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# DETERMINATION OF CHEMICAL FORMULA OF A SMECTITE

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## ABSTRACT

Smectites are dominant clay minerals in bentonites. Each of montmorillonite, beidelite, nontronite, hectorite and saponite minerals is a member of smectite group. They are valuable mineral class for industrial applications because of their high cation exchange capacities, surface area, surface reactivity, adsorptive capacity and catalytic activity. Chemical analysis in combination with other techniques is suitable for the quantitative determination of smectite minerals in natural bentonites. Chemical formula of a smectite which is important to choose its industrial uses can be calculated from chemical analysis. The converting a chemical analysis of a smectite mineral into a chemical formula was discussed in this study depending on various parameters.

**KEYWORDS:** Cation exchange capacity, chemical analysis, chemical formula, exchangeable cations, smectite.

## INTRODUCTION

Smectites are major clay minerals in bentonites. Pure smectite which is seldom found in nature and can be obtain by purification of bentonites [1]. Smectites are important in geology, agriculture, construction, engineering, process industries, and environmental applications [2-4]. They have several traditional applications such as drilling fluids, foundry bondants, liquid barriers, decolorization, catalysts, ceramics, paper, paint, plastics, and chemical carriers [5]. Some high technology materials such as pillared clay, organoclay, and polymer-clay nanocomposites have been obtained by physicochemical modification of smectites [6-10].

Smectites are 2:1 layer clay minerals. The 2:1 layer has two silica tetrahedral (T) sheets bonded to a central octahedral (O) sheet. The 2:1 layer is also named TOT layer. There is considerable substitution in the octahedral sheet of $Fe^{2+,3+}$, and $Mg^{2+}$ for $Al^{3+}$, which creates a charge deficiency in the TOT layer. Also, there is some substitution of in the tetrahedral sheet of $Al^{3+}$ for $Si^{4+}$ which again

creates a charge imbalance. This net positive charge deficiency is balanced by exchangeable cations located between the TOT layers and around the edges. Thus, of the exchangeable cation is $Na^+$ the specific mineral is sodium smectite (NaS), if it is $Ca^{2+}$ it is a calcium smectite (CaS). $Na^+$ and $Ca^{2+}$ are hydrated between the 2:1 (TOT) layers. NaS generally have one water layer between the 2:1 layer and CaS generally have two water layers.

Smectites can be both dioctahedral and trioctahedral like as prophllite, $Al_2Si_4O_{10}(OH)_2$, and talc, $Mg_3Si_4O_{10}(OH)_2$, respectively. In dioctahedral (DO) structure 2/3 of octahedral sites are occupied with trivalent cations such as $Al^{3+}$ and $Fe^{2+}$. All octahedral sites in trioctahedral (TO) structure filled with bivalent cations such as $Mg^{2+}$ for $Fe^{2+}$.

Smectite is the name given to a clay minerals group. The special name and chemical formula unit of each member of smectite group are given below [11].

Montmorillonite (DO) : $M^{+}_{0.33}\,(Al_{1.67}\,Mg_{0.33})\,Si_4\,O_{10}\,(OH)_2.\,nH_2O$

Beidellite (DO) : $M^{+}_{0.33}\,Al_2\,(Si_{3.67}\,Al_{0.33})\,O_{10}\,(OH)_2.\,nH_2O$

Nontronite (DO) : $M^{+}_{0.33}\,Fe^{3+}_{2}\,(Si_{3.67}\,Al_{0.33})\,O_{10}\,(OH)_2.\,nH_2O$

Hektorite (TO) : $M^{+}_{0.33}\,(Mg_{2.67}\,Li_{0.33})\,Si_4\,O_{10}\,(OH)_2.\,nH_2O$

Saponite (TO) : $M^{+}_{0.33}\,(Mg_{2.67}\,R^{3+}_{0.33})\,(Si_{3.34}\,Al_{0.66})\,O_{10}\,(OH)_2.\,nH_2O$

Here, $M^+$ represents the exchangeable cations such as $Na^+$, $K^+$, and $Ca^{2+}$. $R^{3+}$ is a trivalent cation such as $Al^{3+}$, $Fe^{3+}$ and $Cr^{3+}$ and $nH_2O$ is the total water content intra- and interparticles of smectite. These minerals have significantly different physicochemical properties which dictate to a large degree their industrial uses. The two most important industrially are sodium montmorillonite and calcium montmorillonite. However, chemical formula of a smectite is an important parameter to choose of its industrial utilization. Hence, the aim of this study is converting a chemical analysis of a smectite into a chemical formula.

