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Preliminary Assessment of Tuff as CO_2 Sorbent

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Abstract

The removal of carbon dioxide from flue gases can be achieved through adsorption separation technologies. In this framework, zeolites have shown promising results for the separation of CO_2 from gas mixtures and can potentially be used for both TSA/PSA processes. In particular, natural zeolites are inexpensive and can be viable sorbents. The aim of this work is the characterization of a non-synthetic tuff zeolite that could be used as carbon dioxide adsorbent. In order to assess changes in its structural and gas adsorption properties, the tuff was treated with acid solutions. Both the natural and acid treated samples were fully characterized from a chemico-physical point of view: pore size distribution, specific surface, SEM and XRD analyses were performed. The CO_2 adsorption capacity of the samples was measured in a lab-scale fixed bed reactor. Breakthrough curves were determined at a fixed flow rate (15Nl/h) using mixtures of CO_2 and N_2 with different CO_2 concentrations (5-20%vol.). Then, the adsorption isotherms were obtained from experimental data. The experimental results show that tuff, in particular if properly pre-treated, is a promising alternative to synthetic zeolites in adsorption processes for CO_2 removal.

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Keywords: CCS; CO_2 adsorption; natural zeolites; tuff.

1. Introduction

Among all the CCS strategies, post-combustion capture provides a near-term solution for stationary fossil fuel-fired power plants, eliminating the need for substantial modifications to existing combustion processes and facilities

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[1,2]. In this respect, adsorption using solid sorbents has the potential, in terms of energy saving, to complement or replace the current absorption technology [3].

In the design of an adsorption based separation process, the choice of the adsorbent is one of the most crucial design consideration [4]. Indeed, the sorbent should be convenient from the economic point of view but versatile in post-combustion conditions (i.e. low CO_2 partial pressure). Furthermore, the concerns for safe handling and disposal of the exhausted material are relevant for the operating costs of the process. A number of materials have been proposed for carbon dioxide adsorption at low temperature: activated carbons, zeolites [5]: geopolymers [6], metal organic frameworks [7], organic polymers [8].

Synthetic zeolites, commonly used in different gas adsorption applications, are generally characterized by excellent performance in terms of CO_2 adsorption [9]. However, cost and environmental footprint represent a negative contribute to their sustainability. On the contrary, natural zeolites contained in tuff show very interesting selective adsorption properties, associated with its availability in regions, as central Italy. Zeolite tuffs, more specifically, are rocks which contain, besides zeolites, various other crystalline or amorphous phases [10]. One parameter that is especially important in determining the nature of both the formed zeolites and the secondary phases is the silicon content of the original rock [10]. The overall mineralogical composition may vary greatly even in the single deposit, especially in the contents of the various phases, less as regards their nature [10]. Such an inconstancy is ascribable to the chemical and mineralogical heterogeneity of the parent volcanic rocks and also to the different mechanisms of zeolite genesis [10].

In this research, a tuff natural zeolite was studied. In order to assess changes in its structural and gas adsorption properties, the sample was treated with HCl acid solution. Structural and thermal characterization of natural and acid treated tuff samples were carried out using a combination of techniques: X-ray diffraction, BET, porosimetric and SEM analyses. The CO_2 adsorption capacity of the samples was evaluated in a lab-scale fixed bed reactor. All the tests were performed at ambient temperature and pressure with values of CO_2 concentration typical of flue gases (5–20 vol.%). Breakthrough curves were worked out in order to obtain the adsorption isotherms.

2. Experimental

2.1. Materials chemico-physical characterization

A natural yellow tuff from Campania (I) region was used as adsorbent material. First, the sample was crushed and sieved to obtain 250-400 and 400-600 μm fractions. In order to assess the influence of acid treatment on tuff for CO_2 removal, the sample was treated with HCl acid in the following way. The tuff sample was modified by using 100 ml of HCl solution (0.1M) at room temperature for 2 hours. During this mild acid treatment there was no evidence of gas release (e.g. CO_2 from carbonates). After the acid treatment, the sample has been separated and washed with distilled water several times until the filtrate was free from chloride ions and then dried in hoven at 110 °C. Before the experimental procedure, all samples were dried in an oven at 150°C for 24 h and stored in a desiccator.

Prior to the study of CO_2 adsorption, the structural and thermal properties of natural tuff and that of the acid modified form were determined by using XRD, SEM and N_2 adsorption techniques.

In particular, identification of mineral components in the tuff was performed using XRD technique and the XRD diffractograms were obtained with a Bruker D8 Advance powder diffractometer with Cu Kα radiation.

Scanning Electron Microscopy (SEM) analysis was performed with an instrument FEI Quanta 200 (FEI Co., USA), in order to obtain information on the morphology of the samples. Chemical composition of the sorbents was also determined by means of Energy-Dispersive X-ray Spectroscopy (EDS) using an automated analysis system, installed on the SEM instrument.

The BET specific surface areas of the samples were measured by N_2 adsorption at 77 K by using a Quantachrome Autosorb 1-C. The samples were outgassed under vacuum at 150°C before the analysis. Adsorption/desorption data were processed in accordance with the BJH model to evaluate the pore size distribution and volume. This adsorption model provided the best fitting (fitting error < 0.5%) assuming slit pores.