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Smectites: the relationship between their properties and isomorphic substitution

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We have investigated the relationship between the degree of isomorphic substitution in smectites and the green compression strength of sand–smectite–water mixtures. Such a relationship is expressed by a simple mathematical expression which allows the technological behaviour of smectites to be predicted from their degree of isomorphic substitution.

1. Introduction

The technological features of moulding sand (e.g. its resistance to wet and dry compression) are known to be related to some properties of bentonites (swelling capacity, liquid limit etc.) that are directly dependent on the nature of the adsorbed cations and can thus be altered most simply by means of a cation exchange.

While the exchangeable cation is related to some of the properties, it does not seem to appreciably influence others. However, according to our own experience, such properties are indeed related to isomorphic substitutions in bentonites. The aim of this work was to find a relationship between isomorphic substitutions and the technological properties of moulding sands.

2. Experimental procedure

Experiments were carried out on bentonites typically used by foundries in our country. Each sample was collected from three different foundries. The samples were then mixed and homogenized to obtain a single bentonite sample. The nine collected samples were of the following origins: two Spanish, three Moroccan and one each Greek, Italian, American and English.

First, in order to determine both the type and degree of isomorphic substitution of the sample as accurately as possible, we isolated montmorillonite from the other components of the clay sample [1–3] on the basis of the different apparent specific gravities of the minerals suspended in a mixture of ethyl alcohol and bromoform. The results thus obtained are listed in Table I.

The nature and degree of isomorphic substitution were determined according to criteria established elsewhere [1] and summarized in the Appendix. Application of the method called for a precise chemical analysis of montmorillonite; also, in order to avoid potential errors arising from exchangeable cations, we converted the isolated montmorillonite into homoionic samples [4]. The results of the analyses of the homoionic samples as well as the structural formula of each sample are listed in Table II, while the percentage degrees of substitution are given in Table III.

3. Results and discussion

Green compression strength is the accepted universal indicator of the behaviour of a sand–bentonite–water moulding mixture. Changes in cohesion forces are essentially related to the moisture content of the mixture. From the mixture compactability one can determine the optimum moisture content for moulding, which in turn corresponds to a given green compression strength that lies in the wet branch of the compression curve.

We determined the green compression strength [5] and compactability [6, 7] of mixtures prepared through desiccation by successive mixing [7–11] because the results thus obtained are typically quite reproducible [12, 13] and have acceptable dispersions ($\pm$ 10%). The results obtained in these tests are shown in Figs 1–9 as the averages of the values provided by three specimens prepared and tested according to DIN norm 52 401. The figures show the variation of the green compression strength R with the moisture content x. The curves obtained for the nine bentonites assayed conform to a potential function of the form

$$R = R_0 x^a \,(\mathrm{g\,cm^{-2}}) \qquad (1)$$

which was arrived at by regression.

Table IV lists the coefficients R_0 of the nine equations, the exponents a of the bentonites assayed and the correlation coefficient of each. As can be seen, there was quite good correlation: the standard deviation was 0.036 for the average value $\bar{r} = 0.938$. Exponent a is virtually the same for all nine equations because the standard deviation with respect to the average value $\bar{a} = -1.08$ is 0.04. Hence Equation 1 can be written as

$$R = R_0 x^{-1.08} \,(\mathrm{g\,cm^{-2}}) \qquad (2)$$

On relating the coefficients R_0 listed in table IV for each bentonite to the overall degree of substitution in the crystal lattice of the samples it is seen that they conform to the first-order regression equation

$$R_0 = 596 + 159.6\gamma \,(\mathrm{g\,cm^{-2}}) \qquad (3)$$

where γ is the overall degree of substitution (in the

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TABLE I Percentage mineralogical compositions of bentonites assayed on arrival and on flotation[a]

