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Heated blends of clay and phosphate sludge: Microstructure and physical properties

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ABSTRACT

Blends of a naturally occurring clay (0–30 wt.%) and phosphate sludge were heated at different temperatures and times and their microstructures were investigated using impedance spectroscopy, dilatometry, X-ray diffraction and scanning electron microscope. The weights of the effects of the change of temperature, soaking time and clay addition on some physical ceramic properties (shrinkage, water absorption and compressive strength) were assessed. For the latter purpose, the response surface methodology was used. The results showed that the sintering process was effective between 750 and 1000 °C and occurred by melt flow. It was accompanied with low activation energy for ionic conduction (0.20–0.35 eV). Due to the quantitative formation of gehlenite (the unique neoformed phase), the ionic conduction regressed and the melt formation was limited. Also, it was shown that the effects of the experimental factors on physical properties of the blends were well described with the adopted polynomial models, and the weights of the effects of the factors followed the order: temperature > clay content > soaking time. The effects of the interactions between the factors on the properties studied were evaluated and discussed in relation to the microstructure change.

1. Introduction

Phosphate sludge is a by-product commonly composed of fluorapatite, clays, quartz and carbonates [1]. Because of the presence of plastic materials, filler and flux, it could be suitable for ceramics manufacturing. However, because of shortage of alumina and silica, it should be enriched with aluminosilicates such as clays [1].

The physical properties of ceramics are tightly related to the microstructure, which in turn depends on, among others, the firing cycle parameters [2], the shaping method [3], the mineralogical and the chemical compositions of the starting materials [4,5]. To evaluate the effect of these parameters, the microstructure changes are monitored for instance by thermal analysis, dilatometry and examined by electron microscopes. Recently, it has been reported that impedance spectroscopy (IS) is a practical technique to characterize the microstructure of ceramics [6–8]. By the help of this technique, changes due to grains and defects (grain boundaries, pores, etc.) could be distinguished [9–11].

Much less attention has been paid to the potential use of phosphate waste for industrial ceramics manufacturing. Moreover, to the best of our knowledge, no study has been carried out on the sintering process of phosphate waste-based ceramics using impedance spectroscopy.

The aim of this work was to monitor the microstructure of heated clay-phosphate waste blends using, among others, impedance spectroscopy. Furthermore, the effects of the firing cycle parameters and the clay content on some physical ceramic properties were investigated. For the latter goal, the response surface methodology was applied.

2. Materials and methods

2.1. Materials

The phosphate sludge (PS) was from the beneficiation plants of the phosphate rocks of Gantour (Youssoufia, Morocco). The

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Table 1
Chemical and mineralogical compositions (in wt.%) of the phosphate sludge (PS) and the raw clay (SC).

	Chemical composition								
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	[a]LoI
PS	22.8	2.5	0.9	4.1	34.2	0.8	0.4	14.0	19
SC	44.7	8.8	0.9	9.1	10.1	[b]Tr	0.3	0.4	25

	Mineralogical composition				
	F	Q	D	C	M
PS	44	17	7	15	12
SC	–	22	50	–	28

F: fluorapatite; Q: quartz; D: dolomite; C: calcite; M: montmorillonite.
[a] Loss on ignition.
[b] Traces.

Table 2
Experimental design matrix (Doehlert matrix) and the measured values of the studied properties (Y_1: firing shrinkage (%); Y_2: water absorption (%); Y_3: compressive strength (MPa)).

