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Performance and properties of alkali-activated blend of calcined laterite and waste marble powder

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Abstract. This contribution reports on some preliminary studies on the use of lateritic soils from Cameroon as raw materials for the production of alkali-activated binders. These soils contain about 40-60% kaolinite and variable amounts of quartz, hematite and other minor phases. After calcination at 800 °C, this material is blended with up to 30% waste marble powder, which is produced in large amounts during quarrying, cutting and processing of marble.

The results of our tests show that a careful mix design allows a good mechanical performance to be achieved, with values of the cubic compressive strength larger than 30 MPa after 28 days. The role of Fe on the performance of this material is investigated by comparison with Fe-free blends of commercial metakaolin, waste marble powder and quartz. Calorimetric data suggest that the use of alkanolamines as Fe chelating agents may accelerate the early age reactivity, depending on dosage, although the effect on the development of mechanical properties is minor.

It is argued that alkali-activated calcined laterite represents a viable option for the development of sustainable binders, especially for the African market, where it could be used, for example, to produce compressed stabilized earth blocks, in substitution of masonry units based on Portland cement or fired clay bricks. The use of waste marble powder adds further environmental value to this material.

Keywords: Laterite, Alkali activation, Marble powder

1 Introduction

Research into sustainable cement materials based on calcined clays is gaining consensus, as it has now become clear that abundant, worldwide available and relatively lowcost raw materials are necessary in a scenario of rising demand of building materials. Clay minerals are abundant in soils (Fig. 1), particularly in tropical regions and, more in general, in developing countries (Fig. 2).



Fig. 1. Global distribution of kaolinite (top), illite (middle) and smectite (bottom) in soils (modified from [1] CC Attribution 3.0 License.)

Lateritic soils consist of impure, iron-rich kaolinite deposits, which are particularly abundant in the subequatorial areas of the African continent. Laterites may potentially represent a viable raw material for the production of sustainable cement in the African continent, where urbanization is increasing at a fast pace. Recent estimations envisage

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that in 2100 three African cities (Lagos, Kinshasa, Dar-es-Salaam) will become the most highly populated settlements in the world, each with over 70 million inhabitants [2]. Given the current dramatic backlog in providing adequate and affordable housing in the continent, producing sustainable and reliable building materials based on locally available and cheap raw materials, in order to relieve the economic and environmental burden associated with import from other continents, will represent a key technological and societal challenge.



Fig. 2. Real GDP growth in 2019. Growth proportional to the intensity of the green color (compare with clay distribution in Fig. 1). Data from the International Monetary Fund (www.imf.org).

In this study, we test the behavior of alkali-activated calcined clays produced from laterites sampled in Cameroon. Prior to alkali-activation, the calcined laterite is blended with marble powder, a waste material produced during marble quarrying, cutting and polishing. The disposal of this material poses severe environmental issues [3,4], hence the further environmental value of its reuse in cement binders. Previous studies suggested that the addition of waste marble powder may enhance the properties of alkali-activated calcined clays [5].

In the present study, a series of analyses are performed to assess the role of Fe in the processes associated with the alkali activation of calcined clays.

2 Materials and methods

Laterite soil samples were collected in Yaoundé (Cameroon) and consist of kaolinite, quartz, Fe-hydroxide (goethite), Fe-oxide (hematite), Ti-oxide (anatase) and traces of Al-hydroxyde (gibbsite). This material was ground and thermally treated at 800 °C for 5 hours. Upon calcination, goethite is converted to hematite and kaolinite is converted to metakaolinite, as testified by the disappearance of the basal peak at 14.32° 20 and of

the 020 peak at $23.12^{\circ} 2\theta$ in the diffraction pattern (Fig. 3). The starting mix consisted of 70 wt% calcined laterite and 30 wt% marble powder. The latter consists of 100% calcite with Mg impurities. Sodium silicate pentahydrate was used as alkaline activator.



Fig. 3. Calcined laterite XRD pattern. Phase labels: Q = quartz; H = hematite; CR = corundum (internal standard); A = anatase.

Compressive strength tests were performed on the above mix, as well as on a Fe-free mix consisting of commercial metakaolin blended with marble powder and fine quartz. Quartz was added with the aim of diluting the amount of metakaolinite, to match the weight fraction contained in the calcined laterite, in order to separate the effect of Fe with that of metakaolinite content. Moreover, additions of 0.2 wt% alkanolamines were performed with the aim of testing the effect of such additives acting as Fe chelating agents. The amount of this additive was calibrated on the XRF concentration of Fe in the laterite, which is about 20%.

3 Results

The phase composition of the reacted mix after 20 days, as obtained by XRD combined with the PONKCS method [6,7] show that approximately half of the initially present metakaolinite has been dissolved. Calcite (present in the marble powder) and hematite are also partially dissolved. The formation of an X-ray amorphous phase is testified by the presence of a diffuse scattering hump at $30^{\circ} 20$ in the diffraction pattern (Fig. 4).



Fig. 4. *XRD* pattern of the alkali-activated blend. Phase labels: Q = quartz; H = hematite; CR = corundum (internal standard); Cc = calcite.

The maximum measured compressive strength is 29.0 MPa at 7 days and 32.2 MPa at 28 days. The compressive strength of the Fe-free metakaolin sample is approximately 15% higher.

The results of semi-adiabatic calorimetry show that the early-age reaction kinetics is accelerated in the presence of 0.2% alkanolamines (Fig. 5). However, only minor changes in the 7 days compressive strength were detected in the samples containing these additives.

SEM-EDX spot analyses suggest that the composition of the matrix of the reacted material is compatible with that of a N-A-S-H phase, in which non-negligible amounts of Ca and Fe are present. Further research will be needed to clarify the exact nature of the reaction product and whether Fe may play a structural role in it.

4 Conclusions

The results of this study show that alkali-activated cement with an appropriate mechanical performance can be produced using a blend of calcined laterite, a cheap raw material that is particularly abundant in Africa, and waste marble powder, a secondary raw material that is also available in this continent [8,9]. The use of commercial sodium silicate as alkaline activator may pose limitations due to high cost and environmental impact. However, combinations of primary and secondary raw materials rich in Na and Si, such as sodium carbonates present in geological deposits and vegetable ashes or waste glass, could be used as an alternative cheap and less impacting solution. These materials are promptly available in the African continent.



Fig. 5. Heat released by the reference alkali-activated blend of calcined laterite and marble powder, and by the samples with additions of alkanolamines (TIPA: Triisopropanolamine; TEA: triethanolamine).

The presence of Fe seems to affect the development of mechanical strength only to a minor extent. The use of small amounts of Fe chelating agents in the mix improves the early-stage reactivity, although no significant variations in the 7 days compressive strength are observed. Further research will be necessary to understand the exact role of Fe on the dissolution-precipitation pathways.

We conclude that laterite soils represent a promising raw material for the production of sustainable binders in specific geographical locations and encourage additional studies on their exploitation to be performed.

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