CERAMIC DEVELOPMENT FOR DOMESTIC STOVES

Development of a Low Thermal Expansion Ceramic Body for Domestic Charcoal Stoves in Maputo

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ABSTRACT

Although a wealth of information exists on the processing of clay for pottery purposes, very little of the material is geared towards the design of fuel efficient, household, ceramic stoves. Ceramic as a material for stove production holds many potential benefits, most noteably because of its low cost and general availability in areas where improved cooking appliances are needed. However, ceramic or clay stoves do not usually have a long working life and low durability and high breakage of clay stoves results in poor consumers being wary of investing money in the appliance. Household clay stoves are usually produced by small-scale producers, artisans or producer-groups. These producers face many challenges and to improve the long term prospect for producers of improved clay stoves, improved understanding of the use of clay and clay additives was required. The article will describe the results of research into the performance of ceramic materials suitable for the production of, low-cost improved charcoal stoves. Some reasons why clay stoves and stove components typically have low durability are described and to a certain extent, solutions suggested. Lastly, a short overview of the work of the Programme for Biomass Energy Conservation (ProBEC) on clay stoves will be presented. ProBEC is gratefully acknowledged for their support of the research.

Introduction

Energy poverty remains a challenge in developing countries, impacting on the environment, health, security and well-being of an estimated 3 billion people. Around 2.64 billion people or 40% of the world's population lack modern fuels for cooking and heating while 1.6 billion have no access to electricity, three-quarters of them living in rural areas (Litovsky, 2007:1). Households in the SADC region relies heavily on biomass energy resources (firewood, dung, charcoal and agricultural forest residues and crop wastes) which are used mainly for cooking, heating purposes in households as well as income generating activities. More than 80% of the total energy consumed in the household and SME sectors is derived from this primary energy source. Dependence on biomass fuels continues in the region despite attempts made by national governments to modernize the energy sector. Continuing poverty and high costs associated with using modern sources of energy and appliances are some of the factors confining low-income rural and urban households to the use of biomass energy. The way in which biomass energy sources are used also impact negatively on economic, social, environmental and health aspects. Over-harvesting of the resource contributes to deforestation, desertification, increased soil erosion and air pollution. Exposure to smoke from cooking fires is associated with respiratory disease and other health impacts – globally, indoor air pollution from biomass fires is estimated to cause 36% and accounts for 1.6 million premature deaths per annum (WHO, 2002). Other health threats are the use of open fires, which cause burns and fires as well as injuries sustained while collecting or transporting wood fuel.

Citizens of Maputo in the lower and middle income brackets usually cook with charcoal in a brazier made of metal. These range in cost from $1.50 to $10 with a typical home having 3 such stoves in working condition and one or more derelict. In order to develop a replacement stove with improved fuel efficiency, a project was initiated by ProBEC in 2005. It was rapidly concluded that to make a stove with a product target cost of $2-3 meant that a clay stove was almost the only option as a raw material. Historically, clay stoves do not have a long working life – they break – so it was decided that to improve the long term prospect for African producers of improved stoves, a better and publicly accessible understanding of the use of clay and clay additives was needed.

The Maputo Ceramic Stove (MCS) project as it was originally called, was to be the test bed for a better design that the Improved Kenyan Jiko, made from a technically advanced approach to the formulation of the materials used.

Combustion Efficiency

Combustion efficiency can be described as the percentage of heat that could possibly be generated by a fuel divided into the heat that was actually generated. For convenience a researcher is most interested the efficiency with which the carbon portion is burned because most of the heat in a fuel is in the form of carbon. Unburned and partially burned carbon are heat losses. As CO is relatively easy to measure, the ratio of CO to Carbon Dioxide (CO_2) expressed as CO/CO_2 is acceptable as a measure of combustion efficiency. It can also be written in short form as COr (the CO ratio) and expressed as a 'volumetric ratio' in per cent. If the CO is 4 parts and the CO_2 is 65 parts, the COr is

4/65 = 0.615 = 6.15%

The COr for traditional metal braziers ranges from 12% to as high as 100% or more. A 100% figure does not mean that 100% of the carbon is emitted as CO, it means that CO and CO_2 are being emitted in equal amounts.

CO in typical concentrations ignites at a temperature of 850 to 900° C. A cool fire creates a great deal of CO as does a fire starved of Oxygen (O_2) which are the main problems to be dealt with. Because CO is normally produced and burned in a biomass fire, reducing the level means burning more of it, note necessarily generating less.

The easiest way to reduce the production of CO is to increase the temperature of combustion and one way to do that is to use a ceramic stove body that does not conduct as much heat through the walls as a metal stove conducts and to reduce the emissivity of the surface. A second method is to reduce the excess air (EA) passing through the stove which cools the entire flame environment.

As the emissivity of a stove's outside surface is reduced, the temperature rises as the heat does not leave it as easily. As the outer surface increases in temperature, the amount of heat conducted through the wall from inside the stove is reduced. Radiation from rusted metal, which has a very high emissivity, is a major loss. The temperature of combustion chamber wall a typical metal charcoal stove is above 400°.

Carbon Monoxide (CO)

CO is a major health threat. Charcoal stoves are notorious for producing high levels because the flame is not hot enough to properly burn a high carbon fuel and not enough space is left for the flame to finish burning the gases. Any new and improved stove promoted in Maputo should have a lower COr.

Charcoal

Charcoal is produced by artisanal methods in large regions of Moçambique for domestic cooking. It has a high carbon content because the volatile portion of the wood from which it is made has largely been burned off. There are, generally speaking, two qualities of charcoal available at Maputo markets: Shangalane, which is a hard, dense fuel sold in 70 kg bags. It is made from a particular species of tree widely grown in Maputo Province and is increasingly rare due to over-exploitation. 'Other' charcoals are made from other tree species and are usually sold in 35-40 kg bags. The burning characteristics of the two are different but the temperatures reached are similar. From a stove design point of view the different burning characteristics are an important consideration. From a materials point of view, the burning temperature is important.

Charcoal Consumption

The average charcoal use by a family is 70 kg per 6 weeks. This may be purchased in bags of various sizes, by the small pile sold by break-bulk retailers. The consumption for the city of Maputo is roughly 300 tons a day. It is sourced from as far as 600 km to the North and to the provincial borders to the West and South.

Ceramic as a stove material

The income of a typical Maputo home dictates that the stove should be as inexpensive as is practically possible. People are poor, money is very tight and fuel is a major expense. When trying to purchase a stove, initial cost is an important consideration. The least expensive metal stoves are made from thin

(0.5 to 0.8mm) sheet metal. They are destroyed by the fire within a few months. Most stoves are made from 2.0 mm iron sheets tend to last about 18 months after which the sections that burned away are often replaced. Higher quality stoves are made from 4 to 5mm second hand metal. This gives a longer service life but not better combustion because the design is basically the same. After another 18 months the common stove is discarded. After there is major corrosion of the metal, the stove is still useable though the fuel efficiency drops more and more as heat is lost through the holes.

Ceramic materials, typically a blend of clays and fluxes, are quite cheap compared with metal. Clay delivered in Maputo is about $7.00 per ton. If a stove of equal dimensions were to be made from ceramic, it would be a fraction of the cost of a metal equivalent. There is a good chance it will outperform the metal stoves as well.

It was envisioned that the ceramic 'combustor' could be mounted in a metal frame leading to a range of attractive products with an improved lifespan and of course, more fuel efficient.

Clay Stoves

Throughout the world Clay Stoves are produced by artisans (usually potters) and used with wood and charcoal fuels. They have a lifespan of 6 to 9 months in most cases. A clay stove that lasts a year is considered 'top notch'. An attempt was made in East Africa to put a clay liner into a traditional 'Jiko' (metal stove) which resulted in the 'Improved Kenyan Jiko', being a clay-lined metal shell. It was a materials disaster with losses in production exceeding 50%. The was resolved by ceramics engineer Hugh Allen, then with ATI how introduced better material selection and far better production equipment and kilns. At the time the claim was that each IKJ saved two tons of trees from being felled. Over time the design drifted and it is generally taken that the savings are not as large as they were, reduced from the original 50% to perhaps 30% now. One has to be careful to ask what the IKJ is being compared with when making such statements. Though widely reproduced, the IKJ is still no better at burning CO than its metal predecessors.

The IKJ was introduced to the Maputo area by the Eduardo Mondlane University however it predictably ran into ceramic material problems, material costs (it being largely made of metal) and a lack of skilled artisans who knew how to produce the complex parts quickly. Initially it sold for more than $30. The University IKJ suffers from the same problem as the original Jiko which is that it has a very high CO level in the exhaust gases, typically 16% COr when the air door is open and as much as +100% when it is closed. The reason the metal is required is that the clay grate is so weak and easily cracked that it has to be supported in a metal framework. Extensive practical work has been done on IKJ liners but the basic technology remains an artisanal clay or clay blend discovered by trial and error.

It was envisaged that in order to compete against metal stoves and to have the simultaneous saving of fuel and lower CO emissions a new design was needed. The MCS has preheated secondary injection and a carefully angled grate surface that ensures excellent combustion characteristics. An innovative pot stand that can control the fire intensity was also developed.

