Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Assessment of the fluxing potential of igneous rocks in the traditional ceramics industry

Fernanda G. Dias[a], Ana M. Segadães[b,*], Cláudio A. Perottoni[a], Robinson C.D. Cruz[a]

[a] Universidade de Caxias do Sul, Instituto de Materiais Cerâmicos, 95465-000 Bom Princípio, RS, Brazil
[b] University of Aveiro, Department of Materials and Ceramics Engineering (CICECO), 3810-193 Aveiro, Portugal

ARTICLE INFO

Keywords:
Igneous rocks
Hierarchical cluster analysis
Ceramic fluxes
Phase diagrams

ABSTRACT

In this work, the fluxing characteristics of igneous rocks from the Serra Geral Formation (RS, Brazil) were assessed and compared with those of more common fluxes used in the ceramic industry. To this aim, 18 rock samples were characterized (XRF, XRD). Based on their chemical composition, samples were categorized (QAPF–TAS diagrams) and grouped into five major rock types using a hierarchical cluster analysis (HCA). Representative rocks of each type were further characterized in terms of thermal behaviour (TGA-DSC and fusibility tests) and compared with similar characterization results available in the literature for other ceramic fluxes. Tests results showed very good agreement with HCA and the predictions of the SiO_2–Al_2O_3–CaO phase diagram. A synergistic effect was identified between alkali + alkali-earth oxides and iron oxide, suggesting that the fluxing potential can be estimated in terms of the alumina/fluxes weight ratio, resulting in a pleasant dark chocolate sheen of the fired pieces. Thus, the mineral resources identified in the Serra Geral Formation can indeed be used as fluxes and, as such, contribute to the cost-effective production of ceramic materials with higher added value.

1. Introduction

Recent decades have witnessed increased industrialization with intensive extraction and processing of natural resources, as well as humankind's growing concern with the environmental degradation, particularly with wastes disposal. The ceramics industry is no exception, and has generally optimized production processes in order to reduce the amount of wastes produced and the corresponding negative environmental impact. At the same time, the increasing scarceness of conventional ceramic natural raw materials with adequate quality, and their consequent price raise, has been driving the search for alternative and, preferably, less expensive raw materials to reduce production costs and increase competitiveness on the world scenario [1–5].

Ceramic raw materials are selected based on location and availability, in order to reduce transportation costs, and on the roles they must play in ceramics manufacture (*i.e.* plastics, inerts and fluxes). Among those, fluxing materials are used to promote liquid phase formation during firing. A good fluxing agent is recognized by the amount of liquid phase formed at the firing temperature and by its viscosity [5–9]. As such, fluxes determine many of the final ceramic product properties.

In ceramics, alkali (Na_2O and K_2O) and alkali-earth (CaO and MgO) oxides are considered the most efficient fluxing oxides [10–12], their fluxing ability being generally measured against the silica-alumina system. In the corresponding ternary systems, they give rise to liquid phase formation (eutectics) at lower firing temperatures, which promotes sintering and densification of ceramic bodies. It could be reasoned that, the higher the alkali contents in the raw materials, the higher the amount of low viscosity liquid phase formed during firing. The viscosity of the liquid phase depends on the ratio between the glass-forming and refractory oxides (mostly SiO_2 and Al_2O_3) and the modifying oxides (Na_2O and K_2O). But it is also influenced by the Na_2O/K_2O ratio: although the eutectic with K_2O occurs at a lower temperature than that with Na_2O, the latter liquid has lower viscosity [13,14]. Practice shows, however, that raw materials with high fluxing power likely lead to difficulties in controlling pyroplasticity (dimensional stability of fired pieces) [5,15].

