



Ion-exchange in natural zeolite stilbite and significance in defluoridation ability



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ABSTRACT

A preliminary inspection of natural zeolites samples in the north east of Ethiopia showed a large deposit of highly pure stilbite (hereafter called [CaNa]-STI). Rietveld refinement of synchrotron powder diffraction data ($C2/m$, $a = 13.62(1) \text{ \AA}$, $b = 18.2563(1) \text{ \AA}$, $c = 11.28(1) \text{ \AA}$, $\beta = 127.8(2)^\circ$) has shown that both Ca^{2+} and Na^+ ions reside at the intersection of the ten- and eight-ring channels, and are completely surrounded by H_2O molecules that make close contacts with the zeolite framework. Therefore, no coordination of the cations with framework oxygen atoms is observed. In an attempt to improve the defluoridation capacity, [CaNa]-STI was subjected to a NH_4^+ and subsequent Ca^{2+} ion-exchange treatment. Analysis of the diffraction pattern of the [Ca-NH₄]-STI sample revealed the presence of a mixture of crystals with monoclinic and orthorhombic symmetry. This double-exchange treatment notably improved the ability of this material to remove fluoride from water, what is probably related to the formation of connectivity defects that are generated during the exchange treatments.

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1. Introduction

In Ethiopia zeolites are a vast natural resource that remains unexploited because there is a lack of scientific knowledge, available manpower with a geology background and the means to initiate the systematic exploitation of this resource. Previous studies showed abundant resources of mordenite and clinoptilolite near Nazret [1] and of phillipsite and clinoptilolite in the Awassa area [2]. In our attempt to survey the deposits in the north region of the country, several samples have been studied and at least one large and highly-pure deposit of stilbite has been identified in the Hashenge basalt formation, in the locality of Hashenge, Tigray region [3]. However, despite this preliminary survey, a more systematic study of occurrence in the zeolite-abundant areas in Ethiopia has to be carried out, and a critical analysis of the available geological data performed.

Natural zeolites are of volcanic origin and belong to the family of hydrated aluminosilicates. Their microporous structures can accommodate a wide variety of cations such as sodium, potassium

and magnesium. These cations can be exchanged easily by others and this is one of the main applications of these minerals: ionic exchange. Some of the main applications of zeolites in this area include the selective treatment of sewage water, the extraction of ammonia, odor control, heavy metal extraction from nuclear, mining and industrial waste, soil conditioning for agricultural use and even as an additive to animal feed stock [4]. Among these applications of natural zeolites, our focus has been on the ability of natural zeolites in Ethiopia to eliminate fluoride from drinking water [5].

In the course of our work, we investigated the ion-exchange capacity of stilbite in order to build an efficient adsorbent for fluoride [6]. The XRD pattern of the mineral sample reported in this manuscript showed that it belongs to the stilbite family, with the STI framework type [7]. This family consists of three minerals with the same framework topology, but different extraframework cation compositions and symmetries: barrerite, stellerite and stilbite. The framework of stilbite (STI framework type) has two kinds of interconnecting channels, 10-ring channels running parallel to the [100] direction and a smaller 8-ring channels along the [101] direction. A cavity, which also contains 5-rings and 4-rings, is formed at the intersection of these channels [7].

The dehydration of stilbite has been studied in detail, because it is thought to involve a partial collapse of the framework as a result

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of the approach of the strongly polarizing extra-framework cations to the zeolite walls and the fragility of the framework in particular planes [8]. Early attempts to stabilize the stilbite structure involved the investigation of the stabilizing effect of cations on the crystal structure [9]. In the present work, we aim to evaluate the ion exchange capacity of the STI-type zeolite from Ethiopia in order to assess its suitability for application. In an attempt to understand the mobility of the Na^+ and Ca^{2+} ions, the location of the cations before and after ion exchange were studied. We are especially interested in the potential use of this mineral as a cheap and locally available fluoride adsorbent, because the occurrence of groundwater containing high concentrations of fluoride is extensive in Ethiopia and is an endemic problem that needs to be tackled urgently. Prolonged uptake of water with concentrations higher than 1.5 mg/L can lead to dental, or in its most severe form, skeletal fluorosis, and therefore the World Health Organization recommends the reduction of fluoride in drinking water to levels below 1.5 mg/L [10,11]. Existing defluoridation technologies include precipitation-coagulation, membrane-based processes, ion-exchange methods, and adsorption methods. Of these, adsorption is the preferred technique, because of its low cost, ease of operation, high efficiency, easy accessibility and environmental benignity, and because adsorbents can in principle be reused and recycled. Despite the great ion exchange properties of zeolites, very few reports deal with its application in defluoridation. Onyango et al. incorporated trivalent cations, Al^{3+} and La^{3+} , giving place to active sites for the removal of fluoride [12]. Defluoridation was found to be higher for the Al-treated zeolite since in this case F^- was observed to be removed by chemical adsorption. Other studies have also shown that similar exchanges with multivalent cations Zr^{4+} , Fe^{3+} or Ca^{2+} , result in an increased defluoridation capacity of the zeolites [13–17]. These studies show that zeolites can be effectively used for the removal of fluoride, especially if subjected to suitable pre-treatments. Therefore, the final purpose of our work is to test the potential of natural zeolites for removing fluoride from groundwater to provide a cheap and locally available fluoride mitigation solution.

