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The relationship between isomorphic substitutions and swelling in montmorillonites

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A mathematical relation between the overall degree of isomorphic substitution of bentonites and their swelling capacity was investigated. The relation was found to be closely related to surface defects caused by moulding sands.

1. Introduction

The swelling capacity of bentonites is usually employed to assess the amount of water they can adsorb between their particles and is related to the practical behaviour of the moulding sand with regard to the occurrence of surface defects such as scabs, rat tails, etc. [1].

The widely accepted structure of montmorillonite minerals (Fig. 1), which was first proposed in 1933 by Hofmann *et al.* [2], and later modified by Marshall in 1935 [3], Maegdefran and Hofmann [4] in 1937, and Hendricks [5] in 1942, derives from the crystal structure of pyrophyllyte. The elemental crystal unit (a lamella or flake) of pyrophyllyte consists of two tetrahedral layers of silica and a central octahedral layer of alumina. The tetrahedra in each layer associate with one another in such a way that their bases make up hexagons and their fourth apex points to the inside of the crystal unit. The octahedral layer, in turn, associates with the tetrahedral layers in such a way that the apices of the tetrahedra that point to the inside of the crystal unit also make the apices of the octahedral layer. Tetrahedral apices are occupied by oxygen atoms, whereas unshared octahedral apices are occupied by hydroxyl groups. This crystal unit expands along the crystallographic directions *a* and *b* and its thickness (~ 1 nm) is determined by the three constituent layers. Elemental lamellae stack up along the *c*-axis by forming weak bonds that allow for easy exfoliation.

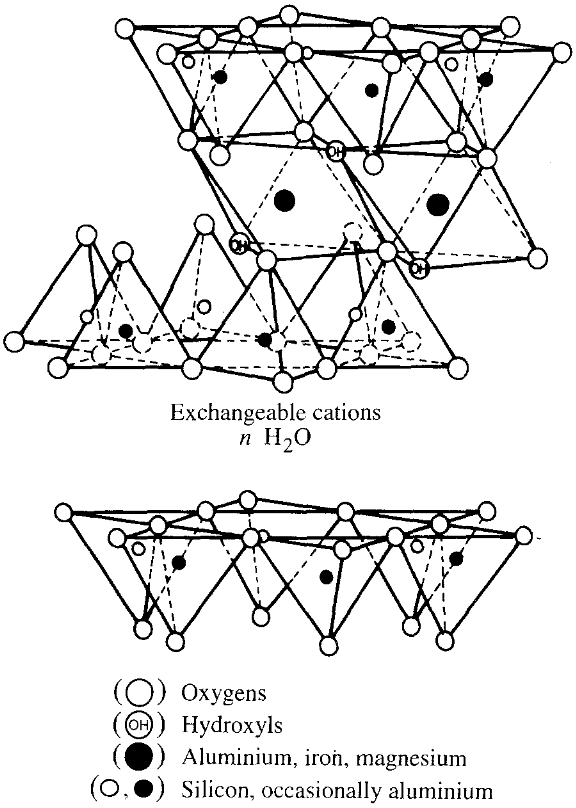

Figure 1 Structure of montmorillonite.

The theoretical formula of the above-described pyrophyllyte structure is $Si_4Al_2O_{10}(OH)_2$, and its theoretical chemical composition is 66.7% SiO_2, 28.3% Al_2O_3 and 5% H_2O.

Montmorillonites, all of which possess the above crystal structure, differ in their theoretical pyrophyllyte formula as a result of isomorphic substitutions of aluminium atoms in the octahedral lattice, which account for their peculiarities and are typical of montmorillonites. The general formula of montmorillonites is thus $[Si_4Al_{2-x}R_x^{2+}O_{10}(OH)_2]EC_x{\cdot}nH_2O$, where R_x^{2+} denotes magnesium in typical montmorillonites but can also represent different cations including iron and manganese in a variety of chemical compositions, and EC_x denotes exchangeable cations (see below). On the other hand, x is indefinite and can vary from 0–2. If all octahedral positions are occupied by magnesium, then the resulting clay mineral is called saponite. Also, if aluminium is replaced with iron, one obtains nontronite.