Natural combinations of those oxides can be found in the feldspar family of aluminosilicates, in which extensive solid solutions are formed among three end members: albite ($NaAlSi_3O_8$), orthoclase (or microcline, $KAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$). The natural alkalis content in feldspars ranges from 9 to 12 wt% [16–18]. Albite and anorthite are isomorphic and constitute the continuous series called plagioclase feldspars, while K-feldspar and albite are known as alkali

* Corresponding author.
E-mail address: segadaes@ua.pt (A.M. Segadães).

http://dx.doi.org/10.1016/j.ceramint.2017.08.190
Received 25 July 2017; Received in revised form 23 August 2017; Accepted 29 August 2017
0272-8842/ © 2017 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

feldspars. For most feldspars, partial or complete melting occurs in the range of 1140–1280 °C and, in the presence of other silicates, initial melting occurs at even lower temperatures.

Feldspathoids are similar to feldspars, the major ones being nepheline ($NaAlSiO_4$) and leucite ($KAlSi_2O_6$) (eventually, also kalsilite, $KAlSiO_4$). The main differences between feldspars and feldspathoids are the crystal structure and the lower (about two-thirds) silica content in the latter. Having higher alkali contents (above ~ 14 wt%), feldspathoids have a fluxing potential higher than that of feldspars and produce less viscous melts, enabling sintering at lower temperatures [6,17,19–21].

At present, feldspars are the main fluxing material used in the ceramic industry, contents ranging from 35 to 50 wt% in the case of porcelain and porcelainized tiles. Thus, feldspar costs significantly contribute to the final product price. Rocks containing feldspars or feldspathoids of commercial importance generally occur in massive igneous intrusions, either coarse-grained (pegmatites) or fine-grained (aplites), such as granite, feldspathic sand, nepheline syenite, phonolite (the volcanic equivalent of nepheline syenite) and basalt [2,16,17,20,22–25].

When dealing with igneous (or magmatic) rocks, the geologist lexicon might be at times bewildering for ceramists, so a brief explanation might be in order. To classify igneous rocks [26,27], geologists mostly rely on petrographic observations such as mineral content, texture (grain size) and colour, which produce descriptions (modal classification) such as "mafic" versus "felsic", or the quartz–(alkali feldspars)–(plagioclase feldspars)–feldspathoids (QAPF) designations. Geologists also rely on chemical composition, particularly the SiO_2 content, which leads to descriptions (normative classification) such as "acidic" versus "basic", or the (total alkali)–silica (TAS) designations. Rock genesis might be called upon too (volcanic or extrusive, and plutonic or intrusive) and the various criteria entwine and overlap each other. For the ceramist, on the other hand, the chemical analysis is particularly important, as it determines processing (specially firing temperature) and the properties of the final product (namely mechanical strength). Because ceramic processing usually involves milling and grinding of some kind, the size of grains in the original rock loses comparative importance. For the ceramist handling igneous rocks, it can therefore be very helpful to bear in mind the volcanic–plutonic pairs of rocks that are compositionally equivalent, typically basalt–gabbro, andesite–diorite, dacite–granodiorite and rhyolite–granite [28]. Similarly, although the TAS diagram was intended for volcanic rocks, its analogue for plutonic rocks, based on those equivalent rock pairs, is used at times instead of the more elaborate QAPF. The two diagrams are based on diverse criteria and are very different but they actually do match each other [29], as shown in Fig. 1.

Roughly, 95% of the Earth's crust is made of igneous rocks, ~ 60% of which are feldspars [30,31]. Although they are abundant in the earth's crust, feldspars are also geopolitically strategic, facing increased market dependency and being on the verge of becoming critical. Turkey, Italy and China account for nearly 60% of the world feldspar production, of which the Brazilian production approaches 1.6% [7,32]. The main feldspar reserves in Brazil [33] are located in the States of Paraná (28.3%), Minas Gerais (13.3%), Paraíba (10.4%), Rio Grande do Norte (10.2%), Rio de Janeiro (10.2%), Bahia (8.9%), São Paulo (8.2%), Santa Catarina (6.2%) and Tocantins (4.3%). Thus, the world scenario is replicated in the acute shortage of feldspars in southern Brazil, one of the main ceramic centres in the country [20,34]. The phonolite found in Santa Catarina is used industrially as a flux in the production of ceramic glazes and glass [22] and, thus, southern consumers often have no other option but to import such raw materials or to use pegmatites from the northeast region, with high transportation costs.

