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**IRON IN THE STRUCTURE OF SOME CLAY MINERALS
AND ITS EXTRACTION WITH 15% H₂SO₄
IN THE LIGHT OF MÖSSBAUER SPECTROSCOPY**

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Abstract. Mössbauer spectroscopy has revealed that iron in the structure of illite, beidellite, mixed-layer illite/montmorillonite and kaolinite is present only in the octahedral sheet, where it may occupy two positions of different crystal field symmetry. Iron ions occupying low-symmetry positions are more readily extractable with 15% H₂SO₄ than the ones at higher symmetry sites. The extraction rate of iron is approximately proportional to the iron content in the structure of a clay mineral. The extraction of iron is most rapid in illite, less so in mixed-layer illite/montmorillonite, and the slowest in beidellite.

INTRODUCTION

Treatment with sulphuric acid is used in the technology of obtaining bleaching earth from clays. Studies of the extraction of iron from clays rich in beidellite, illite, or mixed-layer illite/montmorillonite have shown that it is the cations occupying the octahedral sheet of clay minerals, and in the first place iron ions, that pass into sulphuric acid aqueous solutions (Bahranowski 1980).

The present paper is an attempt to define the position of iron in the structure of illite, beidellite and mixed-layer illite/montmorillonite, and to determine the influence of the crystal field symmetry upon its extraction with sulphuric acid aqueous solutions. Similar investigations were carried out on kaolinite clay containing haematite. The method used was Mössbauer spectroscopy.

Mössbauer spectroscopy has found wide application in the studies of minerals containing iron because the iron isotope ⁵⁷Fe is a Mössbauer

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nuclide that possesses exceptionally advantageous parameters considering both the excited state life-time and the gamma transition energy. Iron in the structure of clay minerals usually occurs in the octahedral sheet (Bancroft 1974; Rozenon, Heller-Kallai 1977; Komusiński, Stoch, Dubiel 1981) although its presence was also suggested in the tetrahedral sheet (Goodman et al. 1976, Goodman 1978).

EXPERIMENTAL

Investigations were carried out on grain fractions $< 2 \mu\text{m}$ or $< 1 \mu\text{m}$ of clays of different mineralogical nature. The were:

The Poznań clay from Kraniec (Lower Silesia). The $< 2 \mu\text{m}$ fraction of this clay consists of about 70% mixed-layer illite/montmorillonite, 10% illite, 10% kaolinite and 10% quartz. The fraction has also been found to contain haematite. The content of swelling layers in the mixed-layer I/M, determined by the methods suggested by Hower and Mowatt (1966) and Reynolds and Hower (1970), amounts to 60%. It is a dioctahedral mineral containing mainly Al^{3+} and Fe^{3+} in the octahedral sheet.

Stagnant clay from Plecewice. The $< 2 \mu\text{m}$ fraction contains about 70% illite, 10% kaolinite and 10% quartz, as well as small amounts of chlorite and mixed-layer I/M.

The Poznań clay from the overburden layer of the "Kazimierz" brown coal mine in Konin. Investigations were carried out on the $< 1 \mu\text{m}$ fraction consisting of about 80% beidellite, 15% kaolinite and 5% quartz (Helios-Rybicka 1975).

Mössbauer spectra were taken at room temperature with a 400-channel spectrometer used in the constant acceleration mode. The source of gamma radiation was ^{57}Co in a chromium matrix. Calibration was made with the aid of chemically pure $\alpha\text{-Fe}_2\text{O}_3$.

The resulting Mössbauer spectra were fitted by digital computer using iterative method. The fitting parameters were: isomer shift (IS), quadrupole splitting (QS) and half-width of line (Γ). In the case of kaolinite from Baranów and mixed-layer I/M from Kraniec, in which haematite was present, another fitting parameter, viz. magnetic splitting (H), was introduced.

After drying and grinding in an agate mortar, the separated fractions were stored overnight in a hygostat at a humidity of 55%.