	C		F		N		O		Q		R		U		V		X	
	OA	OF	OA	OF	OA	OF	OA	OF	OA	OF	OA	OF	OA	OF	OA	OF	OA	OF
Montmorillonite	91.0	95.5	84.0	92.0	93.5	97.2	91.6	95.9	97.3	100	93.2	93.2	90.2	94.7	92.3	96.4	87.4	93.3
α-Cristobalite	2.6	1.2	6.5	3.6	1.7	0.6	2.0	1.3	–	–	1.5	1.6	3.3	1.6	1.1	0.6	2.2	1.2
Quartz	2.3	1.5	5.0	2.7	1.9	1.0	1.5	0.8	0.9	–	2.3	2.3	1.8	1.2	1.6	1.2	2.3	0.7
Mica	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.40	0.34
Feldspars	1.5	1.1	4.5	2.1	2.9	1.2	3.5	1.3	1.8	–	3.0	2.9	3.5	1.8	1.6	–	3.6	2.5
Carbonates	2.6	0.7	–	–	–	–	1.4	0.7	–	–	–	–	1.2	0.7	3.4	1.8	4.1	1.6

[a]OA = on arrival, OF = on flotation.

TABLE II Percentage compositions as oxides and structural formulae $[(Si_{4-\sigma}Al_{\sigma})(Al_{2-\alpha}Fe_{\varphi}Mg_{\mu})O_{10}(OH)_2]M_{\mu+\sigma}$ of the bentonites assayed

Bentonite	Composition (wt %)				α	φ	μ	σ	$M^+ =$ (μ + σ)	Structural formula
	Al_2O_3	Fe_2O_3	MgO	SiO_2						
C	22.8	4.2	2.82	58.0	0.48	0.21	0.27	0.23	0.50	$[(Si_{3.77}Al_{0.23})(Al_{1.52}Fe_{0.21}Mg_{0.27})O_{10}(OH)_2]M^+_{0.50}$
F	20.6	1.86	2.0	50.4	0.33	0.11	0.23	0.18	0.41	$[(Si_{3.82}Al_{0.18})(Al_{1.67}Fe_{0.11}Mg_{0.23})O_{10}(OH)_2]M^+_{0.41}$
N	19.8	3.57	3.0	55.8	0.50	0.19	0.31	0.12	0.43	$[(Si_{3.88}Al_{0.12})(Al_{1.50}Fe_{0.13}Mg_{0.31})O_{10}(OH)_2]M^+_{0.43}$
O	24.8	2.72	2.32	58.0	0.36	0.13	0.22	0.25	0.47	$[(Si_{3.75}Al_{0.25})(Al_{1.64}Fe_{0.13}Mg_{0.22})O_{10}(OH)_2]M^+_{0.47}$
Q	15.5	12.3	3.0	60.0	0.89	0.60	0.29	0.08	0.37	$[(Si_{3.92}Al_{0.08})(Al_{1.11}Fe_{0.60}Mg_{0.29})O_{10}(OH)_2]M^+_{0.37}$
R	22.3	3.43	2.32	57.5	0.40	0.17	0.23	0.16	0.39	$[(Si_{3.84}Al_{0.16})(Al_{1.60}Fe_{0.17}Mg_{0.23})O_{10}(OH)_2]M^+_{0.39}$
U	22.7	2.43	2.16	59.0	0.33	0.12	0.21	0.10	0.31	$[(Si_{3.90}Al_{0.10})(Al_{1.60}Fe_{0.12}Mg_{0.21})O_{10}(OH)_2]M^+_{0.31}$
V	22.0	2.3	4.48	57.7	0.55	0.11	0.44	0.25	0.69	$[(Si_{3.75}Al_{0.25})(Al_{1.45}Fe_{0.11}Mg_{0.44})O_{10}(OH)_2]M^+_{0.69}$
X	19.3	3.29	4.31	57.8	0.60	0.17	0.43	0.12	0.55	$[(Si_{3.88}Al_{0.12})(Al_{1.40}Fe_{0.17}Mg_{0.43})O_{10}(OH)_2]M^+_{0.55}$

