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Gas-Water-Rock Interactions ... / Interactions gaz-eau-roche ...

Gas-Water-Rock Interactions Induced by Reservoir Exploitation, CO_2 Sequestration, and Other Geological Storage*

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1 GLOBAL CHANGE, SUSTAINABLE DEVELOPMENT AND GEOLOGICAL STORAGE

At the opening of the Millenium the planet Earth is confronted with a major open question, namely: what will be the result in the nearby future of the soaring interference between human activities and natural environmental processes? There is an increasing sense of alarm about the anthropogenic threats that exert pressure on the environment, especially if projected towards the future with the growing adoption of the standards of leaving that prevail in developed countries. Modern economies, born from the Industrial Revolution, have developed on the basis of the largely available and relatively inexpensive energy provided by fossil fuels, which are easy to produce, to transport, to store and to use in concentrated power units. In the so-called rich countries basic equipment, energy production means, industrial facilities, lifestyle expectations were shaped by this position with respect to energy, and fastly developing countries today reproduce the same attitude. But for the first time in human history the rising population, the escalating consumption of energy, water, food and raw materials, the increasing production of substances and goods but also of pollutants and wastes, and the expanding demand for mobility and transportation collide with the physical capacities of the planet's resources. Since the "Earth Summit" of the United Nations Conference on Environment and Development (UNCED) held in Rio de Janeiro in 1992 many world leaders and policy makers addressed the risks engendered by such an evolution. With the *Third Assessment Report of the Intergovernmental Panel on Climate Change* (IPCC, 2001), and now with the ratification of the Kyoto Protocol, the questions of climatic change have been rightly brought to the forefront of the political agenda. Because of its abrupt, spectacular and uncontrolled character, they should play an important role in the collective consciousness. However, the emerging and interwoven problems of global change (see for instance Steffen *et al.*, 2004, and reference therein), access to resources, or capability of waste assimilation offered by the planet Earth, are even broader and deeper than the climatic problem on itself. Considering all the present-day trends exhibited by the human population (10 billion people in 2050?), by their levels of consumption (water, food, energy, goods, etc.), and/or by their activities (transportation, urbanization, etc.), one cannot avoid some amount of vertigo and of—at least casual—scepticism. One therefore has to question whether "sustainable development" is still credible? Shouldn't we rephrase the latter concept into a more realistic one of "survival"?

Timing is a key aspect. We are living a kind of dangerous competition between global change and economic growth. On one side, for instance, many recent observations confirm the rhythm of climate alteration already detected and predicted (*e.g.*, ACIA, 2004; Steffen *et al.*, 2004) *(Fig. 1)*. On the other side, industrial and developing countries continue to follow their ascending road towards more consumption. In

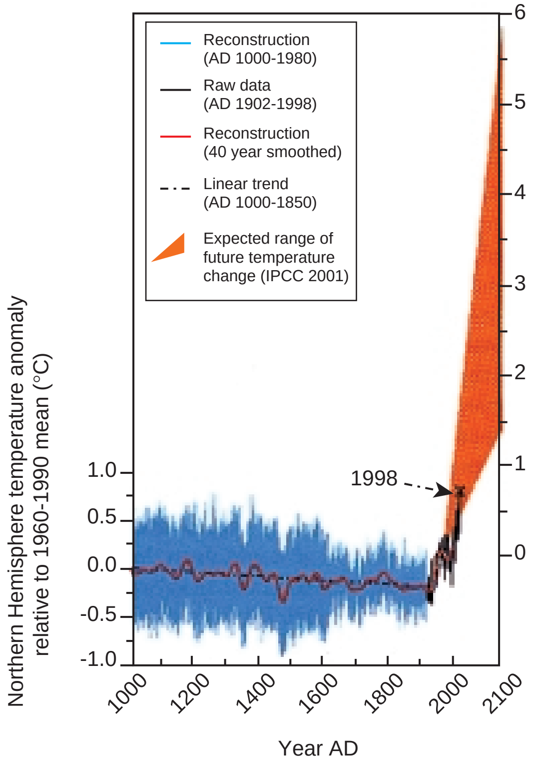

Figure 1

Projections of temperature change in the Northern Hemisphere during the 21st Century, compared to its evolution over the last Millenium (from Steffen *et al*., 2004; see also Bradley *et al*., 2003).

