

Characterization of T-55 sorbent using ^{57}Fe Mössbauer spectroscopy with a high velocity resolution

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Abstract A new sorbent T-55 with mixed ferrocyanide surface modification developed for Cs^+ sorption was characterized using Mössbauer spectroscopy with a high velocity resolution in comparison with $\text{K}_2\text{Ni}[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$ samples. The main sorption active component of T-55 sorbent was determined as $\text{K}_2\text{Ni}[\text{Fe}(\text{CN})_6]$.

Keywords Mössbauer spectroscopy · Sorbent T-55 · Mixed ferrocyanides

1 Introduction

Liquid radioactive wastes resulting from nuclear fuel cycle contain cesium and strontium radionuclides which give the main contribution into activity of these wastes. To extract cesium from the wastes a new sorbent named “T-55” was developed on the basis of surface modification of hydrated titanium dioxide using mixed ferrocyanides [1]. The obtained T-55 sorbent possesses a high specificity and selectivity to Cs^+ ions as well as high capacity, radiation stability and low leaching rates of radionuclides [2]. For further analysis this sorbent was characterized using Mössbauer spectroscopy.

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2 Experimental

Hydrated titanium dioxide with spherical grains ranged in size from 0.2 to 0.4 mm mainly synthesized by sol-gel technology (T-55 sorbent produced by Termoxid company, Russia) was used as a support for T-55 sorbent. The support was preliminary annealed at 400 °C for improving its mechanical features. Then it was saturated by nickel ions, treated by $K_4[Fe(CN)_6]$ solution at elevated temperature and washed by still water. The final drying of synthesized T-55 sorbent was performed at room temperature. For comparison samples of $K_2Ni[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ were used in this study. Commercial chemically pure (> 99 %) $K_4[Fe(CN)_6]$ was used for Mössbauer spectrum measurement and for mixed ferrocyanide preparation by precipitation with commercial chemically pure (> 99 %) $NiSO_4$. The obtained $K_2Ni[Fe(CN)_6]$ was analyzed using X-ray fluorescent spectrometer ARL Quant'X. The molar ratio for metal ions was obtained as K : Ni : Fe = 1 : 0.51 : 0.56 that was close to stoichiometry of $K_2Ni[Fe(CN)_6]$. Powdered samples with a weight less than 10 mg Fe/cm^2 were glued on free from iron aluminum substrate for Mössbauer measurements.

X-ray diffraction patterns of the T-55 sorbent were measured using X-ray diffractometer with system of rapid registration and high-temperature cell X'PERT PRO MPD. Grains of T-55 sorbent were characterized by scanning electron microscopy (SEM) using SIGMA VP microscope (Carl Zeiss). Mössbauer spectra were measured using an automated precision Mössbauer spectrometric system built on the base of the SM-2201 spectrometer with a saw-tooth shape velocity reference signal formed using quantification with 4096 steps. Details and characteristics of this spectrometer and the system were given elsewhere [3, 4]. The 1.8×10^9 Bq ^{57}Co in rhodium matrixes (Ritverc GmbH, St. Petersburg) was used at room temperature. The Mössbauer spectra of studied samples were measured in transmission geometry with moving absorber in the cryostat at room temperature and recorded in 4096 channels. Spectra were measured in velocity range of about ± 2.5 mm/s. For their analysis, spectra were converted into 1024 channels by a consequent summation of four neighboring channels. This was done due to a large atomic absorption of γ -rays by Ti and, therefore, a very long measurement time for the T-55 sorbent Mössbauer spectrum even for presentation in 1024 channels. Statistical count rate in the spectra presented in 1024 channels was $\sim 5.3 \times 10^6$ counts per channel with the signal-to-noise ratio of 29 for Ti containing T-55 sorbent. Statistical count rate for the spectra of $K_2Ni[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ were $\sim 1.3 \times 10^5$ and $\sim 5.6 \times 10^5$ counts per channel and the signal-to-noise ratio was 69 and 143, respectively. The spectra were computer fitted with the least squares procedure using UNIVEM-MS program with a Lorentzian line shape. The spectral parameters such as: isomer shift, δ , quadrupole splitting, ΔE_Q , line width, Γ , relative subspectrum area, S, and statistical quality of the fit, χ^2 , were determined. An instrumental (systematic) error for each spectrum point was ± 0.5 channel (the velocity scale), the instrumental (systematic) error for the hyperfine parameters was ± 1 channel. If an error calculated with the fitting procedure (fitting error) for these parameters exceeded the instrumental (systematic) error we used the larger error instead. Values of δ are given relative to α -Fe at 295 K.