TABLE III Degree of isomorphic substitution

Bentonite	Tetrahedral substitution σ (%)	Octahedral substitution (%)			Overall substitution
		Fe^{3+}(φ)	Mg^{2+}(μ)	α = φ + μ	γ = (α + σ) (%)
C	5.75	10.50	13.50	24.00	29.75
F	4.50	5.50	11.50	17.00	21.50
N	3.00	9.50	15.50	25.00	28.00
O	6.25	6.50	11.00	17.50	23.75
Q	2.00	30.00	14.50	44.50	46.50
R	4.00	8.50	11.50	20.00	24.00
U	2.50	6.00	10.50	16.50	19.00
V	6.25	5.50	22.00	27.50	33.75
X	3.00	8.50	21.50	30.00	33.00

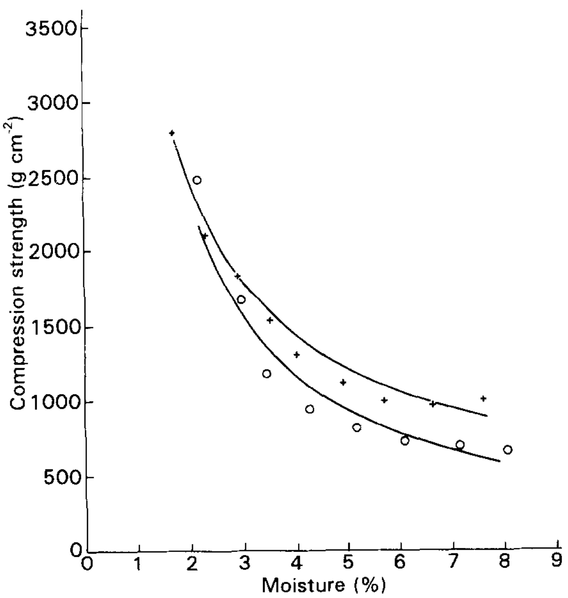

Figure 1 Variation of green compression strength with moisture content for bentonite C: (○) on arrival, (+) homoionic lithium.

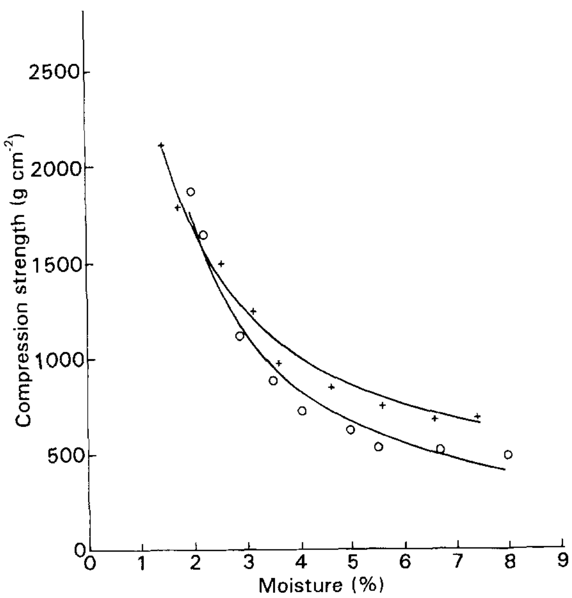

Figure 2 Variation of green compression strength with moisture content for bentonite F: (○) on arrival, (+) homoionic lithium.