Figure 2, for example, the forecast of the International Energy Agency (IEA) for the global energy demand until 2030 is displayed. For both issues, unfortunately the possibility of short term (few decades) slowing down appears very unlikely. The residence time of carbon dioxide in the atmosphere imposes that a substantial amount of global warming is now already inescapable (*e.g.*, Ruddiman, 2001). Conversely, changing heavy infrastructure, and more profoundly, changing minds and ways of life, takes time. In such a context, there is no doubt that any technological option that could be helpful in mitigating the trends has to be fully investigated. With respect to the anthropogenic emissions of Green-House Gases (GHG) the Geological Storage of CO_2 (GS-CO_2)—a final step of the *Capture and Sequestration of Carbon* (Marchetti, 1977; Holloway *et al*., 1996; Herzog *et al*., 1997; Herzog, 2001; IEA-GHG, 2001; DOE, 2002; IEA, 2002; Gale, 2003; Bennaceur *et al*., 2004; among many other references)—is certainly the technological option most widely considered for an application at the industrial level in the nearby future, *i.e*., during at least a couple of decades following 2010.

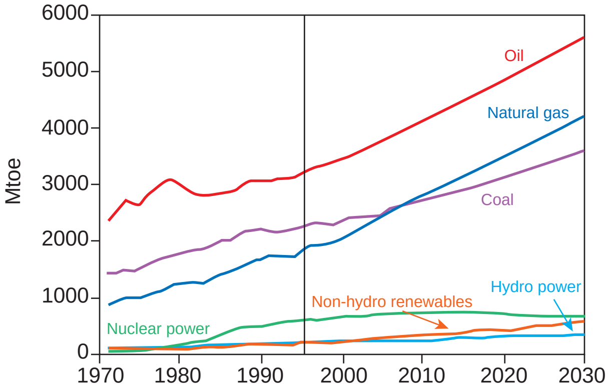

Figure 2

The World demand of commercial energy, anticipated to 2030 by International Energy Agency (from Neef, 2003).

Such a choice rejoins the already existing concept of using appropriate geological formations which are isolated from the biosphere, where by-products of human activity can be disposed in a controlled way. The best known example is radioactive waste (*e.g.*, IAEA, 2003; NEA, 2003), but other contaminant materials might also be concerned in the future, *e.g*., toxic chemical waste. Potential host-rocks such as granite, claystone, salt, or volcanic tuff, are chosen for their long-term stability and confinement properties. To provide support to the design of deep geological disposal of High Level nuclear Wastes (HLW), and to assess the safety functions of such facilities, several countries developed an Underground Research Laboratory (URL). Essentially since the 1980's these facilities have been providing (*e.g.*, in Belgium, Sweden and Switzerland), and will provide (*e.g.*, in France), valuable *in situ* data from scientific experiments, performance assessment from exhaustive engineering testing, and also site characterization for the geological formations which will eventually be chosen for the repository. As opposed to GS-CO_2, in HLW disposal radioactivity, rather than the volume of the waste is the main concern. Furthermore, effects are localised rather than diffuse. The problem of gas production, essentially hydrogen from the corrosion of containers, and its subsequent migration or accumulation, represents a safety issue for such facilities.

The geological permanent storage of industrial activity by-products that are undesirable to be disposed at the Earth's surface (atmosphere, hydrosphere, biosphere) needs expertise from the geoengineering domain. With respect to GS-CO_2 its potential use is now escalating, with volumes required increasing by one or two orders of magnitude. This justifies growing needs for Research & Development (R&D) and some shift of earth science research towards relatively new topics, steered by new questions and demanding cross-disciplinary experience, as it is already the case for geoengineering developed in the framework of deep geological disposal of radioactive wastes.

This also explains the strong interest of specialized meetings such as the *19th Rencontres Scientifiques de l'IFP*, held in Rueil-Malmaison from November 18 to 20 of 2003, on the theme "Gas-Water-Rock Interactions Induced by Reservoir Exploitation, CO_2 Sequestration and other Geological Storage" (http://www.ifp.fr). This meeting was organized to facilitate discussions among scientists involved in the study of underground-waste disposal and its interactions, particularly from the standpoint of geochemistry. It was also meant to bridge the gap between academic and applied research in this field of activity. Special Issues 1 and 2 of 2005 of *Oil & Gas Science & Technology - Revue de l'IFP* contain full papers collected at the end of the conference, mainly from authors of oral or poster presentations, and from other scientists/engineers who attended the meeting. It reflects the spirit in which this event was conceived, *i.e.*, to promote the convergence of scientific expertise and engineer approaches towards some important and urgent problems related to underground storage.

