Applied Clay Science 42 (2009) 657–660

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Effect of the incorporation of a spent catalyst reject from the petroleum industry in clay products

W. Acchar [a,*], B.M. Rulff [b], A.M. Segadães [c]

[a] Federal University of Rio Grande do Norte, Department of Physics, 59072-970 Natal—RN, Brazil
[b] Petrobras/Cenpes/HPE, 21941-915 Rio de Janeiro—RJ, Brazil
[c] University of Aveiro, Ceramics and Glass Engineering Department (CICECO), 3810-193 Aveiro, Portugal

ARTICLE INFO

Article history:
Received 10 January 2008
Received in revised form 19 June 2008
Accepted 22 June 2008
Available online 28 June 2008

Keywords:
Ceramics
Bricks
Recycling
Clays
Catalysts

ABSTRACT

Clay-based materials show a natural forgiveness towards the incorporation of a variety of materials, including potentially hazardous industrial rejects or sub-products. Research from the past few years suggests that the red clay ceramics industry might become the natural end-user of waste materials from other industries. In Brazil, the growth of the petroleum industry is leading to an increasing amount of wastes with high environmental impact and the industry is looking for alternatives to the simple disposal of the wastes. The study reported here shows the changes in properties of an industrial red clay-based mixture, already in use in the production of bricks, due to additions of a spent catalyst reject material (SCR) discarded by the thermal cracking process in the petroleum industry. Samples containing 20 wt.% SCR were extruded and sintered in air in an electric furnace (700–1150 °C, for 1 h). The results obtained (X-ray diffraction and fluorescence, thermal analysis, firing shrinkage, water absorption and mechanical strength) show the effect of the SCR additions and suggest that the incorporation of the SCR material into the clay mixture can constitute a valid route to the amelioration of the environmental concerns.

1. Introduction

The current increasing industrialization, particularly in less developed nations, is placing an enormous pressure on the environment due to the volume of materials consumed, the amount of disposed waste and the amount of energy spent. The ceramics industry, considering the high volume of materials processed, is one of the largest consumers of natural raw materials but has also the capacity and potential to make significant contributions to solving problems associated with wastes (Sorvari, 2003; Shinzato and Hypolito, 2005; Segadães, 2006; Lee et al., 2007). Clay-based materials show a natural forgiveness towards the incorporation of a variety of materials, including potentially hazardous industrial rejects or sub-products (Magalhães et al., 2004; Andreola et al., 2005). Research work carried out over the past two decades has shown that the ceramics industry can incorporate different types of industrial rejects, without degradation of properties (Crespo and Rincón, 2001; Souza and Mansur, 2004; Tucci et al., 2004; Chandra et al., 2005; Jordán et al., 2005; Segadães et al., 2005; Acchar et al., 2006; Raupp-Pereira et al., 2007). Some industrial wastes are similar in composition to the natural raw materials used in the ceramics industry, and often contain materials that are not only compatible but also beneficial in the fabrication of ceramics (Acchar et al., 2005; Segadães et al., 2005).

One such waste material is the spent catalyst reject (SCR) produced in growing amounts by the thermal cracking unit in the petroleum industry, which is becoming a worrying factor for environmentalists. The original catalyst is a zeolite type powder of very large specific surface area, basically constituted of silica and alumina. As a result of the thermal cracking process, metals such as vanadium, nickel, iron and copper, together with coke, are deposit on the catalyst surface, reducing the catalytic activity. The coke deposit can be partially removed by combustion (regeneration) and the regenerated catalyst is fed back into the process and recirculated, until it is too fine or inactive (poisoned catalyst). At the Petrobras refinery in Brazil, the thermal cracking spent catalyst reject is generated at an approximate rate of 50 ton/month. To date, as landfill sites dedicated to the disposal of urban solid waste frequently refuse to accept industrial wastes, there is no definitive solution, from the environmental viewpoint, for the final disposition of this type of reject and the industry becomes responsible for the conditioning and keeping of the waste. From this point of view, it is also in the refinery's interest to find a possible use for the SCR as an alternative to dumping at landfill sites. The local brick making industry seemed to be the obvious choice. The objective of this work is to study the prospective use of the spent catalyst reject and its effect on the sintering/densification behaviour and mechanical properties of a commercial clay-based material already in use in the

* Corresponding author. Fax: +55 84 32153791.
E-mail address: acchar@dfte.ufrn.br (W. Acchar).