Mössbauer spectra of the fractions were taken before and after 14-hour treatment with sulphuric acid. For the illite sample from Plecewice additional spectra were taken after 0.5 and 1-hour treatment. The following procedure was adopted: 2 g samples of a humidity of 55% were weighed out into Erlenmeyer flasks (400 ml in volume) and 200 ml of hot 15% H_2SO_4 was poured on them. To eliminate the evaporation of acid, the flasks were closed with a stopper equipped with a reflux water condenser. The flasks were put on a water bath ensuring a constant reaction temperature of 95°C . The samples were stirred every 15 minutes. After the specified reaction time, the samples were removed from the bath, diluted with cold water, immediately centrifuged and washed with distilled water until the reaction for iron was negative and the neutral solution reaction was obtained. Iron content in the filtrate was determined using atomic absorption spectrophotometry. The precipitate was

dried and kept in a hygostat at a humidity of 55%, and samples for Mössbauer spectroscopy were prepared. The Mössbauer spectra obtained are shown in figures 1—10, whereas the parameters characterizing the spectra are listed in Table 2.

RESULTS

The $< 2 \mu\text{m}$ fraction of the Plecewice clay contains 9.9% Fe_2O_3 . The isomer shift IS and quadrupole splitting QS testify to the presence of iron in the octahedral sheet of clay minerals (Bancroft 1974), specifically of illite. Iron in this sheet occurs in two oxidation states, Fe^{3+} and Fe^{2+} . The amount of ferric iron is about 2.5 times greater than that of ferrous iron. Ferric iron occupies two unequivalent positions in the octahedral sheet: A (of lower symmetry) and B (of higher symmetry), iron in the position A being positively prevalent.

Treatment with sulphuric acid results in systematic extraction of iron from the structure of illite (Table 1). Mössbauer spectra (figs 1—4) have revealed that both Fe^{2+} content and the total content of Fe^{3+} decrease.

Table 1
Extraction of Fe_2O_3 from clay minerals during reaction with 15% H_2SO_4

Sample	Weigh % of Fe_2O_3 in natural sample	Amount of extracted Fe_2O_3 in weight % after		
		0.5 h	1 h	14 h
Illite Plecewice $< 2 \mu\text{m}$	9.90	3.64	3.04	9.49
Illite/montmorillonite Kraniec $< 2 \mu\text{m}$	0.04	1.11	2.54	6.36
Beidellite Konin $< 1 \mu\text{m}$	5.90	0.71	0.36	3.07
Kaolinite Baranów Czerwony $< 2 \mu\text{m}$	11.45	1.85	4.26	10.93

The content of Fe^{2+} decreases fairly rapidly. After 0.5-hour treatment it is four times lower than in the untreated sample. The present investigations failed to ascertain whether this iron was oxidized and remained in the structure as Fe^{3+} , or went into H_2SO_4 solution as Fe^{3+} . After 14-hour treatment no Fe^{2+} was detected in the structure of illite.

The decrease in Fe^{3+} content is caused first of all by the passing of ions from A positions into solution and is approximately 12.5 fold. Iron content at B positions remains more or less at a constant level. It is conceivable, however, that during initial treatment it increases, decreasing during further treatment so that after 14 hours it reaches the level of the untreated sample. Such course of reaction is suggested by the change in parameter ϵ (Table 2). It should be noted, however, that with the increase in this parameter, its measurements are more likely to be in error, in which case the observed tendency may only be apparent. The initial

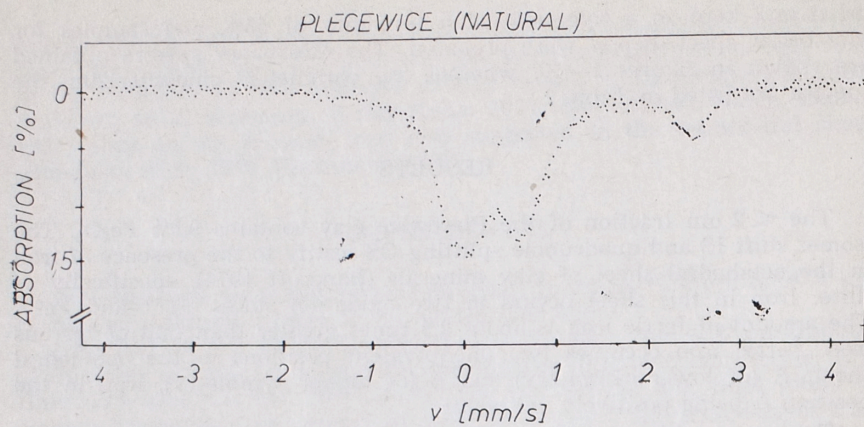


Fig. 1. Mössbauer spectrum of clay from Plecewice (fraction $< 2 \mu\text{m}$)