2 GEOLOGICAL STORAGE: COMMON FEATURES, VARIOUS TYPES AND IMPORTANCE OF GAS-WATER-ROCK INTERACTION

Irrespective of its type, geological storage presents several common features:

- Introducing substances in the subsurface locally creates a strong perturbation of the initial (generally natural) conditions. The processes that take place in the perturbed system as it evolves to a new equilibrium state include transport and reaction mechanisms. Multiple feedbacks and complex interactions between the various parts of the system take place which can produce non-linear responses.
- Water is relatively abundant and forms the basic constituent of the pore space. It is the mediator for most of the interactions occurring between the stored material and the minerals that compose the rock. Interactions between gas, aqueous solution and minerals are some of the key factors that engineers have to take into account to characterize the behaviour of a geological site as an underground storage facility.
- Gas is likely to migrate in the different host lithologies and cap rocks.
- Because of the quantity and / or the activity of the stored material, the initial departure from equilibrium should be resorbed in a delay, from 1000 y to several 100 ky depending on the conditions studied, which is in general shorter than the time scales commonly considered for describing geological phenomena. For instance, a nuclear waste repository will come back to water saturation and ambient temperature in *ca*. 1000 y, whereas concealed canisters and packages will react on longer time scales.
- Whereas geology usually deals with past time, the storage behaviour is an issue to be evaluated versus time ahead. Such a requirement calls for the development of relevant and reliable modelling tools.
- The confinement of the waste material from the Earth's surface is the main goal of storage. The long-term reliability of confinement has to be anticipated with sufficient accuracy.

Two main types of sites for the permanent deep geological disposal of waste or undesirable substances can be outlined. They present very different features. The first type concerns nuclear and chemical waste, whereas the second type concerns CO_2. The volumes to be stored, and the degree of threat to the environment strongly differ between these two cases. For nuclear and chemical waste the confinement must be maximized by choosing geological formations of very low permeability range, in addition to the use of canisters and engineered barriers *(Fig. 3)*. The need to place packages in boreholes or horizontal drifts results in a disposal concept which uses or improves the techniques of the mining industry. In these cases the host formations are relatively shallow (a few hundred meters) and the mine opening creates a partial desaturation of the rock and exposure to atmospheric oxygen.

In contrast, the disposal of CO_2 must consider huge volume capacities of storage, and good injection conditions for decades. This requirement leads to choosing reservoir formations that offer high enough porosity and permeability values, as currently met in depleted hydrocarbon fields or deep saline aquifers *(Fig. 4)*. To benefit from the increase of gas density beyond the critical point, and assuming a standard value of geothermal gradient, a minimum depth of 800 to 1000 m will be favoured. The range of depth values expected for the host reservoirs is 800-2500 m. Gas can be injected and monitored following techniques already available in oil industry (Baklid *et al*., 1996; Arts *et al*., 2003; Torp and Gale, 2003).

2.1 The Storage of Acid Gas

Among the twenty-three articles gathered hereafter twelve refer explicitly to acid gas constituents, and many to GS-CO_2 specifically. Therefore we will first give a brief overview of the technology and of the major related R&D issues. From the moment of gas injection time can be split up into two phases: the injection period (eventually, with an EOR[1] initial step in the case of an oilfield), and the long-term storage period. During the first period the phenomena are dominated by polyphasic fluid flow in the reservoir. The tools of study are mainly those of reservoir engineering. Particular attention must be paid to the thermodynamic properties of acid gas constituents, either for PVT simulations (determination and

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[1] EOR: enhanced oil recovery.