In order to provide a good lifespan and the low cost necessary to make a sustainable improved stove business, it was necessary to make a major leap forward in the type of materials used in the stove in terms of durability.

To last as long as a metal stove it is necessary to overcome the tendency of clay products to crack when heated on one side of the fire chamber which results in 'thermal shock'. The cause of this is the difference in physical size of the two surfaces of a stove component. The hotter side is larger than the cool side, and the bigger the difference in temperature, the bigger the difference in size. This is known as differential thermal expansion. It creates stresses in the material that cause cracks. The exact mechanism is that the hot material tries to expand and the cooler material tried to hold it back. The compressive strength of the hot material is invariably higher than the tensile strength of the cool material. If the difference between them is large enough, the cool material is pulled open by the uncompressible hot portion. This can happen catastrophically or on a very small scale with cracks getting progressively larger with each heating.

There are three common approaches to addressing this problem:

Make the material spongy so that is can accommodate the movement and stress, typically by putting into the mix something like sawdust or rice hulls that burn out and leave a porous clay matrix.
Change the material characteristics. Make the material strong enough to sustain high internal stresses so they are contained and are not able to create a rupture.
Lower the thermal expansion coefficient α so the stresses do not arise in the first place and there will be no need to accommodate them.

In this paper a fourth method will be described: reduction of the free Silica content. The importance of this was identified during the course of the development of the material for a stove in Maputo.

A combination of these four features is usually sought, with producers usually looking for a strong, porous, low expansion ceramic mix that has an acceptable lifetime.

In his book on the production of clay liners for IKJ stoves Hugh Allen described a non-laboratory based approach to the development of a stove body. In essence, the goal is the same, but is based on some experience and a trial-and-error methodology. If one gets a serviceable product, not much is known about why it is performing well. Moving the operation a few kilometres away means starting over again with a new development cycle, typically taking a year to complete. This is an unacceptably long time as hundreds of new producers are needed in Africa. ProBEC needs to be able to select and test clays at a new site in a matter of days, not a year.

In order to get a better understanding of the ceramic body performance and the special needs of stoves, a programme of basic research was commenced in 2005 in collaboration with a consulting ceramics laboratory intending to provide a clear understanding of what was in the clay mix, how it performed and why it did so. To a large extent this has been successful with important findings that can now be applied immediately to any site where clay stove components are going to be produced.

Thermal Expansion

While it is intuitive that materials expand when heated, the phenomenon is more complex than a simple “more heat = bigger size”. It is well known that water, increasing in temperature from 0 degrees to 4 degrees, shrinks slightly. After than, it expands until 100° at which point it undergoes a phase change and boils into steam.

Many material have similar interesting points. Clays are so complex in their makeup that several different complex crystal structures form at different temperatures and all sorts of things happen, some predictable and some not. At certain temperatures, various components may absorb heat, change volume up or down or not expand at all.

Figure 1 shows an example of a small pencil-sized clay sample being fired from 20 to 1100°. The lines represent sample lengths. The hotter it gets, the longer it gets, but only up to a certain point. After about 550°, with each increase in temperature some component of the clay starts to melt. At some point, so much has melted that the entire sample starts to contract as new structures are formed by the molten minerals.   The line showing the length of the two samples starts on the left at 25° C and the expansion is indicated by the line rising to the right.

After 600° the sample represented by the blue line shows that the expansion rate starts to decrease, and at 800 the sample shrinks a little. At 1040° there is a dramatic change in size as components melt and fuse until at 1100° the heat is turned off and the now-vitrified clay cools. When it reaches room temperature the sample is smaller than it was before firing. The shrinkage is permanent.

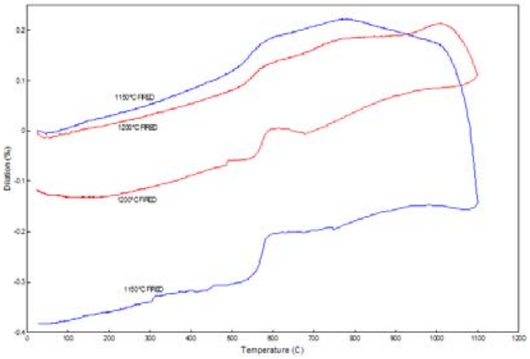
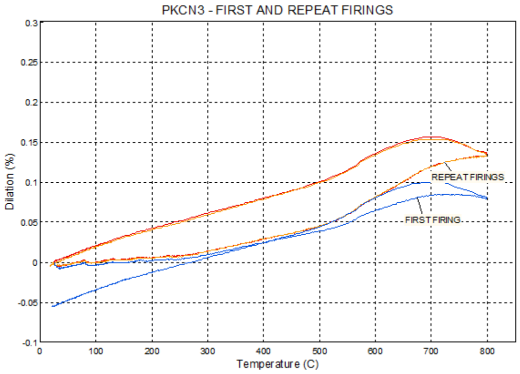


Figure 1 Size changes when firing clay

The first thing to note about the rate of thermal expansion is that it varies with temperature so one cannot state with precision that the α value is at any temperature. α has to be calculated for a stated temperature range. The α expansion coefficient is the linear change in length divided by the number of degrees to get a Specific number (per degree C or K). This coefficient only applies to that whole temperature range, not parts of it or parts beyond it.

In order to standardize measurements, α is usually stated for 0-1200° C, or 0-700° C. Most materials will have a different α value for these two temperature ranges and will not be linear between the two limits. One cannot be guided by the α value alone.

When the fired clay component is reheated (by being used in a stove, for example) the expansion curve is completely different from the one above because it is now a different material. New structures were formed and the 'reversible expansion' curve can now be determined as in Figure 2. Sometimes the sample has to be re-heated two or three times for the chemistry to stabilize and give a truly reversible expansion line that is the same each time.



Notice that the first time this sample was re-heated (blue line) it again shrank slightly. After that, it expands and shrinks in a slightly S-shaped curve. Not only is it not a straight line, the size v.s. temperature is not the same when heating as when cooling. This is because of the complex changes to the crystal structures that take place at different temperatures.

Figure 2 Reversible Expansion Curve

Note that the 'return' cycle of the orange line (the lower portion of the S) is nearly horizontal between 260 and 20°. This indicates that there is nearly no dimensional change over that range when cooling. However it is not true to say that if this material was used between 20 and 260° it would not change in size. The material would expand as shown on the upper line to 260°, then the line would curve down to rejoin the lower line upon cooling.

One of the most important changes that occurs in any clay happens at 573° when free Silica (ordinary Quartz sand) changes from an Alpha to a Beta crystal structure and increases in volume by about 1% over a very small temperature range. There is a very characteristic change in the slope of the curve at exactly this temperature if there is a high free Silica content in the clay. There can be a lot of Silica in clay that is 'tied up' with other minerals and this phase change does not take place. However free Silica mixed into the clay does make this transition. As quartz is a very common component of clay, almost all unprocessed clays exhibit the Silica phase transition expansion phenomenon.

There is a clear example of the Silica phase change in the blue return curve in Figure 1. It is zoomed and repeated here:

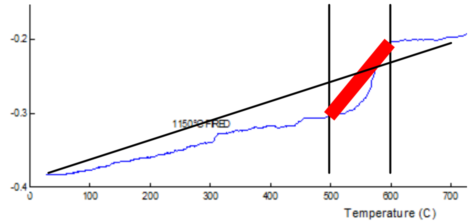
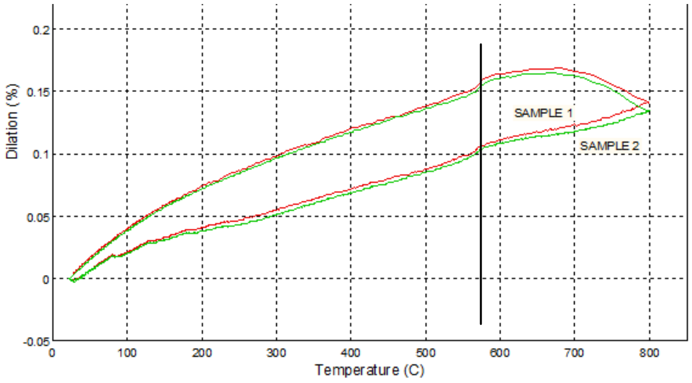


Figure 4 Transition at 573° C

The rate of thermal expansion (or contraction) over the temperature range 550° to 600° is very large (red line), even though the rate from 0 to 700° is not (black line). This means that if one side of a stove body is 600° C and the other is 250°, there can be a very large stress within the thickness of the clay a few millimetres into the material from the hot face because adjacent clay particles are struggling to be different volumes a slightly different temperatures. It is imperative in this case to see that either the temperature of that piece of the stove never reaches any higher than 550° or that if it does, it has to be heated very slowly so the whole thickness of the component rises in temperature and size at pretty much the same rate. Similarly, cooling past this point would have to be done slowly. During the manufacture of ordinary silica glass this is a major issue. It may be the primary reason for the failure of clay stoves, especially grates made from clay.

