Modeling the geochemical impact of an injection of CO2 and associated reactive impurities (SO2 and O2) into a saline reservoir

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MODELING THE GEOCHEMICAL IMPACT OF AN INJECTION OF CO_2 AND ASSOCIATED REACTIVE IMPURITIES (SO₂ ANDO₂) INTO A SALINE RESERVOIR

Laurent ANDRE[1], Mohamed AZAROUAL[1], Christian BERNSTONE[2], Andrea WITTEK[2]

[1]BRGM - Water, Environment and Ecotechnologies Direction, Avenue Claude Guillemin, BP 36009, F-45060 ORLEANSCedex 2 - France

[2] VATTENFALL, R&D Projects, Evenemangsgatan 13, 169 92STOCKHOLM – Sweden

e-mail: l.andre@brgm.fr; m.azaroual@brgm.fr; christian.bernstone@vattenfall.com; andrea.wittek@vattenfall.de

Abstract Carbon dioxide storage in deep geological structures is a strategic technology to mitigate climate change and to promote green development. However, despitecontinuous efforts to develop cost effective capture processes to clean the CO_2 stream before transportation and injection, traces of accessory gases cannot be entirely removed. Consequently, before any injection of these gas mixtures, the impact of impurities on the geochemical reactivity of the system must be evaluated. This paper describes numerical simulations donewith TOUGHREACT that focus on the chemical reactivity of deep reservoir rock impacted by an injection of CO_2 and associated reactive impurities (mainly SO_2 and O_2). A simplified two-dimensional radial geo-model ofthe near wellbore domain of a saline reservoir enabled us to predictits global geochemical behavior. Two $CO_2:SO_2$ratios were studied. The results show the high reactivity of the near-well zone when ancillary gases (SO_2 and O_2) are co-injected with CO_2, which leads to thedissolution of carbonates and the precipitation of sulfateminerals. Major reactions occur in the reservoir formation, whereas clays inthe caprock are only slightly affected by the injection of CO_2 and associated reactive impurities.

Keywords: gas storage, CO₂-SO₂-O₂ gas mixtures, saline reservoir, coupled modeling, geochemical reactivity

1 INTRODUCTION

Carbon dioxide capture and storage (CCS) is anemerging technology for reducinggreenhouse gas emissions and addressing climate change. CO_2 geological storage in deep reservoirs isa promising greenhouse gas sequestrationmethod. However, in order to ensureeffective containment, investigations need to be carried out on reservoir behavior when subjected to physical and chemical perturbations causedby CO_2. Numerical studies have shownthat massive and continuous injection of pure CO_2leads toa disequilibrium of the physical (temperature, gas saturation, pressure, capillary pressure, etc.) (Bielinski et al., 2008; Yamamoto et al., 2009; Hansen et al., 2011)and geochemical (dissolution of supercritical CO_2 in the brine, pH variations, dissolution/ precipitation reactions of the porous rock minerals) characteristics of the host reservoir (Kharaka et al., 2006; Audigane et al., 2007; Gaus et al., 2008; André et al., 2007, 2010; Okuyama et al., 2013).

If CO_2 injection can disrupt the physico-chemical equilibrium of the deep reservoir, the presence of impurities in the CO_2 gas mightalso impair the capture, transport, and injectionprocesses. Some associated reactive gases, i.e. chemical species other than CO_2 in the injected stream – namely SOx, NOx, H_2S, or O_2, might require adaptations of the processes used for theinjection and storageof a pure CO_2stream.

The presence of associated gases in the CO_2 stream in relatively high proportions can affect the compressibility of the injected gas and reduce the CO_2 storage capacity of the reservoir.This is due both to the space taken up by these gases and the unfavorable volume balance of induced geochemical reactions. The effect of impurities on storage capacity has been evaluated using different gas mixture scenarios (IEAGHG, 2011) and results show that, for the unlikely case of high-impurity streams (e.g. 15% non-condensable gases like N_2, Ar, O_2), the storage capacity can be reduced by 10 to 40%, depending on the storage depth (i.e. pressure conditions). An opposite effect is however observed for supercritical CO_2 mixed with a condensable gas such as

SO_2:2.9% SO_2 in the CO_2 stream can increase the storage capacity by 5% at 110 bars because of intrinsic SO_2properties (such as the critical temperature of SO_2, which is higher than that of CO_2). Furthermore, depending on the type of geological storage, the presence of ancillary gases mighthave other specific effects such as trapping performances. When $CO_2$is storedin deep saline formations, the presence of gas impurities affects both the gas solubility in the aqueous phase andthe rate and amount of CO_2 stored through mineral dissolution and precipitation. The presenceofSO_xandNO_x, which causes a dramatic pH decrease of brine, decreases CO_2 solubility.

The behavior of these accessory gases in the context of CO_2storagehas only recentlyinterested the scientific community.Previously, the most important studieswere carried outby the oilindustry and concerned the storage of sourgases in geological structures. Azaroual et al. (2005) analyzed the impact of the injection of a gaseous H_2S-CO_2 mixture (50:50) in a carbonate reservoir. This high proportion ofH_2S was selected to highlight the chemical reactionslikely to occur within the reservoir, along with their impact on reservoir properties and integrity. Gunter et al. (2000, 2004) and Bachu and Gunter (2004) used a coupled numerical and experimental approach to studythe injection of gas mixtures (CO_2-SO_2 and CO_2-H_2S) in Canada, but with H_2S and SO_2 proportions higher than those observed in CO_2storage.

When $CO_2$is stored in deep geological reservoirs, the gas compositionsare expected tovary depending on the treatment processesused and the industrial origin of the stream (Anheden et al., 2004). Over the last decade, R&D efforts have been made to reduce the energy penalty, and CO_2capture in power plants will result in CO_2streams with high CO_2contents. Today's technologies would give >95% CO_2 purity.However, despite continuous efforts to develop cost-effective capture processes to clean the CO_2 stream before transport and injection, traces of accessory gases are notentirely eliminated. For example, at a certain level of cleaning of theoxycombustion process, traces of argon and oxygen are assumed to remain in the injected gas, as well as oxidized forms of sulfur,SO_x,and nitrogen, NOx (IEAGHG, 2011).

Oxygen sulfide (SO_2) is one of the ancillary gases that is most often studied. Palandri and Kharaka (2005a) were among the first to use a numerical approach to study the impact of SO_2 on ferric iron-bearing sediments. They showed that the SO_2 content in the CO_2-dominated gas phase could involve different geochemical pathways. If there is enough SO_2 in the gas phase, dissolved iron is totally reduced as Fe^{2+}, which reacts with dissolved CO_2 to form siderite. However, if there is not enough SO_2, the iron is only partially reduced and less CO_2 is trapped by siderite precipitation. Knauss et al. (2005) also used a numerical approach to investigate the impact of SO_2 (and H_2S) on the mineralogical assemblage modification of a geologic reservoir based on observations of the Frio pilot site (USA). The presence of SO_2 with CO_2 in the injected stream generates significant impacts, in particular near the injection well. The low pH resulting from SO_2 and CO_2 dissolution leads to massive carbonate dissolution (non-stability of calcite) and, under oxidizing conditions, to the precipitation of the sulfate mineral anhydrite. Xu et al. (2007) developed a more advanced conceptual model for the injection of CO_2 with SO_2 (and H_2S) in a sandstone formation. These authors compared numerical modeling results for pure CO_2 and CO_2-SO_2 injections. They showed that the acidified zone is extensive when SO_2 is co-injected with CO_2. They also reported the potential precipitation of alunite and traces of anhydrite and pyrite, whereas CO_2 trapping is due to the precipitation of small quantities of ankerite, dawsonite, and siderite.

