Characterisation of traditional ceramic materials used in the Sotho culture (South Africa) for clay pot making

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Abstract. Different types of clayey soils are readily available as a natural resource in South Africa. Some are used for brick making, some for eating in a geophagia (habit) while some others are used as cosmetic ingredients in cultural ceremonies or in traditional ceramic applications. Among the above mentioned numerous utilisations, clay pot making and trade are claimed to contribute to the improvement of the household income generation in the rural communities. Traditional clay pots are made in Africa by people from different cultures. This study focuses on the suitability of clayey soils used for clay pot production as traditionally made by the Sotho people of the Free State Province of South Africa. Clayey soil raw materials are collected from the local river banks and processed through a shaping, sun drying and firing set of subsequent processes. The knowledge of mineralogical composition, mineral phases formed during the processing of clays and the mastering of physio-chemical properties including plasticity helped to understand the thermal properties of the processed material generated, their forming and shaping, and the application of clay pots produced. Clayey soils, the main raw materials used, were randomly collected from the QwaQwa region of the Free State province and analysed using XRF, XRD, and FTIR. The clayey soil showed plastic limit of 34.36%.

1. Introduction

Ceramics have found large applications in prehistoric and in modern times. Clays are natural materials abundantly found and largely used in the manufacturing of ceramic products such as bricks, porcelain, sanitary ware, floor and roofing tiles and also various industrial applications [8]. With these vast numbers of usages, this paper aims to provide an insight into the characterisation of clayey soils used to make clay pots in QwaQwa, Free State province of South Africa. The sample was received from the Homelands of the Basotho people which lies in the heart of the Karoo sequence rocks, containing mudstones, shales, sandstones and the Drakensberg Basalts forming the youngest capping rocks in a province that is high lying with almost all the land being 1000m above the sea level [7]. In general clay can also be referred to as natural earthy fine grained materials which are powdery when dry, plastic when wet and stone like when baked [2]. In general, clay belongs to a wider group of minerals, however all clay minerals are classified as hydrous aluminium phyllosilicates group with a highly complex structures which are basically characterized by layers where each layer is composed of two types of structural sheets: an octahedral and a tetrahedral. The tetrahedral sheet is composed of silicon-oxygen tetrahedra linked to neighbouring tetrahedra by sharing three corners which is resulting in a hexagonal network on one side and on the other side, the remaining fourth corner of each tetrahedron forms a part to adjacent octahedral sheet. Usually the octahedral sheet is composed of aluminium or magnesium in six-fold coordination with oxygen from the tetrahedral sheet and with hydroxyl. The two sheets together form a layer, and several layers may be joined in a clay crystallite by interlayer cations, Vander Waals force, electrostatic force, or by hydrogen bonding. Based on the clay structure (Figure 1), classification is according to the arrangement of tetrahedral and octahedral sheets. Therefore, it can be 1:1 when the clay mineral has one tetrahedral and one octahedral sheet per clay layer; 2:1 when the clay mineral contains two tetrahedral sheets and one octahedral sheet taken in sandwich between the two tetrahedral sheets; and 2:1:1 when the clay minerals are composed of an octahedral sheet adjacent to a 2:1 layer. Table 1 summarises the classification of clay mineral group in connection to their structures.

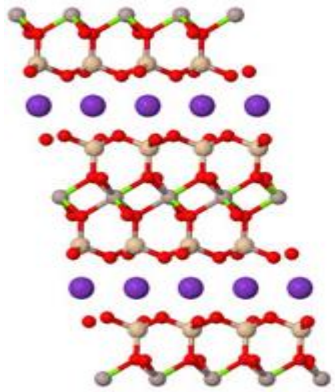

Figure 1. Structure of clay minerals showing tetrahedral and octahedral sheets.
This is a tri octahedral 2:1 [13].

Table 1. Sheet structure for the layers of clay minerals.

Clay mineral	Layer type
Kaolinite	1:1
Montmorillonite	
Or smectite	2:1
Illite	2:1
Vermiculite	2:1
Chlorite	2:1

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Consequently, with respect to variety of the chemical species present in the clay and their arrangement in the clay structure, clay minerals may be divided into four major groups which are mainly in terms of the variation in the layered structure. These include the kaolinite group, the montmorillonite / smectite group, the illite group, with their related associated minerals and general formula as presented in Table 2. In the paper we interchangeably use bentonite, montmorillonite and smectite. Clays and their associated soils have a wide variety of physical characteristics such as plasticity, shrinkage under firing, under air drying, fitness of grain, colour after firing, hardness cohesion and capacity of the surface to take decoration. In general the plasticity is defined by means of its plastic limit and its liquid limit which are defined as the moisture content at which the soil passes from the friable to the plastic state and the moisture content at which the soil passes from the plastic to the liquid state respectively [4]. This study sets to investigate the physical, chemical and mineralogical properties of the clayey soils using x-ray diffraction (XRD), x-ray fluorescence (XRF) and Fourier-transform infrared spectroscopy (FTIR).

Table 2. Major groups of clay minerals [6].