In order to limit failure, it is not enough to create a mix of clays and additives that provide a very low α value, it must also have a heavily suppressed free Silica phase transition. This is most easily achieved by removing the quartz from the clays or choosing clays that do not contain much.

In Figure 5 two samples of the same materials that were fired to 1100° are tested. Their expansion curves from 20 to 800° C are very similar, showing mixing of the ingredients was uniform.

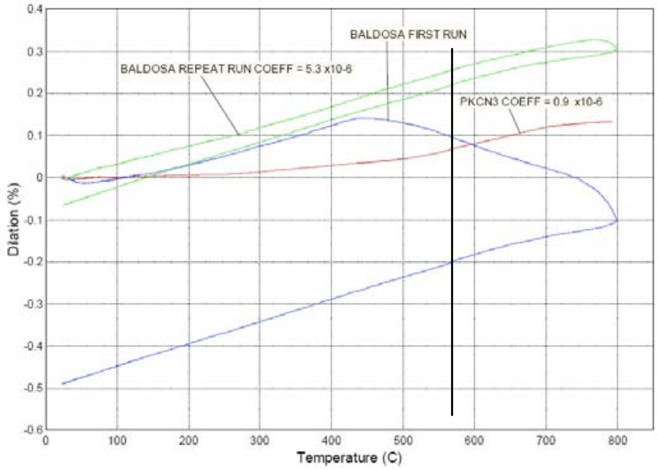


Note that the phase change at 573° C is subdued compared with the sample in Figure 1.

The addition of petalite and potassium feldspar has resulted in the formation of a structure with less free silica though the characteristic change in slope is evident.

Figure 5   Reduced influence of free Silica at 573° C

On occasion, by accident of nature or by design (treating the clay) all the free silica may be missing.



Here a traditional Native American clay tile called "Baldosa" has been re-fired to 800°. Traditionally the material is fired to a lower temperature so there is some shrinkage (0.5%) as seen in the blue line. Following this, repeat runs – the green line – show no evidence of quartz (free silica). Although α is more than six times that of the PKCN3, there is such a dramatic lowering of stress at 573 that the tile can withstand far more thermal stress than might be expected looking at the α value alone.

Figure 6 Baldosa Tile shows zero free silica content

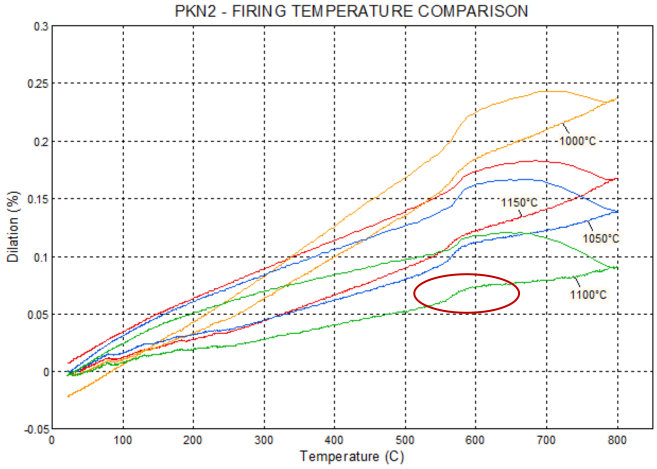
	ORIG	RPT
OXIDE	%	%
SiO2	59.3	62.7
Al2O3	17.3	17.5
Fe2O3	7.0	6.9
TiO2	0.99	1.00
P2O5	0.06	0.06
CaO	2.9	2.8
MgO	0.93	0.93
Na2O	1.84	1.84
K2O	2.3	2.4
LOI	3.4	3.4
TOTAL	96.0	99.5

In spite of being about 60% Silica (SiO_2) this Baldosa tile from El Salvador has virtually no free Silica (Quartz) in it. It can be seen in the chart above where there is no bump near the 573 degree mark. This may be the result of a washing operation to remove it or it just may happen to have ideal qualities for making Silica-shock resistant stove components because a significant cause of fracturing has been entirely suppressed.

The Baldosa α value of $5.3\text{x}10^{-6}$ is high, but can be reduced by the addition of fluxes. This is a very good raw material to start with.

Figure 7 XRF Analysis of the Baldosa Tile

Firing Temperature Affects the Coefficient of Thermal Expansion

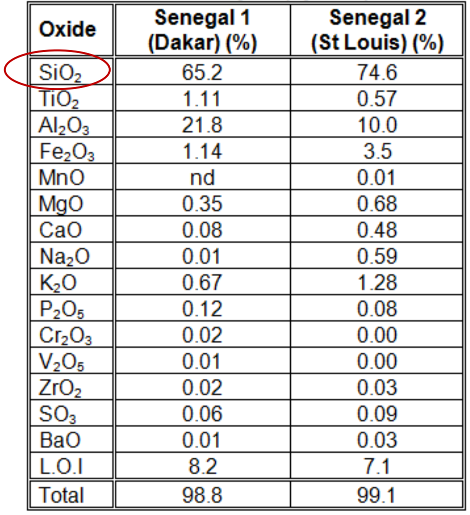


This series of plots shows the effect of the firing temperature. Note that there is a 'sweet spot' at 1100 degrees with this particular blend when the thermal expansion coefficient is lowest. This is because the ceramic chemistry has the highest percentage of low expansion products in it. When fired above 1100 C the mixture changes to a higher expansion set of crystallisations. To the naked eye it may or may not appear 'over-fired'. Only testing can tell. Also note that the slope of the 'Quartz kick' at 573° (circled) is not much affected by the reduction in α.

Figure 8 PKN2 fired at different temperatures

Analysis of the contents of two clay sources from Senegal

Table 1: Chemical analysis (by XRF)



Oxide	Senegal 1 (Dakar) (%)	Senegal 2 (St Louis) (%)
SiO_2	65.2	74.6
TiO_2	1.11	0.57
Al_2O_3	21.8	10.0
Fe_2O_3	1.14	3.5
MnO	nd	0.01
MgO	0.35	0.68
CaO	0.08	0.48
Na_2O	0.01	0.59
K_2O	0.67	1.28
P_2O_5	0.12	0.08
Cr_2O_3	0.02	0.00
V_2O_5	0.01	0.00
ZrO_2	0.02	0.03
SO_3	0.06	0.09
BaO	0.01	0.03
L.O.I	8.2	7.1
Total	98.8	99.1

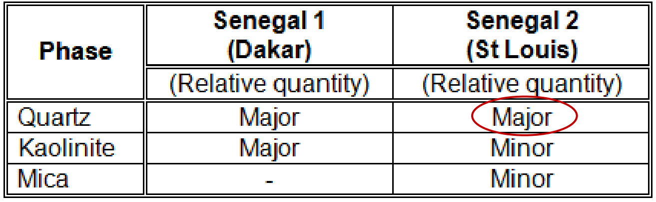
An example analysis of two clays is given in Table 1.

← The type of analysis is X-Ray Florescence. Notice that the first line is Silicon Dioxide. The analysis of Senegal 2 shows that it contains a total of 74.6% Silica.

Whatever portion of Silica is in the form of Quartz will be the cause of expansion problems at 573°.

In the lab report you may see the Mineralogical analysis by X-Ray Diffraction. The Quartz is listed as a 'Major' component of the clay. This is not surprising considering that Silica is ¾ of the sample but is not a yet guarantee. Quartz is Silica but Silica is not necessarily Quartz.

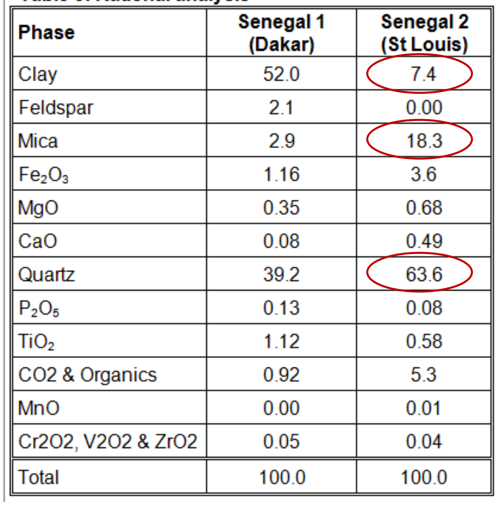
Table 2: Mineralogical analysis (by XRD)



Phase	Senegal 1 (Dakar)	Senegal 2 (St Louis)
	(Relative quantity)	(Relative quantity)
Quartz	Major	Major
Kaolinite	Major	Minor
Mica	-	Minor

In the rational analysis presented in Table 3 the danger of using this clay for a stove becomes apparent.

Table 3: Rational analysis



Phase	Senegal 1 (Dakar)	Senegal 2 (St Louis)
Clay	52.0	7.4
Feldspar	2.1	0.00
Mica	2.9	18.3
Fe_2O_3	1.16	3.6
MgO	0.35	0.68
CaO	0.08	0.49
Quartz	39.2	63.6
P_2O_5	0.13	0.08
TiO_2	1.12	0.58
CO2 & Organics	0.92	5.3
MnO	0.00	0.01
Cr2O2, V2O2 & ZrO2	0.05	0.04
Total	100.0	100.0

In the Rational Analysis the mineral composition of two proposed raw materials calculated.
← There is very little actual clay in Senegal 2.

