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TITRATION OF SOME CLAY MINERALS ACTIVATED WITH SULPHURIC ACID

Abstract. Acid properties of beidellite and kaolinite activated with sulphuric acid were determined from titration curves. It has been found that activation of beidellite leads to the formation of acid centres of different strength on its internal and external surfaces. The number of strong acid centres does not depend on activation time, while the amount of weak acid centres diminishes with prolonged activation time. Activated kaolinite has only weak acid centres, and their number increases with prolonged activation. The "ageing" of beidellite and kaolinite is reflected by the decreased amount of acid centres.

INTRODUCTION

The action of inorganic acids on clay minerals causes the disarrangement of their structure and modifies their surface properties. The structural changes involve the exchange of interlayer cations for hydronium ion and the selective dissolution of octahedral and tetrahedral sheets (Mering 1949; Osthaus 1954, 1956; Granquist, Sumner 1959; Miller 1965; Tiller 1968; Fijał, Kłapyta, Ziętkiewicz, Żyła 1975; Stoch, Bahranowski, Budek, Fijał 1977; Bahranowski, Stoch 1978; Bahranowski 1980; Stoch, Bahranowski 1981). The changes in surface properties consist in the increase of acidic properties of clay minerals (Mills, Holmes, Cornelius 1950; Tamele 1950; Brindley 1952; Stoch, Bahranowski, Gątarz 1979; Fijał, Kłapyta, Żabiński, Żyła 1980). One method of determining acidic properties is to titrate clay suspensions with appropriate bases. On the basis of titration curves it is possible to estimate indirectly the number of protons and the energy of their bonding to the surface of clay minerals.

An equilibrium titration curve is obtained by measuring the pH of suspension after each successive, specified amount of base is added and the system reaches an equilibrium state. It usually takes a long time, from several hours to a few days, to attain equilibrium (Samiullah Khan, Singhal 1967; Jackson 1974), and it is often questionable whether the system has reached an equilibrium state.

Considering this, the method of non-equilibrium titration curves was used in this paper. The curves are plotted on the basis of continuous measurements of the

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pH of suspension during its titration with a base. This method was employed to compare the acidic properties of beidellite and kaolinite activated with sulphuric acid for different lengths of time, and to determine the effect of "ageing" of the activated minerals on their acidic properties.

MATERIALS AND METHODS

Studies were carried out on the Poznań clay (< 1 μm fraction) from the "Kazimierz" strip mine in Konin, and on kaolin from Kalno (< 2 μm fraction).

The < 1 μm fractions of the Poznań clay from Konin contains about 80 wt. % of smectites and admixtures of kaolinite, illite and quartz. Among smectites, beidellite and mixed-layer illite/smectite were identified. This mineral association will be referred to further on as beidellite.

The < 2 μm fraction of kaolin from Kalno contains kaolinite with a well ordered structure and some illite.

The samples were activated with 15% H_2SO_4 on a water bath at a constant reaction temperature of 95°C for 0.5 and 14 hours. Then they were washed with distilled water, dried and stored in weighing bottles.

The acidic properties of samples were studied immediately after their activation and five years after activation.

To obtain titration curves, each sample was dried at 105°C, where upon 250 mg was weighed and a small amount of distilled water was added. After dispergation (15 s) with ultrasounds, the suspension was transferred to a beaker, filling up to a volume of 150 ml, carefully stirred and titrated with 0.05 N NaOH. Titration curves were plotted in the system: pH of suspension — milligram-equivalent of NaOH added per 100 g sample.

RESULTS AND DISCUSSION

The titration curves illustrate the dynamic, non-equilibrium process of neutralization of suspension. The inflexion point (equivalent point) on the curves determine the complete neutralization of acid centres. The corresponding amount of added NaOH depends on the number of acid centres, whereas the corresponding value of pH is related to the strength (kind) of acid centres.