Such constraints, as well as the observed increase in the demand for feldspars, have been causing significant changes in the ceramic industry. This explains the on-going search for alternative mineral resources with fluxing characteristics, capable of reducing firing temperature and the firing time required for a suitable sintering process [8,17,20,23–25,35–38].

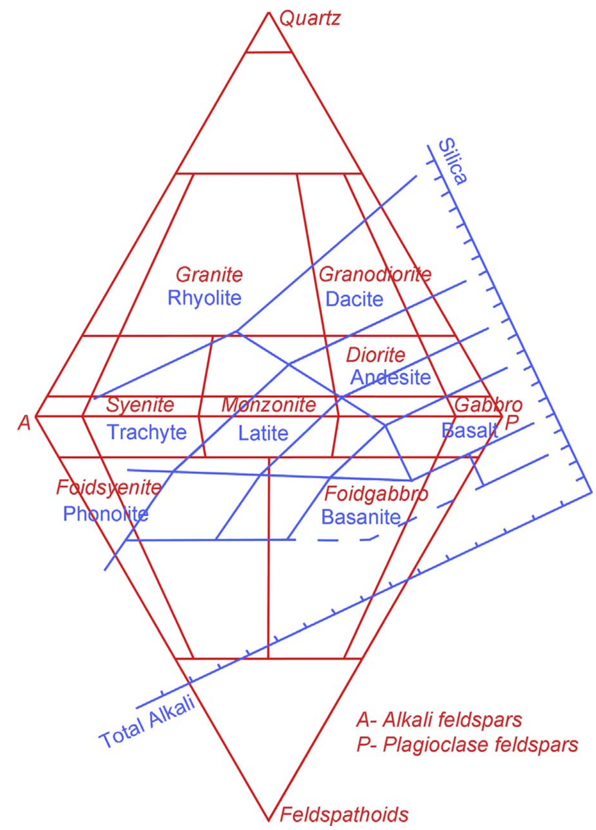

Fig. 1. Superposition of the simplified diagrams Quartz–(Alkali feldspars)–(Plagioclase feldspars)–Feldspathoids (QAPF, in italic) and (Total Alkali)–Silica (TAS, in regular) often used in petrographic classification of igneous rocks, illustrating the composition equivalence between volcanic–plutonic pairs of igneous rocks (adapted from Reference [29]).

Brazil comprises one of the major igneous rocks formations of the western portion of the world: the Serra Geral Formation, stretching over a significant part of the State of Rio Grande do Sul (RS). This magmatic province is mostly (~ 90 vol%) composed of basic tholeiitic basalts (iron-rich with calcic plagioclase), with smaller portions of intermediate tholeiitic basaltic andesites (~ 7 vol%) and acidic rhyolites and dacites (~ 3 vol%). Despite the large amount of basaltic rocks, the Serra Geral Formation is characterized by a diversity of chemically distinct lithotypes, due to the different magmatic spills that took place in the region [39–42].

Thus, the Serra Geral Formation strategic mineral wealth has been drawing the interest of researchers and entrepreneurs alike and the objective of this work is to assess the fluxing characteristics of the igneous rocks from the Serra Geral Formation as compared with those of fluxes commonly used in the ceramic industry, already available in the literature.

2. Experimental

2.1. Characterization of rock samples

Samples of eighteen different igneous rocks (designated by letters A to R) from the Serra Geral Formation were collected directly from the quarries, ground in a jaw crusher, comminuted down and sieved through 0.5 mm. Rock samples were characterized in terms of chemical composition by X-ray fluorescence (XRF, Philips/Panalytical PW 2400 spectrometer with Rh tube) on pressed pellets of 7 g of sample and 1.4 g

Download English Version:

https://daneshyari.com/en/article/5437241

Download Persian Version:

https://daneshyari.com/article/5437241

Daneshyari.com