Other laboratory experiments have been carried out under temperature and pressure conditions similar to those of geological storage in order to gather more information on the impact of the co-injection of SO_2 and CO_2 on water and minerals. Palandri et al. (2005b) carried out laboratory experiments (at 150°C and 300 bars) to test their numerical approach (Palandri and Kharaka, 2005a). These confirmed that the presence of SO_2 in the gas phase can favor the precipitation of stable siderite and, depending on the proportion of SO_2, the potential precipitation of metastable pyrite and elemental sulfur (S°). Murphy et al. (2010) and Murphy et al. (2011) focused their experimental work on the reactivity of ferrihydrite and hematite nanoparticles in the presence of

supercritical CO_2 and sulfide-bearing solutions. They showed that both iron-bearing minerals react to form iron carbonate (siderite), iron sulfide (pyrite) and in specific conditions (at 100 °C with supercritical CO_2) elemental sulfur (S°). They alsoemphasized that the kinetics of the reaction are relatively rapid at temperatures ranging between 70 and 100°C. KummerowandSpangenberg (2011) studiedthe injection of pure CO_2 and a CO_2-SO_2 mixture (99:1 vol/vol)at laboratory scale on sandstone media from the Ketzin reservoir (Germany). They observedthat the injection of pure CO_2does not drastically alter rock properties and identifiedno mineral reactions. However, with the CO_2-SO_2mixture, rockproperties are greatlymodified due, in particular, to the dissolution of intergranularcementation. According to XRD observations, the decrease inrock permeability is not due to precipitation of secondary minerals but to the remobilization of endogen fine particles in the samples. Erzinger et al. (2010) also observedan increaseinthe chemical reactivity when a supercritical CO_2-SO_2mixture (99.5:0.5vol/vol) reacts withdifferentminerals (calcite, siderite, hematite, muscovite, biotite), with a particular increase in sulfate and cation (Fe, Si and Al) concentrations inaqueous solutions. Risse et al. (2011) also observed an increase inchemical reactivity in batch experiments at 120°C and 200 bars. An IEAGHG report (2011) estimated,usinga modeling approach,that 1.5% vol total concentration ofSO_xandNO_xin the injection steam can favor reactivity in limestone, where calcite dissolution increases by about 50%.Atthe same time, clogging can occur, in particular in the dry-out zone, thus limiting injectivity. According to these authors (IEAGHG, 2011), sulfate precipitation can play a role in porosity variations butthese impactsmightbe less significant than those generated by S^0 (Claus reaction). The impact of SO_2 on the chemistry of the brine was also studied by Crandell et al. (2010). Using thermodynamic data such as SO_2solubility, the authors developed a model to calculate the spatial distribution of sulfur in the reservoir depending on storage conditions (T, P, salinity, etc.)., Ellis et al. (2010) used the same approach to analyzethe impact of SO_2 on pH, disregarding the potential mineral reactions that can buffer the pH of aqueous

solutions. SO_2 may form sulfuric acid (H_2SO_4), which is stronger than carbonic acid. Wilke et al. (2012) went further by testing the reactivity of such acidic solutions onreservoir rocks.

Among theother impurities that might be injected with CO_2, traces of oxygen are expected in streams coming from the Oxyfuel capture technology. Previous studies have shown that the presence of high proportions ofO_2(such as the O_2 concentration in air) can generate oxidative reactions (Yu et al., 2010). However, underCO_2 storage conditions, the role of $O_2$is poorly understoodand laboratory experimental resultsare scarce (Heeschen et al., 2011, Langlais et al., 2012). Renard (2010) and Renard et al. (2011) studiedthe impactof SO_2 and O_2 with CO_2 on carbonate rocksunder reservoir conditions. The gas composition they studied was similar to thatof gas comingfrom an oxycombustion process prior toany conditioningprocedure: 82% CO_2, 4% SO_2, 4% O_2, 4% N_2 and 6% Ar(Note that conditioning will always be done, thus increasing the capture rate to >95%). These experiments showedthatthe chemical reactivity of the system increasedwhen SO_2 and O_2wereadded to the gas mixture (with respect to pure CO_2). With pure CO_2, minerals wereslightly altered, whereas massive dissolution of pyrite and calcite wereobserved in the presence of SO_2 and O_2 (Renard et al., 2011). Some precipitation of anhydrite and hematite was alsoobserved.

All of these studies show how important it is that we study the potential impact of these accessory gases on the reservoir. Numerical estimations are needed so that we canpredicthow the gas composition might impact the geochemical reactivity withinthe host reservoir, potentially modifying the porosity and permeability of the medium and influencing long-term well injectivity. This paper describesnumerical simulations using coupled hydrogeological, thermal, and geochemical codes such as TOUGHREACT version 1 (Xu et al., 2006). Thesetools aresuitablefor exploringdifferent evolution scenarios of gas injection in deep geological structures, and determining the behavior of the near-wellbore region of the targeted reservoir. These simulations will provide a methodological basis for future industrial-scale CO_2 storage projects nowbeing developed. The simulationresults (positive or negativeimpact on the caprock

integrity or reservoir injectivity) will condition subsequent simulations and show whether such simulations need to be repeated/improved in order to obtain standard practices (methodologies and tools).

The final objective of this studywas to identify the potential reactivity ofany targetedsystem.Our calculationswere not, therefore, done for a specific site. We modeled a generic (hypothetical) site inspired by existing sites – a sandstone aquifer anda clay caprock formation with properties similar to those of the Nordland Shale formation.Below, we describe the reservoir, caprock and fluid properties in each formation, give the assumptions usedfor modelcalculations, anddescribe two simulations done to study the impact of CO_2, SO_2 and O_2 mixtures on the main physico-chemical characteristics of a deep saline aquifer.The results are compared to those of previous studies that did not consider the presence of impurities in the CO_2injected gas.

2 RESERVOIR PROPERTIES

2.1 Reservoir characteristics

The saline aquifer defined in the modelis a sandstone reservoir approximately 200 m thick. Before injection, the effective pressure is 150 barsand the temperature is 50°C.

Theporosityof both the reservoir rockand the caprock is around15%. This caprockvalueistaken from papers describing the Nordland Shale formation overlyingthe Sleipner reservoir. It is averaged from the porosity values estimated by Johnson et al. (2003) and Gauss et al. (2005) (5 %) and those measuredbyHarrington et al. (2006) and Springer and Lindgren (2006) (about 40 %).The caprock layer has a mean permeability of 0.003 mD (Johnson et al., 2003), whereas the permeability of the saline reservoir is about 300 mD.

Due to the injection of a gas phase (non-wetting phase) intothe deep system, the relative permeability and the capillary pressure of the medium must be defined to accurately describe the relative flow of gas with respect to the aqueous solution. For the sandstone reservoir, we used literature data to define the representative curves and include them in the numerical code (e.g.

