

REDUCTION OF Fe IN MONTMORILLONITE<sup>1</sup>J. Sittek<sup>†</sup>, B. Arvaiová<sup>‡</sup>, I. Tóth<sup>†</sup><sup>†</sup>Department of Nuclear Physics and Technology, STU Bratislava, Slovakia<sup>‡</sup>Institute of Inorganic Chemistry, SAS, Bratislava, Slovakia

Benzidine as a strong reducing agent reacts differently with various smectites. The reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> was studied for montmorillonite from two localities, Wyoming and Jelšovský potok. Wyoming montmorillonite contains Fe<sup>3+</sup> in two sites and Fe<sup>2+</sup> in one site and Jelšovský potok contains only Fe<sup>3+</sup>. The Wyoming sample contains more iron than the Jelšovský potok sample. Benzidine reduced Fe<sup>3+</sup> more efficiently in the Wyoming samples. The reduction process is dependent not only on the pH parameter, but also on the content of Fe<sup>2+</sup> in the parent material.

Reducing agents react differently with dioctahedral smectites. It was also considered to examine whether the nature of the reducing agent affects the product formed and to what extent the course of the reactions is determined by the structure of the clay minerals. Comparison of the reactions of various dioctahedral smectites with hydrazine and dithionite shows [1], that the nature of the reaction products depends both upon the mineral and the reducing agent. Reduction of dioctahedral smectites, particularly montmorillonite, have been studied by several investigators, and by different methods [2, 3, 4].

In the present work, Mössbauer spectroscopy was used to follow reduction of montmorillonite in benzidine solution.

Smectites contain Fe<sup>3+</sup> in the octahedral sites, M1 and M2, [1]. In the Mössbauer spectrum, the first one give rise to the outer doublet with higher, and the second one to the inner doublet with lower value of splitting. The area fractions of the outer and the inner octahedral Fe<sup>3+</sup> doublets are roughly 1/3 and 2/3 respectively. The ratio of the quadrupole splitting of Fe<sup>3+</sup> is approximately 2:1, as predicted in [1]. This ratio could be distorted in various types of smectites or after reduction in different agents. Some samples show an additional weaker doublet, corresponding to Fe<sup>2+</sup>.

The computer fit is usually made with constrained parameters [5, 6]. The spectrum for the montmorillonite was computer fitted with overlapping doublets, initially with only the widths and dips of the component peaks in a particular doublet being constrained equal. In our fit no other constrained parameters were used.

Mössbauer spectra of our montmorillonite samples are shown in Fig. 1. The parameters are given in Table 1 and Table 2. The spectrum of the natural mineral Wyoming

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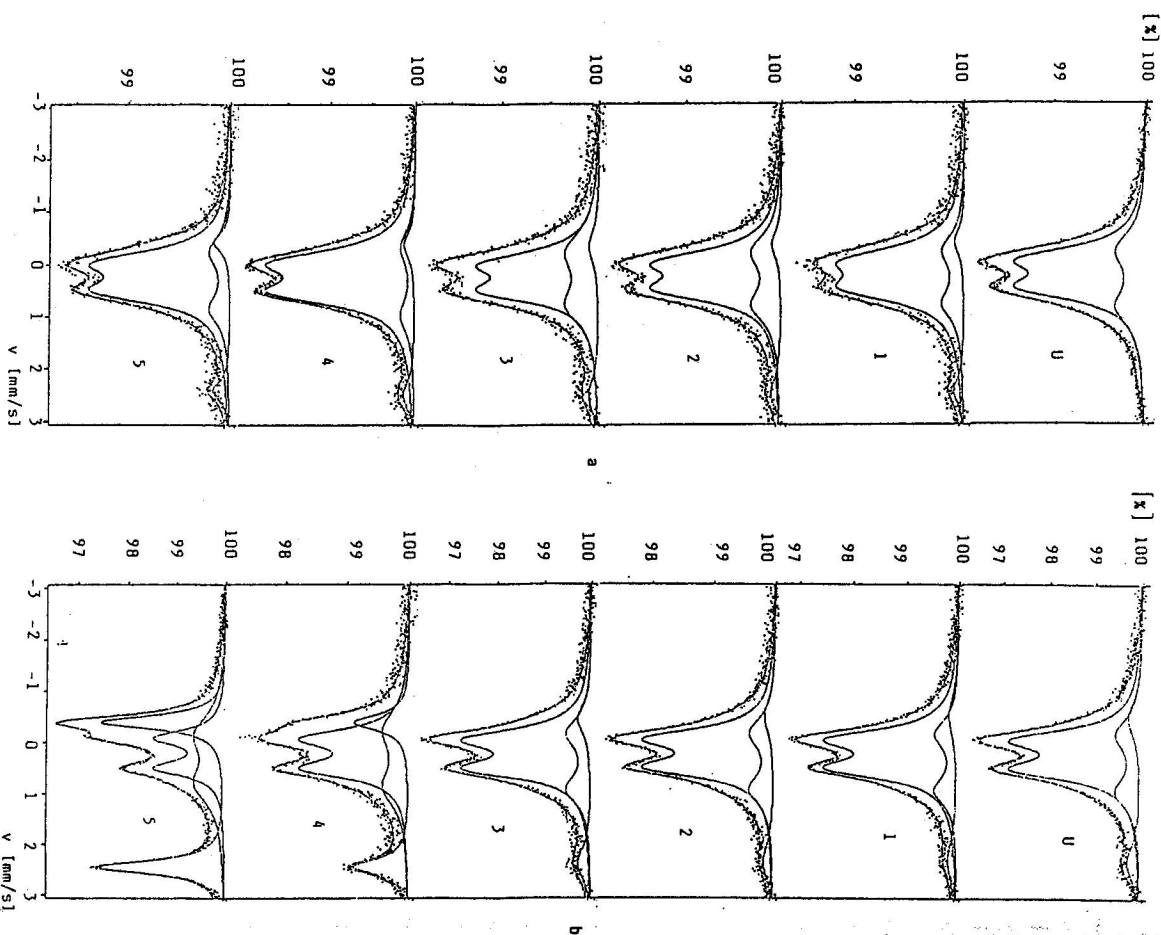


