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Intrusion of CO_2 and impurities in a freshwater aquifer – impact evaluation by reactive transport modelling

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Abstract

Contamination of fresh groundwater is one of the environmental issues of Carbon Capture and Storage. We simulate with the reactive transport code TOUGHREACT the intrusion of CO_2+impurities from oxycombustion capture in a freshwater aquifer model based on a glauconitic sandstone aquifer. We choose an unfavorable scenario where the contaminant gas presents maximal contents in SO_x, NO_x and O_2. Water quality changes after a 10 years intrusion are exposed. French quality standards in pH, Fe, Mn and sulphates concentrations for drinking water are reminded in the results for reference.
Acidification and carbonation of water induces Fe- and Mn-bearing minerals dissolution that increases the concentration of these metals in water. Contamination by sulphates is due to the SO_2 oxidation by O_2, both of these components being carried by the contaminant gas. The vertical extent of contamination is enhanced by both the upward migration of gaseous CO_2 and downward migration of dense carbonated water. The presence of SO_2 and NO in the contaminant gas, even in very low concentrations, induces a negative local pH shift of 1 unit by comparison with a pure-CO_2 contaminant gas. This pH shift has consequences on Fe and Mn release amplitude. The code does not allow realistic modelling of the fate of NO_x in the aquifer. But we hypothesize this component to be oxidized by O_2 into nitrite or nitrates (health-significant substances) that persist into the aquifer. Perspectives are addressed.
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Keywords: CO_2 storage; modelling tools; environmental impacts; drinking water; impurities

1. Introduction

Contamination of fresh groundwater in case of release outside of the intended storage formation is one of the environmental concerns for Carbon Capture and Storage (CCS) [1]. Most current or planned CCS operations deal with an "impure" CO_2-rich gas that can contain up to 10% of impurities depending on the capture process [2]. "Impurities" are diverse components and some are deleterious for aerial but also aquatic environments. For example, SO_x and NO_x (from oxy- and post combustion capture) can potentially generate sulphates, nitrates and nitrites that are of health-significance in water and thus conditioned to quality standards. This study aims to evaluate by reactive transport modelling the quality evolution of a freshwater aquifer in response to the intrusion of CO_2+impurities from

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oxycombustion capture. A companion paper [3] on this issue of the impact on freshwater quality of a CO_2 intrusion focuses on other aspects (pure CO_2 intrusion, trace metals mobilization, remediation) with a slightly different model set-up.

2. Model set-up

We use the multiphasic reactive transport code TOUGHREACT v1.0 [4] with the flow/thermodynamical module ECO2N [5]. The capabilities of the code and the ECO2N module are exposed in [4, 5]. Nevertheless it has to be noted that kinetics of aqueous redox reactions is not implemented in the present version of the code: these reactions proceed at equilibrium.

The model set-up is based on the characteristics of the Albian aquifer of the Paris Basin (France). The domain is 2D, 80 m height along the z-axis, 80 km along the y-axis and 1 m thick along the x-axis (Figure 1). The y and z directions are discretized to form a grid of 944 cells with a y-axis refinement around the intrusion points (Figure 1).

The initial petrophysical properties of the aquifer are supposed homogeneous (porosity, intrinsic permeability, relative permeabilities, diffusion coefficient) and described in [6]. The aquifer is initially fully saturated with water. A constant regional groundwater flow (order of m/yr) and a hydrostatic gradient of 7 bar (65 bar at the basement, 58 bar at the top) are defined. A constant inflow of intrusive fluid is defined either within the top central cell or within the basement central cell, to model either top or basement intrusion lines (Figure 1). We intrude at these points 1 g/s of gaseous CO_2 and 1 g/s of water containing impurities as dissolved species throughout the simulations duration (10 years). We opted for such intrusion procedure (two-phase fluid), following work performed in [7], because the ECO2N module does not account for the gaseous transport and physical properties (phase equilibrium, density, etc…) of the whole mixture CO_2-SO_x-NO_x-O_2-N_2-Ar but only for pure CO_2. The $CO_{2(g)}$ inflow rate value of 1 g/s was chosen to ensure the appearance of a gaseous plume of CO_2.