Bachu and Bennion (2007)). Because of the chosen characteristics of the modeled reservoir (k_{mean} # 300 mD; Φ # 15%; $P_{reservoir}$= 150 bars; T = 50 °C), the Cardium sandstone was used as the reference sandstone (Fig. 1).The characteristic curves for the relative permeability and capillary pressure of the caprock are assumed to be the same as those of the reservoir. The caprock's impermeability is represented by its low intrinsic permeability (0.003 mD).
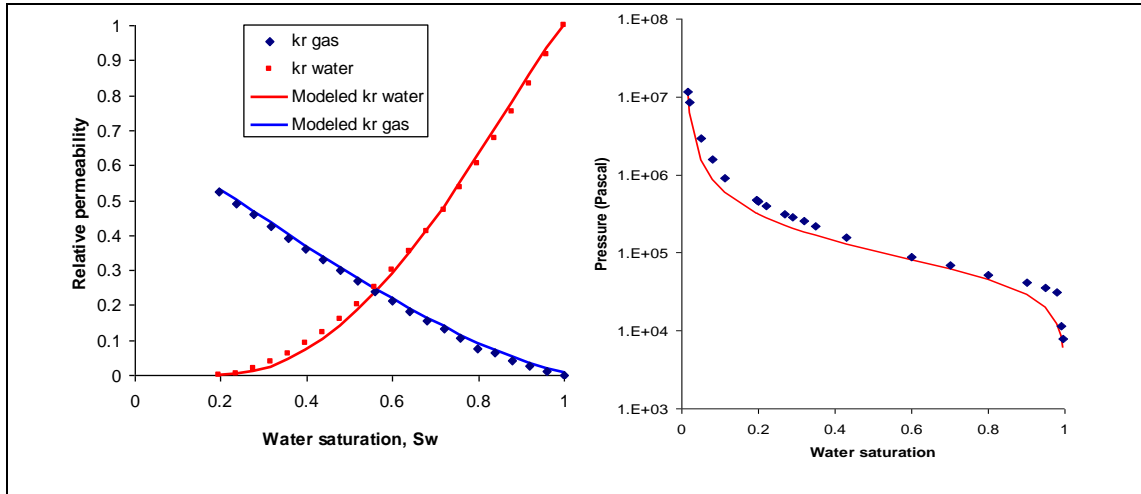

Figure1. Relative permeability (left) and capillary pressure (right) curves for Cardium sandstone (from Bennion and Bachu, 2005). Fitted curves are calculated using TOUGHREACT for both the reservoir and caprock.

Experimental capillary pressure and liquid relative permeability values were fitted using the Van Genuchten model (Van Genuchten, 1980). The parameters used in the simulations for relative permeability and capillary pressure lawsare summarized in Table 1.

Table 1: Van Genuchten parameters used for fitting the characteristic curves of relative permeability and capillary pressure for brine and gas phases

Relative permeability parameters for brine	
m = 1 – 1/n	0.466
Residual liquid saturation	0.197
Liquid saturation	1.000
Residual gas saturation	0.050
Capillary pressure parameters	

m = 1 − 1/n	0.497
Residual liquid saturation	0.197
P_0 (Pa)	60240
P_{max} (Pa)	10^6
Liquid saturation	1.000

2.2 Mineralogical assemblage

For the numerical simulations, the mineral assemblages ofthe caprock and the reservoir weredefinedusingliterature data. The caprock minerals were taken from Gaus et al. (2005) andthe reservoir minerals from Kjoller et al. (2011), who described the mineralogy of the sandstone Gassum reservoir.

The caprock is made up for the most part of illite and quartz (74wt%) while the reservoir rock contains mostly quartz and K-feldspar (91 wt%). In the reservoir and caprock formations, the end-membersalbite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_6$)aresubstituted for theplagioclases series (solid solution)as stated by Gauset al. (2005). The carbonate end member is represented by calcite in the reservoir and by siderite in the caprock.

Chlorite ($Mg_{2.5}Fe_{2.5}Al_2Si_3O_{10}(OH)_8$),siderite and pyrite are iron-bearing minerals in the caprock formation, whereas the reservoir formation does not contain any Fe minerals. Rutile and anatase are common detrital minerals. Anatase, which comes from Ti-bearing minerals, waschosen for this study (Table 2).

Table 2. Mineralogical composition of the caprock and the reservoir rocks

	Minerals	Wt%
	Illite	60
	Quartz	14
	Albite	6
Caprock	Anorthite	3
	Chlorite	5
	K-Feldspar	4

	Pyrite	4
	Siderite	3
	Anatase	1
Reservoir	Quartz	81
	K-Feldspar	10
	Albite	5
	Calcite	3.6
	Anhydrite	0.4

The selection of the secondary minerals that are able to precipitate in the reservoir and caprock formationsis a key parameter since this can have an impact on the overall reactive pathways. As $CO_2$is the major component of the gas phase, variouscarbonates werechosen for the reservoir (dolomite, dawsonite, siderite) and for the caprock (calcite, dolomite, dawsonite). Because of the high redox potential (Eh) of the injected solution due to the presence of O_2 in the gas phase, only oxidized iron-bearing minerals were selected (hematite). The high Eh alsohas an impact on the SO_2, which is fully oxidized as sulfate. Consequently,although we did monitor pyrite behavior during these simulations, we focused primarily on a sulfate mineral. Because of the temperature of the reservoir (50°C), anhydrite was selected. Aluminosilicates (illite, kaolinite and chlorite)were also included in the calculations as potential secondary minerals (newly precipitating) in the reservoir formation.

2.3 Chemical composition of the initial water

Details concerning thephysico-chemical characteristics of the formation water are givenin Table 3. The water is representative of the saline solutions found in the Gassum reservoir (Kjoller et al., 2011).

The water composition for *in situ* conditions (150 bars, 50°C) wasdeterminedusing anappropriatehypothesis and thermodynamic calculations for highly saline aqueous systems using the SCALE2000 code (Azaroual et al., 2004). The pH and bicarbonate concentration of thebrine wererecalculated for the reservoir and caprockpressure and temperature conditions, assuming that the brine is in thermodynamic equilibrium with respect to primary minerals. This

gave a bicarbonate concentration of 103 mg L^{-1} in the reservoir. Under these conditions, the brine remains slightly undersaturated with respect to the evaporitic (halite, sylvite, etc) andiron sulfide (pyrite, pyrrhotite)minerals, but is slightly supersaturated with respect to dolomite. In the caprock, the aqueous solution is supersaturated with respect to dolomite but undersaturated with respect to sulfide (pyrrhotite) and sulfate (anhydrite) minerals.

Table 3. Chemical composition (mg L^{-1})of the waters

Element	Aquifer	Caprock
Na	125,764	78,085
K	21	196.2
Ca	18,872	18,896
Mg	3,059	28,042
Fe	176	540.5
Cl	236,252	238,063
Al	0.002	0.0002
Si (as SiO_2)	10.2	7.4
S (as SO_4^{2-})	723.7	785

2.4 Injected gas mixture

We used two gas steam mixtures provided by Vattenfallin 2008 (Table 4). They contain mostlyCO_2 (90.28 to91.61 % vol) and a range of 8.38 to 9.71 % vol of impurities (i.e. other chemical species). These two mixtures differ mainly in theirSO_2 concentrations (due to different capture options). One has a low SO_2content (0.08 % vol) and is calledhere "Low SO_2-O_2mixture", whereas the otherhas a higher SO_2content (1.53 % vol) and is called"High SO_2-O_2mixture". For O_2, the same concentration is considered for the two injected gases. The other impurities are not discussedhere.

