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Factors involved in the aging process and its implications in the properties of clays for the Ceramic Industry

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Abstract

It is well known that the use of stockpiling systems in the Ceramic Industry provides significant improvements in clays properties. In this system, clays are left to age under the action of environmental elements for periods of time before entering the production process. This renders superior technological properties to clays when compared to those used directly as extracted from the deposit. However, the mechanisms that act during this process are not yet well understood. Chemical and biological factors are generally regarded as the main ones responsible in clay aging. This investigation analyzes the aging of clays, analyzing the most significant mechanisms involved and their implications in the technological properties of clays used in the Ceramic Industry. Clays of the two most important ceramic poles of the States of Rio de Janeiro and São Paulo in Brazil were used in the investigation, which were exposed to aging both indoors and outdoors for a total of six months. Periodic samplings were carried out to monitor the changes in physical, chemical, microbiological and technological properties of the clays with time. Exposure of clays to aging resulted in a significant improvement in the technological properties of the samples during the total period of the investigation. The results demonstrated the importance of biological action in clay aging. Moreover, results also indicated the existence of periods of the year that were most favorable to the aging process.

Key-words: clays, aging, technological properties, enzymatic activity.

1. Introduction

Storing clays in stockpiles and subjecting them to the action of environmental elements during a reasonable period of time before entering the production process is a practice often used in the Ceramic Industry to improve the technological properties of clays. Aging consists of subjecting the clay to the action of environmental elements for periods of time that vary of six months-two years (Zandonadi and Ioshimoto, 1991). The exposure of the extracted material to aging results in washing of soluble salts, the relief of tensions in the clay blocks, improvements in plasticity and provokes the homogenization of the moisture distribution (Anicer, 2005). Clays are deposited in layers forming stockpiles in industry, where the thickness and alternation of the layers depend on the types of clays and the desired properties of the final mixture.

The exposure of clays to aging favors the action of physical, chemical and biological processes that result in improvement in the materials rheological behavior. This improvement in rheology (plasticity) results in better workability of clays during ceramic processing stages such as drawing and pressing. Besides allowing to feed the production process with a clay that is more homogeneous, this process also results in improved productivity, since it allows reducing the proportion of rejects.

The mechanisms that act during the aging process of clays are not yet known well enough. Chemical factors associated to the cation exchange (modification of the electric load and the specific surface of the clay) and oxidation of the organic matter present in the samples are generally considered to be important. Biological factors associated to the bacteriological attack owing to the secretion of polysaccharides that act as ligants between argillaceous micelles, also seem to possess great significance (Abajo, 2000). Indeed, the literature generally considers the biological action to be the most significant mechanism in clay ageing

(Vaiberg et al., 1980; Groudeva and Groudev, 1995; Velde, 1995; Abajo, 2000). Organic acids, mainly citric, gluconic and oxalic acids, are produced as bacterial oxidation of some inorganic composites of sulfur or nitrogen during growth of some bacteria and are set free during this process (Groudeva and Groudev, 1995). These acids are capable of solubilizing ionic species such as Fe^{+3} and Al^{+3} that are present in the clay crystalline structure, modifying their electric charge, pH and specific surface area, which, in conjunction should contribute to increased plasticity (Abajo, 2000). The sorption of H^{+} ionic species by illite or kaolinite clays leads the edge sites to become more positively charged and faces and edges of the clay minerals to remain joined (Velde, 1995). Moreover, some microorganisms are responsible for secretion of polysaccharides, which, when acting as bridges between argillaceous micelles, promote an increase in both plasticity and resistance to drying shrinkage (Abajo, 2000).

The present work aims to assess and identify the main factors that act in the aging process of clays. The benefits brought by this aging process are than quantified in physical, chemical, biological and technological properties of raw materials.

2. Materials and methods

2.1. Clay samples

Samples of two clays from Itaboraí (Rio de Janeiro State) and designated as “red” and “green” clays, and a clay sample from Santa Gertrudes (São Paulo State) were collected for the study. The choice of these raw materials was made on the basis of their different chemical and mineralogical compositions.

After being extracted from the respective mineral deposits, the samples were properly stored in sealed plastic bags and transported to the laboratory for analyses. In the laboratory, the samples were air-dried, crushed using a laboratory smooth double roll crusher, mixed and quartered using a longitudinal pile, with the aim of guaranteeing that the samples were as representative as possible of the original collected material. Varied amounts of sample of the clays were prepared containing about ten kilograms each.