## MATERIALS AND METHODS

A sodium smectite isolated from Reşadiye (Tokat/Turkey) bentonite by purification was used as material in this study [12,13]. Before chemical analysis, the bentonite dried at 105°C for 4h was heated at 1000°C for 2h, and the decrease in mass was taken as the loss on ignition (LOI). For chemical analysis, approximately 0.25g sample was weighed and put into a platinum crucible. This sample was mixed with 3g $LiB_4O_7$ (Merck) and was digested at 1000°C for 1h. The prepared sample was than cooled down to the room temperature. The crucible was placed in beaker containing of 1000mL 10%HCl. The system was heated to 90°C by stirring until the precipitate in crucible was dissolved. The solution was diluted to 250mL in a volumetric flask. The metal content of the sample were analyzed by Hitachi Z-8200 Atomic Adsorption Spectrophotometer. The results were calculated as the mass% of the metal oxides.

## RESULTS AND DISCUSSION

The chemical formula unit for each smectite is given above. In these formulas, $nH_2O$ represents the adsorbed water among and between 2:1 layers of smectite. The amount of this water is exchangeable depend on the type of smectite, moisture in air and temperature. The amount of this water in the investigated smectite is equal to the LOI. The LOI is found as 6.90% by mass. It has not any importance to calculate chemical formula unit. Each of the chemical formula units the $O_{10}(OH)_2$ group having negative electric charge. One mole $H_2O$ form from this group by heating and eleven mole oxygen, $O_{11}$, remains. Therefore, the chemical formula unit of a smectite is based on 11 oxygens, 8 from the tetrahedral sheets and 3 from octahedral sheet of a 2:1 layer. The negative electric charge of 11 oxygens in one chemical formula unit is $\sum Q_- = -22F$, where $F=96485 C mol^{-1}$ represents faraday constant. The value of F is equal to electric charge of one mole electron. The unit of the electric charge is coulomb (C). The charge of an electron $e = 1.60218x10^{-19}$ C. One mole of particles such as electrons, atoms or molecules is represented by Avogadro constant that is $N_A = 6.02214x10^{23} mol^{-1}$. The negative and positive electric charges in a neutral chemical compound must be equal to each other. Hence, the total positive charge in each chemical formula unit must be equal $\sum Q_+ = +22F$. This rule is used by determination the chemical formula unit from the result of chemical analysis.

The determination of chemical formula unit of a smectite by using chemical analysis is summarized in Table 1. Explanations of the 7 columns in this table are as follows [11-14].

1. The oxides of metals in the smectite are represented in first column. The $Si^{4+}$ and a part of $Al^{3+}$ cations are at the tetrahedral positions. The rest of $Al^{3+}$ and also $Ti^{3+}$, $Fe^{3+}$, $Fe^{2+}$, and $Mg^{2+}$ cations are at the octahedral positions. The $Na^+$, $K^+$, and $Ca^{2+}$ are between the 2:1 layers. The $Na^+$ and $Ca^{2+}$ may be easily exchangeable with all the inorganic and organic cations, but $K^+$ does not.