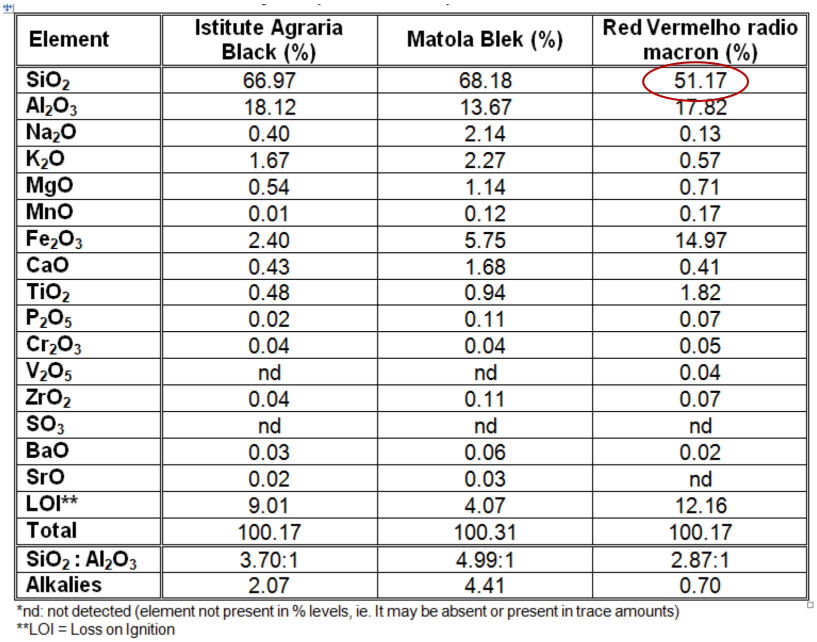
← Mica can work as a clay substitute and the mix can be fired to make pottery. This why people think this material is 'clay'.

← There is a huge amount of Quartz in Senegal 2, nearly all the Silica is 'free'. This is a very bad sign and a large volume change can be expected at 573°, cracking any stove body made from it even if the expansion is, by various additions, reduce to a lower level.

It is not worth testing it further.

Comparing Clays from Several Sites

This example of XRF analysis shows that Vermelho Radio Marconi (the misspelled site name) has the lowest SiO_2 content and is likely to have less Quartz than the other two.



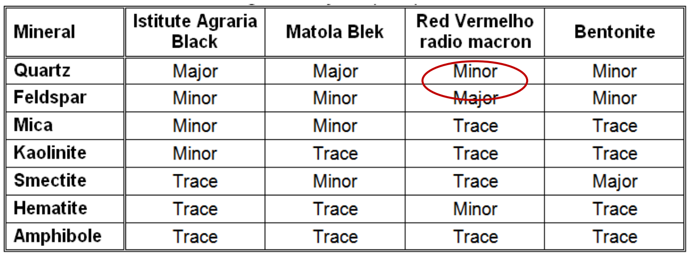
Element	Istitute Agraria Black (%)	Matola Blek (%)	Red Vermelho radio macron (%)
SiO_2	66.97	68.18	51.17
Al_2O_3	18.12	13.67	17.82
Na_2O	0.40	2.14	0.13
K_2O	1.67	2.27	0.57
MgO	0.54	1.14	0.71
MnO	0.01	0.12	0.17
Fe_2O_3	2.40	5.75	14.97
CaO	0.43	1.68	0.41
TiO_2	0.48	0.94	1.82
P_2O_5	0.02	0.11	0.07
Cr_2O_3	0.04	0.04	0.05
V_2O_5	nd	nd	0.04
ZrO_2	0.04	0.11	0.07
SO_3	nd	nd	nd
BaO	0.03	0.06	0.02
SrO	0.02	0.03	nd
LOI**	9.01	4.07	12.16
Total	100.17	100.31	100.17
$SiO_2 : Al_2O_3$	3.70:1	4.99:1	2.87:1
Alkalies	2.07	4.41	0.70

*nd: not detected (element not present in % levels, ie. It may be absent or present in trace amounts)
**LOI = Loss on Ignition

← Lower Silicon Dioxide content

Table 4 Comparative analysis of 3 Maputo area clays

Next, the XRD shows the relative quantities of the major components. The Radio Marconi site looks very attractive now.

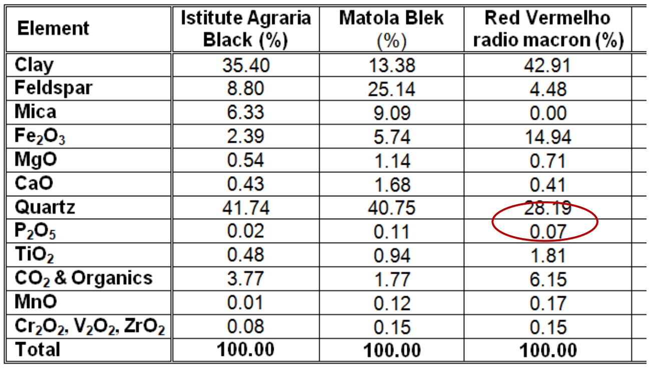


Mineral	Istitute Agraria Black	Matola Blek	Red Vermelho radio macron	Bentonite
Quartz	Major	Major	Minor	Minor
Feldspar	Minor	Minor	Major	Minor
Mica	Minor	Minor	Trace	Trace
Kaolinite	Minor	Trace	Trace	Trace
Smectite	Trace	Minor	Trace	Major
Hematite	Trace	Trace	Minor	Trace
Amphibole	Trace	Trace	Trace	Trace

← XRD for four clay sources. Bentonite will be added in small quantities to increase workability and green strength.

Table 5 XRD for 4 Maputo area clays

Here is the Rational Analysis showing that indeed the lowest Quartz level is from the Radio Marconi site.



Element	Istitute Agraria Black (%)	Matola Blek (%)	Red Vermelho radio macron (%)
Clay	35.40	13.38	42.91
Feldspar	8.80	25.14	4.48
Mica	6.33	9.09	0.00
Fe_2O_3	2.39	5.74	14.94
MgO	0.54	1.14	0.71
CaO	0.43	1.68	0.41
Quartz	41.74	40.75	28.19
P_2O_5	0.02	0.11	0.07
TiO_2	0.48	0.94	1.81
CO_2 & Organics	3.77	1.77	6.15
MnO	0.01	0.12	0.17
Cr_2O_2, V_2O_2, ZrO_2	0.08	0.15	0.15
Total	**100.00**	**100.00**	**100.00**

Figure 9 Rational Analysis of 3 Clays

← The addition of fluxes to this clay can reduce the expansion, as can washing some of the Quartz out with standard clay treatment. The PKN5 is based on this clay.

During 2006 and 2007 the lab performance of PK11 was very impressive. Ceramic bars made from it could be heated to 1000 C and dropped into water without breaking. Production issues in Maputo were a problem but the mix itself looked good. It's green strength was surprisingly high, it was easy to work with and produced a reasonably smooth finish. Importantly, it sticks to itself very well so the grate rests are easy to add and are reliable in service.

It was discovered after some time during a customer survey that the stoves were being slightly over-fired resulting in excessive fracturing. Reducing the firing temperature from 1150 to 1100 reduced the number fractures. This is explained by the fact that the production of the lowest expansion crystal/mineral mix occurred at 1100 and above that they started to deteriorate into other formations.

	PK11	PKN5
	%	%
Potassium Feldspar	5.0%	5.4%
Petalite	45.0%	48.9%
Istitute Agraria Black	33.4%	
Bentonite	3.8%	4.1%
Matola Black	2.8%	
Vermehlo Radio Marconi		39.3%
Charcoal	10.0%	
Paper Fibre		2.2%
TOTAL	100%	100%

Table 6 Contents of PK11 and PKN5

In light of the discovery that lowering the free Silica could offer even better performance at high temperatures, another set of tests was conducted producing a new mix based on the low Quartz red clay from Radio Marconi. This resulted in a new formulation called PKN5 emerged. A comparison of the formulations of PK11 and PKN5 is shown in Figure 8. The newly selected clay from Radio Marconi dominates PKN5. There are only 5 ingredients in the new mix. The substitution of paper fibre for pounded and sifted charcoal saves money, time and increases green strength. Both the charcoal and paper burn away leaving pores.

Comparing the α value of PK11 and PKN5

The use of the lowest Quartz local clay reduced the expansion coefficient and the overall effect of Quartz, but not the slope of the line during the Silica phase change.

