SANS/VSANS investigation of porosity microstructure in rocks from a natural CO_2 reservoir.

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Carbon capture and storage (CCS) is considered a valid option to reduce the CO_2 concentration in atmosphere. The gas is collected from industrial plants, then injected and stored underground in geological reservoir. A very wide range of information about chemical-physical characteristics of the sequestration site is therefore needed and, among them, data on porosity microstructure are crucial. Part of the processes which affect microporosity and act during and after the rocks formation can be reconstructed by studying the micro-porosity features. We have therefore performed a couple of SANS and VSANS experiments on rocks coming from a CO_2 reservoir (which represents a natural analogue of a CCS site) in order to define the role and the possible effects of CO_2 alteration in determining the micro-porosity and to check the sealing potential of rocks overlying the reservoir, which act as a barrier with respect to CO_2-rich gas. The collected data are expected to be beneficial for developing theoretical model about the effects of CO_2 sequestration in deep geological reservoirs.

Introduction

Sequestration of CO_2 in deep geological reservoirs represents one of the potential methods to reduce anthropogenic emissions into the atmosphere. In the long term, the injected fluid dissolves into the local formation of rocks and, when present, in saline deep aquifers, participating to a variety of geochemical reactions. The overall impact of these processes produces changes in mineralogy, texture, permeability and porous structure of the rocks, to a level which depends on the different lithology of the rocks. These changes can be investigated by considering what occurs in rocks with natural CO_2 accumulations, as analogues for geological sequestration. Also, computer simulations based on thermodynamics, kinetics and geochemical modelling can be beneficial. On the other hand, reliable data concerning the porous structure, which is so important to trap CO_2, can be hardly extracted from computer simulations. Here the preliminary results of a SANS and VSANS investigation on rocks pertaining to a geological context (located in Eastern Tuscany, Central Italy) characterized by the presence of a deep gas reservoir are presented. The reservoir was intercepted at ~3,700 m depth by a bore-well drilled in the eighties and is presently hosting supercritical CO_2 (calculated density ~860 kg/m3) at the estimated pressure and temperature of 670 bars and 120 °C. Texture and mineralogy of volcanic rocks samples, from drill cores located into the reservoir in the 3,864 to 3,871 m depth range, were found heavily modified by the interaction with CO_2-rich fluids [1].

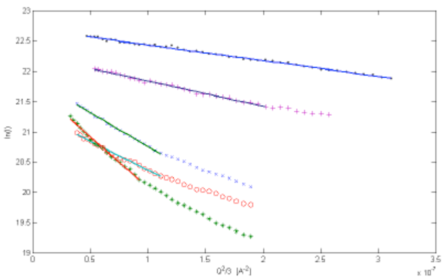

Figure 1: Guinier-like plots on some of the TPA data (λ = 12 Å): Burano rocks (•), Volcanic rocks IG1(+) and IG3 (o) not affected by CO_2, and Volcanic rocks 3864 (x) and 3870 (*) from the bore-well, therefore affected by CO_2. Straight lines represent the linear fit results. Statistical uncertainties are within the size of the symbols.

Experimental Settings

SANS experiments on sedimentary, volcanic and metamorphic rocks have been reported since late eighties (e.g. [2],[3] and [4]). This non-destructive method was proven to be a powerful tool for getting information about porosity microstructure in rocks (e.g. dimension, distribution and shape of pores, see [5] and references therein). We have carried out two neutron scattering experiments: the first one using the PAXE diffractometer and the second one with the VSANS (Very Small Angle Neutron Scattering) TPA diffractometer. The two experiments covered globally the ~ $6 \cdot 10^{-4}$ to ~ $3 \cdot 10^{-1}$ Å^{-1} Q range, which in direct *d*-space means from ~ 1 µm to ~ 4 nm. Samples of rocks from the reservoir and a selection of possible analogues of the same volcanic rocks, unaffected by CO_2 presence, were chosen for the experiments together with rocks, from outcrops, corresponding to the geological layers immediately overlying the reservoir. These samples are representative of different volcanic rocks and of sedimentary rocks bearing gypsum, dolomite, calcite. Samples have been thinned down to 2 and 5 mm thick slices; also, the sample corresponding to 3,870 m depth was cut in 5 different slices from 0.7 to 5 mm thickness, respectively. Indeed, previous studies [4] showed evidence that, depending on the wavelength, for thicknesses larger than 2 mm and for Q values smaller than 10^{-3} Å^{-1} the effect of multiple scattering (MS) can be of some relevance.