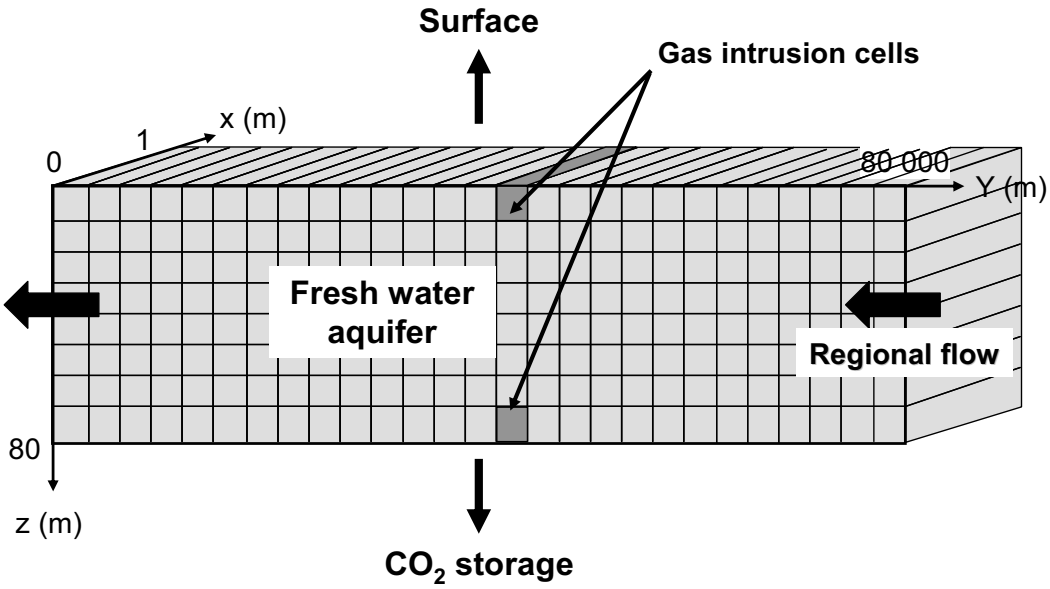

Figure 1 Simplified geometry and hydrodynamics of the reactive transport model.

The initial chemistry (interstitial water composition and solid matrix mineralogy) of the aquifer is supposed to be homogeneous. The solid matrix is a glauconitic sandstone with some amounts of clay and carbonate minerals. The details are exposed in [6]. The interstitial water composition (Table 1) reflects the equilibrium with the solid matrix and is close to the *in-situ* water composition as retrieved from field sampling. Sulphate (gypsum) and iron oxides (lepidocrocite) are defined as secondary minerals *i.e.* not present initially but expected to precipitate. Dissolution

and precipitations of minerals are kinetically-constrained. The kinetic laws implemented in TOUGHREACT are exposed in [4] and the intrinsic kinetic parameters of the minerals in [6]. A specific aqueous chemical system was chosen to account for the foreseeable contrasts of pH and redox potential (the initial water is neutral-reductive while the intrusive fluid is acidic-oxidative). The thermodynamic constants of the aqueous and mineral equilibria are taken from the THERMODDEM database (2008 release, [8]).

Table 1 Calculated composition of the fresh water aquifer and of the intrusive fluid (concentrations in mol/kg of H_2O). "Fe" and "S(+6)" respectively mean total iron and total sulphur under the oxidation state +VI (sulphates), etc….

Element/ Valence	Concentration	
	Fresh water	Intrusive water
pH	7.4	0.4
$O_{2(aq)}$ (pe)	1.3E-70 (-3,4)	1.0E-03 (20.3)
Fe	1.4E-05	1.4E-05
Mn	3.0E-05	3.0E-05
N	1.0E-15	1.0E-01
N(-3)	1.0E-15	2.4E-49
N(0)	5.1E-23	5.0E-04
N(+5)	2.1E-33	1.0E-01
S(+6)	3.5E-04	4.0E-01