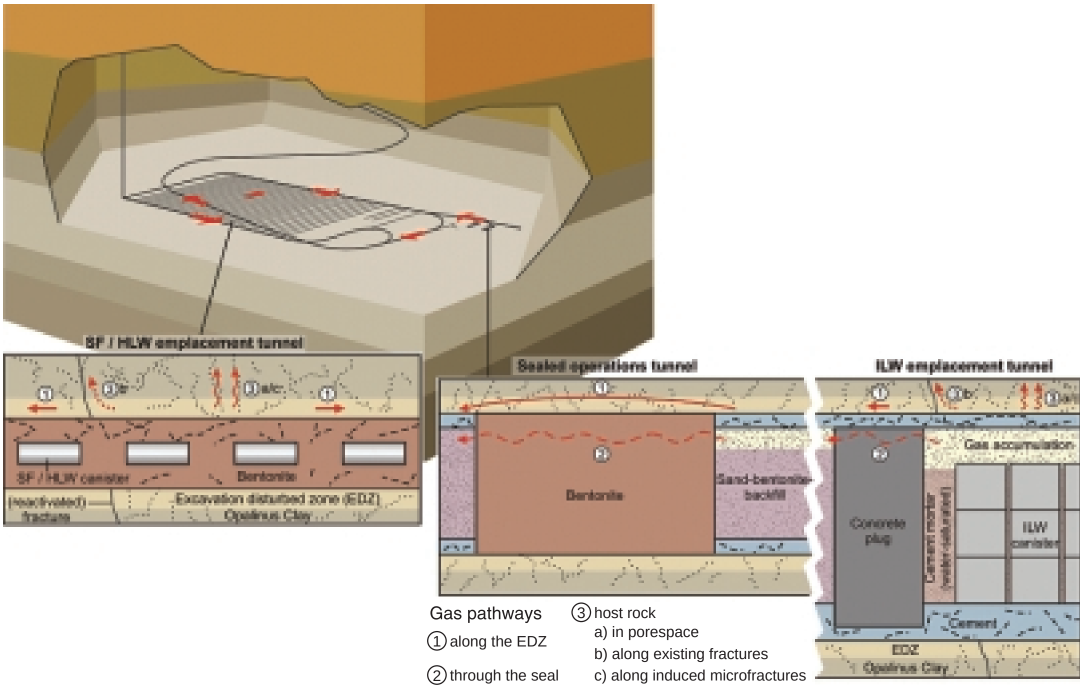

Figure 3

Geological isolation of radioactive waste in low-permeability host rock formations – Example of the Swiss concept of deep geological disposal in Opalinus Clay, for spent fuel (SF)/high-level and long-lived intermediate-level waste (HLW)/intermediate-level waste (ILW). The release of degradation and corrosion gases accumulated in the SF/HLW tunnels and ILW tunnels is a key issue in the assessment of long-term safety of the repository. Possible routes of gas escape are along the backfilled tunnels, through the microscopic pore space of the intact rock matrix and along existing/induced fractures (Nagra, 2004).

composition of fluid phases in the reservoir at given temperature T and pressure P) or for transport calculation (values of density, viscosity, interfacial tension). Most of the data available to constrain the models to be used are relevant to systems which contain only one acid gas constituent. In contrast, data are relatively scarce for mixtures (*e.g.*, CO_2 and H_2S). The concern about H_2S was raised because this gas, or a CO_2-H_2S mixture, is co-produced with natural gas in a number of large fields throughout the world. For both ecological and economic reasons oil companies increasingly want to reinject these constituents into the subsurface.

The contrast of transport properties between CO_2 gas and the other fluid phases can produce fingering effects, largely amplified by the sedimentary heterogeneity. To consider their influence on the solubilization of CO_2 in oil or in water is a real challenge for reservoir modelling. A correct appraisal of the dissolution timing in water is particularly important because as it dissolves the acid gas makes the aqueous solution aggressive with respect to the host-rock minerals. Depending on lithology the impact can be seen in the short term (Perkins *et al.*, 2003), or will only be noticed on long term (Holloway *et al.*, 2002). The occurrence of short time scale reactions, during gas injection, has to be evaluated with high accuracy since reactions can be strongly enhanced when coupled to water movement and mass transport, and because effects of these reactions on petrophysical and mechanical properties can have a considerable impact on injection.

Dissolution of minerals able to provide cations, and combination of these cations with bicarbonate to precipitate carbonate minerals, forms the basis of the popular "mineral trapping" concept (*e.g.*, Gunter *et al.*, 1997). In a favourable mineral environment this mechanism is likely to become really significant in terms of mass balance if the following conditions are met:

– the dissolved gas is efficiently transferred to "fresh", reactive rock, *e.g.*, by natural hydrodynamism;
– the precipitation kinetics are not too slow;
– the less soluble elements released by mineral dissolution, *e.g.*, Al from feldspar, can be accomodated in secondary solid phases. The possibility to form dawsonite, a carbonate mineral that contains Al, is particularly attractive as pointed out by Johnson *et al*. (2004). However, in geological sites where natural CO_2 has been abundant this mineral is not systematically reported.

As far as primary minerals are concerned, basalts and other mafic rocks are very good candidates for mineral trapping. Unfortunately, the hydraulic conductivity in such rocks is often much lower than in sandstones (Matter *et al.*, 2003; 2005).