Run	X_1	X_2	X_3	τ (wt.%)	T (°C)	t (h)	Y_1	Y_2	Y_3
1	1	0	0	30.00	1050.00	2.00	4.57	21.40	10.52
2	−1	0	0	5.00	1050.00	2.00	3.90	18.29	6.97
3	0.5	0.866	0	23.75	1179.90	2.00	6.55	5.11	19.52
4	−1	−0.866	0	11.25	920.10	2.00	1.28	22.73	2.23
5	0.5	−0.866	0	23.75	920.10	2.00	1.88	24.48	3.17
6	−1	0.866	0	11.25	1179.90	2.00	6.08	8.11	17.91
7	0.5	0.2887	0.8165	23.75	1093.31	3.63	5.08	16.10	12.57
8	−1	−0.289	−0.817	11.25	1006.70	0.37	3.23	19.12	7.92
9	0.5	−0.289	−0.817	23.75	1006.70	0.37	3.72	19.92	8.72
10	0	0.5774	−0.817	17.50	1136.61	0.37	5.48	9.87	16.49
11	−1	0.2887	0.8165	11.25	1093.31	3.63	4.96	14.18	13.98
12	0	−0.577	0.8165	17.50	963.39	3.63	2.13	21.07	4.26
13	0	0	0	17.50	1050.00	2.00	4.09	20.60	8.56
14	0	0	0	17.50	1050.00	2.00	4.17	20.39	8.52
15	0	0	0	17.50	1050.00	2.00	4.14	20.52	8.21
16	0	0	0	17.50	1050.00	2.00	4.15	20.45	8.36

alumina- and silica-bearing material was a swelling raw clay (SC) from the phosphate basin area. The chemical and mineralogical compositions of both materials are given in Table 1. In this respect, it may be noted that the amounts of the identified minerals were estimated by the Rietveld method, and the chemical compositions were determined with inductively coupled plasma atomic emission spectroscopy (ICP-AES), using a Perkin Elmer Optima 3100 RL apparatus. Some physical characteristics of PS and SC are given elsewhere [1].

2.2. Experimental procedures

Blends of the phosphate sludge and the clay (up to 30 wt.%) were damped (water/solid = 40%) and kneaded for 30 min. Pellets (<2 cm diameter) were shaped from the paste and dried at ambient temperature, then at 105 °C. The samples were heated at 900–1100 °C for up to 4 h.

The impedance spectroscopy measurements were carried out at 650–1100 °C using a Solartron SI 1260 impedance analyzer. The voltage used was 2000 mV and the frequency varied from 0.1 to 10^6 Hz.

Phase identification was performed by means of X-ray diffraction (XRD) and scanning electron microscope (SEM). The XRD patterns were recorded with a Philips X'Pert MPD diffractometer equipped with a copper anode (K_α = 1.5418 Å). The SEM examinations were carried out with a JEOL JMS 5500 apparatus equipped with an EDAX Falcon spectrophotometer. For this purpose, the samples were coated with a thin layer of gold.

Shrinkage was measured by following the sample dimensions before and after heating. For water absorption measurement, the weights of the heated sample were determined before and after immersion in boiled water for 2 h. The compressive strength of the heated samples was measured with an Instron 3369 apparatus. The load and loading speed were 50 kN and 0.1 mm/min, respectively.

2.3. Experiments design

The effects of the clay content (τ), sintering temperature (T) and soaking time (t) on a physical property (Y) of the sample were evaluated by using the following equation [12,13]:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3$$

X_1, X_2 and X_3 are the coded variables related to the real factors (τ, T and t) as follows:

$$X_1 = \frac{(\tau - \tau_0)}{\Delta\tau}; \quad X_2 = \frac{(T - T_0)}{\Delta T}; \quad X_3 = \frac{(t - t_0)}{\Delta t}$$

τ_0, T_0 and t_0 are the clay content, sintering temperature and soaking time at the centers of the experimental domains (τ_0 = 17.5 wt.%, T_0 = 1050 °C and t_0 = 2 h). $\Delta\tau$, ΔT and Δt are the variation steps of the natural variables ($\Delta\tau$ = 12.5 wt.%, ΔT = 150 °C and Δt = 2 h).a_0 is a constant, and a_1, a_2 and a_3 are the weights of the effects of τ, T and t, respectively. a_{ii} is considered as a curve shape parameter, and a_{ij} represents the weight of the effect of interactions between i and j factors. The coefficients were determined by least-squares regression using the software: New Efficient Methodology for Research using Optimal Design (Nemrod) [14]. For this goal, 16 experiments, planned according to the Doehlert matrix design, were realized. The planned experiments and the experimental values of the corresponding properties are given in Table 2.