Before escaping of the underneath storage and penetrating within the above aquifer, the injected gas would be depleted in impurities (due to reactions with water-reservoir rock and -caprock). Nevertheless, our model considers a contamination of the aquifer by a gas having the composition of an oxygas stream designed for injection (Table 2) because it is difficult to predict the gas composition evolution after its injection. The contaminant gas is characterized by the presence of SO_x, NO_x and O_2 with maximal concentrations for the reason mentioned just before. The intrusion of these impurities in the aquifer is modelled by inflowing a water containing impurities as dissolved species. This water is called "impurities-enriched water". The composition of the impurities-enriched water is the result of the equilibrium between the contaminant gas and the aquifer water calculated by the PHREEQC software [9]. The impurities-enriched water is very acidic-oxidative, concentrated in sulphates and nitrates after the reactions of SO_2, NO and O_2 with water:

$$SO_{2(aq)} + 0.5\ O_{2(aq)} + H_2O \rightarrow 2\ H^+ + SO_4^{2-} \quad (1)$$

$$NO_{(aq)} + 0.75\ O_{2(aq)} + 0.5\ H_2O \rightarrow H^+ + NO_3^- \quad (2)$$

Table 2 Gas composition from oxycombustion capture considered in the study (proportions in vol. %). Data from Anheden et al. (2007).

Component	Proportion
CO_2	90.2
Ar	5.6
O_2	1.6
SO_2	1.5
N_2	0.6
NO	0.2
H_2O	0.1

3. Results and discussion

Maps of pH, Fe, Mn, sulphates (S(+6)) and N concentrations after 10 years continuous CO_2+impurities intrusion located at the top and basement of aquifer are exposed in the following figures (2, 3). We also present the results of simulations considering pure-CO_2 intrusion to discriminate the impurities effect. The French quality standards values for drinking water [10] are noted on the figures (black bracket) for reference, for the elements they apply to. For our study, they only concern pH, Fe, Mn, sulphates and nitrates (N(+5)).

3.1. Intrusion at the top of the aquifer

A low-pH plume migrates downward, accumulates at the basement of the aquifer and spreads laterally by advection and dispersion up to about 1 km width (Figure 2, a). Gaseous CO_2 dissolves into water while it enters the aquifer inducing a densification of water (carbonated water). This carbonated water migrates downward by density contrast with the CO_2-free water (Figure 3, left). High-Fe- and high-Mn-concentration plumes moving downward with shapes similar to the high-pH plume appear in the aquifer (Figure 2, b and c). Acid-induced dissolution of Fe-carbonate (siderite), Fe-clay (glauconite) and Mn-carbonate (rhodocrosite) minerals is responsible of the increase in these metals concentrations. High-sulphate and high-N concentration plumes moving downward are also observed (Figure 2, d and e). Those substances are carried by the intrusive fluid. $N_{2(aq)}$ species make up the majority of the total dissolved N suggesting the nitrates are reduced. This reaction is unlikely to occur as it is highly kinetically limited in abiotic conditions. As mentioned before, kinetics of redox reactions are not implemented in the current version of TOUGHREACT. Realistic migration of nitrates can therefore not be modeled. We hypothesize the high-N concentration plume to be dominated by nitrates.

The minimal pH encountered in the aquifer after pure-CO_2 intrusion is 5.0-5.5 (Figure 2, right side) while it is 4.0-4.5 after CO_2+impurities intrusion. This result depicts the strong acidic character of SO_2 and NO even in low concentrations (here the SO_2/CO_2 and NO/CO_2 ratios of the injected gas are ~2 and 0.2 % respectively). This negative pH shift induced by the presence of SO_2 and NO results in a Fe and Mn concentrations increase by comparison to pure-CO_2 intrusion. These effects remain very localized (about 50m horizontally) around the intrusion point however.