0169-1317/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.clay.2008.06.007

Table 1
Chemical composition (wt.%) of the raw materials used, as determined by XRF

	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MgO	TiO_2	P_2O_5	MnO	La_2O_3	NiO
Clay	54.66	28.28	6.69	3.17	0.26	3.87	0.90	1.40	0.17	0.09	–	–
SCR	52.08	42.82	0.52	0.07	0.59	0.09	–	–	0.59	–	2.90	0.19

local brick making industry, in order to minimize the SCR negative impact on the environment.

2. Experimental procedure

A typical brick making clay mixture of medium plasticity and a spent catalyst reject (SCR) collected directed from the petroleum industry were selected as raw materials and characterized. The characterization included chemical composition (X-ray fluorescence (XRF), Shimadzu EDX-700), mineralogical composition (X-ray diffraction (XRD), Shimadzu XRD-60) and thermal behaviour (dilatometry, BP Engineering RB-3000, differential thermal analysis (DTA), Shimadzu DTA-50, and thermogravimetric analysis (TGA), Shimadzu TGA-51). Given that the clay material is regularly used in the extrusion of bricks, extrusion was chosen as the shaping technique. Another reason for this option was the differences usually observed between the characteristics (and specifications) of industrial products and laboratory results obtained from small test-pieces frequently produced by different shaping techniques (e.g. uniaxial pressing). However, given the limited amount of the SCR sample made available and because both the shaping process and the available equipment require a rather high amount of material, only mixtures containing 20 wt.% of SCR (constant) were investigated. The mixtures were prepared, homogenised with 10–12 wt.% water (dry basis) and extruded (Verdès 035-051 laboratory extruder). The dried test-pieces ($25 \times 17 \times 95$ mm^3) were sintered in air in an electric furnace between 700 and 1150 °C for 1 h, with a heating rate of 300 °C/h. The mechanical strength of the sintered samples (average of five specimens for each value) was measured with a universal testing machine (Zwick-Roell, 2.5 kN) in three-point bending tests at a constant cross-head speed of 0.5 mm/min. Apparent density and water absorption were determined using the Archimedes water displacement method, as specified by the European Standard EN 99 (ISO 10545-3, 1991), and the crystalline phases present after sintering were identified by X-ray diffraction.