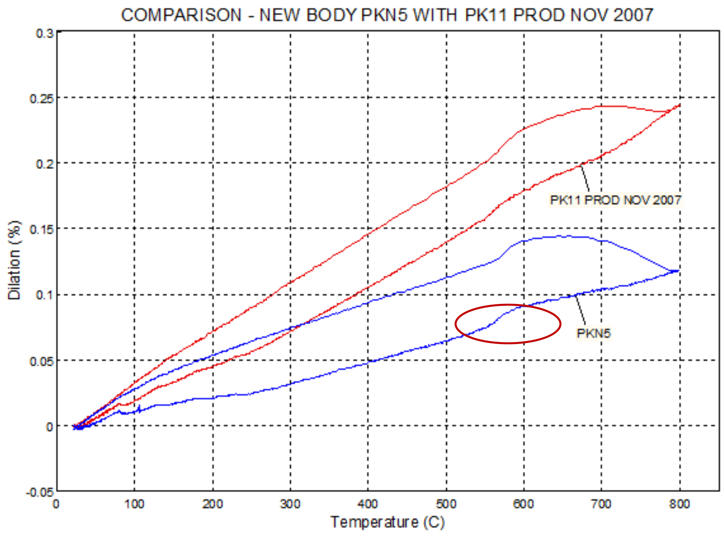


Figure 16: Comparison PKN5 with PK11 from Production

The Cermalab report reads:

"Figure 16 [of their report] shows a comparison 800°C thermal expansion plot of 1100°C Fired PKN5 with the Production PK11 sample of November 2007. The PKN5 body has thermal expansion coefficients 25°C to 500°C of 1.38 x10^{-6} and 25°C to 700°C of 1.56 x10^{-6}, while the PK11 Production body has coefficients in the same temperature ranges of 2.95 x10^{-6} and 3.05 x10^{-6}."

A bump at 573 degrees is evident (circled). It appears however that the slope of the line is not less steep than the PK11 and the overall expansion is about half so this is a significant improvement but the threat remains from Quartz. If it is used in a part of the stove that does not exceed 550°, no problem. Bars of

PKN5 heated to 1000 degrees and dropped into water did not shatter. The reason seems to be that the PNK5 is even stronger in tension than PK11, giving it more crack resistance. As charcoal has been replaced by hammer-milled paper fibre the number of pores increased, their size was reduced and the green strength – very important for de-moulding – was improved.

Figure 16 above with its highlighted change in the rate of thermal expansion at the silica transition point provides an insight into a different type of component failure.

If the thermal expansion of a material was pretty much a straight line, like the Baldosa tile in Figure 6, the stress on the component is only related to the difference between the temperature of the two sides, called Delta T (ΔT). This is the simplest understanding and applies to a situation when there is a constant and established heat flow.

When the heat is initially applied (which happens to a stove each time it is lit) a heat wave passes into the cold ceramic wall. The rate of temperature increase is determined by the particular mix used. The stress created by the hotter material trying to get bigger while the rest remains cool can be accommodated only up to a certain critical threshold after which it cracks.

In pottery kiln walls which are heated slowly, the rate of temperature change is slow enough not to stress the material much and the number of cycles is comparatively smaller. In addition, the materials tend to be of high quality. Domestic stoves unfortunately are subject to additional stresses because the walls change temperature rapidly and frequently.

Next Page:

LEFT COLUMN: The rectangles with a break line on each end represent the top views of the wall of a stove with the heat applied at the bottom of the picture. In the first figure the fire is out and the temperature on both sides is the same. The vertical lines indicate that everything is without stress (no stretching or expansion).

The ΔT per millimetre within the material is not always the same as the ΔT from one side to the other because the temperature does not rise immediately in the whole thickness. Also there can be localized points of higher stress. As heat from a new fire is penetrating the cold material, and if the fire is intense, most of the thickness of the material is at ambient temperature while a wave of heat is affecting the hot face alone. The ΔT of the first 2 millimetres may well be higher at that moment than will be the case 20 minutes later for the entire thickness. The stress generated by the inside of the stove being heated to, say, 275 degrees while the centre of a 10 mm stove wall is still 25 degrees is related to the ΔT of 250 degrees over 5 mm or 50 C/mm. If the level of thermal expansion of the material cannot be contained by its strength and 'sponginess', the hotter portion will try to stretch the colder portion, which will crack. As the heat wave passes through the material, it will push the crack ahead of it until it reaches the opposite surface.

RIGHT COLUMN: A schematic illustration of the effect of a heat wave rapidly entering the material. The material cracks immediately. The crack is then chased through the wall by the heat wave. When the material has a high rate of thermal expansion, the rate that heat enters the material has to be low enough to avoid cracking, even in the temperature range from ambient to the Silica transition point. For each material composition, there is a maximum rate that heat can be allowed to penetrate it.

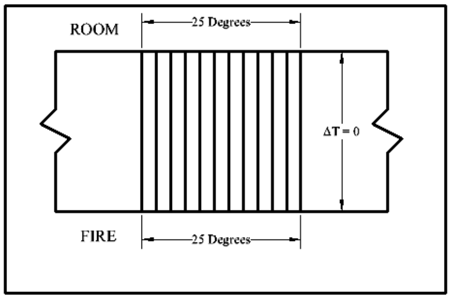


Fig 17 Room temperature, no stress.

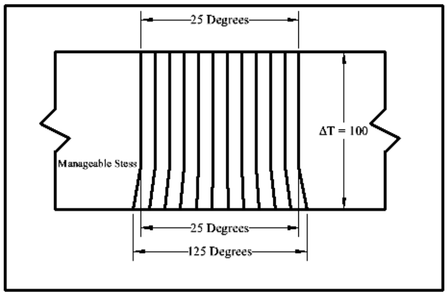


Fig 18 Heat is applied to one face. It is heating slowly enough for thermal expansion to be accomodated by the material.

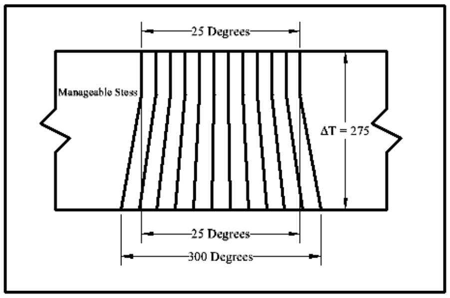


Fig 19 Heat penetrates the material Everything expands.

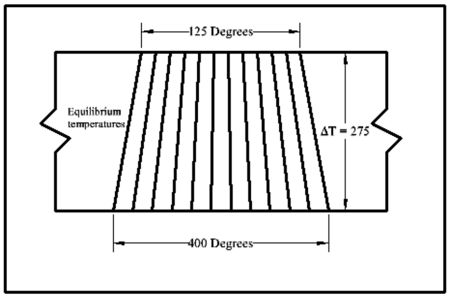


Fig 20 Equilibrium is eventually attained with a ΔT of 275° C. The stress is manageable.

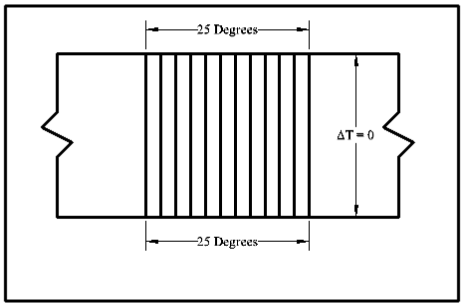


Fig 21 The same starting conditions.

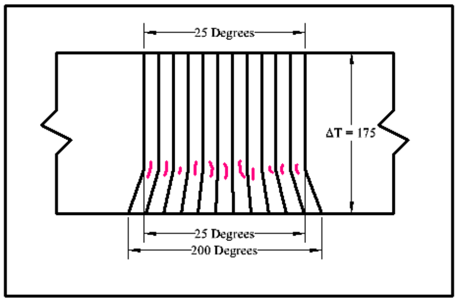


Fig 22 Initial rapid heating immediately produces cracks in the material.

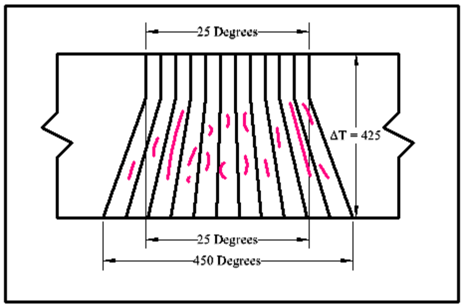


Fig 23 The heat wave passes through the material cracking it as the ‘front’ passes.

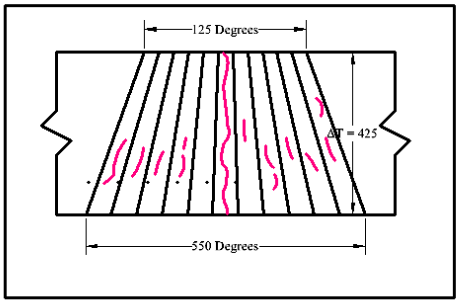


Fig 24 The result is a crack from one side to the other.

A ceramic material may perform very well in all respects up to the Silica transition point, then the A-B phase problem arises: the rate of thermal expansion suddenly changes. Even if the rate of temperature increase in the material remains the same, there is a change in the mechanical stress generated because the material is not reacting in the same manner. The stress can be thought of as being first derivative of the slope of the line. For any given rate of change in temperature, a change in slope on the expansion plot indicates a change in stress if some part of the component is at that temperature.

