica and Cosmochimica Acta*, Vol. 56. Pp. 1451- 1460, 1992.

Duan Z., Sunc R., An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar, *Chemical Geology* 193, 257– 271, 2003.

Metz V., Schüßler W., Kienzler B., Fanghängel Th., Geochemically derived non-gaseous radionuclide source term for Asse salt mine-assessment for the use of a Mg(OH)₂-based backfill material, *Radiochim. Acta* 92, 819-825, 2004.

Pusch G, Alkan H, Cinar Y., Mechanical and hydraulic characteristics of disturbed zones of the caverns excavated in rock salt Asse. Technical Report 2002; BMBF Project 02-CO598, Germany.

Trotignon T., Didot A., Bildstein O., Lagneau V., Margerit Y., Design of a 2-D cementation experiment in porous medium using numerical simulation, *Oil&Gas Science and Technology*, rev. IFP, Vol. 60, No.2, 307-318, 2005.

Xu, T., Sonnenthal, E., Spycher N., Pruess K., *Toughreact User's Guide*, Berkeley National Laboratory, Berkeley, Calif., 2004.