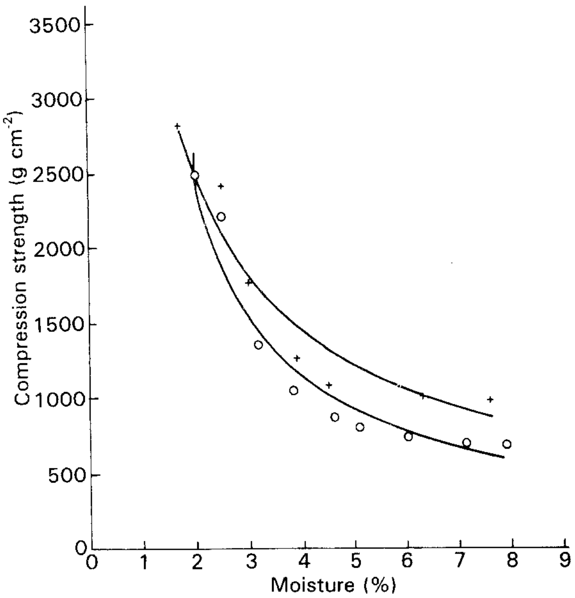

Figure 3 Variation of green compression strength with moisture content for bentonite N: (○) on arrival, (+) homoionic lithium.

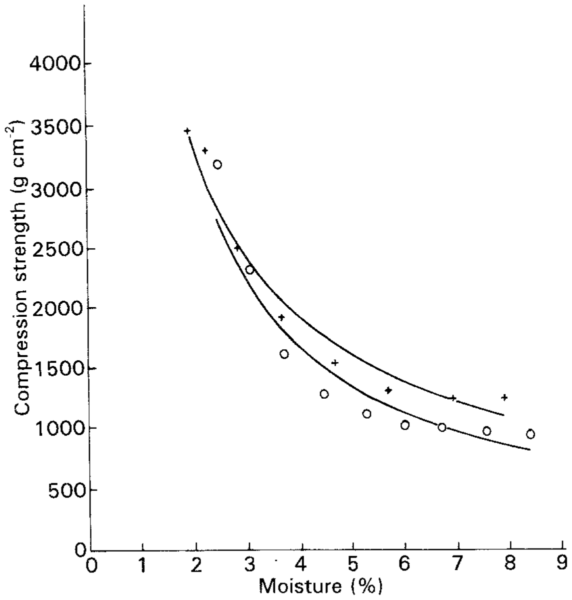

Figure 5 Variation of green compression strength with moisture content for bentonite Q: (○) on arrival, (+) homoionic lithium.

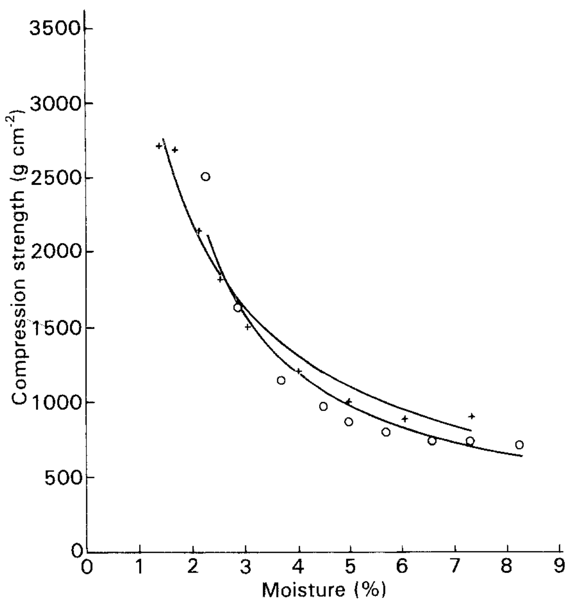

Figure 4 Variation of green compression strength with moisture content for bentonite O: (○) on arrival, (+) homoionic lithium.