It appears that the slope of the thermal expansion at 573 degrees in Figure 16 is not affected much by the change in the thermal expansion rate. This means that even if you have a material with a α of 1.0 x 10^-6 and it has a high Quartz level, the material will perform well up to 500 but still change size rapidly around the 573 degree mark. It is not instantaneous as it is moderated by the strength of the non-silica materials around it, but there is a characteristic 'S' shape which reveals the presence of the Quartz. It is this change, indicated by the change in the slope of the line, which in addition to the thermal expansion factor described above, determines whether or not the material will still crack. Just as a wave of heat flows through the wall, there is a wave of 'suddenly bigger' as well. This creates micro-cracks ahead of the wave. This 'Quartz phase transition wave' will chase the crack through to material to the other edge.

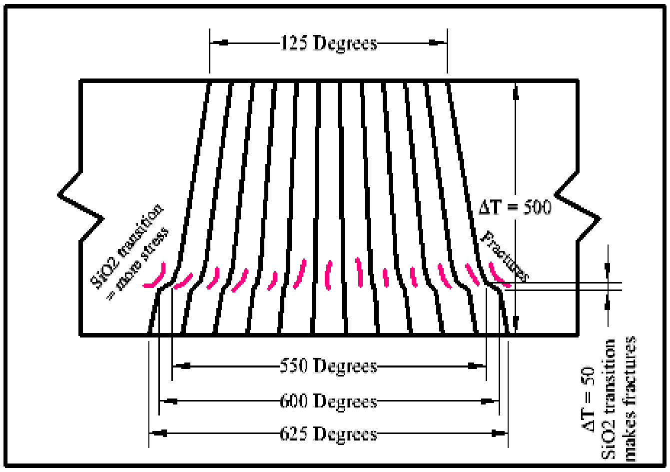


Figure 25 Quartz transition wave mimics thermal expansion damage

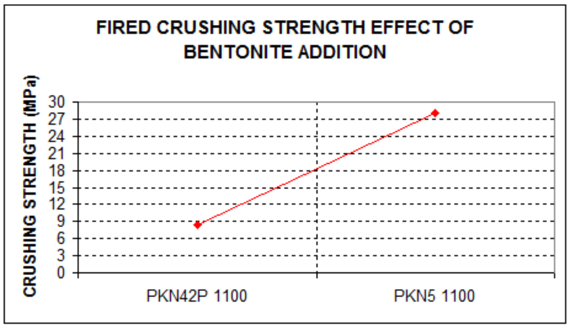
In Figure 25 a stove component that is already hot, is being slowly increased in temperature past the Silica transition point. The sudden or 'faster' expansion due to the Silica change from Phase A to Phase B reproduces the same sort of stresses in the material and the same cracks as a high rate of heating even though the ΔT is the same.

Thus seeking to reduce the α value alone does not necessarily eliminate cracking. It is also necessary to limit or remove the Quartz threat so that any ΔT that cannot crack the stove at low temperatures and will not do so when some portion of material inside the component is at 573 degrees.

As the free Silica content is reduced, the 'S' in the expansion becomes stretched and flatter. The slope of the line changes less. The PKCN3 expansion line in Figure 6 clearly indicates some Quartz.

Stoves ceramics are a challenge because they are cycled rapidly through wide temperature ranges.
During these investigations certain relationships appeared to consistently influence the tendency to crack. They are given here only as a suggestion for the purpose of assisting others to further the development of suitable materials.

The effect of Bentonite on the crushing strength of PKN5



The strength of a clay stove before it is fired is important because it has to be handled several times. The addition of small amounts of Bentonite (3 to 5%) to the PKN5 mix increased the green and fired crushing strength by a factor of 3.3 fold.

Figure 26 Fired strength of Bentonite addition

Proposed Formula for Predicting the Tendency to Crack

Cracking Tendency, factors influencing the propensity to fracture.

The relative influence of these parameters is unknown at this time.

[1] $$Ct = \frac{(\alpha * C * Qz)}{(K * T * Po * El)}$$

Where:
Ct = Tendency to Crack
C = Compressive Strength
K = Coefficient of Heat Conduction
Po = Porosity including quasi-porosity
α = Coefficient of Thermal Expansion
Qz = Quartz (free Silica)
T = Tensile Strength
El = Elongation

Topics for Further Investigation
Determining the *E* of the materials by reverse engineering the deflection and compression data on multiple samples.
Make a sieving operation with a 75 µm screen a standard part of the clay test in order to know what the effect of removing the +75 µm particles will have on the free Silica level. This sieving the clays at 75 µm and separately analysing the fractions above and below that size fraction. From this one will be able to predict what will happen if the larger fraction is removed.

Additional Findings
The inclusion of bentonite in the mix increases the workability without increasing the moisture content, reducing the amount of drying needed and the shrinkage that results from it.
The use of charcoal powder as a substitute for spherical prills produces irregular pores with sharp edges and uneven size.
Milled paper is a better additive than pounded charcoal in that it is easier to produce and work with.
Paper fibre (0.4 or 0.5 mm) greatly increases the green strength and creates a fine porous structure. Clay bodies formed in a jigger-jolley de-mould better as a result.
Cracked green stove bodies can be successfully patched using the PKN5 mix, something quite difficult before.
The use of a jigger is very practical for intermediate production rates in a low-tech factory that operates above the artisanal level.
Electric firing is necessary to control the ultimate temperature reached. In most cases this is 1100 C and the mixes were designed to be fired at this temp.

RESULTS Chemical analyses results

Table 7: Chemical analyses (XRF method) 3 Clays

Element	Institute Agraria Black (%)	Matola Black (%)	Red Vermelho Radio Marconi (%)
SiO_2	66.97	68.18	51.17
Al_2O_3	18.12	13.67	17.82
Na_2O	0.40	2.14	0.13
K_2O	1.67	2.27	0.57
MgO	0.54	1.14	0.71
MnO	0.01	0.12	0.17
Fe_2O_3	2.40	5.75	14.97
CaO	0.43	1.68	0.41
TiO_2	0.48	0.94	1.82
P_2O_5	0.02	0.11	0.07
Cr_2O_3	0.04	0.04	0.05
V_2O_5	nd	nd	0.04
ZrO_2	0.04	0.11	0.07
SO_3	nd	nd	nd
BaO	0.03	0.06	0.02
SrO	0.02	0.03	nd
LOI**	9.01	4.07	12.16
Total	100.17	100.31	100.17
SiO_2 : Al_2O_3	3.70:1	4.99:1	2.87:1
Alkalies	2.07	4.41	0.70

*nd: not detected (element not present in % levels, ie. It may be absent or present in trace amounts)
**LOI = Loss on Ignition

Table 8: Chemical analysis (XRF method) 4 Clays

Element	Bentonite (%)	Feldspar (%)	Petalite (%)
SiO_2	73.37	65.34	77.69
Al_2O_3	12.07	18.46	16.72
Na_2O	1.62	3.06	0.54
K_2O	0.20	9.13	0.36
MgO	2.54	0.02	0.04
MnO	0.01	0.01	0.01
Fe_2O_3	2.85	nd	nd
CaO	0.83	0.13	0.09
TiO_2	0.20	nd	nd
P_2O_5	0.01	0.27	0.01
Cr_2O_3	0.01	0.01	0.01
V_2O_5	nd	nd	nd
ZrO_2	0.08	0.01	0.03
SO_3	nd	nd	nd
BaO	0.02	0.02	nd
SrO	0.02	nd	nd
LOI**	5.70	0.66	0.78
Li_2O	-	0.327	4.20
Total	99.54	97.45	100.48
$SiO_2 : Al_2O_3$	6.08:1	3.54:1	4.65:1
Alkalies	1.82	12.20	0.90

*nd: not detected (element not present in % levels, ie. It may be absent or present in trace amounts)
**LOI = Loss on Ignition

Mineralogical analyses (XRD) and chemical analyses (XRF)

Table 9: Qualitative mineralogical analyses (XRD)

Mineral	Institute Agraria Black	Matola Black	Red Vermelho Radio Marconi	Bentonite
Quartz	Major	Major	Minor	Minor
Feldspar				
Mica				
Kaolinite				
Smectite	Trace		Trace	Major
Hematite	Trace		Minor	Trace
Amphibole	Trace		Trace	Trace

Table 10: Rational analyses, 4 Clays

Element	Institute Agraria Black (%)	Matola Black (%)	Red Vermelho Radio Marconi (%)	Bentonite (%)
Clay	35.40	13.38	42.91	23.37
Feldspar	8.80	25.14	4.48	14.95
Mica	6.33	9.09	0.00	0.00
Fe_2O_3	2.39	5.74	14.94	2.87
MgO	0.54	1.14	0.71	2.55
CaO	0.43	1.68	0.41	0.84
Quartz	41.74	40.75	28.19	52.65
P_2O_5	0.02	0.11	0.07	0.01
TiO_2	0.48	0.94	1.81	0.20
CO_2 & Organics	3.77	1.77	6.15	2.47
MnO	0.01	0.12	0.17	0.01
Cr_2O_2, V_2O_2, ZrO_2	0.08	0.15	0.15	0.09
Total	**100.00**	**100.00**	**100.00**	**100.00**