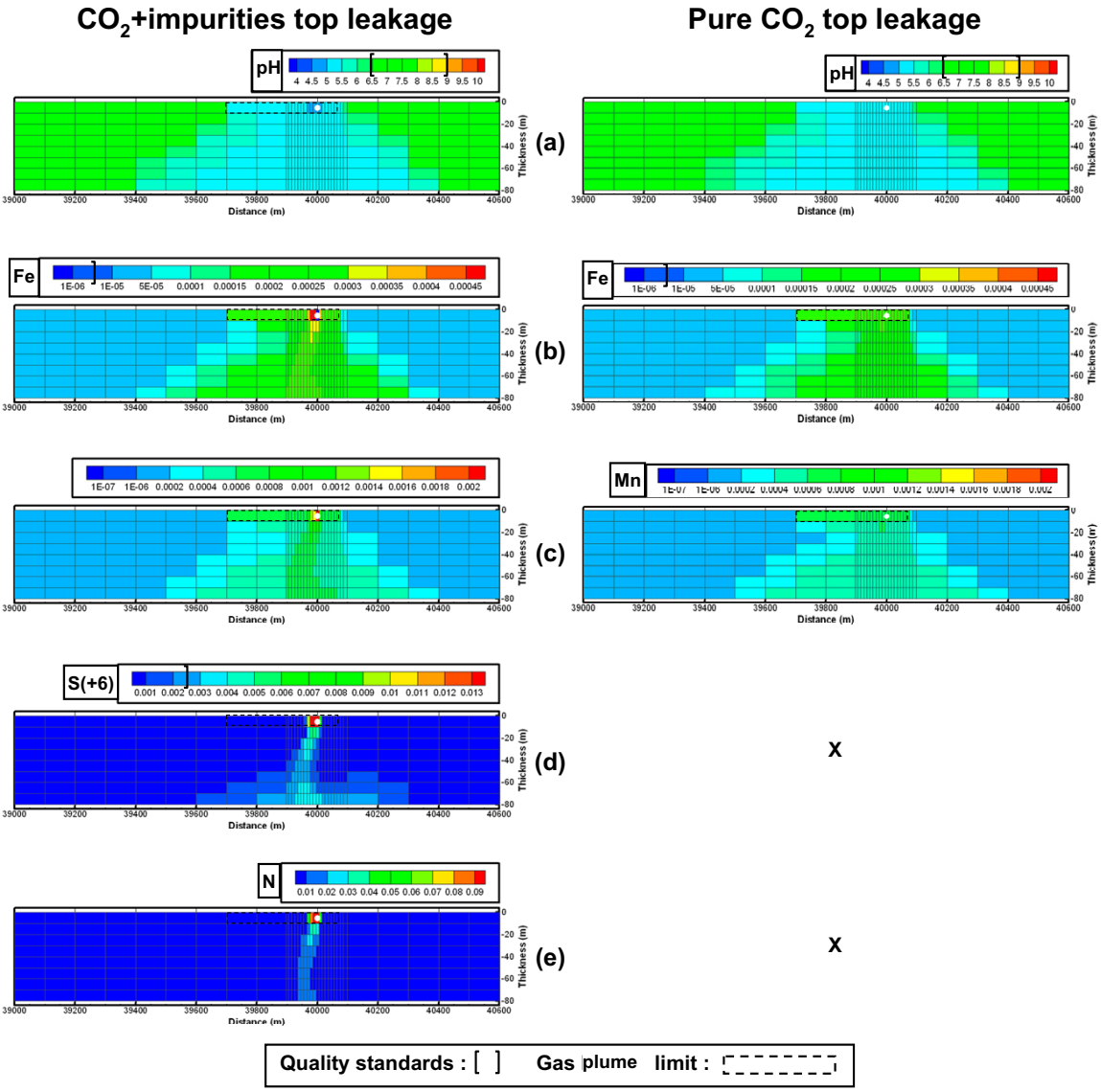

Figure 2 Concentration of Fe (b), Mn (c), S(+6) (d) and N (e) and pH (a) after 10 years continuous intrusion of CO_2+impurities (left side) and pure CO_2 (right side) at the top of the freshwater aquifer. The white dot indicates the position of the gas intrusion. The concentrations are expressed in mol/kg of H_2O.