The results are listed in Table 1. Titration curves, each being the mean of two parallel determinations, are shown in Figures 1 and 2.

The titration curves for beidellite, obtained immediately after its activation (1982), have two equivalent points (Fig. 1). One corresponds to the neutralization of strong acid centres (I), i.e. protons present in the interlayer spaces of beidellite, weakly bound to the surface of mineral. The other equivalent point determines the complete neutralization of weak acid centres (II), mainly protons located at the edges of layers. Such behaviour of titration curves is typical of the hydrogen forms of beidellite (Wilgat 1982). The small amount of strong acid centres may be attributed to the relatively strong bonding of protons in the interlayer spaces of beidellite. In this case, their exchange for sodium during titration with 0.05 N NaOH is a slow and gradual process.

The prolongation of activation time from 0.5 to 14 hours does not affect the amount or strength of centres with strong acid properties but reduces the number of weak acid centres. Prolonged, 14-hour acid activation disarranges appreciably the structure of beidellite (Bahranowski 1980). Its dissolution begins at the peri-

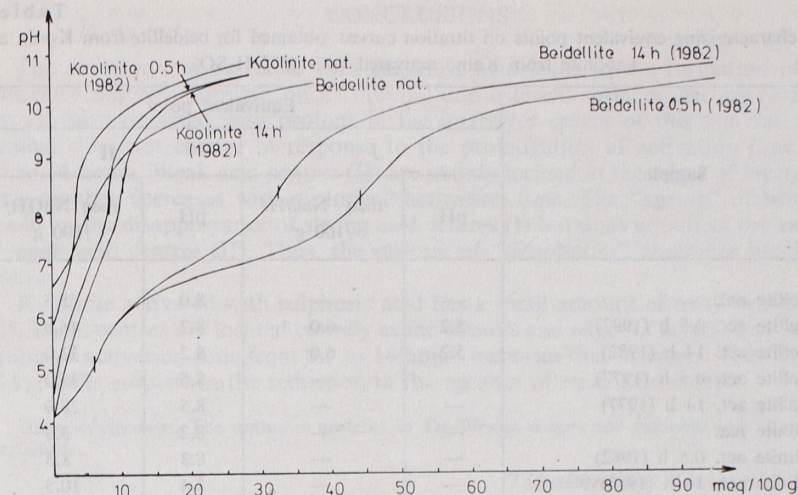


Fig. 1. Titration curves obtained for beidellite from Konin and kaolinite from Kalno immediately after their activation

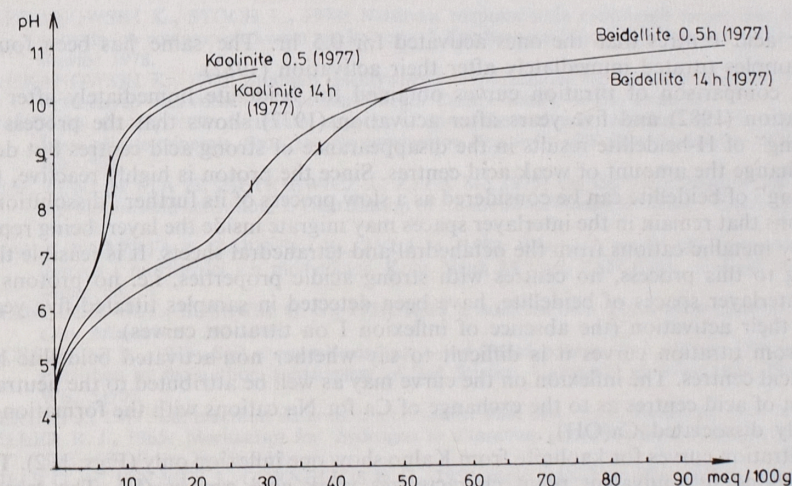


Fig. 2. Titration curves obtained for beidellite from Konin and kaolinite from Kalno five years after their activation

pheries, proceeding inwards (Bahranowski 1980). It appears, therefore, that the extraction of metallic cations from the octahedral sheet into solution may lead to the reduction in the number of weak acid centres connected with the edges of layers.