Fig. 1. Mössbauer spectra of a) Jelský potok montmorillonite, U - untreated sample, pH (1 - 1.52; 2 - 1.71; 3 - 2.15; 4 - 4.82 and 5 - 8.75), b) Wyoming montmorillonite. U - untreated sample, pH (1 - 1.52; 2 - 1.71; 3 - 2.29; 4 - 4.80 and 5 - 10.64

sample (W) consists of three doublets, corresponding to one bivalent, and two trivalent sites of Fe. Mössbauer spectrum of the Jelský potok sample (JP) shows that iron

Table 1. Parameters of Wyoming montmorillonite U - untreated sample, IS - isomer shift against Fe, QS - quadrupole splitting, A - relative area

Sample	Fe <sup>3+</sup>					Fe <sup>2+</sup>					pH	Colour	
	IS	QS	A	IS	A	IS	QS	A	IS	QS			A
U	0.38	1.03	24	0.33	64	0.91	2.84	12	1.38	2.84	12	1.38	yellow
1	0.38	1.01	23	0.33	65	0.89	2.84	12	1.71	2.84	11	1.71	yellow
2	0.39	1.02	22	0.33	67	0.92	2.84	12	2.29	2.84	12	2.29	yellow
3	0.38	1.00	20	0.33	68	0.96	2.84	12	4.80	2.84	24	4.80	blue
4	0.37	1.01	26	0.33	50	1.04	2.82	24	10.64	2.88	45	10.64	blue
5	0.37	0.96	28	0.32	27	1.03	2.84	9					blue

Table 2. Parameters of Jelský potok montmorillonite U - untreated sample, IS - isomer shift against Fe, QS - quadrupole splitting, A - relative area

Sample	Fe <sup>3+</sup>					Fe <sup>2+</sup>					pH	Colour	
	IS	QS	A	IS	A	IS	QS	A	IS	QS			A
U	0.38	1.07	28	0.33	72	1.03	2.84	8	1.52	2.84	8	1.52	yellow
1	0.38	1.02	24	0.34	68	1.05	2.84	8	1.71	2.84	8	1.71	yellow
2	0.38	1.02	29	0.34	60	1.08	2.84	9	2.15	2.84	8	2.15	brown
3	0.37	1.01	31	0.34	69	1.05	2.84	8	4.82	2.84	8	4.82	blue
4	0.37	1.01	23	0.33	69	1.05	2.84	9	8.75	2.84	9	8.75	blue
5	0.37	1.08	26	0.33	65	0.99	2.84	9					blue

occurs in trivalent form only. Comparison of the W-spectrum with the JP-spectrum shows that the line intensity in the W-spectrum is higher than that in the JP-spectrum indicating different contents of iron, which was confirmed also by a chemical analysis.

Mössbauer spectra of benzidine treated montmorillonite show that the reaction is dependent on the pH of the solution. Reduction in the W-montmorillonite is more significant than in the JP one. The Mössbauer spectra, again, consist of three doublets, of which one corresponds to Fe<sup>2+</sup>. For the first three samples, the amount of reduced iron is nearly equal (approximately 12%). A sudden increase of Fe<sup>2+</sup> occurred in the fourth, and the fifth sample, up to 24% or to 45%, respectively. In the last two cases, the isomer shift and the quadrupole splitting slightly changed for Fe<sup>3+</sup> (M1) only.

Reduction with benzidine affects the distribution of Fe<sup>3+</sup> ions. The population of the sites with a smaller quadrupole splitting decreased relatively to the others. We propose that Fe<sup>3+</sup> is preferentially reduced to Fe<sup>2+</sup> in one site (M2).

Mössbauer spectra of JP-sample after benzidine treatment, were resolved also into three doublets corresponding to one Fe<sup>2+</sup> site and two Fe<sup>3+</sup> sites. However, the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> was not significant. The fraction of reduced iron increased only slowly, and the change is within the experimental error. Other Mössbauer parameters did not change substantially.

Most discussed is isomer shift of montmorillonite. Its value varied from 0.29 to 0.35 mm/s for the inner doublet and from 0.37 to 0.46 mm/s for the outer doublet [3,5]. The differences could have arisen not only from the fit of the spectrum but also from

the variability of such natural materials. Our results correspond to the values within the given range.

The interaction of montmorillonite with benzidine gave rise to two coloured substances, depending on the pH of the system. The benzidine transformed to a blue monovalent radical cation while  $\text{Fe}^{3+}$  in smectite reduced to  $\text{Fe}^{2+}$ . The blue radical cation transformed to a yellow divalent radical cation, when the pH of the system dropped below 3. For JP sample we found between yellow and blue a brown colour.

The presence of radical cations can be seen on the colours of the samples. Colours and pH are given in Table 1 and Table 2.

Our results confirmed that a reduction of W-montmorillonite is strongly pH dependent. On the other hand, the reduction of JP-montmorillonite is almost independent on pH. We propose that the reduction process depends on the iron amount, first of all on the  $\text{Fe}^{2+}$  content in prior to the reducing treatment. Our results showed that when using benzidine as a reducing agent, we obtained suspensions of different colours, according to pH.

#### References:

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