Table 4: Gas stream mixture compositions (in vol%) to be injected. Data provided by Vattenfall.

	Low SO_2-O_2 mixture	High SO_2-O_2 mixture
CO_2	91.61	90.28
Ar	5.70	5.62
O_2	1.60	1.58
N_2	0.61	0.60

NO	0.25	0.24
H_2O	0.14	0.14
SO_2	0.08	1.53
Total of impurities	8.38	9.71
Total	99.99	100.00

These two compositions were specifically chosen so that we could determine the consequences of relatively large amounts of impurities. The likely compositions are constantly being updatedand the CO_2content would currently exceed95%.

3 NUMERICAL APPROACH

3.1 Calculation code

TOUGHREACT (version 1 - Xuet al., 2006) wasused for all simulations. This code, which was developed by introducing reactive chemistry into TOUGH2 V2 (Pruess et al., 1999), couples thermal, hydraulic and chemical (THC) processes and is applicable to one-, two-, or three-dimensional geologic systems with physical and chemical heterogeneity. TOUGHREACT is coupled with ECO2n (Pruess, 2005), a fluid property module developed specifically to simulate geologic sequestration of CO_2 in saline aquifers. It can be used to model isothermal or non-isothermal multiphase flow in water/brine/CO_2 systems.

TOUGHREACT simulates the chemical reactivity of systems using an extended thermodynamic database. We used the database providedwith the program, i.e., a modified version of the EQ3/6 database (Wolery, 1992).

Thermodynamic equilibrium between the gas phase and the aqueous phase is assumed for CO_2 dissolution. An extension of Henry's law, including salting-out effect, is used to estimate the solubility of CO_2 in the aqueous phase at high pressure and high salinity.

For this work, the advancement of dissolution and precipitation reactions of minerals wasmodeled under kinetic constraints.The general form of the rate law proposed by Lasaga (1984) was applied for both the dissolution and precipitation of minerals:

$$r_n = \pm k_n A_n \left| 1 - \Omega_n^{\theta} \right|^{\eta}$$

Positive values for r_n correspond to the dissolution of the mineral n (negative values for precipitation), $k_n$isthe rate constant (mol m^{-2} s^{-1}), $A_n$is the specific reactive surface area per kg$_{H2O}$, $\Omega_n$isthe saturation ratio of the mineral n ($\Omega_n = Q_n/K_n$), and θandη are empirical parameters determined from experiments, usually taken as 1.

The dependence of the rate constant $k_n$ontemperature is calculated using the Arrhenius equation:

$$k_n = k_{25} \exp\left[\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right]$$

whereE_a is the activation energy (J mol^{-1}), $k_{25}$is the rate constant at 25°C, R is the gas constant (J mol^{-1} K^{-1}), and $T$is the temperature in Kelvin.

For some minerals, specifically alumino-silicates and salts, dissolution and precipitation also depend on H$^+$ (acid mechanism) and OH$^-$ (alkaline mechanism) concentrations, in addition to the neutral mechanism. In this case, k_n is calculated using the following equation:

$$k_n = k_{25}^{nu} \exp\left[\frac{-E_a^{nu}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] + k_{25}^{H} \exp\left[\frac{-E_a^{H}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{n_H} + k_{25}^{OH} \exp\left[\frac{-E_a^{OH}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{n_{OH}}$$

where superscripts and subscripts *nu, H*, and *OH* indicate neutral, acid, and alkaline mechanisms, respectively, and *a* is the activity of the species.

For carbonate minerals, dissolution/precipitation mechanisms are catalyzed by HCO$_3^-$, and reaction rates depend on the activity of aqueous CO$_2$. k_n is calculated according to:

$$k_n = k_{25}^{nu} \exp\left[\frac{-E_a^{nu}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] + k_{25}^{H} \exp\left[\frac{-E_a^{H}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{n_H} + k_{25}^{CO_2} \exp\left[\frac{-E_a^{CO_2}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_{CO_{2.aq}}^{nCO_2}$$

The kinetic parameters used for the last two equations are given in Table 5 and come from Palandri and Kharaka (2004). The dissolution rates depend on the three mechanisms proposed in Table 5, whereas the precipitation rate depends only on the neutral mechanism. The kinetic parameters for siderite are assumed to be the ones of dolomite rates (Gunter et al., 2000)

Table 5 – Kinetic parameters for mineral dissolution and precipitation (C stands for minerals from the caprock and R for minerals from the reservoir). k (calculated at 25°C and pH=0) = Rate constant in mol m^{-2} s^{-1}, E = Arrhenius activation energy in kJ mol^{-1}, n_H and n_{OH}= reaction order with respect to H$^+$ and OH$^-$, n_{CO2} = reaction order with respect to CO_2

		Acid mechanism			Neutral mechanism		Base/Carbonate mechanism		
		Log k	E	n_H	Log k	E	Log k	E	n_{OH}/n_{CO2}
C	Illite	-12.71	48.0	0.220	-14.41	48.0	-14.41	48.0	-0.130
C&R	Quartz	--	--	--	-13.40	90.9	--	--	--
C&R	Plagioclase (Albite)	-10.16	65.0	0.457	-12.56	69.8	-15.60	71.0	-0.572
C&R	Plagioclase (Anorthite)	-3.50	16.6	1.411	-9.12	17.8			
C&R	Chlorite	-11.11	88.0	0.500	-12.52	88.00	--	--	--
C	K-Feldspar	-10.06	51.7	0.500	-12.41	38.0	-21.20	94.1	-0.823
C	Hematite	-9.39	66.2	1.000	-14.60	66.2	--	--	--
C	Siderite	-3.19	36.1	0.500	-7.53	52.2	-5.11	34.8	0.500
R	Calcite	-0.30	14.4	1.000	-5.81	23.5	-3.48	35.4	1.000
R	Anhydrite	--	--	--	-3.19	14.3	--	--	--
C	Rutile	Assumed to beat equilibrium							
C	Pyrite	Assumed to be at equilibrium							

The reactive surface area of the dissolving minerals is a complex factor since the dissolution rate depends on the available surface area in contact with the aqueous solution. This contact surface is difficult to estimate. According toWhite and Peterson(1990), it can vary between 1 and 3 orders of magnitude with respect to the total surface area measured using the BET method. We assumed that all of the minerals except illite have the same specific surface area (about 10 cm².g^{-1}). A value of 100 cm².g^{-1}wasused for illite. These values are consistent with the data chosen by Xu et al. (2007).

Mineral dissolution and precipitation reactions causetemporal changes in reservoir porosity. Indeed, variations in the mineral volume fraction owing to chemical reactions make it possible tocalculatethe resulting porosity. Permeability variations were not calculated in this study

because of the poor knowledge of the relationship between permeability evolution and porosity changes.