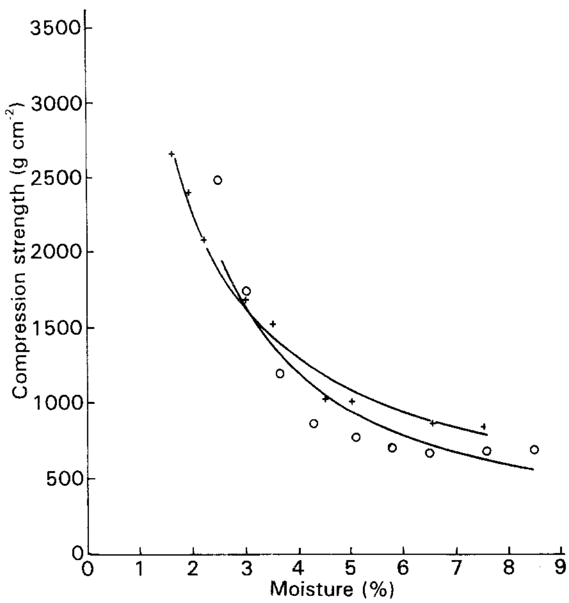

Figure 6 Variation of green compression strength with moisture content for bentonite R: (○) on arrival, (+) homoionic lithium.

tetrahedral layers and the octahedral layer). The correlation coefficient of Equation 3, $r = 0.857$, indicates that the coefficients R_0 are essentially a linear function of the degree of substitution of the bentonite concerned.

Substitution of the R_0 value provided by Equation 3 into Equation 2 yields

$$R = (596 + 159.6\gamma)x^{-1.08}\,(\mathrm{g\,cm^{-2}}) \qquad (4)$$

which gives the green compression strength of a moulding sand as a function of the overall degree of substitution and moisture of the mixture (both expressed as percentages). Table V gives the green compression strengths calculated from Equation 4 and experimental moisture contents, as well as the experimental strengths obtained at the same moisture values. The average dispersion was 0.37% and the standard deviation 14.7, so Equation 4 accurately accounts for the behaviour of the nine bentonites assayed.

Table VI compares the green compression strength calculated from Equation 4 with the value obtained by applying each bentonite its own Equation 1 at a fixed moisture content of 3.5%. As can be seen from the table, the average dispersion between values was 0.31% and the standard deviation was 9.4, which indicates that the general Equation 4 is accurately descriptive of the behaviour of the bentonites. Accordingly, the green compression strength of sand–bentonite–water mixtures can be accurately calculated in terms of the degree of substitution of the bentonite lattice and the moisture content of the mixture by

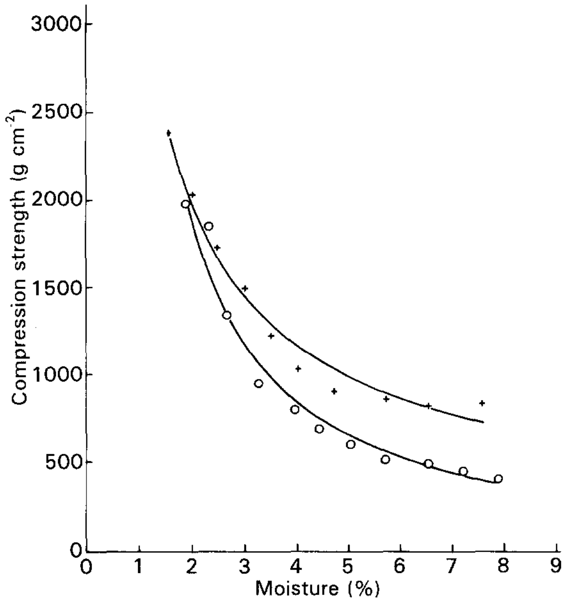

Figure 7 Variation of green compression strength with moisture content for bentonite U: (○) on arrival, (+) homoionic lithium.