Titration curves obtained for beidellite five years after its activation (1977) have a different shape (Fig. 2). They show only one inflexion, corresponding to the neutralization of weak acid centres. Samples activated for 14 hours have

Table 1

Data characterizing equivalent points on titration curves obtained for beidellite from Konin and kaolinite from Kalno activated with 15% H₂SO₄

Sample	Equivalent point			
	I		II	
	pH	meq NaOH/ /100 g	pH	meq NaOH/ /100 g
Beidellite nat.	—	—	8.0	5.5
Beidellite act. 0.5 h (1982)	5.2	6.0	8.2	45.0
Beidellite act. 14 h (1982)	5.2	6.0	8.2	33.0
Beidellite act. 0.5 h (1977)	—	—	8.5	39.0
Beidellite act. 14 h (1977)	—	—	8.5	28.0
Kaolinite nat.	—	—	8.2	3.5
Kaolinite act. 0.5 h (1982)	—	—	8.3	8.5
Kaolinite act. 14 h (1982)	—	—	8.4	10.5
Kaolinite act. 0.5 h (1977)	—	—	8.3	7.5
Kaolinite act. 14 h (1977)	—	—	8.3	8.8

fewer acid centres than the ones activated for 0.5 hr. The same has been found for samples titrated immediately after their activation (1982).

A comparison of titration curves obtained for beidellite immediately after its activation (1982) and five years after activation (1977) shows that the process of "ageing" of H-beidellite results in the disappearance of strong acid centres but does not change the amount of weak acid centres. Since the proton is highly reactive, the "ageing" of beidellite can be considered as a slow process of its further "dissolution". Protons that remain in the interlayer spaces may migrate inside the layer, being replaced by metallic cations from the octahedral and tetrahedral sheets. It is feasible that owing to this process, no centres with strong acidic properties, i.e. no protons in the interlayer spaces of beidellite, have been detected in samples titrated five years after their activation (the absence of inflexion I on titration curves).

From titration curves it is difficult to say whether non-activated beidellite has any acid centres. The inflexion on the curve may as well be attributed to the neutralization of acid centres as to the exchange of Ca for Na cations with the formation of weakly dissociated Ca(OH)₂.

Titration curves for kaolinite from Kalno show one inflexion only (Figs. 1, 2). The corresponding equivalent point characterizes weak acid centres (II). The sample activated for 0.5 hr has twice as many acid centres as the untreated sample. On the other hand, 14-hour activation causes a nearly 20% increase in the number of acid centres compared with 0.5-hour activation (Table 1). The disarrangement of the structure of kaolinite during activation with sulphuric acid is considerably less than in beidellite. In this process, mainly aluminium is extracted from the structure of kaolinite (Bahranowski 1980). The activation of kaolinite proceeds at a slower rate than the activation of beidellite, hence samples activated for 14 hours have a greater number of acid centres than the ones activated for 0.5 hr.

The "ageing" of activated kaolinite manifests itself in the decrease in the number of acid centres.

CONCLUSIONS

The activation of beidellite with sulphuric acid leads to the formation of acid centres of different strength on its internal and external surfaces. Strong acid centres (I) are associated with protons in the interlayer spaces of this mineral. Their number does not change in response to the prolongation of activation time from 0.5 to 14 hours. Weak acid centres (II) are mainly located at the edges of layers, and their number decreases with prolonged activation time. The "ageing" of beidellite results in the disappearance of strong acid centres (I) but does not affect the amount of weak acid centres (II). Thus, the process of "dissolution" continues but is less intense.

Kaolinite activated with sulphuric acid has a small amount of weak acid centres (II). These centres are located entirely at the corners and edges of layers. The prolongation of activation time from 0.5 to 14 hours increases their number. The "ageing" of kaolinite consists in the reduction in the number of weak acid centres.