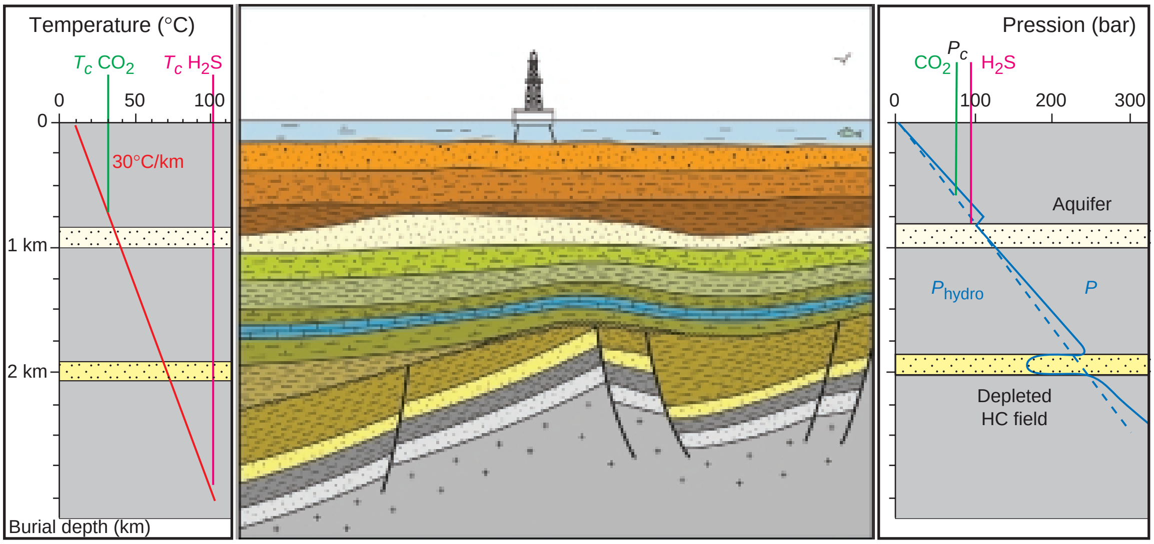

Figure 4

The concept of CO_2 storage in deep permeable reservoirs, either saline aquifers or depleted hydrocarbon fields. Critical temperature and pressure of pure CO_2 and H_2S, respectively, are indicated. Typical geothermal gradient and pressure gradient are reported. Geological conditions can be chosen in order to maximize storage capacity (dense fluid phase above critical point, average porosity value, etc.) and injectivity (average permeability value, etc.), and / or to minimize the injection cost (burial depth, etc.).

The need for huge reservoir capacities has a counterpart. The confining role is transferred to the cap rock and to the whole sedimentary cover (*e.g.*, Pacala, 2003). For a hydrocarbon field, especially if it contained some gas, a definite sealing efficiency does exist. In general this is much less certain for aquifers. In any case the specific properties of the fluids containing acid gas constituents, in particular the pH value of aqueous solutions, have to be considered to study the possible reactive transfers through cap rock. The risks of leakage created by the long-term alteration of cement in abandoned wells is an additional area of serious concern.

2.2 The Disposal of Nuclear Waste

The safe disposal of HLW can be achieved through a system of several natural and engineered (*e.g.*, glass matrix, metal canisters, bentonite) barriers. The latter should provide primary containment of the waste. It is therefore expected that most radioelements will decay to insignificant levels within these barriers. To favour further immobilization of radioelements, the main natural barrier will be the host-rock. It should be characterized by stable pH and Eh conditions at the location of disposal, and this over time periods of several ten thousands years and if possible geologic time periods. In case of waste leakage out of the repository, the natural natural barrier should also provide retardation and dilution of the contaminant plume. This should reduce the toxicity to a point where the impact is minimal when the plume reaches the biosphere.