2.2. Exposure to aging

The samples were placed in 20-liter uncovered plastic containers. After being placed in the containers, the samples of approximately 10 kg were subject to aging under two different conditions: indoors and outdoors. Samples subject to ageing outdoors were subjected to the action of environmental elements and thus to more drastic climatic variations. Samples subject to aging indoors were placed in a covered area within the laboratory. The exposure of the samples indoors had the aim of allowing to establish a reference for comparison to the samples left outdoors, since the earlier were not subjected to such significant variations in temperature and moisture.

Besides the samples that were exposed to ageing both indoors and outdoors, two other samples of each clay were prepared. One of the samples was used in initial clay characterization and the other was used as reference. These reference samples remained stored in sealed plastic bags under controlled temperature and moisture during the period of six months samples of the study.

The study was conducted during the total period of six months, with periodic collections of the samples. These had as objective of monitoring the changes in clay properties the exposure time. For each of these sample collections, a representative sample was used in the biological characterization (measurement of enzymatic activity). This particular sample was collected from different points and depths within the contained with the aid of a sterile spatula. Additional samples were then collected for chemical, physical and technological characterization studies.

2.3. Initial characterization of the samples

Mineralogical analyzes have been carried out by X-Ray diffraction. These analyzes have been conducted with samples of the clay fraction (natural, heated and intercalated with ethylene glycol) of each raw material, in dust form, using Cu-k_{α} radiation with sweeping angles 2θ varying from 3 to 60º (Albers et al., 2001). The chemical composition of the raw materials has been determined by X-ray fluorescence spectrometry, in which the elements are presented in the form of oxides. The loss on ignition and the moisture content were determined by gravimetric methods. The plasticity of the clays was determined according to NBR 6459-84 and NBR 7180-84 for calculation of Atterberg limits.

2.4. Experiments after exposure to aging

After the end of the storage period, chemical, biological and technological characterization tests have been carried out. Chemical characterization consisted of pH measures in water and KCl (Thomas, 1996), oxidation and reduction potential using potenciometric methods (Patrick et al., 1996) and measurement of amount of organic matter with the Walkley & Black methodology (Embrapa, 1997). The cation exchange capacity was determined by two methods: the methylene blue adsorption for the total cation exchange (ASTM C 837-81) and the determination of exchangeable cations Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, H^{+} and Al^{+3} in accordance to the methodology used by Embrapa (Embrapa, 1997). Biological characterization was conducted by measuring the enzymatic activity of each clay (Adam & Duncam, 2001).

Technological characterization of the samples consisted of first preparing test bodies measuring 11.4x2.5x1.0 cm at 30 MPa using a uniaxial press. After drying at 110ºC, the test bodies were then sintered in the laboratory at 1050ºC, with 10ºC/min of heating/cooling ramp, while keeping at the set temperature for 1 hour. The following parameters were then measured from the samples: apparent density, linear retraction, modulus of rupture flexion (ASTM C 674-77), water absorption (ASTM C 373-72) and loss on ignition.

The chemical and technological assays described previously were carried out with the clay samples collected after exposure to aging. In this paper, only results from analyses that showed more significant variation during ageing are presented. The complete set of results may be found elsewhere (Gaidzinski, 2006).

3. Results and discussion

The mineralogical characterization by means of X-ray diffraction and later semi-quantitative analyzes (Santos, 1998) showed the presence of 9% of illite and 64% of kaolinite for the red clay from Itaboraí. The mineralogical analysis of the green clay from Itaboraí showed the presence of the clay minerals illite (24%), kaolinite and smectite, whereas the presence of illite (47%), kaolinite, quartz, smectite-vermiculite interstratificated was found for Santa Gertrudes clay. Itaboraí clays then present high clay minerals contents, which are in agreement with their chemical analyzes, being classified as highly plastic materials (plasticity index of 15%). The Santa Gertrudes clay presents a low clay minerals content, also in agreement with chemical analyzes, presenting an average plasticity (7% < plasticity index < 15%).

Table 1 presents selected biological and physical properties of the clays before and after exposure to aging. It was generally observed an increase in the green flexural strength of the samples with the time of exposition to aging. This fact can be an indication that exposure to aging provided improvements in the technological properties of these clays, besides also promoting greater homogeneity for the feed to the productive process.

For Itaboraí red and Santa Gertrudes clay samples, aging outdoors was more favorable, since it resulted in greater green flexural strengths of the samples. This improvement in the technological properties in relation to the initial sample seems to be related mainly to the increase in moisture content of the samples subject to outdoor exposure. For Itaboraí red clay, indoor exposure became unfavorable due to the progressive loss of moisture of the samples with time. This progressive loss of moisture was likely to be responsible for the reduction in the green flexural strength of the material in comparison to the initial sample. In this case, it would be advisable to use canvases for covering the clay stockpile in order to prevent such loss of moisture during exposure. In fact, this is a procedure that is already adopted in Brazil with clays from Santa Gertrudes region.