Both montmorillonite and nontronite preserve the dioctahedral structure of pyrophyllyte (only two-thirds of all octahedral holes are occupied by trivalent cations), whereas saponite possesses a trioctahedral structure (all octahedral holes are occupied by divalent cations).

The most frequent natural occurrences of montmorillonites are dioctahedral aluminium-containing varieties with fairly low degrees of substitution of aluminium by magnesium and/or iron. Bentonite

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clays have been found to consist chiefly of a mixture of montmorillonites with two or more isomorphically substituted cations [6].

Isomorphic substitutions in montmorillonite involve replacement of one trivalent aluminium cation with other divalent cations, so the original electron balance is disturbed. Excess charges are generally balanced by cations that occupy the surfaces of the elemental lamellae – the imbalance can also be partly offset by replacement of hydroxyl groups with oxygen atoms in the octahedral layer. Likewise, the lower degree of isomorphic substitution in the tetrahedral layer (aluminium by silicon) results in an electron imbalance that is also compensated by cations or hydroxyl groups.

The nature of the balanced cations involved influences in the properties of montmorillonites and hence those of bentonites. Such cations are essentially sodium (monovalent) and calcium (divalent), hence the denominations "sodium bentonites" and "calcium bentonites". These cations are electrochemically bonded in montmorillonite, so they are highly water-soluble and can be readily replaced by cation exchange, which is why they are called "exchangeable cations" in montmorillonite (EC_x in the general formula). As lamellae stack up along the *c*-axis, exchangeable cations lie between them forming weak bonds, hence their also being known as "interlayer cations".

The most immediate implication of the montmorilonite structure is that water and other polar molecules can be intercalated between elemental lamellae, which are thus separated along the *c*-axis. This phenomenon is known as swelling. On immersion in water, the original volume of sodium montmorillonite increases by a factor as high as 30, whereas that of calcium montmorillonite can increase by a factor of ~ 10 at the most. Swelling is reversible unless the crystal structure concerned is altered or destroyed by heating.

Ion exchange is of great theoretical and practical significance to swelling because the nature of exchangeable cations can have a marked effect on the physical properties of the material in question and hence on the technological features of the resulting moulding sand. Thus, the swelling capacity, liquid limit, wet compression resistance, etc., all depend on the exchangeable cation involved and can thus be altered within given ranges by cation exchange (in practical terms, all these properties are dependent on the "degree of activation" to a greater or lesser extent.

As noted earlier, isomorphic substitutions facilitate the adsorption of exchangeable cations which, in turn, determine the reversible water adsorption capacity of the material, provided the bentonite in question has not been subjected to temperatures above a given limit.

2. Experimental procedure

The bentonites used in this work were taken from foundries, where they are routinely employed as moulding sand.

Samples were treated as required in order to determine their nature and degree of isomorphic substitution according to procedures reported elsewhere [7, 8].

3. Results and discussion

As stated above, the swelling of montmorillonites is an immediate result of the hydration of exchangeable cations and is very sensitive to their nature. In principle, there must be no easy way of deriving a relation between the swelling capacity and isomorphic substitutions in bentonites on arrival, which typically contain various exchangeable cations (primarily Na^+ and Ca^{2+}). Let us consider Fig. 2 by way of example. It shows a plot of swelling capacity against the overall isomorphic substitution that was constructed from the data given in Table I. As can be seen, there is no clear orientation whatsoever.