The studies on deep geological disposal of HLW are concerned with the persistence of the confinement conditions over a long period of time in repository facilities. In almost all the concepts studied in the world, clay materials play an important role as a constituent of the engineered barriers and/or as host rock. A great deal of R&D activity is therefore focused on the long term behaviour and especially on the interactions between the different materials that will be used in repositories: clay, concrete, iron, steel (canisters and structures), and waste matrices (mainly spent fuel and vitrified wastes). These interactions are studied under various conditions which correspond to different stages in the life of the repository. An initial stage is when transient thermal-hydraulic-mechanical (THM) conditions will prevail and corresponding to the resaturation phase in the near field after emplacement of the canisters and closure of the repository. Crossed water and vapour flow under temperature gradients will occur during this stage. At the end of the resaturation phase, the temperature should have decreased close to the background value. Coupled geochemical interactions and transport will then dominate, leading to the gradual alteration of the different materials in the repository. Transient HM conditions may prevail during this stage due to the potential production of significant amounts of gases, *e.g.*, hydrogen from the corrosion of steel canisters. Specific problems are related to gas: overpressuring that can cause damage to barriers; release of volatile radionuclides such as ^{14}C and iodide. The ultimate stage starts after the failure of canisters, with the alteration of the waste matrices and the subsequent migration of radionuclides.

With this wide range of constitutive material types, THM conditions and the time scale to investigate in HLW repositories, the tools used to study these systems vary accordingly. Parametric laboratory experiments provide basic physical and chemical data for pertinent processes and one-to-one scale experiments in URL allow for an integration of these processes and for the understanding of couplings in realistic conditions. Natural and archeological analogues provide valuable, mostly qualitative, information on the long term behaviour and interactions between different materials. However, the latter are usually only relevant to sub-systems in the repository. Numerical modelling is used at all different scales and with different degrees of complexity either to study sub-systems or to look at the full-scale, including the various coupled system inherent to the repository. For instance, safety assessment calculations may be performed using a simple representation of the thermal-hydraulic-mechanical-chemical (THMC) processes but looking at the scale of the repository and with the complex geometry of galleries and tunnels. Performance assessment calculations may be conducted at the scale of the near-field (waste packages, engineered barrier systems and disturbed host-rock) to capture the long-term behaviour of the system using a sophisticated description of the phenomena.

Physical and chemical data are basically available for isolated phenomena and constitutive laws, but seldom found for coupled phenomena, *e.g.*, for THM behaviour of clay in undersaturated conditions with a possible alteration of the plastic properties of these materials; HMC behaviour of clay during hydrogen gas production with the creation of preferential pathways for transport, changing of porosity and permeability; corrosion of steel or concrete, and alteration of clay modifying its sorption capacity and mechanical properties (formation of iron-rich clay minerals); etc.

2.3 Common R&D Approaches for Addressing Gas-Water-Rock Interaction

Albeit different, the two types of storage both lead to complex interactions between fluid and mineral phases. Moreover, the behaviour of any storage site is heavily determined by the properties of the rocks and materials used for confinement. Common problems call for common approaches, either on the modelling side or on the experimental side.

The interaction between gas constituents, aqueous species and mineral phases involves a number of different parameters. The composition of rocks and fluids, the degree of openness of the system with respect to underground fluid flows (gas, water, possibly hydrocarbons) and, of course, the temperature and pressure of the site are the main determinants.

Effects and feedbacks include:
- changes in the composition of both minerals and fluids;
- modification of porosity, rock fabric, permeability;
- loss or gain in mechanical strength and in retention (sorption) properties.

The complexity and non-linearity of involved phenomena, the necessity of quantitative simulations and the risk assessment lead scientists to develop an approach that combines numerical models and laboratory experiments (up to a certain point, natural analogues can also provide information).

Among the problems that are currently met when using modelling approaches, which require additional experimental investigations, one can cite:
- the migration of gas and the occurrence of at least two fluid phases in the porous medium;
- the damage of engineered/geological barriers by gas overpressures, and the need for improved understanding of HM coupling;
- the expulsion of contaminated porewater from the reservoir, and the need to address completely multi-component mass tranfers;
- the gap between the reaction rates measured in the lab (*e.g.*, the dissolution of calcite) and observed in the field (*e.g.*, the formation of karst) (see for instance White and Brantley, 2003, and reference therein);
- the appraisal of reactive surface areas and the feedback of the reactions on the rock fabric;
- the choice of an appropriate model for mineral nucleation (Lasaga, 1998);
- the integration of sediment heterogeneity or fracture networks in reaction-transport modelling;
- the coupling between reactions, transport and mechanics;
- interactions between concrete, steel and clay.

3 A BRIEF PRESENTATION OF THE ARTICLES

We now briefly introduce the rationale that governed the organization of the volume. A first set of articles, grouped in this issue, strongly relies on observation. They provide descriptions of systems, either natural or experimental, from which the effects of reactions between gas, water and minerals can be depicted. Four papers, [1-4], concern natural systems where acid gas is involved. The two following ones, [5, 6], characterize the confining properties of clay-rich sediment or material. Finally, the papers [7-10] provide data on experiments that reproduce situations likely to occur in acid gas storage, or relevant in this context.