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REFERENCES

- BAHRANOWSKI K., STOCH L., 1978: Kinetyka rozpuszczania niektórych minerałów ilastych w wodnych roztworach kwasu siarkowego. I Konferencja Mineraly i Surowce Ilaste, Boleśławiec 1978.
- BAHRANOWSKI K., 1980: Studium selektywnego rozpuszczania niektórych minerałów ilastych w wodnych roztworach kwasu siarkowego. Doctor thesis, AGH, Cracow.
- BRINDLEY G. W., 1952: Structural aspects of some thermal and chemical transformation of layer silicate minerals. Proc. Int. Symposium on Reactivity of Solids. Gothenberg (Sweden), 349—361.
- FIJAŁ J., KŁAPYTA Z., ZIĘTKIEWICZ J., ŻYŁA M., 1975: On the mechanism of the montmorillonite acid activation. I. Degradation of Ca-montmorillonite structure. *Miner. Pol.* 6, 1, 29—43.
- FIJAŁ J., KŁAPYTA Z., ŻABIŃSKI W., ŻYŁA M., 1980: Własności powierzchniowe minerałów ilastych i możliwości ich modyfikacji. Kom. Nauk Mineral. PAN Oddz. w Krakowie, *Pr. Miner.* 65.
- GRANQUIST W. T., SUMNER G. G., 1959: Acid dissolution of a Texas bentonite. *Clays and Clay Minerals* 6, 292—308.
- JACKSON M. L., 1974: Soil chemical analysis — advanced course. 2nd edition, 9th printing. Published by the author. Department of Soil Science. University of Wisconsin, Madison, Wis. 53706.
- MERING J., 1949: Les reactions de la montmorillonite. *Bull. Soc. Chim. France D*, 218—223.
- MILLER R. J., 1965: Mechanism for hydrogen to aluminum transformation in clays. *Soil Sci. Soc. Am. Proc.* 29, 36—39.
- MILLS G. A., HOLMES J., CORNELIUS E. G., 1950: Acid activation of some bentonite clays. *J. Phys. Chem. Coll. Chem.* 54, 1170—1185.
- OSTHAUS B., 1954: Chemical determination of tetrahedral ions in nontronite and montmorillonite. *Clays and Clay Minerals*. Nat. Acad. Sci. Nat. Res. Council Publ. 327, 404—417.
- OSTHAUS B., 1965: Kinetic studies on montmorillonites and nontronites by the acid dissolution techniques. *Clays and Clay Minerals* 4, 301—321.
- SAMIULLAH KHAN, SINGHAL J. P., 1967: Titrations of hydrogen clays with nicotine. *Soil. Sci.* 104, 427—432.
- STOCH L., BAHRANOWSKI K., BUDEK L., FIJAŁ J., 1977: Bleaching properties of non-bentonitic clay materials and their modification. I. Acid activation of the Miocene clays from Machów. *Miner. Polon.* 8, 1, 31—51.
- STOCH L., BAHRANOWSKI K., GAJARZ Z., 1979: Bleaching properties of non-bentonitic clay materials and their modification. II. Bleaching ability of natural and activated Krakowice clays from Machów. *Miner. Polon.* 10, 2, 21—38.

- STOCH L., BAHRANOWSKI K., 1981: Mechanism and kinetics of iron and aluminium extraction from clay minerals by acid solutions. 7th International Clay Conference, Bologna and Pavia (Italy), 6—12 September, 1981.
- TAMELE M. W., 1950: Chemistry of surface and the activity of aluminosilica cracking catalysts. *Disc. Farad. Soc.* 8, 270—279.
- TILLER K. G., 1968: Stability of hectorite in weakly acidic solutions. I. A chemical study of the dissolution of hectorite with special reference to the release of silica. *Clay Minerals* 7, 245—260.
- TILLER K. G., 1968: Stability of hectorite in weakly acidic solutions. II. Studies of the chemical equilibrium and the calculation of free energy. *Clay Minerals* 7, 261—345.
- WILGAT M., 1982: Charakterystyka mineralogiczna i niektóre właściwości fizykochemiczne smektytów w wybranych glebach Polski. Doctor thesis. AGH, Cracow.