Group name	Member minerals	General formula	Indications
kaolinite	kaolinite, dickite, nacrite	$Al_2Si_2O_5\ (OH)_4$	members are polymorphs (composed of the same formula and different structure)
montmorillonite or smectite	montmorillonite, pyrophyllite, talc, vermiculite, glauconite, saponite, nontronite	$(Ca,Na,H)(Al,Mg,Fe,Zn)_2\ (Si,Al)_4O_{10}(OH)_2\text{-}xH_2O$	X indicates varying level of water in mineral type
illite	illite	$(K,H)Al_2\ (Si,Al)_4\ O_{10}(OH)_2xH_2O$	X indicates varying level of water in mineral type

2. Materials and Methods

Clayey soils were received from the potter who collected them from the river banks of Phutaditshaba, QwaQwa (Figure 2). The sample was then oven dried at 105° for 24 hours. The dried sample was crushed and sieved using ASTM sieve. Materials > 45µm were utilised. Three spectroscopic techniques (XRF, XRD, and FTIR) were used. The chemical composition of clayey soils used in this work represented was studied using the X-ray fluorescence Rigaku Primus II. About 2g of the dry and pulverised sample used to determine the phase identification was studied using the XRD Rigaku Ultima IV. Vibration and stretching bands were determined using FTIR Thermo Scientific Nicolet iS10 with a spectral range of a wave number between 400 - 4000 cm^{-1}. The loss of ignition was calculated by placing 46.45g of the sample in a furnace at 1000°C for 2 hours. The weight of the dried sample was then measured as soon as the sample was removed from the furnace. This was done in order to determine the weight loss of the clayey soils. Plasticity of clayey soils was determined using the Atterberg limits. The ASTM procedure was used [1]. The plastic limit, liquid limit, moisture content and linear shrinkage were calculated from this experiment. The sample was placed in the liquid limit device, and 25 blows were counted in order to reach the point of contact for the clayey soils. The sample was collected at the junction point then put in the oven at 105° for 24 hours. This sample was then weighed, dried and the liquid limit was then measured

3. Results and Discussions

Figure 2. Map of South Africa showing the position of QwaQwa where clay pots are made

Figure 3. Photo showing a clay pot made in QwaQwa, Free State

QwaQwa clay pots generally have bright motives as seen on Figure 3.The dexterity of the potter is appreciated in order to produce such amenable and durable clay pots. Interviews conducted with the potters revealed that the exercise of clay pot making is an indigenous skill of the Sotho people and helps to create sustainable income for the potters from the rural lands of QwaQwa Free State. The knowledge and skill of pot making runs a risk of being lost because the current generation finds no interest in acquiring these pot making skills. The traditional uses of these pots include simple decoration in households, water storage and for everyday use of drinking water, grain storage, for drinking traditional beer at cultural events such as weddings, funerals and family gatherings.

The chemical composition of a soil type influences its technological properties. The results show major elements that include Al (24.33%) and Si (56.42%), leaving other minerals such as Fe (8.43%) and K (4.25%) in trace elements as per XRF results (Table 3). The large amount of silicate present in the clay is associated with the crystalline phase quartz which is combined to alumina in the alumina silicate structure [11]. The low Ca content (less than 5%) is an indication of non-calcareous clays therefore limiting shrinkage. The presence of K, Ca, Mg and Ti help to melt silicates and bind particles together during firing. Aluminium oxide in kaolinite leads to increased plasticity [9]. The X-Ray Diffraction was used in order to explore the mineral assemblages of the clayey soil as depicted in Figure 4 with the presence of quartz, montmorillonite, illite and kaolinite. The semi-quantitative XRD denote 75% quartz, 4% illite, 5% Kaolinte.and 16% montmorillonite, these crystallite minerals are represented as peaks in figure 4. The high montmorillonite/kaolinite + quartz ratio of 3 makes this clayey soil usable in pot making as it has a higher plasticity index value of 64.85 which is in the range of a montmorillonite rich clay [1]. The higher amount of montmorillonite (16%) in the sample is then confirmed.The strength of the clay pot depends on the composition of the raw materials that are used. Quartz and montmorillonite are seen to be in abundance as compared to kaolinite and illite while other minerals are presented as trace minerals. The high presence of quartz further justified the high content of Si as seen in Table 3.

FTIR can determine many and very small mineral contents that are present within a sample. Vibration and stretching bands were identified as seen on Figure 5. Weak bands due to absorbed water are observed at wavenumbers 1633cm^{-1} and 1536cm^{-1}. Vibration bands were identified at different wavenumbers respectively, 993cm^{-1} corresponds to Si-O stretching band, 1416 cm^{-1} –OH-stretching band, 3693.63 cm^{1} –OH asymmetric band and weak band M-O at 688 cm^{-1} ,788 cm^{-1} and 910 cm^{-1} .C-H stretching vibrations which can be attributed to organic contribution are present at peaks 2848 cm^{-1} and 2919 cm^{-1}. All these peaks observed on Figure 5 were identified by comparing the observed wave numbers with available literature.

