

# Th CO2 P07

# Simulated Fluid-Rock Interactions During Storage Of Temporally Varying Impure CO2 Streams

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# Summary

Impurities in CO2 streams influence the chemical reactivity in and mineral alterations of CO2 storage formations. Fluid-rock interactions have been investigated by means of reactive transport simulations using TOUGHREACT V3.0-OMG. A novel method has been established through which co-injection of SO2, NO2, O2 and H2 with temporally varying concentrations can be implemented in reactive transport model scenarios. The paper presents (i) model testing and validation against simulation results obtained by Xu et al. (2007), and (ii) results acquired from 1D-radial multiphase reactive transport simulations investigating two generic Bunter Sandstone reservoir formations. Results gained applying the novel hybrid approach show that modelling-based inaccuracies have largely been eliminated and inconsistencies are minimized. For the investigated generic Bunter Sandstone reservoir formations, two major geochemical processes are apparent. While the acidifying impurities SO2 and NO2 trigger carbonate dissolution coupled to anhydrite precipitation, presence of O2 leads to dissolution of iron-rich chlorite and subsequent goethite precipitation. Absolute changes of porosity for the two generic Bunter Sandstone formations are below 1 %. The total quantitative impact of SO2, NO2, O2 and H2 on mineral reactions is rather limited and their impacts on the petrophysical properties of the two investigated generic Bunter Sandstone formations are geotechnically negligible.



# Introduction

In recent years, impurities in  $CO_2$  streams and their potential chemico-physical effects on transport and geological  $CO_2$  storage gained more and more attention in the CCS research community. Impurities in  $CO_2$  streams, like  $H_2S$ ,  $SO_2$  and  $NO_2$ , commonly occur in flue or process gases captured at energy or industrial facilities. These impurities may influence both chemical reactivity and physical properties of  $CO_2$  streams. These influences are the focus of the project CLUSTER "Impacts of impurities in  $CO_2$  streams captured from different emitters in a regional cluster on transport, injection and storage".

The project CLUSTER aims at establishing recommendations for defining "minimum composition thresholds" that  $CO_2$  streams must meet according to EU Directive 2009/31/EC when accessing a shared transport and storage infrastructure. For this, potential impacts of different, temporally varying  $CO_2$ -stream compositions are examined along the whole CCS chain. These variations originate from a defined base scenario comprising a regional cluster of eleven  $CO_2$  emitters (power stations and industrial plants) whose captured  $CO_2$  streams contain different impurities and vary in mass flow rate (Kahlke *et al.* 2017). In this base scenario, captured  $CO_2$  streams of individual emitters are collected in a regional pipeline network and jointly transported to a generic geological  $CO_2$  storage site through a 400 km long trunk line. This contribution focuses on investigations of fluid-rock interactions in the two generic reservoir formations based on reactive transport simulations using TOUGHREACT V3.0. These reservoir formations comprise generic saline aquifers in Bunter Sandstone that differ in petrophysical rock properties and mineralogical composition.

### Methodological approach

In order to analyze the impact of temporally varying  $CO_2$ -stream compositions on petrophysical rock properties, a set of 1D radial multiphase reactive transport simulations have been conducted. For these simulations, TOUGHREACT V3.0-OMP (Xu *et al.* 2014) with ECO2N EOS module was used as a basis. Presence of impurities in  $CO_2$  streams enhances chemical complexity in the storage system mainly due to variations in impurity concentrations both on spatial and temporal scale impacting fluid-rock interactions. This challenges accurate simulations of a  $CO_2$  storage system compared to injection scenarios with pure  $CO_2$  or  $CO_2$  streams of constant composition. To handle this chemical complexity, a method was developed in which TOUGHREACT-MATLAB-TOUGHREACT simulation runs are sequentially computed (Wolf 2017). With this method it is possible to implement co-injection of SO<sub>2</sub>, NO<sub>2</sub>, O<sub>2</sub> as well as H<sub>2</sub> with temporally varying concentrations into reactive transport model scenarios.

Further, a novel approach has been established for TOUGHREACT simulations. In this hybrid approach advantages of the frequently applied approaches *additional brine injection* (ABI) and *trace gas transport* (TGT) are combined (*mobile additional brine injection* (mABI); Wolf *et al.* 2017). In brief, based on the gas saturation profile for a pure CO<sub>2</sub> injection scenario, a pre-calculated amount of dissolved impurity species is injected into the various grid cells of the radial 1D reservoir model. This way, CO<sub>2</sub>-phase transport and consecutive dissolution of impurity species is mimicked by "moving the point" of impurity injection through the individual grid cells of the reservoir model.

# Model testing and validation

The methodological approach was tested and validated by comparing the results of Xu *et al.* (2007) with those we obtained using our approach for their system. Xu *et al.* implemented SO<sub>2</sub> as an aqueous phase impurity, i.e. by injection of additional brine, in their simulations. For benchmarking, we applied three model approaches: 1. Injection of SO<sub>2</sub>(aq) dissolved in additional brine (ABI); 2. Injection of CO<sub>2</sub> containing 2.5 mol.% SO<sub>2</sub>(g) (TGT); 3. Injection of SO<sub>2</sub> using our hybrid approach (mABI).