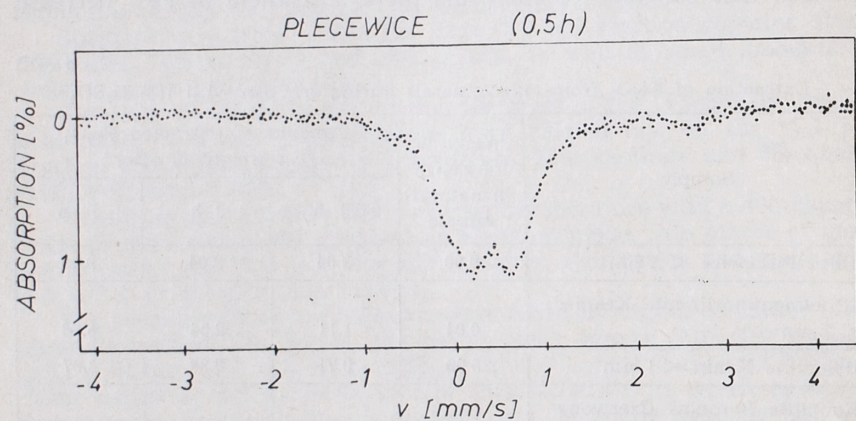


Fig. 2. Mössbauer spectrum of clay from Plecewice (fraction $< 2 \mu\text{m}$) treated 0.5 h with 15% H_2SO_4

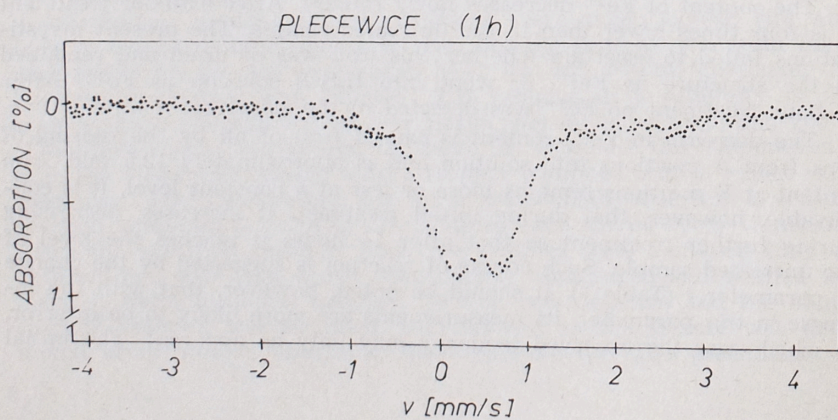


Fig. 3. Mössbauer spectrum of clay from Plecewice (fraction $< 2 \mu\text{m}$) treated 1 h with 15% H_2SO_4

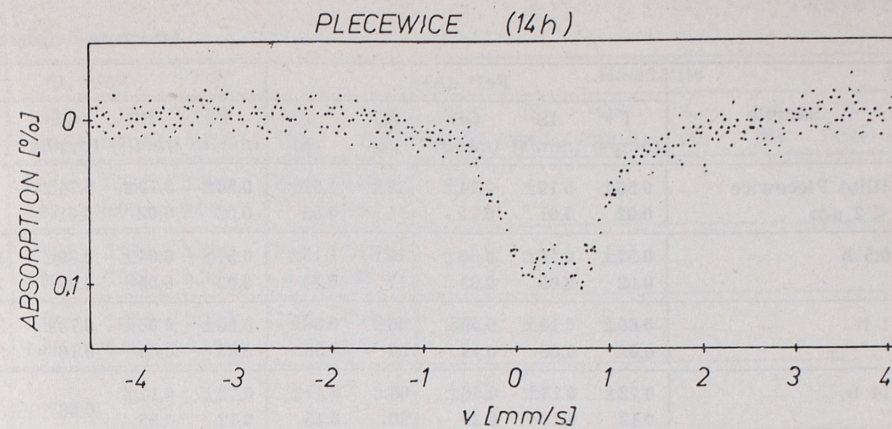


Fig. 4. Mössbauer spectrum of clay from Plecewice (fraction $< 2 \mu\text{m}$) treated 14 h with 15% H_2SO_4