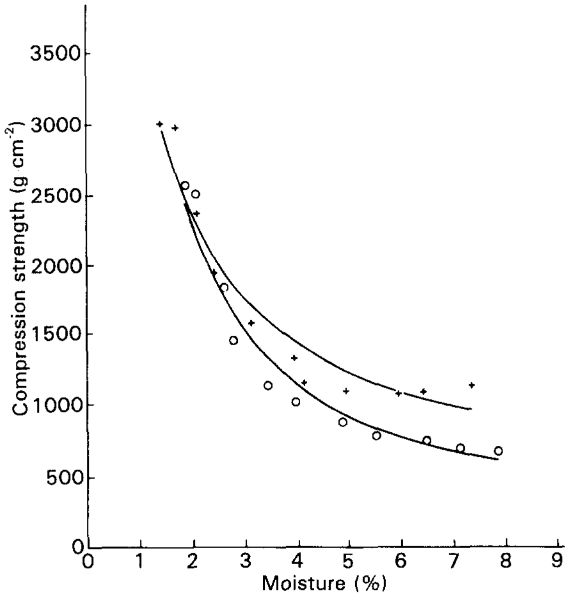

Figure 9 Variation of green compression strength with moisture content for bentonite X: (○) on arrival, (+) homoionic lithium.

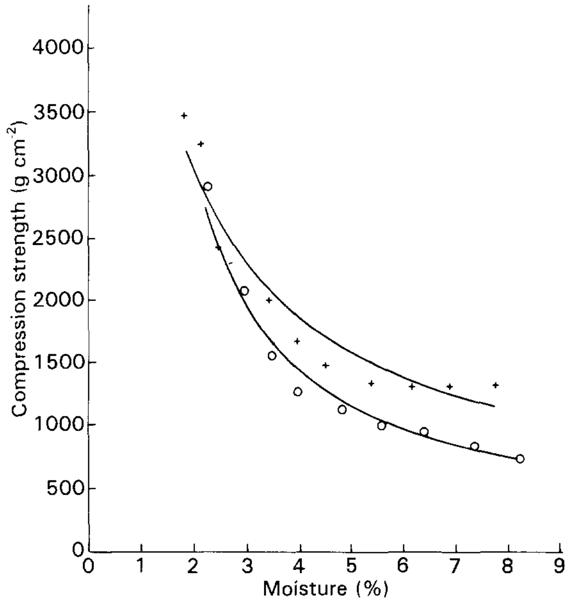

Figure 8 Variation of green compression strength with moisture content for bentonite V: (○) on arrival, (+) homoionic lithium.

TABLE IV Overall degree of substitution γ, coefficient R_0, exponent a and correlation coefficient r of the function $R = R_0 x^a$ for the bentonites on arrival

Bentonite	γ (%)	R_0 (g cm^{-2})	a	r
C	29.75	4936	− 1.04	0.938
F	21.5	3369	− 1.02	0.970
N	28.0	5024	− 1.09	0.948
O	23.75	4967	− 1.11	0.921
Q	46.50	7869	− 1.11	0.911
R	24.0	4596	− 1.01	0.861
U	19.0	3686	− 1.09	0.960
V	33.75	6976	− 1.13	0.974
X	33.0	5252	− 1.12	0.958

using Equation 4 throughout the isomorphic substitution range studied.

In order to determine the effect of exchangeable cations, the bentonites were converted into homoionic lithium substances by using a procedure reported elsewhere [1]. By using the experimental green compression strength data (Table IV) and the same treatment as with the original samples we obtained Figs 1–9. The curves shown in these figures conform to a potential function similar to Equation 1:

$$R^{\mathrm{Li}} = R_0^{\mathrm{Li}} x^a \,(\mathrm{g\,cm^{-2}}) \quad (5)$$

which was also determined by a regression procedure.

Table VII lists the coefficients R_0^{Li} of the nine samples as well as the exponents a and corresponding correlation coefficients. As can be seen, there is good correlation here as well: the standard deviation was 0.024 for an average value $\bar{r} = 0.964$. Exponent a was also virtually invariable here as the standard deviation from the average value $\bar{a} = -0.78$ was 0.04. Hence, Equation 5 can be generalized to

$$R^{\mathrm{Li}} = R_0^{\mathrm{Li}} x^{-0.78} \,(\mathrm{g\,cm^{-2}}) \quad (6)$$

On relating the coefficients R_0^{Li} given in Table VII to the overall degree of substitution γ, they are also found to conform to a first-order regression equation:

$$R_0^{\mathrm{Li}} = 1454 + 94.64\gamma \,(\mathrm{g\,cm^{-2}}) \quad (7)$$

with a correlation coefficient $r = 0.821$. Hence the coefficients R_0^{Li} are also essentially a linear function of the degree of substitution of the bentonite.