For the clay of Santa Gertrudes, indoor exposure was more favorable due to the low initial moisture content of the sample. For this clay sample, which presents very low initial moisture, outdoor exposure resulted in some improvement in its properties. For the clays of the two regions studied, the increase in moisture during the exposure to aging seems to be of great significance, since samples exposed outdoors presented highest green flexural strength than those exposed outdoors for the same period of time. Moreover, this increase in moisture content seemed to be even more important for the Santa Gertrudes clay, given its low initial moisture content. The results show that only Santa Gertrudes clay presented a significant increase in the enzymatic activity during the entire period of exposure. These results can be an indication that the larger proportion of water contained in the sample yielded an increase in its microbial population.

For Itaboraí green clay, which presents greater capacity of moisture retention and also higher initial plasticity, exposure of the samples to aging seemed more favorable when carried out indoors, since no significant loss of moisture took place in time. This constancy in the moisture content seems to be the main responsible for the observed increase in plasticity and green flexural strength of the samples.

In respect to moisture, the three clays presented similar behavior during the exposure to aging during periods of time of low pluviometric index that succeeded the rainiest periods (Table II). The great losses of moisture during short periods of time proved to be deleterious to the clay properties, since a loss of the acquired mechanical properties in the periods most favorable to aging could occur. For all clay samples subjected to ageing under these climatic conditions, a reduction in their moisture content was also followed by a reduction of the enzymatic activity. These results suggest that the swelling and drying resulting from the variation of moisture of clay particles could be harmful to the survival of the microbial populations (Van Gestel, 1993; Kostopoulou and Zotos, 2005). This can also be an indication that clay ageing during these significant climatic variations must be prevented, such that appropriate periods of the year should be selected for improved effects of ageing. This has also been demonstrated by a previous work carried out using industrial-sized stockpiles (Gaidzinski et.al., 2005).

Table I: Clay properties before and after exposure to ageing indoors and outdoors (coefficients of variation in parentheses)

Clay	Exposure place	Exposure time (months)	Moisture content (%)	Enzymatic activity (μg/min.g)	Mechanical strength green (MPa)	Mechanical strength sintered (MPa)
Itaboraí red	None	0	15.43 (0.3)	0.0304 (26.2)	2.06 (12.4)	5.19 (11.3)
	Indoors	1	6.97 (0.0)	0.0537 (20.9)	2.36 (10.0)	6.70 (13.6)
		2	5.25 (2.8)	0.0202 (16.4)	2.07 (10.1)	5.24 (12.8)
		4	4.24 (3.6)	0.0420 (13.1)	2.04 (4.8)	5.12 (14.8)
		6	4.01 (1.1)	0,0131 (8.6)	1.77 (14.7)	4.45 (3.7)
	Outdoors	1	38.42 (1.3)	0.0399 (37.3)	2.67 (12.0)	7.15 (16.8)
		2	44.19 (0.5)	0.0212 (17.8)	3.30 (13.3)	7.42 (15.6)
		4	38.39 (1.7)	0.0266 (15.9)	2.27 (10.5)	5.51 (12.7)
		6	13.70 (0.5)	0.0089 (14.5)	1.75 (16.1)	5.93 (12.0)
	Reference	6	14.61 (0.9)	0.0125 (10.4)	1.80 (5.6)	4.85 (17.4)
Itaboraí green	None	0	7.12 (0.4)	0.0744 (30.9)	2.24 (23.0)	6.52 (23.1)
	Indoors	2	8.12 (1.6)	0.0343 (26.9)	2.94 (11.4)	7.52 (10.5)
		4	7.95 (3.6)	0.0127 (9.9)	2.46 (17.1)	7.95 (11.7)
		6	7.15 (1.7)	0.0107 (46.9)	2.33 (29.8)	7.74 (1.8)
	Outdoors	2	29.64 (1.1)	0.0112 (66.3)	2.63 (5.5)	6.81 (7.4)
		4	28.65 (1.1)	0.0213 (33.7)	2.85 (17.3)	7.26 (23.1)
		6	12.44 (2.0)	0.0097 (22.2)	1.86 (9.6)	4.85 (14.0)
	Reference	6	7.14 (0.8)	0.0012 (27.2)	2.72 (8.4)	7.89 (14.8)
Santa Gertrudes	None	0	3.70 (1.5)	0.0378 (10.5)	3.00 (13.3)	28.03 (7.1)
	Indoors	1	3.97 (0.1)	0.0473 (14.8)	3.53 (7.0)	31.39 (4.1)
		2	4.40 (0.1)	0.0400 (10.0)	3.00 (4.1)	29.15 (8.7)
		4	4.16 (1.9)	0.0264 (28.6)	2.26 (6.0)	27.16 (4.4)
		6	4.11 (1.6)	0.0171 (20.2)	2.16 (10.0)	26.77 (1.8)
	Outdoors	1	27.37 (1.1)	0.0368 (10.5)	3.41 (7.8)	30.56 (6.1)
		2	27.46 (3.4)	0.1023 (14.9)	3.61 (8.0)	31.60 (6.5)
		4	26.26 (2.7)	0.0836 (10.5)	2.24 (0.9)	27.19 (8.7)
		6	9.47 (1.6)	0.0362 (16.9)	2.30 (12.2)	23.32 (10.8)
	Reference	6	3.53 (0.9)	0.0232 (22.8)	1.86 (3.0)	25.45 (1.2)

