Ion exchange equilibrium and structural changes in clinoptilolite irradiated with β- and γ-radiation: Monovalent cations

DANIEL MORAETIS,* GEORGE E. CHRISTIDIS, AND VASILIOS PERDIKATSIS

Department of Mineral Resources Engineering, Technical University of Crete, 73100, Chania, Greece

ABSTRACT

Thermodynamic calculations of ion-exchange reactions were applied for clinoptilolite in a natural state and after irradiation with three doses of β-radiation \((10^{12}, 10^{15}, 3 \times 10^{16} \text{ e/cm}^2)\) and γ-radiation \((70 \text{ Mrad})\). Samples were equilibrated with binary systems of \(K^+ \leftrightarrow Na^+\) and \(Cs^+ \leftrightarrow Na^+\) at 25°C and a total normality of 0.025 \(N\). Selectivity for K was not affected after β-radiation with doses of \(10^{12}\) and \(10^{15} \text{ e/cm}^2\) \((\Delta G^\circ = -6.37 \text{ kJ/equiv}, \ln K\alpha = 2.58\) for the original clinoptilolite), whereas it increased considerably after 70 Mrad of γ-radiation \((\Delta G^\circ = -7.88 \text{ kJ/equiv}, \ln K\alpha = 3.18)\). Selectivity for Cs\(^+\) increased for the clinoptilolite irradiated with β-radiation \((10^{12}, 10^{15}, 3 \times 10^{16} \text{ e/cm}^2)\) and γ-radiation \((70 \text{ Mrad})\). \(\Delta G^\circ\) and \(\ln K\alpha\) for original sample and Cs\(^+\) \(\leftrightarrow Na^+\) were \(-7.33 \text{ kJ/equiv and} 2.96\), respectively. Irradiated samples with β-radiation \(10^{12}, 10^{15}, 3 \times 10^{16} \text{ e/cm}^2\) and 70 Mrad γ-radiation yielded \(\Delta G^\circ\) and \(\ln K\alpha\) for original sample and Cs\(^+\) \(\leftrightarrow Na^+\) were \(-7.88 \text{ kJ/equiv and} 3.18\), respectively. Remarkable amorphization of clinoptilolite was observed after exposure at the highest dose of β-radiation \((3 \times 10^{16} \text{ e/cm}^2)\) with a concomitant decrease in cation-exchange capacity (CEC). Crystallographic parameters and especially exchangeable cation site coordinates were refined for all samples with the Rietveld method. Cesium-saturated samples exhibited changes in the cation sites Cs2 and Cs3, which are next to clinoptilolite channel walls with lower Al\(^3+\) for Si\(^4+\) substitution. The observed changes include a shift in cation sites Cs2 and Cs3 toward channel walls and occupancy decrease in site Cs2.

Keywords: Clinoptilolite, ion exchange, β-radiation, γ-radiation, thermodynamics, Rietveld refinement

INTRODUCTION

Clinoptilolite, a HEU-type zeolite, occurs in various geological environments and forms mainly by alteration of volcanic glass, biogenic silica, and clay minerals (Hay 1977; Gottardi 1989; Hay and Sheppard 2001). The ion exchange properties of clinoptilolite have been thoroughly studied in the past by numerous researchers (Ames 1960; Loizidou 1982; Loizidou and Townsend 1987; Pabalan 1994, among others). The ion-exchange properties of zeolites are utilized in environmental applications such as the removal of NH\(_3\) from municipal wastewater, the removal of heavy metals mainly from industrial processes (Zamzow et al. 1990; Inglezakis et al. 2004; Petrus and Warchol et al. 2005; Melamed and Benvindo da Luz 2006), or other processes such as the removal and recovery of \(p\)-phenylenediamines developing compounds from photofinishing lab-wastewater (Vlessidis et al. 2001). In addition, the nuclear industry has invested time and financial resources to solve the problem of nuclear wastewater treatment (treatment of low- and high-level effluents). In the past, several workers have demonstrated the ion-exchange selectivity of clinoptilolite for the removal of radioactive elements like \(^{137}\)Cs from aqueous solutions (Mercer and Ames 1978; Faghhiian et al. 1999; Elizondo et al. 2000; Abusafa and Yücel 2002). A more practical application for nuclear wastewater treatment is the Yucca Mountain project in Nevada, U.S.A., which is being investigated as a site for a high-level waste geologic repository. In this example, zeolitized tuffs could act as naturally occurring barriers against radionuclide transport (Bodvarsson et al. 1999; Vaniman et al. 2001). In the case of nuclear spillage, natural barriers could act as natural containment barriers via ion-exchange processes and prevent extensive diffusion of harmful elements.

The application of clinoptilolite as a barrier for nuclear waste disposal is supported by its assumed resistance to degradation after γ-radiation. However, data on this topic is rather limited. Fullerton (1961) did not observe changes in the uptake of Na\(^+\), Cs\(^+\), and Ba\(^+\) after γ-radiation of clinoptilolite with a dose of 9.6 Grad, and demonstrated a 42% decrease in the distribution coefficient of clinoptilolite for Ca\(^2+\) ions after exposure to γ-radiation of 9.6 Grad. Limited information on the stability after irradiation exists also for other zeolites. Pillay and Palau (1982) reported a slight decrease of cation-exchange capacity (CEC) by 3% of a