2. The content of each metal oxide obtained from chemical analysis is given in second column. The mass percentage (mass %) may be taken as mass (m/g) of metal oxide in 100g of the smectite.
3. The molar mass ($M/gmol^{-1}$) of each metal oxide calculated from adding the molar masses of the elements within the oxides are given in third columns.
4. The equivalent mass ($E/g\ eqv^{-1}$) of each metal oxide calculated from dividing the molar mass by the total cation charge in the oxide is given in fourth column. For example, for $Fe_2O_3$, divide $159.691 gmol^{-1}$ to 6 to get $26.615 g\ eqv^{-1}$ because there are $2Fe^{3+}$ cations in this oxide.
5. The positive electric charge ($q_+/F$) in each metal oxide formed from 100g of the smectite is calculated from dividing the mass by the equivalent mass, $q_+=m/E$, is given in fifth column. For example, again for $Fe_2O_3$, divide m= 4.88g by E= $26.615 g\ eqv^{-1}$ to get 0.183 eqv which means $q_+$= 0.183F. The total positive electric

**Table 1**. The steps for determination of chemical formula unit of the smectite by using chemical analysis ($\Sigma q_+$= 5.731F, $\Sigma Q_-$= -22F, $\Sigma Q_+$= 22F, f= $\Sigma q_+/\Sigma Q_+$= 5.731/22= 0.2605)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| Metal | m (mass%) | M | $E=M/\Sigma z_+$ | $q_+=m/E$ | $Q_+=q_+/f$ | $x_+=Q_+/z_+$ |
| oxide | g | $g\ mol^{-1}$ | $g\ eqv^{-1}$ | F | F | - |
| $SiO_2$ | 61.65 | 60.084 | 15.021 | 4.104 | 15.754 | 3.939 |
| $TiO_2$ | 0.30 | 79.894 | 19.979 | 0.015 | 0.058 | 0.015 |
| $Al_2O_3$ | 21.10 | 101.959 | 16.993 | 1.242 | 4.768 | 1.589 |
| $Fe_2O_3$ | 4.88 | 159.691 | 26.615 | 0.183 | 0.702 | 0.234 |
| MgO | 1.98 | 40.304 | 20.152 | 0.098 | 0.376 | 0.188 |
| CaO | 0.36 | 56.079 | 28.040 | 0.013 | 0.050 | 0.025 |
| $Na_2O$ | 2.14 | 61.979 | 30.990 | 0.069 | 0.265 | 0.265 |
| $K_2O$ | 0.34 | 94.195 | 47.097 | 0.007 | 0.027 | 0.027 |

charge in all metal oxides formed from 100g smectite is calculated as $\Sigma q_+$= 5.731F. This value is lower than the total negative charge in the chemical formula unit of the smectite.

6. The total positive electric charge for the chemical formula unit must be $\Sigma Q_+$= 22F according to the eletroneutrality. A convertion factor between these values is defined as f= $\Sigma q_+/\ \Sigma Q_+$= 5.731/22=0.2605. The positive electric charge ($Q_+/F$) in each metal oxide formed from the chemical formula unit is calculated from

$q_+/0.2605$ ratio and given in sixth column. For example, for $Al_2O_3$, divide $q_+= 1.242F$ by 0.2605 to get $Q_+= 4.768F$.

7. The molar content ($x_+$) of each cation in the chemical formula unit obtained from dividing the $Q_+$ value by positive electric charge ($z_+$) of the cation is given in seventh column. For example, for $Al_2O_3$, divide $Q_+= 4.768F$ by $z_+=3F$ to get $x_+= 1.589$.

The obtain the chemical formula unit, cations are assigned always to the tetrahedral sheet first, then to the octahedral sheet, and than to the interlayer cation positions. If there had not been at least 4 mole $Si^{4+}$ cations in the formula unit, then you would have had to take enough $Al^{3+}$ to have 4mole cations in the tetrahedral sheet. Hence, the cations in the tetrahedral sheets must be $Si^{4+}_{3.939}\ Al^{3+}_{0.061}$. The remainders of the $Al^{3+}$ cations as 1.586-0.061= 1.528 mole are in the octahedral sheet. As for the rest of the elements, $Fe^{3+}$ is not found as an interlayer cation and will not be found in the tetrahedral sheet if $Al^{3+}$ is present, so it is assigned to the octahedral sheet along with $Mg^{2+}$ and $Ti^{3+}$. The other cations such as $Na^+$, $K^+$ and $Ca^{2+}$ are present interlayer. Now, the sum of the positive charges of the interlayer cations, 0.265+0.027+2x0.025= 0.342, must be balanced by the negative layer charge. A part of the negative layer charge originated from the tetrahedral sheets is 0.061. The reminder layer charge, 0.342-0.061= 0.281, must be originated from the octahedral sheet. It is seen from seventh column in Table 1 as 0.188 which is mole content of $Mg^{2+}$ cations. According to charge balance a part of Fe cations must be bivalent. The subscripts of the $Fe^{2+}$ and $Fe^{3+}$ cations in the octahedral sheet are calculated as 0.281-0.188= 0.093 and 0.234-0.093= 0.141, respectively. According to this discussion, the final chemical formula unit of the smectite is written as follows,