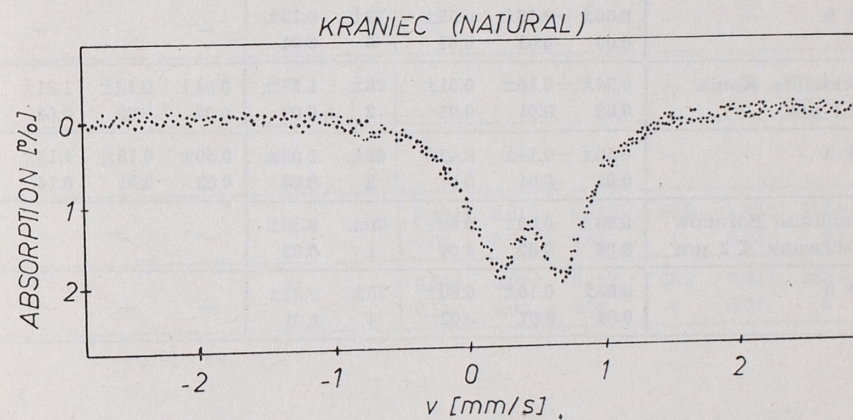


Fig. 5. Mössbauer spectrum of clay from Kraniec (fraction $< 2 \mu\text{m}$)

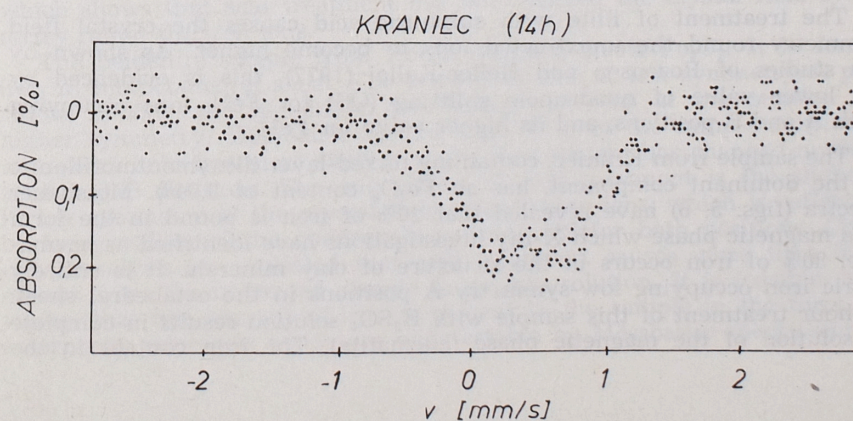


Fig. 6. Mössbauer spectrum of clay from Kraniec (fraction $< 2 \mu\text{m}$) treated 14 h with 15% H_2SO_4

Mössbauer parameters

Sample	Fe ³⁺ (A)					Fe ³⁺ (B)			
	Γ (mm/s)	IS (mm/s)	QS (mm/s)	A _o (%)	ε (%)	Γ (mm/s)	IS (mm/s)	QS (mm/s)	A _o (%)
Illite Plecewice < 2 μm	0.56± 0.02	0.19± 0.01	0.74± 0.01	73± 1	1.52± 0.05	0.56± 0.02	0.12± 0.02	0.74± 0.01	3± 2
0.5 h	0.57± 0.02	0.16± 0.05	0.50± 0.03	79± 17	1.15± 0.24	0.57± 0.02	0.04± 0.05	0.39± 0.28	11± 18
1 h	0.60± 0.03	0.14± 0.06	0.50± 0.13	56± 36	0.86± 0.56	0.60± 0.03	0.06± 0.04	0.73± 0.16	34.5± 35
14 h	0.72± 0.12	0.13± 0.19	0.56± 0.20	65± 20	0.12± 0.15	0.72± 0.12	0.12± 0.35	0.66	35
Illite/montmorillonite Kraniec < 2 μm	0.48± 0.01	-0.12± 0.01	0.53± 0.01	81± 1	1.96± 0.01	—	—	—	—
14 h	0.66± 0.05	-0.16± 0.02	0.55± 0.02	79± 6	0.22± 0.04	—	—	—	—
Beidellite Konin < 1 μm	0.54± 0.02	-0.16± 0.01	0.51± 0.01	88± 2	1.17± 0.02	0.54± 0.02	0.13± 0.03	1.31± 0.08	12± 3
14 h	0.50± 0.03	-0.14± 0.01	0.45± 0.01	88± 2	1.00± 0.03	0.50± 0.03	0.19± 0.01	1.13± 0.14	86± 4
Kaolinite Baranów Czerwony < 2 μm	0.90± 0.08	0.09± 0.02	0.60± 0.04	20± 1	0.36± 0.02	—	—	—	—
14 h	0.68± 0.04	0.10± 0.01	0.60± 0.02	75± 4	0.32± 0.01	—	—	—	—