3.2Geometrical Model

The saline aquifer is represented by a 2D-radial model that includesthe reservoir and caprock units (Fig.2).
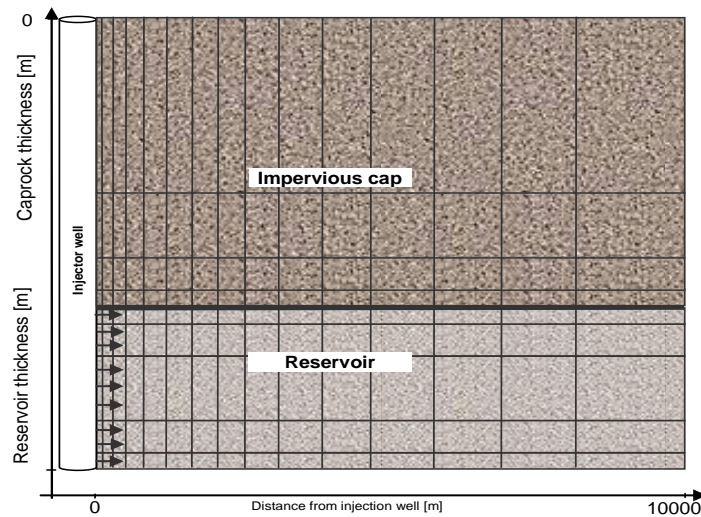

Figure 2.   The geometrical 2-D radial model (vertical cross-section)

This conceptual model is able to calculatethe evolution of the geochemical reactivity induced by gas injection inboth time and space. The 200-mthick reservoir is centered on a vertical injection well with a radius of 0.2 m.The maximum radial extent is 100 km. The system is represented by 800grid blocksmaking upthe model mesh. Along the radius axis, there are 29 grid cells between 0.2 m and 1 km, 50 grid cells between 1 km and 10 km, and 20 grid cells between 10 and 100 km. In each interval, the width of the radial elements follows a logarithmic scale. Vertical discretization is achieved by dividing the reservoir into 5 layers,20, 40, 80, 40, and 20 m thick, from bottom to top, and the caprock into 3 layers, 5, 10, and 25 m thick. The objective of this greaterrefinement near the injection well is to more preciselyidentify both the details of geochemical processes and the migration of the desiccation front in the near-well region.

3.3 Injecting supercritical CO_2 with SO_2 and O_2 impurities

TOUGHREACT cannot handle CO_2-SO_2-O_2-H_2O gas mixtures – only CO_2-H_2O mixtures (specificity of the ECO2n module).A mixture of supercritical CO_2 and reservoir brine containing dissolved SO_2 and O_2 (hereafter called "SO_2-O_2mixture") were thereforeco-injected into the reservoir.

The injection rates of supercritical CO_2 and SO_2-O_2 dissolved in brinewere 30 kg s^{-1}and 15 kg s^{-1}, respectively. The mass ratio of 2 was arbitrary chosen for the simulations. Gas and brine were injected over the total thickness of the reservoir during an assumed exploitation period of 30 years. The specific injection rates were 0.15 kg s^{-1} m^{-1} for CO_2 and 0.075 kg s^{-1} m^{-1} for brine containing dissolved SO_2-O_2 because of the thickness of the reservoir formation. Since the reservoir had a high permeability (about 300 mD), the pressure buildup was limited to about 10 bars and enabled a long injection period.

Two gas stream mixtures are studied:

- "Low SO_2-O_2mixture" containing CO_2 (91.61 % vol) and 9.71 % vol of impurities, including a negligible amount of SO_2 (0.08 % vol) and 1.6 % vol of O_2 (Table 4);

- "High SO_2-O_2mixture" containing 90.28 % vol of CO_2, 1.53 % vol of SO_2, and 1.6 % vol of O_2 (Table 4)

The chemical composition of the SO_2-O_2-acidified brine(co-injected with supercritical CO_2) wasdetermined in different steps:

- First, the injected brine wasequilibrated with the reservoirminerals at the reservoir temperature.

- SO_2 and O_2 gases werethen dissolved in the brine. Given the chosen mass ratio of 2 between the injected mass of supercritical CO_2 and the mass of SO_2-O_2 brine, the SO_2

and O_2 concentrations in the solution weredefined to ensure consistency with the gas composition of an oxy-combustion capture process (given data from the industry).

These preliminary simulations were done with the batch option of the PHREEQC code (Parkhurst and Appelo, 1992). The hypothesis that SO_2 is totally dissolved in the SO_2-O_2 brine is acceptable since its solubility is very high at such temperatures (Ellis et al., 2010).

3.4 Initial Conditions

The following assumptions were used fornumerical modeling:

- *Hydrostatic equilibrium*: no regional flow is considered, and a hydrostatic pressure is imposed in the outermost column of the mesh.

- *Thermal equilibrium*: before starting gas injection, reservoir and caprock are at the same temperature, i.e., 50°C.The numerical simulations are donein isothermal mode.

- *Geochemical equilibrium*: the aqueous solutions initially present in the reservoir and caprock are in equilibrium with their respective mineral assemblages at the temperature of the system.

The Davies modelwas used as the activity model in the batch simulations with PHREEQC.The TOUGHREACT code uses an extended Debye-Hückel model, although these models are poorlyadapted tohighly saline solutions such as those in the reservoir (Table 2). For this reason, and for more reliable results, the elemental concentrations of each species of the acidified water weredivided by 10 in order to decrease the ionic strength of the solution (Table 6). This artificial dilution does not drastically modify the simulation results and thereaction paths, but it can change thedissolution/precipitation magnitudes of minerals.Another change related to the dilution is the initial saturation state of water with respect to rock minerals. After dilution, the "low SO_2-O_2 mixture" is undersaturated with respect to anhydrite, whereas the "high SO_2-O_2mixture" is supersaturated with respect to anhydrite. The consequences on numerical results will be analyzed in paragraph 4.2.

Table 6. Chemical characteristics of the fluids used for numerical calculations

	Reservoir brine	Low SO_2-O_2mixture	High SO_2-O_2mixture
pH	7.9	1.5	0.2
pe	-3.9	17.7	19.0
TDS (g/kg_{H2O})	38.6	~38.6	~38.6
$[SO_4^{-2}]$(mol/L)	1.7e-02	5.0e-02	7.2e-01

The "SO_2-O_2mixtures" are highlyacidic, with oxidative and sulfateconcentrations higher than in the reservoir brines. These brines wereexpected to be highly reactive with reservoir minerals.

4 RESULTS AND INTERPRETATION
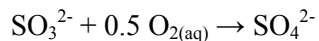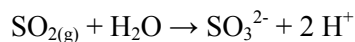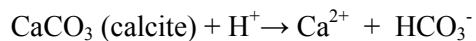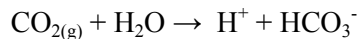
4.1 Case 1: Injection of a"Low SO_2-O_2mixture"

The injection ofgas and water in the reservoir changes the physical parameters (gas saturation, pressure, etc.)and geochemical properties at different scales, with a major impact on the near-wellbore zone.

The injection of the gas/solution mixture changesthe gas saturation around the injection well. Because the supercritical CO_2 densityislower than that of the formation brine, CO_2reachesthe top of the aquifer and spreads outalong it (Fig. 3). Although the caprock isless permeable than the reservoir, the supercritical $CO_2$is able topenetrate itovera few centimeters.The pressurearound the injector, initially between 143 and 160 bars between the top and the bottom of the reservoir,increasesto 167 bars by the end of the injection period.