$$Na^{+}_{0.265}\,K^{+}_{0.027}\,Ca^{2+}_{0.025}\,(Al^{3+}_{1.528}\,Ti^{3+}_{0.015}\,Fe^{3+}_{0.141}\,Fe^{2+}_{0.093}\,Mg_{0.188})$$
$$(Si_{3.939}\,Al_{0.061})\,O_{10}\,(OH)_2\,,nH_2O.$$

8. This formula shows that the mineral approximately is a sodium montmorillonite.

## BİR SMEKTİTİN KİMYASAL FORMÜLÜNÜN BULUNMASI


### ÖZET

Smektitler bentonitler içinde yer alan ana kil mineralleridir. Montmorillonit, baydellit, nontronit, hektorit ve saponit minerallerinden her biri simektit grubunun bir üyesidir. Yüksek katyon değiştirme kapasitesi, yüzey alanı, yüzey aktifliği, adsorpsiyon kapasitesi ve katalitik aktifliğe sahip olan smektitler endüstriyel uygulamalar için değerli bir mineral sınıfıdır. Diğer tekniklerle birleştirildiğinde kimyasal analiz bentonitler içindeki simektitlerin nicel olarak belirlenmesinde uygun bir yöntemdir. Endüstriyel kullanım alanlarının belirlenmesinde önemli bir yeri olan kimyasal formül smektitlerin kimyasal analizinden belirlenebilir. Kimyasal analizin kimyasal formüle dönüştürülmesi çeşitli parametrelere bağlı olarak bu çalışma içinde tartışılmıştır.

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## REFERENCES

1. Grim, R.E. *Clay Mineralogy*, 2nd edition, McGraw-Hill, New York, 1968.
2. Murray, H.H. *Appl. Clay Sci.*, 1991, 5, 379-395
3. Murray, H.H. *Clay Miner.*, 1999, 34, 39-49.
4. Murray, H.H. *Appl. Clay Sci.*, 2000, 17, 207-221.
5. Grim, R.E.; Güven, N. *Bentonites-Geology, Mineralogy, Properties and Uses. (Developments in Sedimentology, 24)*, Elsevier, New York, 1978.
6. Adams, J.M. *Appl. Clay.Sci.*, 1987, 2, 309-342.
7. Breen, C.; Zahoor, F.D.; Madejovà, J.; Komadel, P. *J. Phys. Chem. B.,* 1997, 101 ,5324-5331.
8. Chitnis, S.R.; Sharma, M.M. *Reac. Func. Polym.*, 1997, 32, 93-115.
9. Le Baron, P.C.; Wang, Z.; Pinnavaia, T.J. *Appl. Clay Sci.*, 1999, 15, 11-29.
10. Meier, L.P.; Nueesch, R.; Madsen, F.T. *J. Colloid Interf. Sci.*, 2001, 238, 24-32.
11. Moore, D.M.; Reynolds, Jr., R.C. *X-Ray Diffraction and the Identification and Analysis of Clay Minerals*, 2nd edition, Oxford University Press, New York, 1997.
12. Önal, M.; Sarıkaya, Y.; Alemdaroğlu, T. *Turk. J. Chem.*, 2001, 25, 241-249.
13. Önal, M.; Sarıkaya, Y.; Alemdaroğlu, T.; Bozdoğan, İ. *Turk. J. Chem.*, 2003, 27, 683-693.
14. Newman, A.C.D. (Ed.) *Chemistry of Clays and Clay Minerals,* Monograph No.6, Mineragical Society, London, 1987.