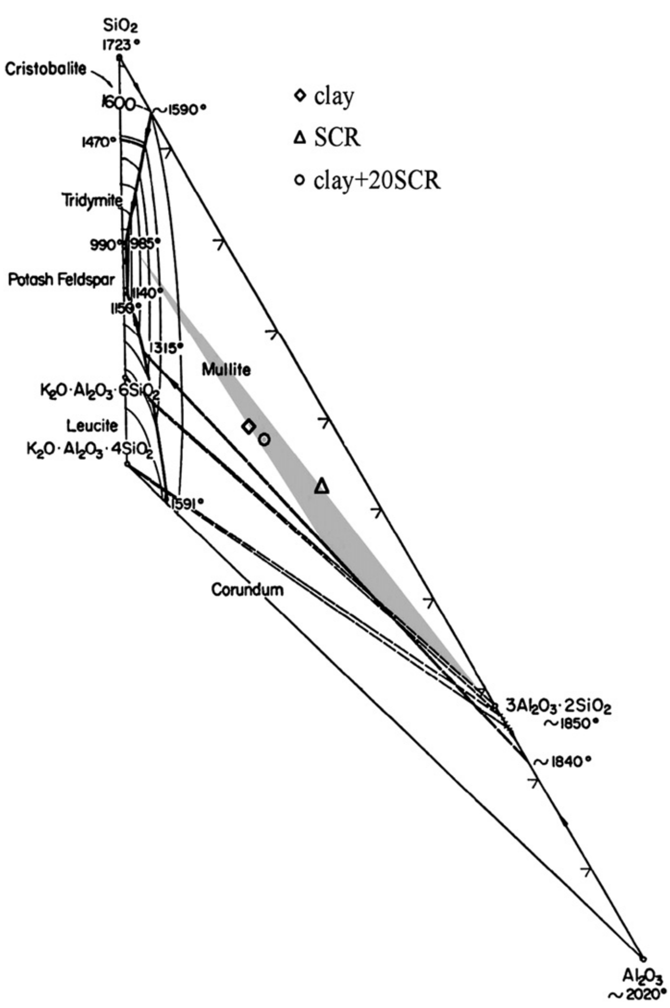

Fig. 1. Silica–mullite–feldspar compatibility triangle in the Al_2O_3–SiO_2–K_2O phase diagram, showing the location of the clay, SCR and the mixture containing 20 wt.% SCR. The shaded area represents the movement of the first-liquid tie-line when composition changes from clay to SCR.

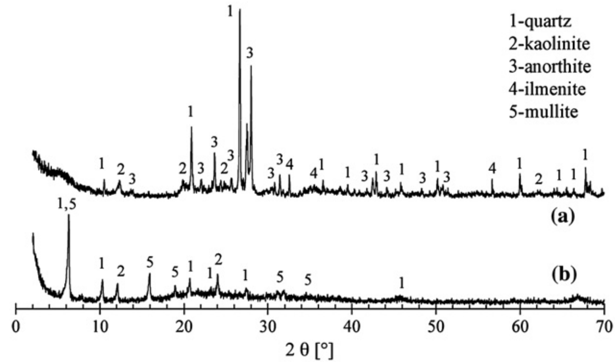

Fig. 2. X-ray diffraction patterns: a) clay; b) SCR.

3. Results and discussion

Table 1 gives the chemical composition of the commercial clay mixture and the SCR material. The clay mixture shows the expected typical composition: rich in silica and alumina with a small amount of CaO and K_2O (minor contents of Mg, Ti and Na oxides), accompanied by a significant amount of iron oxide (6.69 wt.%), a high temperature fluxing agent which is responsible for the dark colour of the fired pieces. The SCR material basically contains SiO_2 and Al_2O_3 in a proportion like in kaolinite, indicating its aluminosilicate origin. Small amounts of La_2O_3, Fe_2O_3 and P_2O_5 are also present, likely resulting from metal pick-up during catalyst service. In terms of chemical composition, the major differences between the two materials (hence, those that might induce some changes in the clay mixture behaviour, upon the reject additions) lie in the higher alumina content of the SCR. Considering the otherwise

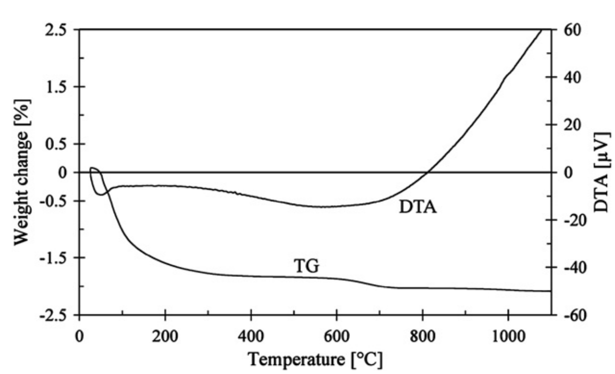

Fig. 3. Thermal analysis (TG and DTA) of SCR.