In order to eliminate the influence of the nature of interlayer cations, we purified bentonite samples as reported elsewhere [7, 9, 10, 11] and converted them into homoionic lithium substrates because Li^+ ions result in the greatest swelling. Obviously, a lack of isomorphic substitution denotes the absence of exchangeable cations between the elemental lamellae and hence the lack of swellability; in fact, pyrophyllyte does not swell at all. It therefore remained to be seen how swellability varied with the overall degree of isomorphic substitution in homoionic samples. As noted earlier, lithium was the sole interlayer cation present.

Fig. 3 shows a plot of the swelling capacity of the lithium samples (in $cm^3/2$ g as recommended by the 1A International Commission on Bonding Clays, CYAFTF [1]) against the overall degree of substitution, γ (%). Compared to Fig. 2 (bentonites on arrival), Fig. 3 shows not only substantially increased swellability as a result of the presence of Li^+, but also more orderly experimental values. The linear function obtained by polynomial regression for this plot was

$$H = 55 - 0.62\gamma \qquad (1)$$

where H is the swelling capacity of the lithium samples

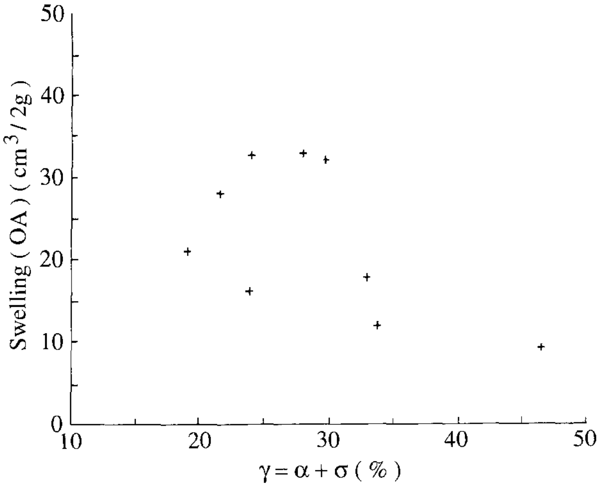

Figure 2 Variation of the swelling capacity of the samples on arrival with the overall degree of isomorphic.

TABLE I Swelling index and degree of isomorphic substitution of the bentonites studied

	Swelling index ($cm^3/2$ g)		Tetrahedral substitution	Octahedral substitution (%)			Overall substitution
Bentonite	OA[a]	LiB[b]	σ (%)	Fe^{3+} (φ)	Mg^{2+} (μ)	Total, $\alpha = \varphi + \mu$	$\gamma = \alpha + \sigma$
C	32	46	5.75	10.50	13.50	24.00	29.75
F	28	44	4.50	5.50	11.50	17.00	21.50
N	33	39	3.00	9.50	15.50	25.00	28.00
O	16	46	6.25	6.50	11.00	17.50	23.75
Q	9	18	2.00	30.00	14.50	44.50	46.50
R	33	45	4.00	8.50	11.50	20.00	24.00
U	21	41	2.50	6.00	10.50	16.50	19.00
V	12	25	6.25	5.50	22.00	27.50	33.75
X	18	33	3.00	8.50	21.50	30.00	33.00

[a] OA, on arrival.

[b] LiB, homoionic lithium bentonite.

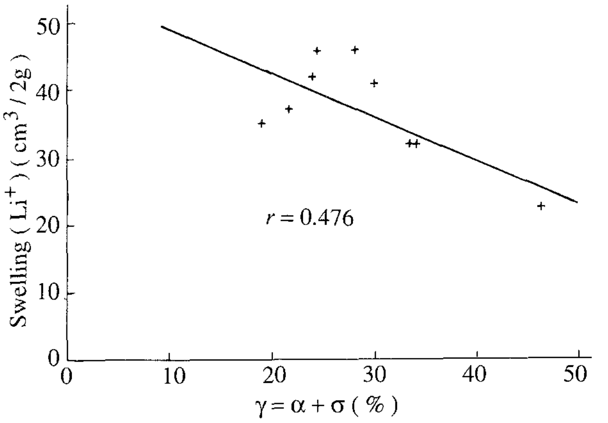

Figure 3 Variation of the swelling capacity of homoionic samples with the overall degree of isomorphic substitution.