increase in Fe³⁺ content at B-type lattice sites can be accounted for by the oxidation of Fe²⁺ occupying these positions.

The treatment of illite with sulphuric acid causes the crystal field symmetry round the unextracted ions to become higher. As shown by the studies of Rozenson and Heller-Kallai (1977), this is evidenced by the lower value of quadrupole splitting (QS) for Fe³⁺ ions occupying both A and B positions, and its higher value for Fe²⁺.

The sample from Kraniec, containing mixed-layer illite/montmorillonite as the dominant component, has an Fe₂O₃ content of 8.04%. Mössbauer spectra (figs. 5, 6) have revealed that 20% of iron is bound in the form of a magnetic phase which X-ray investigations have identified as haematite. 80% of iron occurs in the structure of clay minerals. It is entirely ferric iron occupying low-symmetry A positions in the octahedral sheet. 14-hour treatment of this sample with H₂SO₄ solution results in complete dissolution of the magnetic phase (haematite). The iron content in the

of investigated samples

ε (%)	Fe ²⁺					Haematite					
	Γ (mm/s)	IS (mm/s)	QS (mm/s)	A _o (%)	ε (%)	Γ (mm/s)	IS (mm/s)	QS (mm/s)	A _o (%)	ε (%)	H (kQe)
0.07± 0.06	0.44± 0.02	1.22± 0.02	2.28± 0.02	24± 0.3	0.63± 0.01	—	—	—	—	—	—
0.16± 0.27	0.51± 0.06	0.95± 0.36	2.60± 0.36	10± 0.4	0.16± 0.01	—	—	—	—	—	—
0.53± 0.54	0.46± 0.02	1.09± 0.09	2.27± 0.17	12± 1	0.19± 0.01	—	—	—	—	—	—
0.07	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	0.48± 0.02	0.0006	0.22± 0.04	19± 2	—	492.2± 1.6
—	—	—	—	—	—	—	—	—	—	—	—
0.16± 0.04	—	—	—	—	—	—	—	—	—	—	—
0.14± 0.05	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	0.40± 0.03	0.01± 0.01	0.11± 0.01	80± 1	1.45± 0.02	512.6± 0.1
—	—	—	—	—	—	0.54± 0.11	0.02± 0.02	0.10± 0.02	25± 9	0.04± 0.01	505.8± 2

octahedral sheets of clay minerals decreases 6.5-fold. The values of quadrupole splitting QS and isomer shift IS remain virtually unchanged, which shows that acid treatment has not changed the crystal field symmetry round the iron ions.

The beidellite sample from Konin contains 5.90% Fe₂O₃. It is ferric iron in the octahedral sheet. The content of iron at low-symmetry A positions is 88%, the remaining part being iron ions at the position of higher symmetry. Mössbauer spectra (figs 7, 8) of the sample subjected to 14-hour acid treatment show that the iron content has changed neither at A nor B positions. The only effect of acid treatment is the slightly higher symmetry of the crystal field round these ions, which is reflected by lower values of the quadrupole splitting QS for both positions. Chemical analysis has revealed that acid treatment causes more than 50% of iron from the untreated sample to go into solution. It is feasible, however, that this amount of iron is present in the sample in the form of amorphous siderogels which are undetectable by Mössbauer spectroscopy.