Substitution of the R_0^{Li} values given by Equation 7 into Equation 6 yields

$$R^{\mathrm{Li}} = (1454 + 94.64\gamma) x^{-0.78} \,(\mathrm{g\,cm^{-2}}) \quad (8)$$

On comparing Equations 3 and 7 it is seen that R_0 is a linear function of the overall degree of substitution, γ, in both; however, their respective parameter values are different, as they roughly depend on the nature of

TABLE V Comparison between calculated ($R_{cal} = R_0 x^{-1.08}$) and experimental (R_{exp}) green compression strengths obtained at the same moisture content

Bentonite	γ (%)	$R_0 = 596 + 159.6\gamma$	x_{exp} (% H_2O)	R_{cal}	R_{exp}	Dispersion (%)
C	29.75	5344	3	1631	1677	− 2.8
F	21.5	4027	2.90	1275	1107	+ 13.2
N	28.0	5065	3.2	1442	1310	+ 9.2
O	23.75	4387	2.8	1443	1580	− 9.5
Q	46.5	8017	3.2	2283	2330	− 2.1
R	24.0	4426	2.9	1402	1707	− 21.8
U	19.0	3628	3.2	1033	930	+ 10.0
V	33.75	5983	2.9	1895	2200	− 16.1
X	33.0	5863	2.9	1857	1427	+ 23.2

TABLE VI Comparison between the green compression strength obtained by using the general Equation 4 (R_{cal}) and that for each bentonite (Equation 1, R_{part}).

Bentonite	γ (%)	x (% H_2O)	R_{cal}	R_{part}	Dispersion (%)
C	29.75	3.5	1381	1341	+ 2.9
F	21.5	3.5	1041	939	+ 9.8
N	28.0	3.5	1309	1282	+ 2.1
O	23.75	3.5	1134	1236	− 9.0
Q	46.5	3.5	2072	1959	+ 5.5
R	24.0	3.5	1144	1297	− 13.4
U	19.0	3.5	938	841	− 0.3
V	33.75	3.5	1546	1694	− 9.6
X	33.0	3.5	1515	1291	+ 14.8

TABLE VII Overall degree of substitution γ, coefficient R_0^{Li}, exponent a and correlation coefficient r of the function $R^{Li} = R_0^{Li} x^a$ for the homoionic lithium bentonites

Bentonite	γ (%)	R_0^{Li}	a	r
C	29.75	4307	− 0.80	0.978
F	21.5	2898	− 0.76	0.987
N	28.0	4242	− 0.78	0.931
O	23.75	3999	− 0.79	0.975
Q	46.50	5913	− 0.79	0.968
R	24.0	3843	− 0.84	0.988
U	19.0	3484	− 0.81	0.929
V	33.75	5011	− 0.71	0.929
X	33.0	3928	− 0.71	0.942

the exchangeable cation. Also, on comparing Equations 4 and 8 it is seen that the exponent of the moisture content of the mixture is different, i.e. it is roughly dependent on the nature of the exchangeable cation.

In summary, the green compression strength of moulding sands is given by the general expression

$$R = R_0 x^a (\text{g cm}^{-2}) \quad (9)$$

or alternatively

$$R = (A + B\gamma) x^a$$

where x is the moisture percentage of the sample, γ is the overall degree of substitution (percentage) in the bentonite lattice, a depends on the nature of the exchangeable cation in the bentonite binder and R_0 is a function of the overall degree of substitution and the nature of the exchangeable cation.