3 Results and discussion

XRD patterns of T-55 sorbent are shown in Fig. 1. These patterns demonstrate the main peaks of TiO_2 in two structural modifications (rutile and anatase). Peaks related to ferrocyanides cannot be revealed from these patterns due to its low intensities and overlapping with the main peaks of TiO_2 . SEM images of T-55 sorbent are shown in Fig. 2. It is clearly

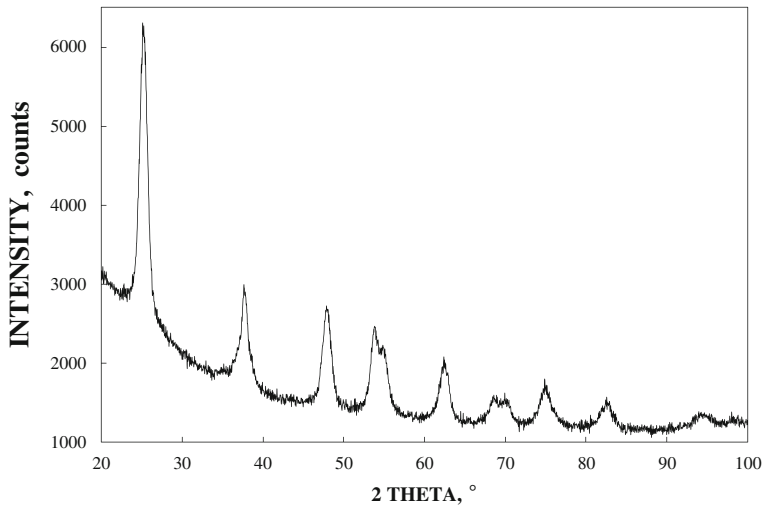


Fig. 1 XRD patterns of the T-55 sorbent sample

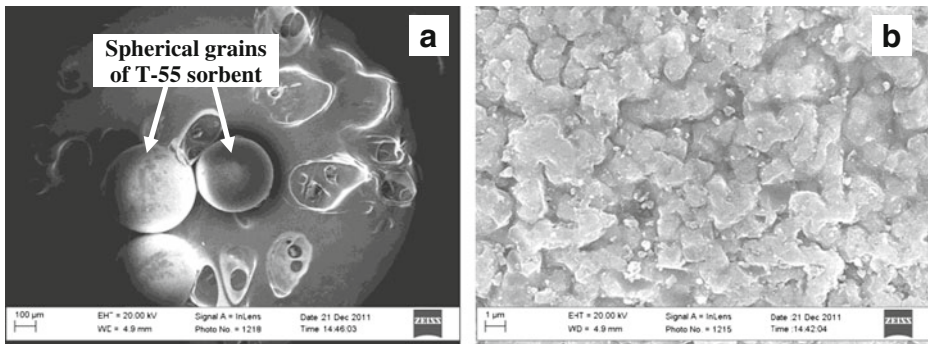


Fig. 2 Scanning electron microscopy images of T-55 sorbent spherical grains (a) and porous surface of the grain (b)

seen spherical shape of grains. Each grain demonstrates porous surface providing Cs^+ ions transport inside the grain.

Mössbauer spectra of T-55 sorbent sample and samples of $\text{K}_2\text{Ni}[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$ are shown in Fig. 3. These spectra look like single absorption peak shapes with significantly different absorption effect. This is a result of the presence of Ti atoms in the sorbent sample which substantially decrease an absorption effect. The best fits of these spectra showed that the Mössbauer spectrum of T-55 sorbent consists of the main singlet component and two weak quadrupole doublets ($\delta = 0.11 \pm 0.02$ mm/s, $\Delta E_Q = 0.58 \pm 0.04$ mm/s and $\delta = 0.41 \pm 0.04$ mm/s, $\Delta E_Q = 0.73 \pm 0.06$ mm/s for components 2 and 3, respectively) while the spectrum of $\text{K}_2\text{Ni}[\text{Fe}(\text{CN})_6]$ consists of the main singlet line and one weak quadrupole doublet ($\delta = 0.14 \pm 0.02$ mm/s, $\Delta E_Q = 1.20 \pm 0.04$ mm/s). The spectrum of $\text{K}_4[\text{Fe}(\text{CN})_6]$ demonstrates well-known singlet line only. In the present study we omit from consideration small spectral components demonstrating Mössbauer hyperfine parameters for three different ferric compounds. The exact identification of these