Results of the two ABI simulations, i.e. the original one from Xu *et al.* (2007) and our reproduction (termed "SO<sub>2</sub>(aq)" in Fig. 1), show very similar spatial distribution of dissolved species, and minor differences regarding mineral reactions within the reservoir leading to somewhat higher porosities in our simulations. The latter might be due to differences in database settings. In close proximity to the injection well both simulations show an increased porosity due to the injection of additional brine. This is because a dry-out zone does not form when additional brine is injected. Hence, the reservoir brine is continuously undersaturated regarding some minerals and fluid-rock interactions may occur over longer time periods compared to the other simulations.



**Figure 1** Results of reactive transport simulations during co-injection of  $SO_2$  and  $CO_2$  into an arkose formation. Displayed is the obtained porosity versus distance from the point of injection for the time intervals 10 and 100 years, respectively. A: Results adapted from Xu et al. (2007). B: Results obtained by using our new approach for the different scenarios – ABI ("SO<sub>2</sub>(aq)"), TGT ("SO<sub>2</sub>(g)"), mABI (Hybrid).

In the TGT simulation (termed "SO<sub>2</sub>(g)" in Fig. 1), a dry-out zone forms around the injection well. The dry-out zone reaches a distance of approximately 15 m after 10 years and approximately 50 m after 100 years of injection, respectively. Dissolution of SO<sub>2</sub>(g) into the reservoir brine triggers mineral reactions that lead to exceeding TOUGHREACT's default limit of the ionic strength. Hence, further computation of mineral reactions in the individual cells is stopped (Wolf *et al.* 2016). This causes significant differences in the TGT simulation results compared to those of the ABI approach. Differences comprise underestimation of SO<sub>2</sub> dissolution into reservoir brine as well as subsequent mineral reactions, and implausible simulation of changes in porosity.

In the mABI simulation (termed "Hybrid" in Fig. 1), a dry-out zone forms around the injection well with similar extents compared to the TGT approach. After 100 years of injection, the pressure in the first reservoir cell is approximately 10 % lower compared to the ABI approach, although the pore volume is even lower. Simulated mineral reactions are similar to those observed in the ABI and TGT simulations. Main difference are higher pH values in the mABI simulation. These higher pH values may affect the kinetics of mineral reactions.

Results of the mABI simulation reveal that advantages of the ABI and TGT approaches were successfully combined and modelling-based inaccuracies were largely eliminated in this hybrid approach. The biases of injecting additional brine on the dry-out zone formation, on the reservoir pressure increase as well as on an increased mineral reactivity were minimized. Also, the TOUGHREACT ionic strength threshold limit was not exceeded in the mABI simulation. The newly developed methodological approach was subsequently applied for modelling the various scenarios in the CLUSTER project. Besides parameter variations also temporally varying impurity concentrations and different impurity combinations were simulated.



#### **Results and discussion**

Modelling results show that reactive impurities exhibit different spatial extents of migration into the reservoir. This is mainly due to the different abundances and solubilities of the individual impurity species. The dominant time periods of varying impurity concentrations in the injected  $CO_2$  stream are reflected in the spatial mineral alteration profiles of the reservoir rocks after a given injection time.

For the investigated generic Bunter Sandstone reservoir formations, two major geochemical processes were apparent (Figure 2A). Firstly, presence of the acidifying impurities  $SO_2$  and  $NO_2$  triggers carbonate dissolution that buffers the pH of the reservoir brine. Accordingly,  $Ca^{2+}$  is released into solution, which – in combination with aqueous  $SO_4^{2-}$  (from  $SO_2$  oxidation) – directly leads to anhydrite (CaSO<sub>4</sub>) precipitation. Secondly, the presence of  $O_2$  leads to dissolution of iron-rich chlorite and subsequent goethite precipitation. The geochemical impact of H<sub>2</sub> on the reservoir was negligible.

The mineralogical reactions described above have a direct impact on the pore space of the considered generic reservoir formations. Due to the coupled dissolution-precipitation reactions also the porosity is affected (Figure 2B). These changes in porosity differ in the individual scenarios and strongly depend on the presence and concentration of the individual impurity. For the two Bunter Sandstone formations absolute changes of the porosity are, on average, below 1%.

Further, simulation results show that induced mineralogical changes also strongly depend on the primary mineral phases in the reservoir rocks (data not shown here).



**Figure 2** Results obtained from reactive transport simulations including  $SO_2$ ,  $NO_2$ ,  $O_2$  and  $H_2$  during  $CO_2$  injection into a generic Bunter Sandstone reservoir. Grey areas denote the extent of the dry-out zone. *A*: Simulated changes of mineral volume fractions for the coupled reactions anhydrite-calcite and chlorite-goethite, respectively, after one year of injection. Note the scale difference on the y-axis of the two diagrams. *B*: Simulated changes of total porosity including individual contributions of the coupled mineral reactions as shown in *A*.

# Conclusions

The total amount of injected impurities determines the total geochemically affected rock volume of the reservoir. Individual impurity species trigger different chemical reactions. Presence of  $SO_2$  and  $NO_2$  in  $CO_2$  streams trigger acid-induced reactions with calcium-rich mineral phases, namely dissolution of carbonates and precipitation of anhydrite. Presence of  $O_2$  controls redox-induced reactions, e.g. with iron-rich mineral phases. These reactions are characterized by the dissolution of chlorite and precipitation of goethite. Overall, the total quantitative impact of the investigated impurity species  $SO_2$ ,  $NO_2$ ,  $O_2$  and  $H_2$  on mineral reactions is rather limited and their impacts on the petrophysical properties of the two investigated generic Bunter Sandstone formations are geotechnically negligible.



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