3.2. Intrusion at the basement of the aquifer

A low-pH plume extends along the entire height of the aquifer, accumulates at the basement and spreads laterally by advection-dispersion up to the same width than in the previous case (1 km, Figure 4, a). The vertical extension is explained by the upward migration of gaseous CO_2 driven by density contrast (Figure 3, right side). Also, the

accumulation of the low-pH plume at the basement is explained by the downward migration of denser carbonated brine (Figure 3, right side). High-Fe and high-Mn concentrations plumes with shapes similar to the low-pH plume are predicted by the simulation (Figure 4, b and c). Dissolution of glauconite and rhodocrosite minerals is responsible of the increase in these metals concentrations. High-sulphates and high-nitrogen concentrations plumes occur only at the basement of the aquifer and spread laterally by advection-dispersion (Figure 4, d and e). The containment of sulphates and nitrogen at the basement is a consequence of impurities intrusion as dissolved species. As SO_2 and NO invade the aquifer, they are quickly dissolved in water (because of their high solubility) so that no gaseous SO_2 and NO exist and migrate upward through gas phase. But the containment of sulphates and N at the basement would also be a consequence of the impurities introduction procedure (as dissolved species). If they were introduced in the aquifer as gaseous species, they may migrate upward through gas phase like CO_2.

Similarly to the intrusion at the aquifer's top, a negative pH shift occurs by comparison to a pure-CO_2 intrusion scenario. This shift is due to the presence of impurities such as SO_2 and NO in the CO_2-rich gas. The higher acidity increases dissolution of Fe- and Mn-bearing minerals that then results in a Fe and Mn concentrations increase. Although still very localized for pH and Mn, this effect affects a wider area (in the order of 300m) for Fe.

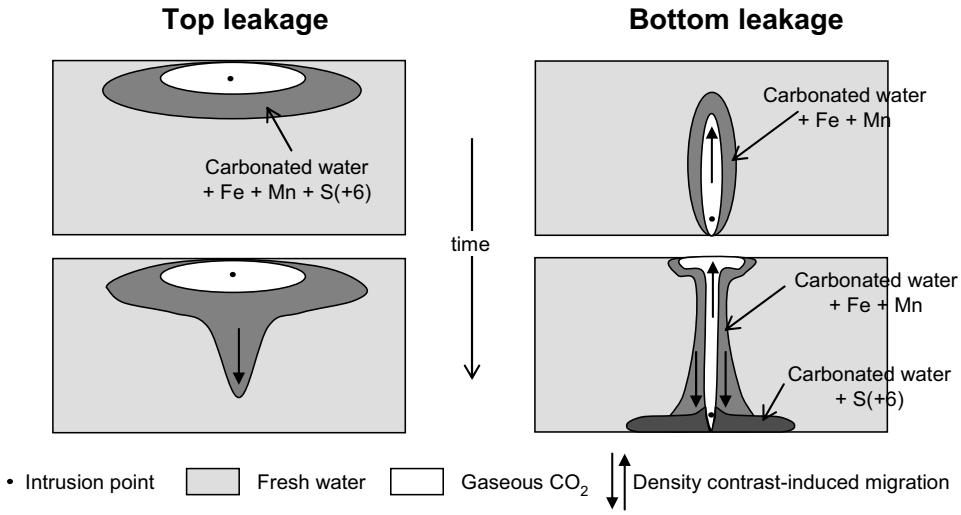

Figure 3 Schematic representation of the contamination plumes migration processes.