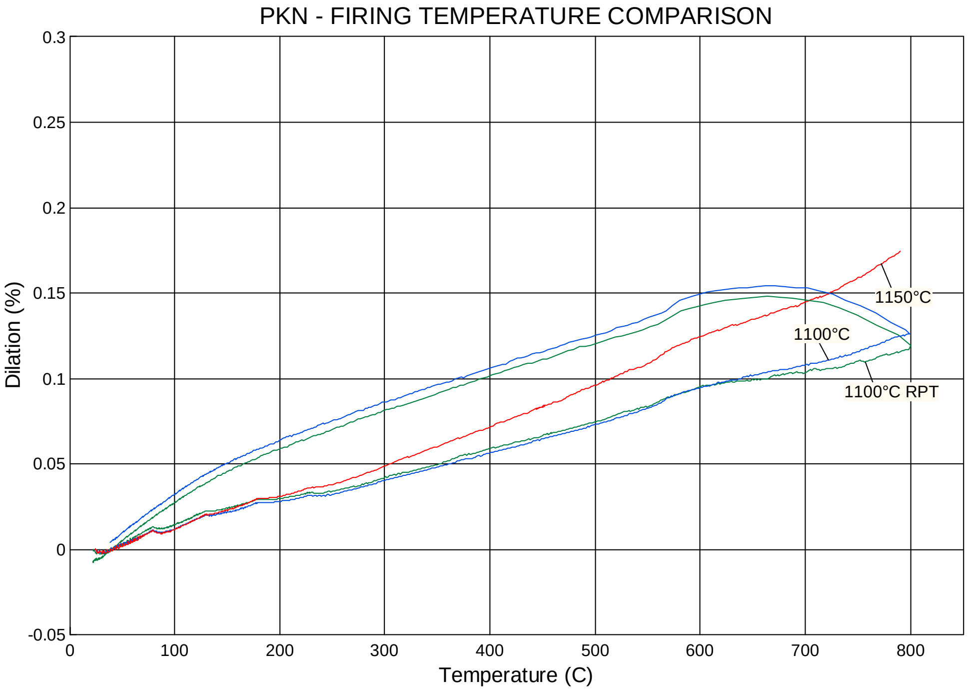


Figure 27: PKN after Firing at 1100°C and 1150°C

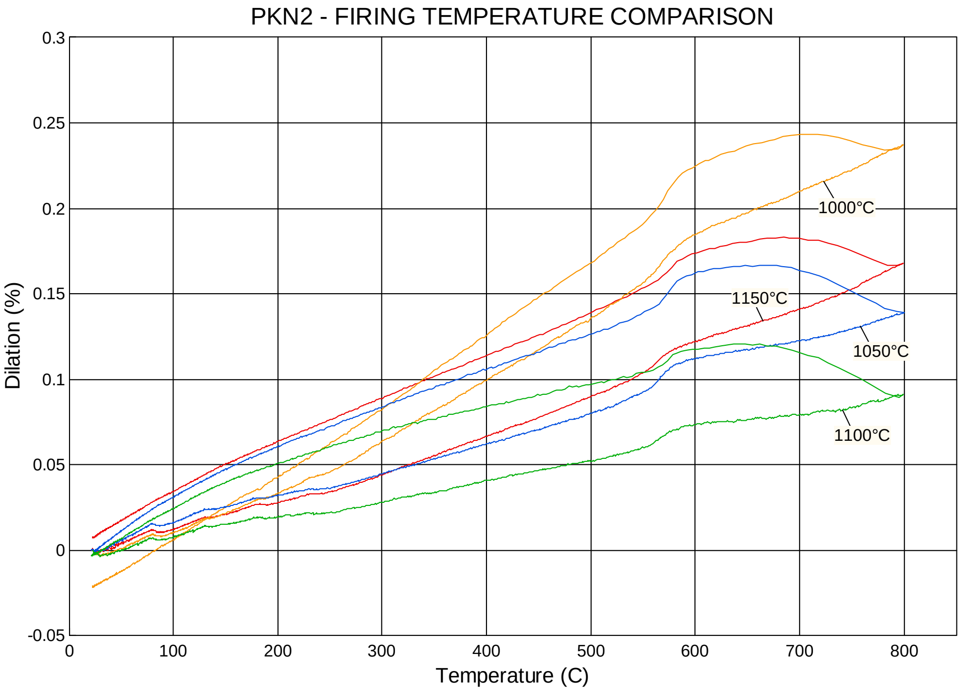


Figure 28: PKN2 after Firing at 1000°C, 1050°C, 1100°C and 1150°C

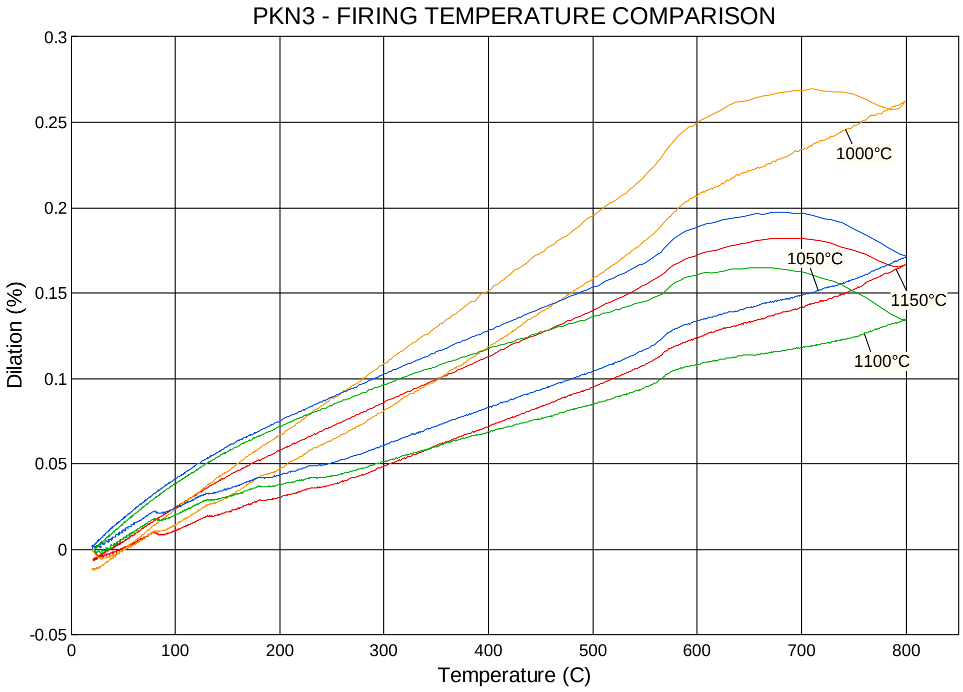


Figure 29: PKN3 after Firing at 1000°C, 1050°C, 1100°C and 1150°C

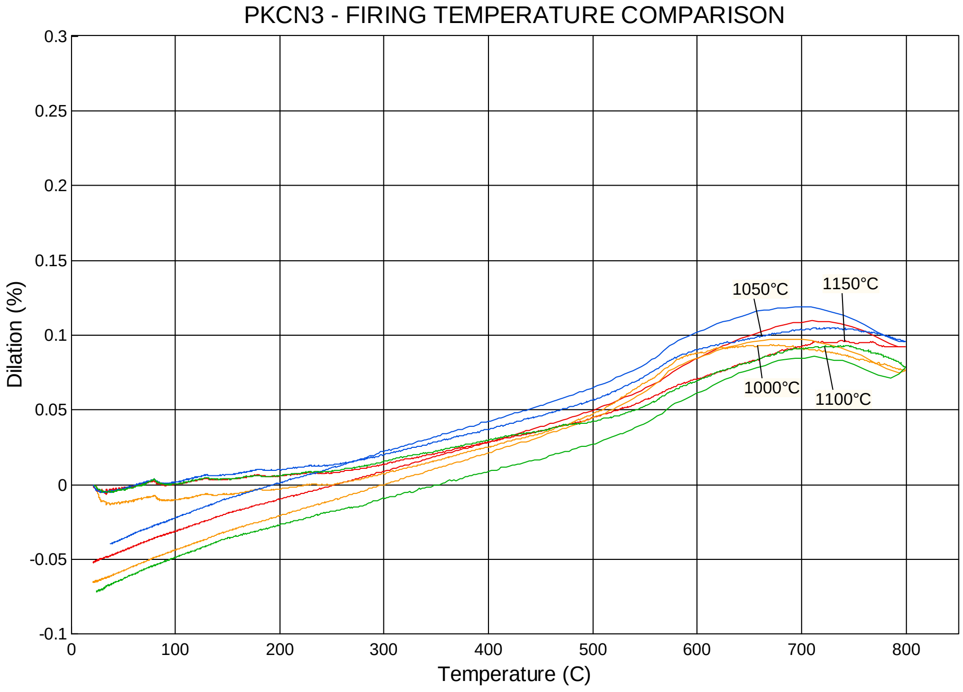