Table II: Monthly precipitation and temperature average of the time of clay samples exposition to aging

Aging exposure of Itaboraí clays (months)	Aging exposure of Santa Gertrudes clay (months)	Average temperature (ºC)	Average monthly precipitation (mm)
0		24.7	112.8
1	0	24.4	116.6
2	1	22.4	51.8
3	2	21.2	30.0
4	3	19.8	67.6
5	4	21.9	5.4
6	5	20.9	49.6
-	6	23.5	42.0

The increase of the green flexural strength can be related to an increase in the plasticity of the samples. Besides mineralogy, particle size distribution, lamellar habit of the clay minerals, electric load of crystals and organic matter, the cation exchange capacity also has great influence in the plasticity of the samples. The nature of exchangeable cations also has great importance for the technological properties. Some cations exert great influence, over all in the viscosity and plasticity of the watery suspensions of clays (Fernandes, 1998). However, the results showed that for three clays studied, the increase in green flexural strength (and the consequent increase in plasticity), was not followed by increase in the cation exchange capacity of the samples (Gaidzinski, 2006). These results can be an indicative that, in this in case, an increase in plasticity of the samples could not be associated directly to chemical factors such as organic matter and cation exchange capacity. The increase in plasticity could be a consequence of the action of microorganisms, or either, of biological processes, since no improvement in the chemical properties was observed during the six months of exposure of the samples to ageing. The microorganisms present in the samples would be responsible for the secretion of polysaccharides that would act as ligants between argillaceous micelles, in accordance with the literature (Groudeva et al., 1995).

Results also suggest that the major factors that seem to affect the aging of clays are the moisture content and the action of microorganisms. Indeed, it is suggested that moisture favors the growth and/or development of the microbial population, being more significant for clays with very low initial moisture content, such as Santa Gertrudes. However, moisture seems to be beneficial up to a certain upper limit. When moisture increases beyond a certain level, part of population of microorganisms may die, leading to worsening of the technological properties of the clays.

4. Conclusions

Improvements in the technological properties of the clays studied were obtained under certain conditions of the aging process, which is in agreement with both the technical literature and results from a previous study by the authors (Gaidzinski et.al., 2005). These improvements in the technological properties are, in general, translated in increase in their flexural strength, both of the green body and after sintering, and a reduction of water absorption of the samples with the time of exposition to aging.

The results from clay ageing, however, depend on the initial characteristics of the clays. The present study showed that clays with lower contents of clay minerals and low initial plasticity have a greater potential benefit from ageing.

Different responses were found for the clays when subjected to aging indoors or outdoors. For clays that present low initial moisture or that do not possess high capacity of moisture retention, aging seems to be unfavorable indoors, so that the use of canvases to cover the stockpile is recommended in order to minimize water loss. On the other hand, for clays that possess higher initial plasticity and capacity to retain moisture, aging indoors with no canvas may be advisable. Exposure of clays to aging outdoors also becomes unfavorable during periods of high pluviometric index followed of times of drought. Exposure during these periods resulted in deleterious effects in their technological properties in comparison to the improvements already capitalized during the previous months of exposure. Moreover, during these periods, significant reductions in the cation exchange capacity and in enzymatic activity were also observed.

The reduction in the enzymatic activity can be associated to the lack of time that the microorganisms may have had for adapting to these new climatic conditions. The moisture is presented as one of the main factors responsible for the increase in the green flexural strength of the samples with the exposure time. Generality, the increase in moisture content favors the increase in green flexural strength of clays, although no changes in the chemical properties of the samples were observed.

The moisture is presented as a factor of great importance in the aging process of clays. In the case of the action of microorganisms in the process, the moisture also could favor the development and/or growth of the microbial populations present in the samples. In this case, the mechanism of performance of the microorganisms would be by means of the secretion of polysaccharides that would act as ligants between argillaceous micelles, increasing the plasticity of the samples.

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