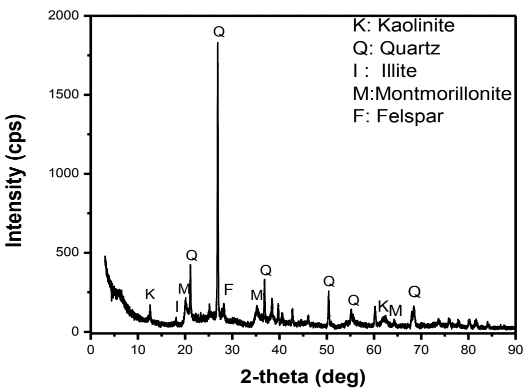

Figure 4. XRD spectrum of clayey soils showing their mineral contents .Smectite and kaolinite are observed.

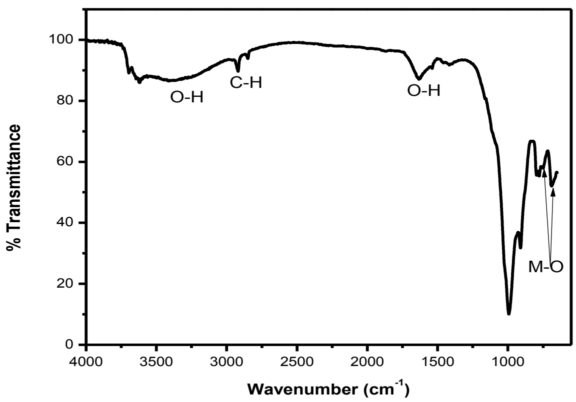

Figure 5. FTIR spectrum of pot clayey soils showing the vibration and stretching bands. O-H stretching band; C-H stretching band; Si-O stretching band.

Table 3. Main elements in the clayey soil used. XRF results

Element	Al	Ca	Fe	K	Mg	Mn	Na	P	Si	Ti	Zn
Mass%	24.33	2.58	8.43	4.25	1.38	0.04	0.60	0.06	56.42	1.38	0.02

In the present study, the plasticity was determined using the Atterberg limits, due to the useful information it provides on the plastic properties [1].The moisture content was calculated at 9.3 %, the high moisture content is associated with high plasticity, meanwhile a low moisture content will cause cracking during moulding. Because between 4-10% of linear shrinkage is within an acceptable range for clays, the QwaQwa pot clayey soils have a linear shrinkage calculated at 7.3% therefore classifying it as a good material to use that limits cracking and warping. Taking into consideration the heat factor during the firing process, heat is directly proportional to the shrinkage. The loss of ignition was calculated at 3.38%. The liquid limit is taken as the water content of the soil at which it will just begin to flow when jarred in a specific manner [1] .Liquid limit was calculated at 99.21% and plastic limit at

34.36%. The plastic index was therefore derived at 64.85%. When the plastic index is above 35, its high value is associated with low water permeability therefore making the QwaQwa pot clayey soils with 64.85% PI a good sealable product.. The property of plasticity is generally dependent on the mineralogical composition of the soil and smectite is generally sticky and plastic. The high plasticity of these clayey soils enables the potter to create different shapes in ceramic applications

4. Conclusion
The investigations performed on the clayey soils were done with an intention to understand the importance of the mineralogical and chemical composition of the clayey soils used to make clay pots. From this study it was obtained that clayey soils from QwaQwa are composed mainly of Si, Al and Fe and montmorillonite, kaolinite, illite and quartz as major minerals. The clayey soils were of excellent industrial quality for ceramic production making clay pots that were durable and suitable for diverse applications.

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References
[1] Bain J.A. 1971 *Clay Minerals* **9** 1
[2] Bam S.A, G A. 2014. *Journal of Multidisciplinary Engineering and Technology* **5** 10
[3] Catuneau O, Wopfner H, Eriksson P.G, Cairncross B, Rubidge B.S, Smith R,M,H, & Hancox P.J. 2005 *Journal of African Earth Sciences* **211** 253
[4] Dumbleton M. & West G. 1966 *Clay Minerals* **6** 179
[5] Ekosse G.-I., de Jager L., & Ngole V. 2010 *Journal of Biotechnology***, 9** (47) 8058
[6] FAHEEM U. 2008 *The Minerals, Metals & Materials Society and ASM International,* 39A
[7] Johson M R, Van Vuuren C.J, Hegenberger W F, Key R, & Shoko U. 1996 *Journal of African Earth Sciences* **23** 3
[8] Mahanoharan C. S. 2012 *Journal Cerâmica* **58** 412
[9] Maria G M 2002 *Universitatis Babe¯***(**Bolyai,Geolgia) XLVII 1 77
[10] Murray H. 2007 *Applied Clay Mineralogy* (first edition ed. Netherlands)
[11] Nwajagu C O, Aneke L.E. 2001 *Journal of Nigerian Society of Chemical Engineering* **5** 1
[12] Sumner P D, Hall K J, van Rooy J L & Meik l. 2006. *Journal of African Earth Sciences* 236
[13] http://www.claysandminerals.com/minerals/clayminerals. [Accessed 3 June 2016]