1 **Franz May** takes the mineral composition of wallrocks and the chemistry of CO_2-rich mineral waters, characterized from fractured rocks of the Rhenish Massif (Germany), as indicative of water-CO_2-rock interaction processes, and as constraints to evaluate the results of geochemical modelling.

2 **Stuart Haszeldine *et al.*** show the interest of studying natural CO_2 (palaeo-) accumulations, for instance those of the Colorado Plateau (United States) that form nice outcrops, because they give constraints on the by-products of interaction on appropriate time and space scales. Geochemical modelling should consider such constraints.

3 **Hans Machel** depicts a type of hydrocarbon pool overpressured and hydrodynamically isolated, rich in H_2S and CO_2. These are present for example in the Nisku Formation (Alberta, Canada). Once depleted, they offer a strong sealing capacity for the injection and the long-term disposal of acid gas (see Gunter *et al*., 2005, for an approach of the mineral trapping in this context).

4 **François Roure *et al.*** address a variety of mineral-water reactions in the natural context of thrust belts (Albania, Canada, Columbia, Mexico, Pakistan, Venezuela). Some of them concern sour gas (thermo-sulphate reduction).

A reliable long-term confinement of the substances trapped is the main property sought in underground disposal. As mentioned above, clay has a distinguished position, either in the engineered barriers used in the repositories of radioactive waste, or in the geological barriers.

5 **Michel Jullien *et al.*** describe the various mechanisms that operate during gas-water-rock interaction in clay-rich sediment or material, and what observations, experiments, specific analytical techniques and modelling tools are available to characterize the relevant parameters and behaviours.

6 **Paul Marschall *et al***. review the transport properties of non-wetting and partially soluble gas through water-saturated claystone. They present in particular the Opalinus Clay considered in Switzerland as a possible host rock for nuclear waste. It is a formation in which clay minerals represent more than 50% of the rock matrix. Porosity, intrinsic permeability and gas entry pressure can be evaluated experimentally or from field tests. The behaviour of the formation with respect to transport depends on these properties, and also on the mechanical situation created by the stress field and the tensile strength of the rock.

7 **Christos Tsakiroglou *et al***. illustrate how a pore network can help to understand what governing parameters determine the prevailing flow-regime pattern in a situation where two fluids of very different density, such as CO_2 and brine, mix together in a heterogeneous porous medium.

8 **Keith Bateman *et al*.** achieved a long-term (7.5 months) column experiment in which the sand of the Utsira Formation (North Sea), host reservoir of the carbon dioxide injected at the Sleipner site since 1996 (*e.g.*, Torp and Gale, 2003), was percolated by an equivalent of the Utsira pore water equilibrated with CO_2 at 100 bar pressure. Post-experiment petrography serves as a basis of discussion of the results obtained using a reaction-transport model.

9 **Catherine Noiriel *et al***. describe a plug-flow experiment designed to capture the evolution of the porous medium, observed in three dimension at the high resolution allowed by non destructive synchrotron microtomography. This experiment was also conceived to test the application of reaction-transport modelling (see below).

10 **Nicolas Jacquemet *et al***. adapted the technique of synthetic fluid inclusions to disentangle the complex interactions that occur in the systems CO_2-H_2S-brine-cement-steel. Many observations can be drawn from such experiments, which are relevant to the understanding of well bore integrity in the context of acid gas trapping.

The thirteen remaining papers, grouped in issue 2 of 2005, of *Oil & Gas Science and Technology – Revue de l'Institut Français du Pétrole* are more oriented towards modelling. The development of simulation software codes, particularly those which integrate complex couplings between phenomena, is a time-consuming job. It needs the long-term converging efforts of various talents and disciplines (geochemistry, thermodynamics, petrophysics, applied mathematics, informatics, etc.) to meet the real demands of industrial applications. Unfortunately, very few organizations—if any—manage to perform this effort with the required stable task force. Another aspect is that the more numerically efficient a computation code is for addressing strong couplings on large and heterogenous grid blocks, the more difficult it is to modify. These facts have several consequences. First, the availability of modelling tools able to capture reaction-transport problems in the context of at least two fluid phases (gas and aqueous solution) is only emerging today, and, to our knowledge, there is no existing software accounting for coupled interaction between polyphasic flow, heterogenous reactions and mechanics. Secondly, a numerical code cannot be specifically elaborated for any new problem. A version of a code is developed with the perspective of being used in a relatively broad range of situations. In doing so, a certain amount of simplification and empirism is considered. A striking example is the way rock-fabric structure and evolution are represented by reaction-transport codes. The users have to consider these limitations and to define the appropriate calibrations that can make a model applicable to a given context.