($cm^3/2$ g) and γ is the overall degree of isomorphic substitution (%). The correlation coefficient obtained was $r = 0.476$.

Taking into account the origin of swelling, it was, in principle, logical to obtain a direct, positive relationship between the increase in isomorphic substitutions and the swelling capacity. However, our experimental data proved that the opposite was true: the swelling capacity decreased with increase in the overall degree of isomorphic substitution. In any case, this conclusion cannot be extrapolated because it is only valid for the studied range. In fact, according to the independent term in the above equation, nil isomorphic substitution would result in a swelling capacity of 68 $cm^3/2$ g; in fact, pyrophyllyte does not swell at all. The lack of samples with degrees of isomorphic substitution between 0% and 20% precluded obtainment of data for that range, however, one can assume that the swelling capacity must gradually increase from 0 cm $^3/2$ g to 45 $cm^3/2$ g as the degree of substitution increases between the previous two values. Whatever is the shape of the curve for the variation of the swelling capacity over this range, this property of montmorillonites must go by a maximum.

Thus, the phenomenon can be better described in mathematical terms by using a second-order equation. Fig. 4, which was constructed from the same experimental data as Fig. 3 plus those of pyrophyllyte (0,0), shows the graphical representation of the following second-order polynomial function

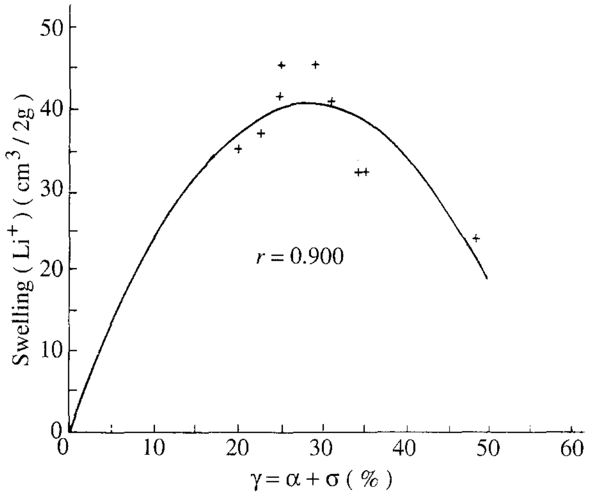

Figure 4 Variation of the swelling capacity of homoionic samples including pyrophllyte with the overall degree of isomorphic substitutions.

$$H = 2 + 3.2\gamma - 0.06\,\gamma^2 \qquad (2)$$

with a correlation coefficient $r = 0.900$.

The intercept of the plot is close to zero (the pyrophyllyte value) and the maximum swelling capacity corresponds to a degree of isomorphic substitution of ~ 25%.

Determining the influence of each of the various isomorphic substitutions (silicon by aluminium in the tetrahedral layer and aluminium by magnesium in the octahedral layer) was impossible. The second-order polynomial functions obtained were identical to that corresponding to complete isomorphic substitution except for their correlation coefficients, which were somewhat lower. In as much as swelling and isomorphic substitution are not related directly, but through interlayer cations, the nature of the substitution is masked, so only the influence of the overall substitutions is observed.

4. Conclusion

Careful analysis of the above experimental results allows one to draw the following conclusions.

1. Establishing a relation between swelling and isomorphic substitution is only possible if the interlayer cations in bentonites are of the same nature, i.e. if the bentonites are homoionic.

2. The relationship between the swelling capacity and overall degree of isomorphic substitution can be expressed by means of a second-order equation in which the former variable reaches a maximum at a degree of isomorphic substitution of $\sim 25\%$.

3. In as much as the relationship is established through the interlayer or exchangeable cations, one can only detect the influence of the overall substitutions.

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