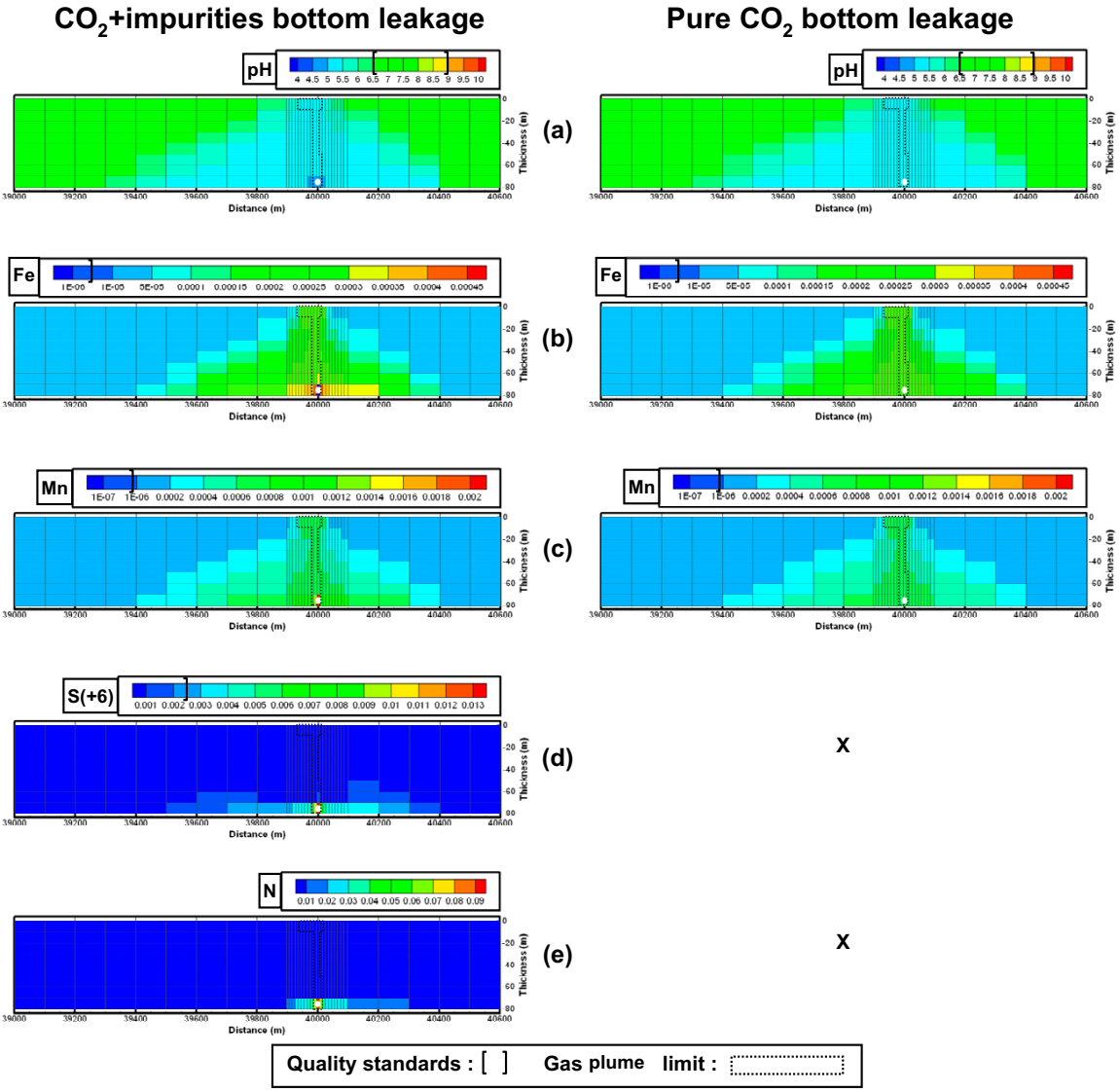

Figure 4 Concentration of Fe (b), Mn (c), S(+6) (d) and N (e) and pH (a) after 10 years of continuous leakage of CO_2+impurities (left side) and pure CO_2 (right side) at the basementof the freshwater aquifer. The white dot indicates the position of the gas intrusion. The concentrations are expressed in mol/kg of H_2O.

4. Conclusion

We simulated a continuous intrusion of CO_2+impurities from oxycombustion capture in a freshwater aquifer model based on characteristics of a glauconitic sandstone aquifer (Albian aquifer, Paris Basin, France). We chose an unfavorable model where the contaminant gas presents maximal contents in SO_x, NO_x and O_2. A first run simulated the gas intrusion at the top of the aquifer and a second one at its basement. A continuous inflow rate of 1 g/s of contaminant gas was chosen for both cases. This value allows the persistence of a gas plume within the aquifer.

Water quality changes are showed after a 10 years intrusion. We compared them to simulation results considering the intrusion of pure-CO_2 gas to discriminate the impurities effect on the water quality changes.