Experimental Results and Discussion

In this work we address two questions: a) which is the average pore size and b) which are the fractal dimensions shown by the selected rocks. For point a) the average pore size has been evaluated on samples with 2 mm thickness looking at the lower Q-range investigated with TPA (λ = 12 Å) and applying to the data a Guinier-like model

$ln(I) = AQ^2 + B$, where I is the detected intensity as a function of the wavevector Q. Some of the resulting curves are shown in Fig. 1. The radius of the assumed spherical pores, related to the A coefficient, comes out to be roughly between 3300 and 4100 Å with a 0.1% uncertainty for the volcanic rocks samples of the bore-well, while is significantly smaller, *i.e.* approximately between 2000 and 3100 Å (± 0.1 %) for the possible analogues of the same volcanic rocks coming from outcrops and therefore believed not affected by CO_2. Moreover, it is worth mentioning that the radius for the Burano samples comes out to be by far the smaller, being roughly 1600 Å, so confirming the sealing role of those rocks overlying the reservoir. Concerning point b), if the data are modeled with a generalized Porod behaviour, *i.e.* with a power law $I(Q) = I_1Q^{-x} + B$, from the exponent x the fractal dimension D_s for surface ($3 < x < 4$, with $D_s = 6-x$) or D_m for mass/volume ($2 < x < 3$, with $D_m = x$) can be derived [6]. We have applied this approach to the PAXE data (λ = 7.8 Å) in the 1.13-5.58·10^{-2} Å^{-1} range. Some of the results curves are displayed in Tab. 1. The values of D_s for the CO_2 altered volcanic rocks lay in a wide range from 2.11±0.03 (depth 3,864 m) to 2.76±0.05 (depth 3,870 m), showing differences of more than 30%. A similar dispersion of values is also present in the bulk chemical (ICP-MS analysis) and mineralogical composition (XRD Rietveld refinement) of the investigated rocks. Both chemistry and mineralogical assemblage are consistently different from sample to sample, although they pertain to a contiguous drill core which is less than 10 meters long. In contrast, the D_S values relative to the analogue volcanic rocks, unaffected by CO_2 alteration, are confined between 2.33±0.04 and 2.52±0.04, although these rocks come from different geological context. In the bore-well rocks the very different chemical and mineralogical composition and the wide range of D_s values found, can be interpreted considering that chemical alteration due to CO_2-rich fluids proceeded not homogenously, likely due to the circulation of fluids in preferential paths. Moreover, it is worth mentioning that, for those rocks, there is a direct correlation between the radius of gyration and the D_s, i.e. higher values of surface fractal dimension are associated with larger pores sizes.

Table 1: Surface fractal dimension Ds from a generalized Porod law applied to some of the PAXE data (λ = 7.8 Å).

Sample ID	D_s
Rocks not affected by CO_2	
Burano	2.41± 0.09
IG1	2.36± 0.05
IG3	2.52± 0.04
IG2	2.33± 0.04
Rocks affected by CO_2	
3864	2.11± 0.03
3866	2.13± 0.06
3867	2.45± 0.05
3868	2.34± 0.05
3870	2.76± 0.05
3871	2.63± 0.05

Conclusions

Several experimental approaches have been combined to get microscopic information on porosity and fractal features of rocks coming from a natural CO_2 reservoir as compared to similar rocks not affected by CO_2. Among these approaches, the VSANS experiment allowed a preliminary determination of the average pore sizes, with indications of possible effects due to the CO_2 presence. Work is still in progress to deepen the analysis so that the shape of the pores can be evaluated and also a quantitative assessment of the porosity can be achieved. The SANS results about the surface fractal properties indicate a dispersion of the fractal dimensions for the bore-well rocks significantly larger than for the values found in rocks not affected by CO_2 presence. This confirms the results of chemical and mineralogical analysis, which give clear indications that chemical alteration due to CO_2-rich fluids has affected the rocks along the paths chosen preferentially by those fluids. The collected data are expected to provide some help for developing theoretical model about the effects of CO_2 sequestration in deep geological reservoirs.

References

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