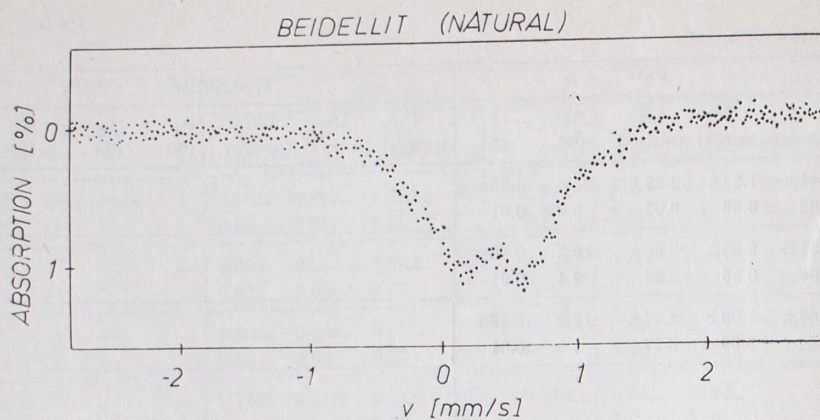


Fig. 7. Mössbauer spectrum of clay from Konin (fraction $< 1 \mu\text{m}$)

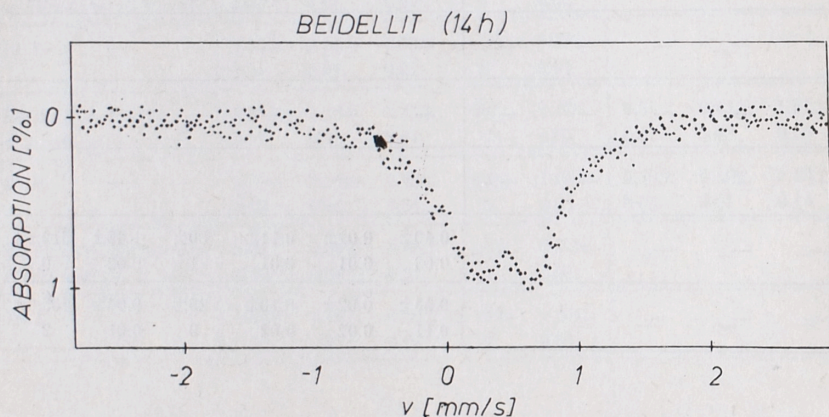


Fig. 8. Mössbauer spectrum of clay from Konin (fraction $< 1 \mu\text{m}$) treated 14 h with 15% H_2SO_4

DISCUSSION

From the above investigations it appears that acid treatment of clay samples rich in illite, beidellit and mixed-layer illite/montmorillonite causes in the first place the dissolution of siderogels and haematite.

The next to be extracted is iron bound in the structure of clay minerals. The rate of iron extraction from the structure of clay minerals varies for each mineral. It is most rapid for the Plecewice illite, moderately rapid for the mixed-layer illite/montmorillonite from Kraniec, and the slowest for the beidellit from Konin. These results are in agreement with the studies of iron extraction kinetics by chemical methods (Bahranowski 1980).

There is a distinct correlation between the content of structural iron and the rate of its extraction by sulphuric acid solution. The iron extraction rate is approximately proportional to its content in the structure of a clay mineral. Moreover, the iron ions occupying lower-symmetry positions in the octahedral sheet are more readily extractable than the ones at the positions of higher crystal field symmetry.

The extraction of Al, Mg and Fe cations occupying the octahedral sites and the vacant cationic sites left in this sheet may cause changes in the symmetry of these positions. The crystal field symmetry round the iron ions that failed to be extracted from the structure becomes higher.

In kaolinite (the $< 2 \mu\text{m}$ fraction of the Baranów clay) treatment with 15% H_2SO_4 results in the dissolution of haematite while the content of structural iron decreases insignificantly (Table 2, figs. 9, 10). Also no changes in the crystal field symmetry of iron ions have been noted.

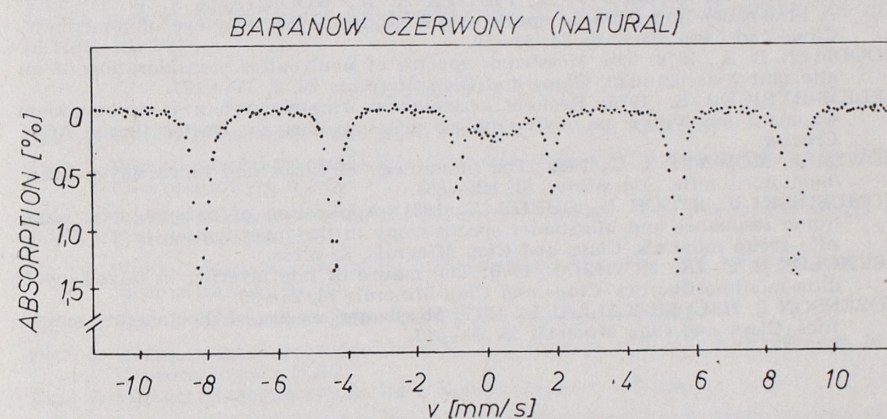


Fig. 9. Mössbauer spectrum of clay from Baranów (fraction $< 2 \mu\text{m}$)

