

## **Ion exchange equilibrium and structural changes in clinoptilolite irradiated with $\beta$ - and $\gamma$ -radiation: Monovalent cations**

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### **ABSTRACT**

Thermodynamic calculations of ion-exchange reactions were applied for clinoptilolite in a natural state and after irradiation with three doses of  $\beta$ -radiation ( $10^{12}$ ,  $10^{15}$ ,  $3 \times 10^{16}$  e/cm<sup>2</sup>) and  $\gamma$ -radiation (70 Mrad). Samples were equilibrated with binary systems of  $K^+ \leftrightarrow Na^+$  and  $Cs^+ \leftrightarrow Na^+$  at 25° and a total normality of 0.025 *N*. Selectivity for K was not affected after  $\beta$ -radiation with doses of  $10^{12}$  and  $10^{15}$  e/cm<sup>2</sup> ( $\Delta G^\circ = -6.37$  kJ/equiv,  $\ln K\alpha = 2.58$  for the original clinoptilolite), whereas it increased considerably after 70 Mrad of  $\gamma$ -radiation ( $\Delta G^\circ = -7.88$  kJ/equiv,  $\ln K\alpha = 3.18$ ). Selectivity for Cs<sup>+</sup> increased for the clinoptilolite irradiated with  $\beta$ -radiation ( $10^{12}$ ,  $10^{15}$ ,  $3 \times 10^{16}$  e/cm<sup>2</sup>) and  $\gamma$ -radiation (70 Mrad).  $\Delta G^\circ$  and  $\ln K\alpha$  for original sample and  $Cs^+ \leftrightarrow Na^+$  were  $-7.33$  kJ/equiv and 2.96, respectively. Irradiated samples with  $\beta$ -radiation  $10^{12}$ ,  $10^{15}$ ,  $3 \times 10^{16}$  e/cm<sup>2</sup> and 70 Mrad  $\gamma$ -radiation yielded  $\Delta G^\circ$  and  $\ln K\alpha$   $-7.41$ ,  $-8.83$ ,  $-8.60$ ,  $-8.25$  kJ/equiv and 2.99, 3.57, 3.47, 3.33 for  $Cs^+ \leftrightarrow Na^+$ , respectively. Remarkable amorphization of clinoptilolite was observed after exposure at the highest dose of  $\beta$ -radiation ( $3 \times 10^{16}$  e/cm<sup>2</sup>) 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<sup>3+</sup> for Si<sup>4+</sup> 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,  $\beta$ -radiation,  $\gamma$ -radiation, thermodynamics, Rietveld refinement