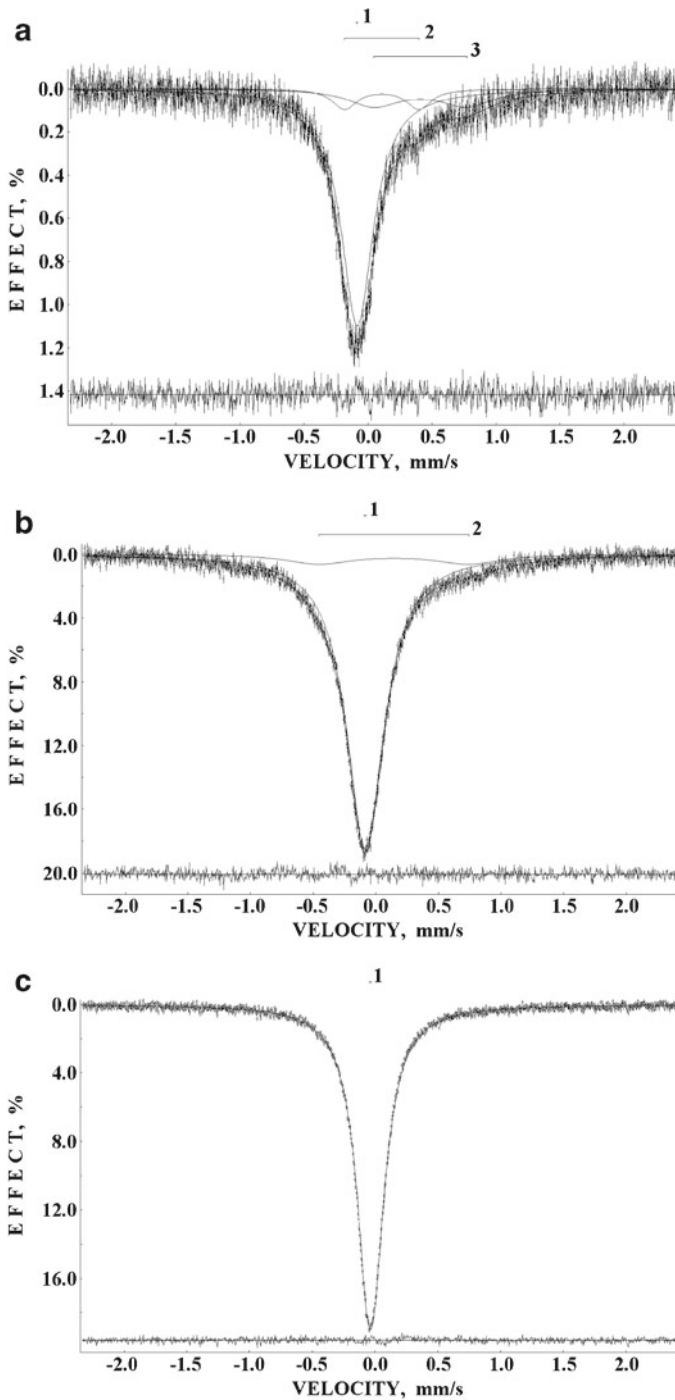


Fig. 3 Mössbauer spectra of the T-55 sorbent (a), $K_2Ni[Fe(CN)_6]$ (b) and $K_4[Fe(CN)_6]$ (c) measured at 295 K and presented in 1024 channels. Indicated components are the results of the best fits. Differential spectra are shown below

compounds is not possible yet. We assume that these minor compounds may be considered as contaminations resulting from formation of various ferro- and/or ferricyanides (for instance, see Mössbauer parameters δ and ΔE_Q for similar compounds in [5]). The values of isomer shift for the main singlet lines were -0.083 ± 0.005 mm/s (T-55 sorbent), -0.084 ± 0.005 mm/s ($\text{K}_2\text{Ni}[\text{Fe}(\text{CN})_6]$) and -0.036 ± 0.005 mm/s ($\text{K}_4[\text{Fe}(\text{CN})_6]$). The later value of δ is the same for $\text{K}_4[\text{Fe}(\text{CN})_6]$ sample ($\delta = -0.050 \pm 0.025$ mm/s) obtained in [6]. Therefore, these results indicate that T-55 sorbent contains $\text{K}_2\text{Ni}[\text{Fe}(\text{CN})_6]$ as the main iron containing component. This mixed ferrocyanide formed during the surface modification of TiO_2 grains as a result of Ni^{2+} ions interaction with $\text{K}_4[\text{Fe}(\text{CN})_6]$. Finally, $\text{K}_2\text{Ni}[\text{Fe}(\text{CN})_6]$ appeared to be the main sorption active component in T-55 sorbent which realizes a good selective sorption of Cs^+ ions observed in [1, 2].

4 Conclusion

Characterization of T-55 sorbent in comparison with $\text{K}_2\text{Ni}[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$ samples was carried out using Mössbauer spectroscopy with a high velocity resolution. The results obtained demonstrated that surface modification of hydrated titanium dioxide grains using nickel ions and potassium ferrocyanide led to the mixed potassium-nickel ferrocyanide formation mainly. This potassium-nickel ferrocyanide is the main active component which realizes a good selective sorption of Cs^+ ions that was shown in [1, 2].

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