Acidification and carbonation of water induces Fe- and Mn-bearing minerals dissolution that increases the concentration of these metals in water. Contamination by sulphates is due to the SO_2 oxidation by O_2, both components being carried by the contaminant gas. The vertical extent of contamination is enhanced by both the upward migration of gaseous CO_2 and downward migration of dense carbonated water. The presence of SO_2 and NO in the contaminant gas even in very low concentrations induces a local negative pH shift of 1 unit by comparison to a pure-CO_2 contaminant gas. This pH shift results in an increased release of Fe and Mn.

The code used does not account for the gaseous transport and for the physical properties of complex gas mixtures such as oxycombustion flue gas. The impurities were thus introduced within the aquifer under the form of dissolved aqueous species. The transport of low-soluble components like $O_{2(g)}$, $N_{2(g)}$ and $Ar_{(g)}$, expected to persist as gaseous species, could not be modelled. Another limitation of the study relates to the aqueous redox equilibrium assumption (current code version limitation). This did not allow to realistically modeling the fate of NO_x in the aquifer. $NO_{(g)}$ is oxidized into nitrite or nitrates by $O_{2(g)}$, both NO(g) and $O_{2(g)}$ being carried by the contaminant gas. Then we expect the nitrites or nitrates (health-significant substances) to persist into the aquifer contrary to the outcomes of the model. The aqueous redox equilibrium assumption could also have effects on the whole system redox behavior. A detailed study of nitrogen redox reactions would be necessary in the future. Finally, punctual intrusions in 2D axisymetric and 3D cartesian models, lower inflow rate (with no appearance of gas phase) and additional chemical processes such as ionic exchange and sorption (on clay minerals and oxy-hydroxydes) could be tested.

5. References

[1] Damen K, Faaij A, Turkenburg W. Health, Safety and environmental risks of underground CO_2 Storage - overview of mechanisms and current knowledge. Climatic Change 2006 ;74: 289-318.

[2] Jacquemet N. Gaus I, Azaroual M, Audigane P, Yan J, von Dalwigk I, Anheden M, Bernstone C, Le Gallo Y, Estublier A, Lachet V. CO_2 streams containing associated components - a review of the thermodynamic and geochemical properties and assessment of some reactive transport codes. Energy Procedia 2008 ; proceedings of the GHGT-9.

[3] Vong CQ, Jacquemet N, Picot-Colbeaux G, Lions J, Rohmer J, Bouc O. Reactive transport modelling for impact assessment of a CO_2 intrusion on trace elements mobility within fresh groundwater and its natural attenuation for potential remediation. Energy Procedia 2010; proceedings of the GHGT-10.

[4] Xu T, Sonnenthal EL, Spycher N, Pruess K. Toughreact user's guide. Lawrence Berkeley National Laboratory Report No. 55460; 2004

[5] Pruess K. ECO2N: a TOUGH2 fluid property module for mixtures of water, NaCl and CO_2. Lawrence Berkeley National Laboratory Report No. 57952; 2005.

[6] Jacquemet N, Picot-Colbeaux G, Vong CQ, Lions J, Bouc O. Intrusion de CO_2 contenant des impuretés dans un aquifère d'eau potable - évaluation de l'impact par modélisation en transport réactif. BRGM report No. RP-58-534-FR, available online at www.brgm.fr.

[7] Xu T, Apps JA, Pruess K, Yamamoto H. Numerical modeling of injection and mineral trapping of CO_2 with H_2S and SO_2 in a sandstone formation. Chem Geol 2007 ;242, 319-346.

[8] Blanc P, Lassin A, Piantone P. Thermoddem a database devoted to waste minerals; 2010. Available online at http://thermoddem.brgm.fr.

[9] Parkhurst DL, Appelo CAJ. User's guide to phreeqc (version 2) - a computer program for speciation,batch-reaction, one-dimensional transport,and inverse geochemical calculations. USGS Water-Resources Investigations Report 99-4259, 1999.

[10] Journal Officiel de la République Française. Arrêté du 11 janvier 2007 relatif aux limites et références de qualité des eaux brutes et des eaux destinées à la consommation humaine mentionnées aux articles R. 1321-2, R. 1321-3, R. 1321-7 et R. 1321-38 du code de la santé publique. Annexes I et II, 2007.