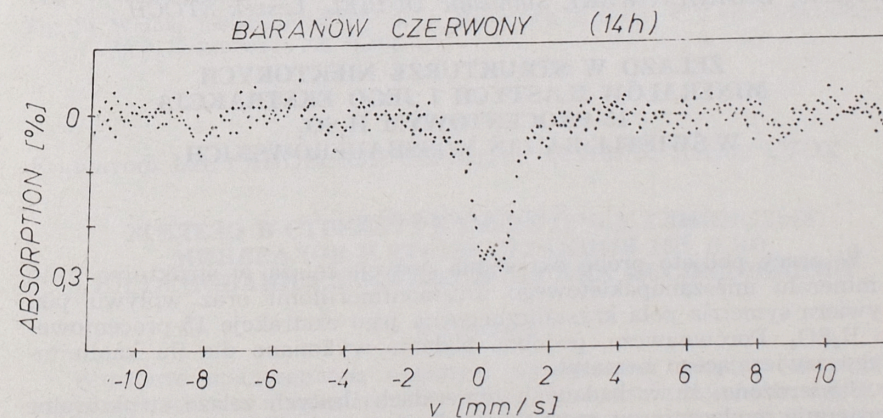


Fig. 10. Mössbauer spectrum of clay from Baranów (fraction $< 2 \mu\text{m}$) treated 14 h with 15% H_2SO_4

Mössbauer spectroscopy has proved to be a satisfactory method for the investigation of iron extraction from clays. It allows one to follow the process of extraction of iron occurring in different mineralogical forms (haematite, structural iron of layered silicates), as well as to determine changes in the crystal field symmetry of ferric and ferrous iron.

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Krzysztof BAHRANOWSKI, Stanisław DUBIEL, Leszek STOCH

ZELAZO W STRUKTURZE NIEKTÓRYCH MINERAŁÓW ILASTYCH I JEGO EKSTRAKCYJA 15-PROCENTOWYM H_2SO_4 W ŚWIETLE BADAŃ MÖSSBAUERÓWSKICH

Streszczenie

W pracy podjęto próbę określenia pozycji żelaza w strukturze illitu i minerału mieszanopacketowego illit/montmorillonit oraz wpływu jaki wywiera symetria pola krystalicznego na jego ekstrakcję 15-procentowego H_2SO_4 . Porównawczo, podobne badania wykonano dla ilu kaolinitowego zawierającego hematyt.

Stwierdzono, że w badanych minerałach ilastych żelazo strukturalne występuje wyłącznie w warstwie oktaedrycznej. Może zajmować tam dwie pozycje, różniące się symetrią pola krystalicznego. Plość żelaza w pozycjach o wysokiej symetrii pola krystalicznego jest niewielka, prze-

waża żelazo w pozycjach niskosymetrycznych. Jony żelaza zajmujące pozycje niskosymetryczne są łatwiej usuwalne w wodnym roztworze kwasu siarkowego, niż znajdujące się na pozycjach o wyższej symetrii pola krystalicznego.

Ekstrakcja kationów Al, Mg i Fe z warstwy oktaedrycznej minerałów ilastych i powstanie luk w pozycjach kationowych w warstwie oktaedrycznej może powodować zmianę symetrii tych pozycji. Symetria pola krystalicznego wokół niewyekstrahowanych ze struktury jonów żelaza ulega podwyższeniu.

Szybkość usuwania żelaza ze struktury minerałów ilastych jest różna dla różnych minerałów. Najszybciej usuwane jest żelazo z illitu z Plecewicz, wolniej z minerału mieszanopacketowego illit/montmorillonit z Krańca, najwolniej z beidelitu z Konina. Zaznacza się ponadto wyraźna zależność pomiędzy zawartością żelaza strukturalnego a szybkością jego ekstrakcji do roztworu pod wpływem kwasu siarkowego. Szybkość usuwania żelaza jest w przybliżeniu proporcjonalna do jego ilości w strukturze minerału ilastego.