The pH of the formation water iscontrolled by water-rock interactions. Initially, the formation water isinequilibrium with the mineral assemblage of the reservoir: the pH isclose to 7.9 (Table 6). Co-injection of supercritical CO_2 and SO_2-O_2 brinemodifiesthis equilibrium.The evolution of pH followsthe evolution of the gas saturation in the reservoir, with the impacted zone extending up to 3000 m from the injector after an injection period of 30 years (Fig. 3b). Consequently, the

formation water around the injector acidifies,becomesundersaturated with respect to all minerals, and dissolvesthem (preferentially the carbonates).Calcite dissolution is illustrated by the increase in the calcium concentration in the low pH zone (Fig. 3c). As long as reactive carbonates arepresent, the aqueous solution isin equilibrium with them and the pH isbuffered. However, continued injection exhaustssome minerals.All of the carbonates areconsumed around the injector and the buffering stops. pHisno longercontrolled and decreasesto very low values. Near the well, the mineral assemblage isdrastically modified, and the pH decreasesto a minimum value of 1.4, similar to that of the injected fluid (Table 6). Further within the impacted zone of the reservoir, the pH isbuffered to a value ranging between 4 and 6, since not all of the carbonatesareconsumed.The pH does not change in the non-impacted zone.

Because of this acidification of the medium, calcite isthe mineral most affected by the injection of the acid solution. It dissolvesnear the injection well (50 m around it), but isnot significantlyimpacted elsewhere in the reservoir (Fig. 3e).Anhydrite is also affected by gas and water injection.The behavior of anhydrite differsin time and space.Atfirst, anhydrite precipitates near the injection well because the injected fluid contains sulfur,which is oxidized tosulfateby oxygen.Calcite is dissolved by the acidified injected water, releasing Ca^{2+} in solution (Fig. 3c). With SO_4^{2-} present in the injected water (Fig.3d), these ions combine to form anhydrite according to the following successive geochemical reactions:

$$CO_{2(g)} + H_2O \rightarrow H^+ + HCO_3^-$$

$$CaCO_3 \text{ (calcite)} + H^+ \rightarrow Ca^{2+} + HCO_3^-$$

$$SO_{2(g)} + H_2O \rightarrow SO_3^{2-} + 2\ H^+$$

$$SO_3^{2-} + 0.5\ O_{2(aq)} \rightarrow SO_4^{2-}$$

$$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4(\text{anhydrite})$$
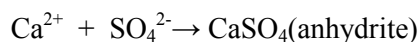
However, when all of the calcite has beenconsumed, the Ca^{2+} source disappears and anhydrite precipitation stops. Because the injected solution is undersaturated with respect to anhydrite, the

secondary precipitated anhydrite and the original anhydrite (initially present in reservoir) dissolve. This is why some zones showa deficit inanhydrite, whereas others showa positive balance of anhydrite compared to its initial amount (Fig. 3f). However, because of the amount of sulfate injected, the dissolution and precipitation of anhydrite have a limited impact on sulfate concentration.

As a consequence of calcite and anhydrite reactivity, porosity increases near the injector (Fig. 3g). After 30 years of injection, it is estimated that the porosity 10 m from the injection well is around 19 % (due to calcite and anhydrite dissolution). In any case, these values must be considered to beindicative (qualitative) and not quantitative, because of some limiting working hypotheses (dilution of the initial brine, limitations of kinetic parameters, restrictions of multiphase reactive transport, etc.).
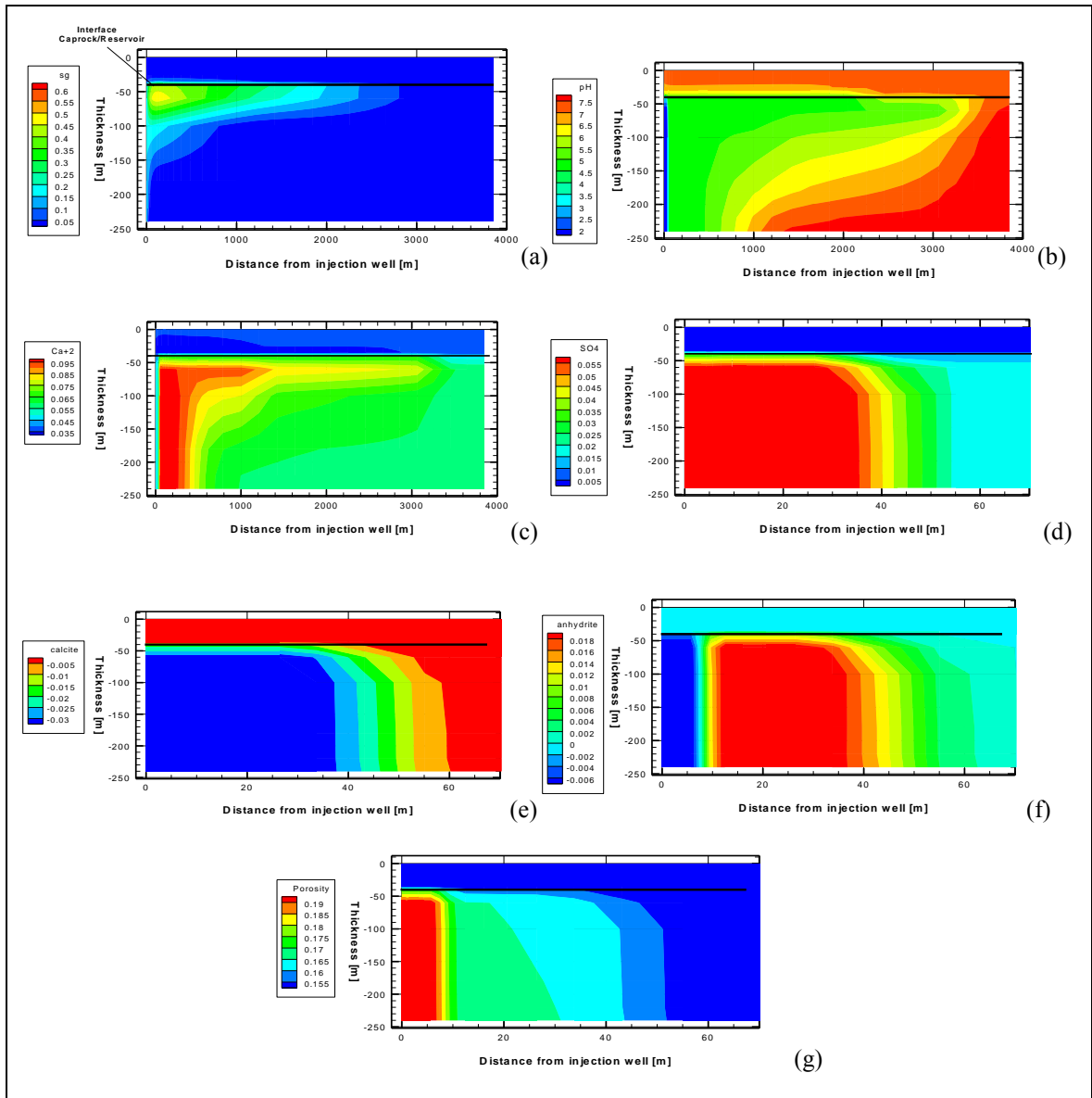
Figure 3.State of the reservoir and caprock after a 30-yearinjection period. a)Gas saturation (Sg), b) pH pattern, c) Calcium concentration (mol/kg$_{H2O}$)with x-axis up to 4000 m, d) Sulfate concentration (mol/kg$_{H2O}$), e) Volumic fraction of calcite, f) Volumic fraction of anhydrite, g) Porosity with x-axis up to 70 m from injection well

All other minerals in the reservoir react, but less than calcite and anhydrite (by 2 to 5 orders of magnitude) and their impact on porosity isnegligible.