4. Conclusions

The results discussed above allow us to draw the following conclusions:

(a) The green compression strength of sand–bentonite–water mixtures for foundry moulding is an exponential function of the moisture content of the mixture, $R = R_0 x^a$.

(b) The exponent in this general equation is roughly dependent exclusively on the nature of the exchangeable cation.

(c) Coefficient R_0 is also roughly a function of the overall degree of substitution and the nature of the exchangeable cation.

Appendix: Determination of the structural formulae of the montmorillonites from the results of their chemical analyses

The structural formula of a montmorillonite can be considered to derive from that of pyrophillite by isomorphic substitution of its tetrahedral and octahedral cations. Since the formula of pyrophillite is $Si_4Al_2O_{10}(OH)_2$ or, in oxide form, $4SiO_2 \cdot Al_2O_3 \cdot H_2O$, that of montmorillonite will be

$$(Si_{4-\sigma}Al_\sigma)\cdot(Al_{2-\alpha}Fe_\phi^{3+}Mg_\mu)\cdot O_{10}\cdot(OH)_2\cdot(\sigma + \mu)M^+$$

where σ denotes the number of tetrahedral Si atoms that are replaced by Al (which introduces a deficiency of positive charges in the structural formula of pyrophillite); α is the number of octahedral Al atoms substituted by Fe or Mg; ϕ is the number of Fe atoms that partly replace octahedral Al (usually in trivalent form, so no further deficiency of positive charges is introduced); μ is the number of Mg atoms that replace other Al atoms and hence cause a further deficiency of positive charges; $\alpha = \phi + \mu$; and $(\sigma + \mu)M^+$ are the exchangeable cations (assumed to be univalent) that offset the charge deficiencies arising from the isomorphic substitutions. For divalent cations the expression would be $[(\sigma + \mu)/2]M^{2+}$, or in oxide form

$$(4-\sigma)SiO_2\cdot\left(\frac{2-\alpha+\sigma}{2}\right)Al_2O_3\cdot\frac{\phi}{2}Fe_2O_3\cdot$$

$$\mu MgO\cdot H_2O\cdot\left(\frac{\sigma+\mu}{2}\right)M_2O$$

which is a general formula where parameters α, ϕ, μ and σ vary in each instance.

If we denote the molecular weight of the above formula (unknown) and those of SiO_2 (60.1), Al_2O_3 (102.0), Fe_2O_3 (159.7) and MgO (40.3) by P, S, A, F and M, respectively, then the percentage weights of the oxides in the structural formula (s, a, f and m) will be as follows:

$$s = 100\frac{(4-\sigma)S}{P}$$

$$a = 100\frac{(2-\alpha+\sigma)A}{2P}$$

$$f = 100\frac{\phi F}{2P}$$

$$m = 100\frac{\mu M}{P}$$

with which one can construct a system of four equations in four unknowns: α, ϕ, μ and σ.

Inasmuch as P is not known, it is actually another unknown that calls for a fifth equation, $\alpha = \phi + \mu$. Thus, the final equation system to be used is

$$\begin{aligned}100A\alpha - 100A\sigma &= 2100A - 2Pa\\ 100S\sigma &= 4100S - Ps\\ 100F\phi &= 2Pf\\ 100M\mu &= Pm\\ \alpha - \phi - \mu &= 0\end{aligned}$$

By solving this equation system one can obtain the following α, ϕ, μ and σ values from the results of the chemical analyses:

$$\alpha = \frac{6m + 3.029f}{m + 0.791a + 0.505f + 0.671s}$$

$$\phi = \frac{3.029f}{m + 0.791a + 0.505f + 0.671s}$$

$$\mu = \frac{6m}{m + 0.791a + 0.505f + 0.671s}$$

$$\sigma = 4 - \frac{4.025s}{m + 0.791s + 0.505f + 0.671s}$$

which allows the structural formula of the corresponding montmorillonite to be established.

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