OBJAŚNIENIA FIGUR

- Fig. 1. Widmo mössbauerowskie ilu z Plecewicz (frakcja $< 2 \mu m$)
- Fig. 2. Widmo mössbauerowskie ilu z Plecewicz (frakcja $< 2 \mu m$) traktowanego 0,5 h 15-procentowym H_2SO_4
- Fig. 3. Widmo mössbauerowskie ilu z Plecewicz (frakcja $< 2 \mu m$) traktowanego 1h 15-procentowym H_2SO_4
- Fig. 4. Widmo mössbauerowskie ilu z Plecewicz (frakcja $< 2 \mu m$) traktowanego 14 h 15-procentowym H_2SO_4
- Fig. 5. Widmo mössbauerowskie ilu z Krańca (frakcja $< 2 \mu m$)
- Fig. 6. Widmo mössbauerowskie ilu z Krańca (frakcja $< 2 \mu m$) traktowanego 14 h 15-procentowym H_2SO_4
- Fig. 7. Widmo mössbauerowskie ilu z Konina (frakcja $< 1 \mu m$)
- Fig. 8. Widmo mössbauerowskie ilu z Konina (frakcja $< 1 \mu m$) traktowanego 14 h 15-procentowym H_2SO_4
- Fig. 9. Widmo mössbauerowskie ilu z Baranowa (frakcja $< 2 \mu m$)
- Fig. 10. Widmo mössbauerowskie ilu z Baranowa (frakcja $< 2 \mu m$) traktowanego 14 h 15-procentowym H_2SO_4

Кришитоф БАГРАНОВСКИ, Станислав ДУБЕЛЬ, Лешек СТОХ

ЖЕЛЕЗО В СТРУКТУРЕ НЕКОТОРЫХ ГЛИНИСТЫХ МИНЕРАЛОВ И ЕГО ЭКСТРАКЦИЯ 15% H_2SO_4 НА ОСНОВАНИИ МОССБАУЭРОВСКИХ ИССЛЕДОВАНИИ

Резюме

В работе представлена попытка определения позиции железа в структуре иллита и смешаннопачкового минерала иллита/монтмориллонит, а также влияние какое оказывает симметрия кристаллического поля на его экстракцию 15% H_2SO_4 . Для сравнения подобные исследования проведены для каолинитовой глины содержащей гематит.

Констатировано, что в исследованных глинистых минералах структурное железо находится только в октаэдрическом слое. Может занимать там две позиции отличающиеся симметрией кристаллического поля. На позициях с высокой симметрией кристаллического поля количество железа небольшое, преобладает железо на низкосимметрических позициях. Ионы железа занимающие низкосимметрические позиции легче уstraняются в водном растворе серной кислоты, чем находящиеся на позициях с более высокой симметрией кристаллического поля.

Экстракция катионов Al, Mg и Fe из октаэдрического слоя глинистых минералов и образование пробелов в позициях катионов в октаэдрическом слое может обуславливать изменение симметрии этих позиций. Симметрия кристаллического поля становится более высокой вокруг неэкстрагированных из структуры ионов железа.

Скорость удаления железа из структуры глинистых минералов является разной для разных минералов. Быстрее всего железо уstraняется из иллита из Плецевиц, медленнее из смешаннопачкового минерала иллит/монтмориллонит из Краньца, еще медленнее из бейделлита из Кони́на. Кроме того отмечается четкая зависимость между содержанием структурного железа а скоростью его экстракции в раствор под влиянием серной кислоты. Скорость удаления железа приблизительно пропорциональна его количеству в структуре глинистого минерала.

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- Фиг. 1. Моссбауэровский спектр глины из Плецевиц (фракция $< 2 \mu\text{м}$)
- Фиг. 2. Моссбауэровский спектр глины из Плецевиц (фракция $< 2 \mu\text{м}$) продерживанной 0,5 часа в 15% H_2SO_4
- Фиг. 3. Моссбауэровский спектр глины из Плецевиц (фракция $< 2 \mu\text{м}$) продерживанной 1 час в 15% H_2SO_4
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