2. Experimental

The stilbite sample was collected in the Hashenge basalt formation, in the locality of Hashenge, Tigray, Ethiopia, by the Earth Science Department at Addis Ababa University [3]. Raw zeolite samples were grounded with a disc mill and sieved to an average particle size between 75 μm and 105 μm for ion exchange and defluoridation studies.

The sample underwent different treatments to exchange extra-framework cations with NH_4 ions. A 1 M solution of NH_4Cl was prepared; the zeolite sample was then added to the solution in a 1(g)/10(ml) ratio, and the mixture was stirred under reflux (95 °C) for 16 h (sample $[\text{NH}_4]\text{-STI}$). We then studied a further ion-exchange of the $[\text{NH}_4]\text{-STI}$ sample with Ca ions, in order to have a fully exchanged Ca-stilbite zeolite (Ca- $\text{NH}_4\text{-STI}$). The ion-exchange was carried out in the same conditions as before, with a 1 M CaCl_2 solution (1 g/10 ml) at 95 °C for 16 h. In order to remove all possible Ca ions from the surface, the Ca-exchanged sample was thoroughly washed with deionized water until no Ca was observed in the water after washing ($[\text{Ca}]_{\text{water}} = 10^{-5}$ M). Finally, a direct ion-exchange with Ca ions, without going through the intermediate NH_4 exchange (Ca-direct-STI), was carried out under the same conditions (1 M CaCl_2 at 95 °C), again taking special care in washing the sample thoroughly to remove the surface Ca (final Ca concentration of 10^{-6} M).

The nature of the crystalline phases was determined from X-ray diffraction data (PANalytical X'Pert PRO-MPD diffractometer, $\text{CuK}\alpha$

radiation). The composition of the samples was determined by ICP-AES in an ICP Winlab Optima 3300 DV Perkin–Elmer spectrometer. The N content of the samples was determined by elemental analysis with a Perkin–Elmer 2400 CHN analyser. The crystal morphology of the samples was determined by scanning electron microscopy (JEOL JSM 6400 Philips XL30 electron microscope, operating at 20 kV). For the structure analysis, powder diffraction data were collected on the Materials Science–Powder X04SA Beamline at the Swiss Light Source (SLS) at Paul Scherrer Institut in Villigen, Switzerland [18]. Data collection details are given in Table 1. The Rietveld refinement was performed using the program package XRS-82 [19], and the structure drawings were produced using the program CrystalMaker [20]. The plots with observed, calculated and differences patterns were prepared with the programme ppp13 [21]. Throughout the rest of the manuscript, water oxygen atoms will be referred to as O_w to distinguish them from framework oxygen atoms.

Defluoridation experiments were carried out at room temperature (~ 23 °C), with a contact time of 20 h under continuous agitation. The concentration of fluoride in the initial solution and after equilibrium upon the addition of the adsorbent was measured by the Ion Selective Electrode technique with a pH&Ion-meter GLP 22 CRYSON.

3. Results

3.1. CaNa-STI X-ray powder diffraction

The diffraction pattern of the original CaNa-STI sample corresponds to the stilbite family of zeolite minerals (Fig. 1). There are three distinct minerals in the stilbite group which share the same framework topology (STI [7]) but differ in the space group and chemical composition: barrerite (orthorhombic *Amma*, $\text{Na}_8(\text{Al}_8\text{Si}_{28}\text{O}_{72})\cdot 26\text{H}_2\text{O}$), stilbite (monoclinic *C2/m*, $\text{NaCa}_4(\text{Al}_9\text{Si}_{27}\text{O}_{72})\cdot 30\text{H}_2\text{O}$) and stellerite (orthorhombic *Fmmm*, $\text{Ca}_4(\text{Al}_8\text{Si}_{28}\text{O}_{72})\cdot 28\text{H}_2\text{O}$). Barrerite and stellerite are the sodium- and calcium-rich members of the family, respectively, while stilbite contains both types of cations, whose content can vary over a large range. The symmetry of the various zeolites of the stilbite group is related to the number of cations per unit cell. The three types of minerals can be easily differentiated by chemical analysis and X-ray diffraction. Orthorhombic and monoclinic phases can be differentiated from the positions of their reflections [22]. The diffraction pattern of sample CaNa-STI can be indexed in a monoclinic unit cell. No peaks corresponding to an orthorhombic phase are observed in this pattern (see inset of Fig. 1).

3.2. CaNa-STI composition studies: ICP and SEM–EDX

Stilbite samples contain Si and Al as tetrahedral framework atoms, and mono- and divalent cations as extraframework cations that compensate for the negative charge introduced by the

Table 1
X-ray data collection parameters for CaNa-STI and Ca-STI samples.

Synchrotron facility	SLS
Beamline	Material science
Diffraction geometry	Debye–Scherrer
Detector	Mythen II Si microstrip
Monochromator	Si 111
Wavelength	1.000 Å
Sample	Rotating 0.3 mm capillary
Nominal step size	0.004°2 θ
Detector positions	4
Time per pattern	10 s
2 θ range	6.0–80°2 θ

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