Because of the assumptions made regarding caprock permeability, supercritical CO_2 is able to penetrate it slightly, which causes some reactivity, in particular at the interface between reservoir

and caprock formations. The amount of CO_2infiltrating the caprockistoo low and the impact on chemical reactivity and porosity variations are too limited to be seen in the graphs.Some reactivity of Fe minerals is however observed. In relation to the extent of the CO_2 gas bubble (spreading about 2,000 m from the injection well) and the decrease in pH, siderite and chlorite are the most impacted minerals, with dissolution of these two minerals over a few centimeters inside the caprock. There is little dissolution of minerals but it causes an increase in the iron (III) concentration and a potential precipitation of hematite at the interface.

One key concern associated withCO_2storage in geological reservoirs is the potential durable trapping of gas as minerals. For this specific case,CO_2could be stored as carbonate but because of the acidity of the injected fluid, no mineral precipitation is observed. The primary carbonates are totally dissolved (close to the injection well),which leads to a release of carbon in the reservoir instead of trapping. The only gas storage observed was that of SO_2, which is stored as anhydrite (after oxidation as sulfate). However, because of the low amount of calcium in solution (coming from carbonate dissolution), the trapped fraction of SO_2 is relatively low and has a low impact on the sulfate concentration (Fig. 3d).

4.2Case 2: Injection of a "High SO_2-O_2mixture"

At the temperature of the reservoir (i.e. 50°C), the "High SO_2-O_2 mixture" is slightly oversaturated with respect to anhydrite. Consequently, after 12 years ofinjection, anhydrite precipitation has fully cloggedthe porosity nearthe injection well,putting an end to injection if no corrective measures have beentaken.

In order to studyanhydrite precipitation conditions, we rananother simulation,injectinga differentsolution. This time, the reservoir brine, once again diluted 10-fold,was not initially equilibrated with the mineralogical assemblage of the reservoir before theSO$_2$ and O_2 were added, and the injected solution was undersaturatedwith respect to anhydrite.
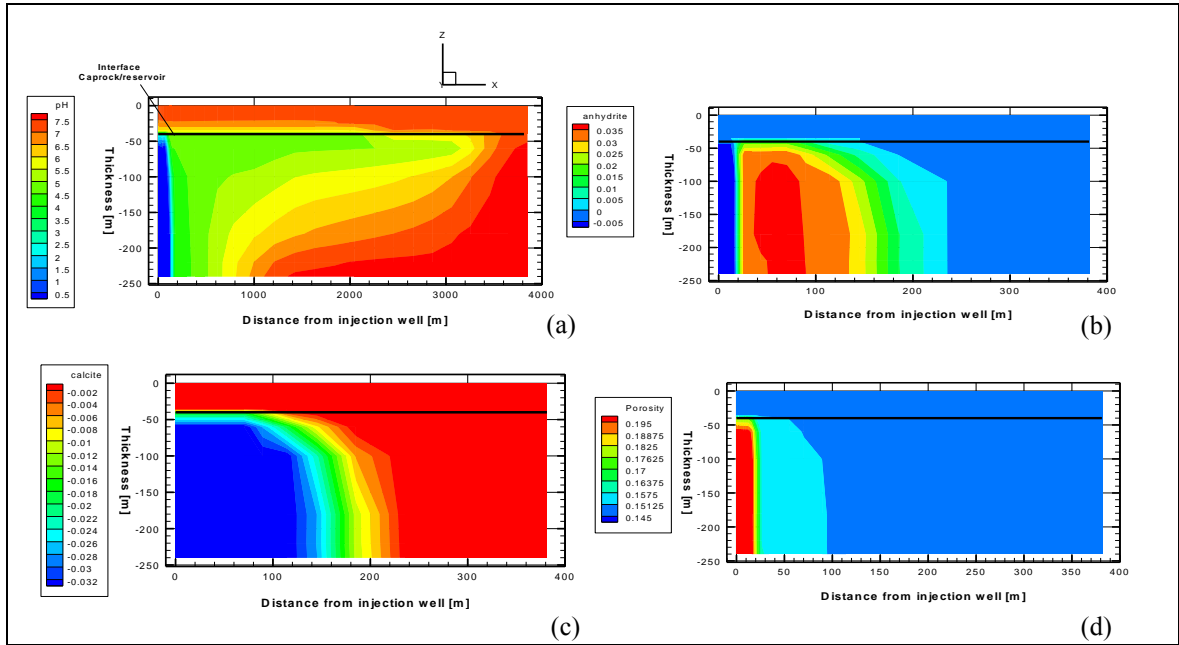
Figure 4. State of the reservoir and caprock after an injection period of 30 years. a) pH pattern with x-axis up to 4000 m, b) Volumic fraction of anhydrite, c) Volumic fraction of calcite, d) Porosity with x-axis up to 400 m from inejction well.

The impact of the co-injection of supercritical CO_2 and acidified brine is a decrease in pH around the injection well and a co-dissolution of both carbonates and anhydrite (since the solution is undersaturatedwith respect to anhydrite) (Fig. 4). Since the acidity is higher than that ofthe "low SO_2-O_2 mixture" (Table 3), the impacted zone is larger than in the first case (about 50 m in case 1 and 200 m in case 2).
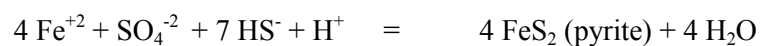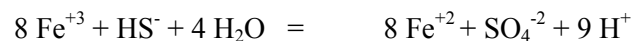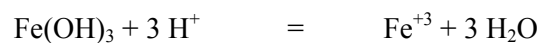
The other minerals of the assemblage arealso impacted by this strong acidification. They areless impacted than carbonates or anhydrite, but the dissolution of some (K-feldspar) and the precipitation of others (quartz, kaolinite) must be carefully monitored.

The higher acidity of the injected fluid in this caseis neutralized to a lesser extent by reactions with minerals. Smaller variationsin porosity are observed in the near-well region, whereas the impacted zone is enlargedby the mineral dissolution and precipitation reactions.

4.3 Discussion

In order to determine the effect of impurities (SO_2 and O_2) co-injected with CO_2 in deep saline reservoirs, we comparedour results with those of Audigane et al. (2007), which were obtained with the injection of pure CO_2. The initial mineralogical assemblage and the secondary minerals in our study were the same as those of Audigane et al. (2007). These authors investigated both the injection period (25 years) and the post injection period (10,000 years). During the injection period, theypredicted a minor alteration of the alumino-silicates (chlorite, albite, muscovite). Calcite is the most reactive mineral with dissolutionmainly in the reservoir formation and some precipitation of secondary calcite near the shale layers at the interface between the CO_2-saturated brine and the initial brine. Our study gives the same results with predominantly carbonate dissolution (no traces of secondary precipitations) and only weak reactivity of alumino-silicates.