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KRZYWE MIARECZKOWANIA NIEKTÓRYCH MINERAŁÓW ILASTYCH AKTYWOWANYCH KWASEM SIARKOWYM

Streszczenie

Aktywacja beidellitu kwasem siarkowym prowadzi do powstania na jego wewnętrznej i zewnętrznej powierzchni centrów kwasowych o różnej mocy. Silne centra kwasowe (I) związane są z protonami w przestrzeniach międzypakietowych. Ilość ich nie ulega zmianie przy wydłużaniu czasu aktywacji od 0,5 do 14 godzin. Centra o słabych właściwościach kwasowych (II) zlokalizowane są głównie na krawędziach pakietu. Ilość ich maleje z wydłużaniem czasu aktywacji od 0,5 do 14 godzin. „Starzenie” się beidellitu prowadzi do zaniku centrów o silnych właściwościach kwasowych (I) i nie powoduje zmiany ilości centrów o słabych właściwościach kwasowych (II). Proces „roztwarzania” minerału przebiega więc nadal, lecz z mniejszą intensywnością.

Kaolinit aktywowany kwasem siarkowym posiada małą ilość centrów o słabych właściwościach kwasowych (II). Centra te zlokalizowane są wyłącznie na narożach i krawędziach pakietu. Wydłużanie czasu aktywacji od 0,5 do 14 godzin powoduje wzrost ich ilości. „Starzenie” się kaolinitu przejawia się zmniejszaniem ilości centrów o słabych właściwościach kwasowych.

OBJAŚNIENIA FIGUR

- Fig. 1. Krzywe miareczkowania beidellitu z Konina i kaolinitu z Kalna wykonane bezpośrednio po ich aktywowaniu
- Fig. 2. Krzywe miareczkowania beidellitu z Konina i kaolinitu z Kalna wykonane pięć lat po ich aktywowaniu

Кишиниоф БАХРАНОВСКИ

КРИВЫЕ ТИТРОВАНИЯ НЕКОТОРЫХ ГЛИНИСТЫХ МИНЕРАЛОВ АКТИВИРОВАННЫХ СЕРНОЙ КИСЛОТОЙ

Резюме

Активация бейделлита серной кислотой ведет к образованию на его внешней и внутренней поверхностях кислотных центров различной интенсивности. Сильные кислотные центры (I) связаны с протонами в межпакетных пространствах. Количество их не подвергается изменению при удлинении времени активации от 0,5 до 14 часов. Центры о слабых кислотных свойствах (II) располагаются преимущественно на ребрах пакета. Их количество сокращается с удлинением времени активации от 0,5 до 14 часов. «Старение» бейделлита приводит к исчезновении центров с сильными кислотными свойствами (I) и не вызывает изменения количества центров со слабыми кислотными свойствами. Процесс «растворения» минерала проходит однако по-прежнему но с меньшей интенсивностью.

Активированный серной кислотой каолинит имеет небольшое количество центров со слабыми кислотными свойствами (II). Эти центры располагаются исключительно в углах и на ребрах пакета. Увеличение времени активации с 0,5 до 14 часов вызывает увеличение их количества. «Старение» каолинита проявляется в сокращении количества центров со слабыми кислотными свойствами.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Кривые титрования бейделлита из Конина и каолинита из Кальна, полученные непосредственно после их активации
- Фиг. 2. Кривые титрования бейделлита из Конина и каолинита из Кальна, полученные 5 лет спустя после их активации