In the second set of articles a first group, [11-14], use existing numerical models, in particular geochemical software, to understand natural behaviours or to evaluate storage performance. Paper [15] combines the two aspects. A second group of articles, [16-18], focuses on the question of model calibration, or validation, that can be drawn from well defined experiments. Finally, papers [19-23] present new or improved modelling tools from a very large range of topics, from liquid-vapour equilibria to more prospective future *ab initio* molecular calculations, through activity corrections, coupling between chemistry and mechanics, and solid solutions.

11 Carole Frima *et al.* rely on a reaction-transport code to extrapolate an experimental rate law of calcite growth to natural systems. The model is applied to evaluate the delay of fracture sealing in veins related to an active normal fault in the Gulf of Corinth (Greece).

The two following papers address the question of mineral trapping in the context of CO_2 storage in aquifers.

12 Vincent Lagneau *et al.* applied a reaction-transport code to the simulation of long-term reservoir evolution, either in a carbonate reservoir (Dogger of the Paris Basin), or in an arkosic sandstone (Bunter of the North Sea). They show the striking difference between the two types of lithology, but also the difficulty to predict accurately the long-term behaviour of the storage.

13 Naoko Zwingmann *et al.* estimate from geochemical software that the potential of mineral trapping in a sandstone rich in volcanogenic fragments could be large (Haizume formation of the Niigata Basin, Japan).

In both cases the modelling results are useful indications to go further, *i.e.*, to improve the modelling tool, or to perform experiments. Finally,

14 Marcelo Ketzer *et al.* define an approach to CO_2 confinement in a mature oilfield (Forties, North Sea), based on basin modelling simulations constrained by available data on the hydraulic regimes.

15 Laurent Richard *et al.* elaborated a thermodynamic model that correctly accounts for high partial pressures of H_2S generated by thermochemical sulfate reduction in carbonate reservoirs. The model is applied to predict a possible sink of sulfur in the context of H_2S sequestration.

16 Étienne Brosse *et al.* applied a reaction-transport code to simulate the experiments presented by C. Noiriel *et al.* (see above). They discuss the problem of estimating a reactive surface area of the rock when use is made of a mineral rate law that depends on mineral surface.

17 Laurent Trotignon *et al.* use reaction-transport modelling to define an experiment in which transport, mineral reactions and correlative petrophysical evolution should be strongly coupled and should progress rapid enough to allow observations on a reasonable time scale. Such an experiment would constitute an invaluable validation test for a model.

18 Bruno Lecerf *et al.* present a method that allows the calibration of a reaction-transport model from few experiments performed on well-chosen samples, in the specific context of sandstone acidizing treatments. Once calibrated, the model can be successfully applied to reservoirs for which the samples are relevant.

19 Dubessy *et al.* built a model that calculates the liquid-vapor equilibrium and the solubility of gas in brine, in the context of acid gas storage (either CO_2 or H_2S).

20 Kervévan *et al.* evaluate the effect of the various correction terms that have to be introduced in a thermodynamic model to correctly account for gas-brine equilibria in a large range of T, P and salinity values. They show an application of the model to a scenario of CO_2 injection in the Smackover Formation (Gulf Coast, United States).

21 Renard *et al.* present a new numerical model that is able to calculate the effects of pervasive pressure solution creep in limestones where CO_2 is injected. Such a model, which has the potential to be compared to natural situations or calibrated by experiments, shows a significant enhancement of the pressure-solution process in presence of high partial pressures of the acid gas.

22 Nourtier *et al.* improved an existing geochemical code by the implementation of a new model able to kinetically precipitate solid solutions. For studies of CO_2 mineral trapping such a model, provided thermodynamic data are available, can have a great interest.

And finally,

23 Toulhoat *et al.* review several recent performances of the density functional theory (DFT), a particular *ab initio* method, in accurately predicting a variety of thermodynamic properties of minerals.

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3 H.G. Machel. Geological and Hydrogeological Evaluation of the Nisku Q-Pool in Alberta, Canada, for H_2S and/or CO_2 Storage.

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