The main difference is the reactivity of sulfur-bearing minerals. When SO_2 is co-injected with CO_2, the geochemistry of the system is controlled primarily by the sulfur, in particular its reduced form S(-II). Redox reactions are activated by the presence of sulfide in solution. Because of acidification, iron-bearing minerals like ferrihydrite ($Fe(OH)_3$) and hematite (Fe_2O_3) are dissolved, releasing Fe(III) in solution. Because of reduced conditions, iron III is reduced to iron II, which can react with dissolved CO_2 to form siderite (mineral trapping of CO_2) or H_2S (coming from the solubilizationof SO_2) to form pyrite.

$$Fe_2O_3 + 6\ H^+ \quad = \quad 2\ Fe^{+3} + 3\ H_2O$$

$$Fe(OH)_3 + 3\ H^+ \quad = \quad Fe^{+3} + 3\ H_2O$$

$$8\ Fe^{+3} + HS^- + 4\ H_2O \quad = \quad 8\ Fe^{+2} + SO_4^{-2} + 9\ H^+$$

$$Fe^{+2} + CO_3^{-2} \quad = \quad FeCO_3\ (siderite)$$

$$4\ Fe^{+2} + SO_4^{-2} + 7\ HS^- + H^+ \quad = \quad 4\ FeS_2\ (pyrite) + 4\ H_2O$$

In our calculations, enough oxygen is injected to fully oxidize the injected SO_2. Consequently, the geochemical system is dominated by the reactions involving sulfates and carbonates with complex links with oxygen (through pH and redox conditions). Sulfate minerals play a major role, in relation to the carbonates – the precipitation of the former being correlated with the dissolution of the latter. Simulations predict anhydrite precipitation, in agreement with Renard et al. (2011). Wilke et al. (2012) carried out laboratory experiments and reported the presence of gypsum as a secondary mineral. The nature of sulfate minerals is complex and frequently debated because it can have a major influence on rock properties: the molar volume of anhydrite is about 46 cm^3/mol (under standard conditions), whereas that of gypsum is 60% higher (about 74.7 cm^3/mol). Consequently, gypsum precipitation might have a significant impact on the porosity of the porous medium. According to the thermodynamic properties of sulfate minerals, anhydrite is more stable than gypsum above 40°C. Moreover, recent experiments with micro-capillary tubes have shown that gypsum, in the presence of anhydrous CO_2, can change into either bassanite or anhydrite, depending on temperature (Pironon et al., 2012). We can then assume that, in a deep CO_2 storage reservoir, anhydrite will be the main sulfate mineral that is able to precipitate.

Brines present in the reservoir are modified by acid gases. CO_2 dissolution generates carbonic acid and SO_2 + O_2 produce sulfates, both of which lead to a decrease in pH. Because of mineral reactions (carbonate dissolution), the pH does not drop below 4, which is in agreement with the observations of Ellis et al. (2010). This pH-buffering capacity is, however, controlled by carbonates only as long as these minerals are present in the mineralogical assemblage (Gunter et al., 2000).

The high solubility of SO_2 causes a massive dissolution of this gas, which is oxidized by the O_2 co-injected with the CO_2. This oxidation produces sulfates, as described by Rumpf and Maurer (1993), whereas no precipitation of hematite is predicted, despite the presence of iron in the initial solution (Table 3). This is probably due to the absence in the initial mineral

assemblage of iron-bearing minerals such as pyrite (Renard et al. 2011) or daphnite (Thibeau et al. 2009), which could release iron in solution.

Althoughsimulation results seem to corroborateexperimental results, they must be interpreted with caution because of the many assumptions made to do the calculations.First of all, the gases are not all injected as a gas phase. Some of them (O_2 and SO_2) are dissolved in brine. This has an impact on the variations in gas saturation inside the reservoir and on the chemical reactions that might occur in the aqueous phase. Secondly, the activity model used in TOUGHREACT does not handle highly saline solutions. As demonstrated by André et al. (2007) by calculations with different numerical codes and activity models, the use of a specific approach (such as the one proposed in the Pitzer formalism) might increase the accuracy of geochemical predictions, in particular the quantitative results. This is crucial because the predicted amounts of minerals able to precipitate or dissolve depend entirely on these calculations in the aqueous phase. Furthermore, there is noEquation of State (EoS) for the fugacity correction for the complex gas mixture (CO_2-SO_2-O_2-(H_2O)).The calculation of porosity variations might, therefore,be highly uncertain, even though the overalltrend seems to make sense. Thirdly,there are few data concerning the reactivity and the kinetic behavior of alumino-silicate minerals when these are exposed to acidified brines. Many studies emphasize the high reactivity of carbonates and inter-granular cementation in sandstone. Studies (numerical and experimental) must be done to analyze the possible long-term effect of these acid gases on alumino-silicates after the buffering effect of carbonates has disappeared.

5CONCLUSIONS

The objectives of this paper were to present the results ofnumerical simulations of the co-injection of acid gases in a deep saline aquifer. Since the TOUGHREACT code cannot represent the co-injection of these components in a gaseous (non-wetting phase) mixture, some limiting

hypotheses were used: CO_2injection was simulated in a supercritical form, whereas SO_2 and O_2injections were simulated as dissolved species in an aqueous solution. After an injection period of 30 years, simulation results indicate:

- The injected supercritical CO_2 dissolves in solution, increasing its ability to dissolve carbonates. Since calcite is one of the components of the mineralogical assemblage, it dissolves around the injection well and therebyincreases porosity. However,because of the negligibleinitial amount of calcite in the mineralogical assemblage, the impact on pore volume is limited.

- SO_2 reacts rapidly around the injection well, forming sulfatesdue tothe traces of oxygen in the injected gas. Bythe recombining of Ca^{2+} (from calcite) and SO_4^{2-} (from SO_2 and O_2), anhydrite precipitates. The SO_2 concentration determinesthe extent of the anhydrite deposition occurring around the injection well.

- The higher the SO_2 concentration in the injected stream, the larger the radius of anhydrite deposition around the well. However, the SO_2 concentration seems to have no effecton the geochemical mechanisms in terms of, for instance,reaction paths.

- Calcite and anhydrite are the most reactive minerals. All of the other initial minerals are also affected by the injection of the acid solution, but to a lesser extentand with a minor impact on porosity.

- When calcite and anhydrite haveopposite behaviors, numerical simulations predictthat calcite dissolution will have a greater impact on porosity than anhydrite precipitation. Consequently, increasing porosity is expected around the injection well, assumingan increase in well injectivity and a potential long-term injection period.

However, these results are onlyqualitative and highlight only the global trends of the system under investigation. Indeed, the real (quantitative)impact is still very hardto predict. For example, how the dissolution/precipitation of a particular mineral will affect rock porosity

depends on the characteristics of the rock (e.g., micro/macro porosity, connected porosity). Our results must, therefore, be interpreted with caution.

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