Figure 30: PKCN3 after Firing at 1000°C, 1050°C, 1100°C and 1150°C

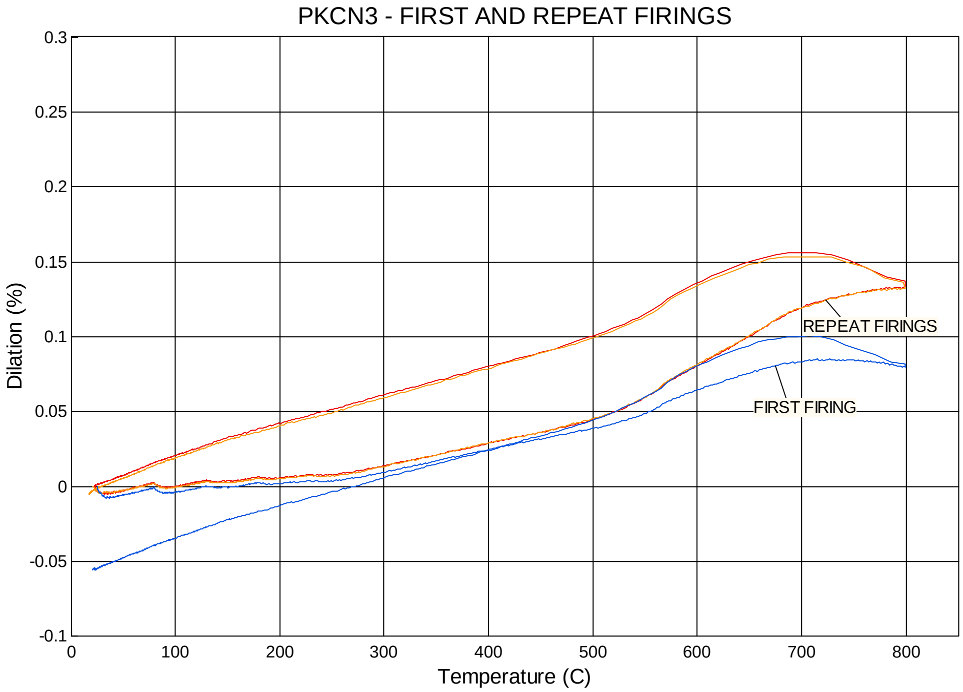


Figure 31: Three Runs of 1100°C Fired PKCN3

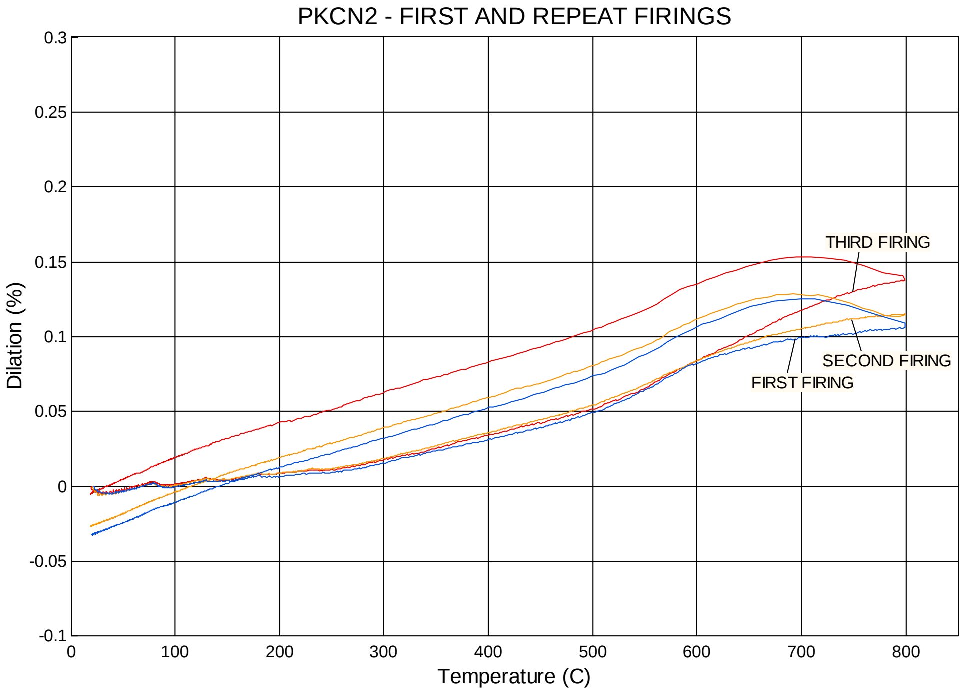


Figure 32: Three Runs of 1100°C Fired PKCN2

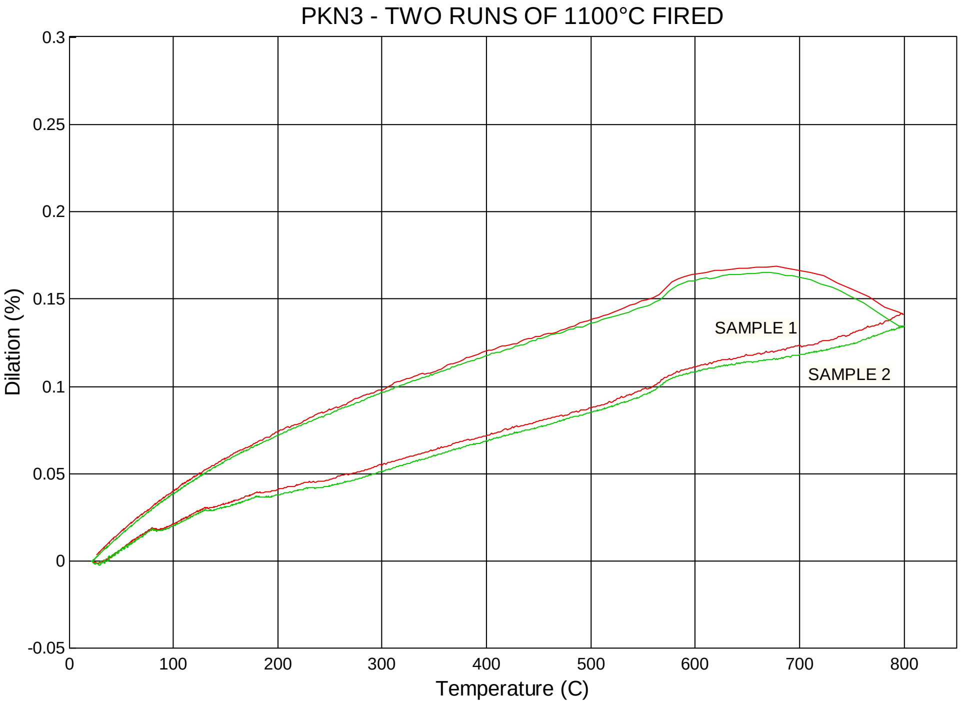


Figure 33: Two Samples 1100°C Fired PKN3

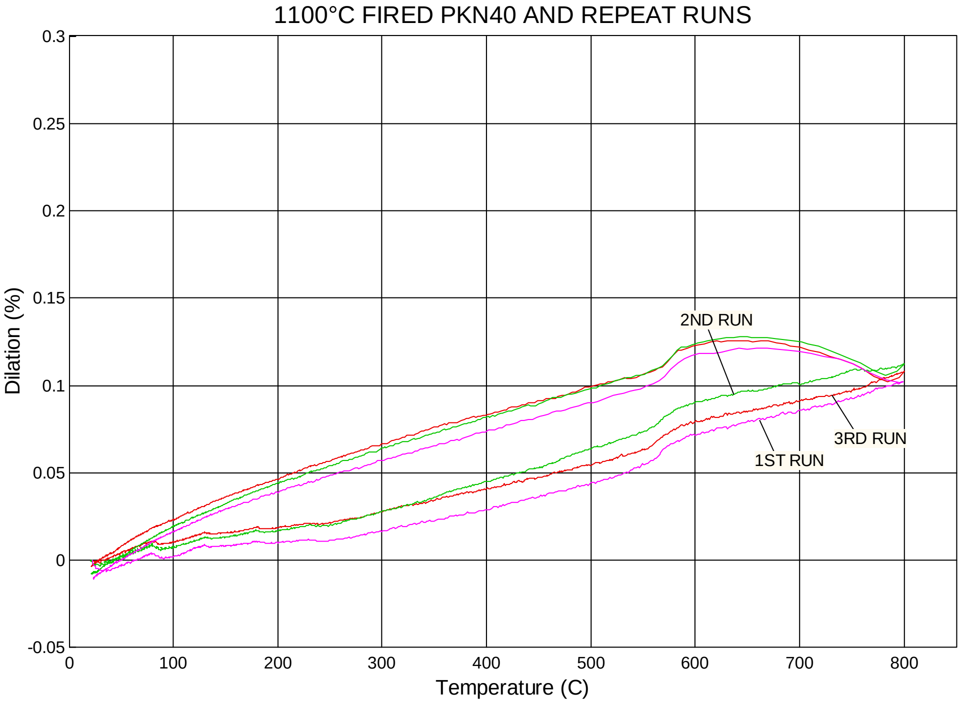


Figure 34: Three Runs of 1100°C Fired PKN40

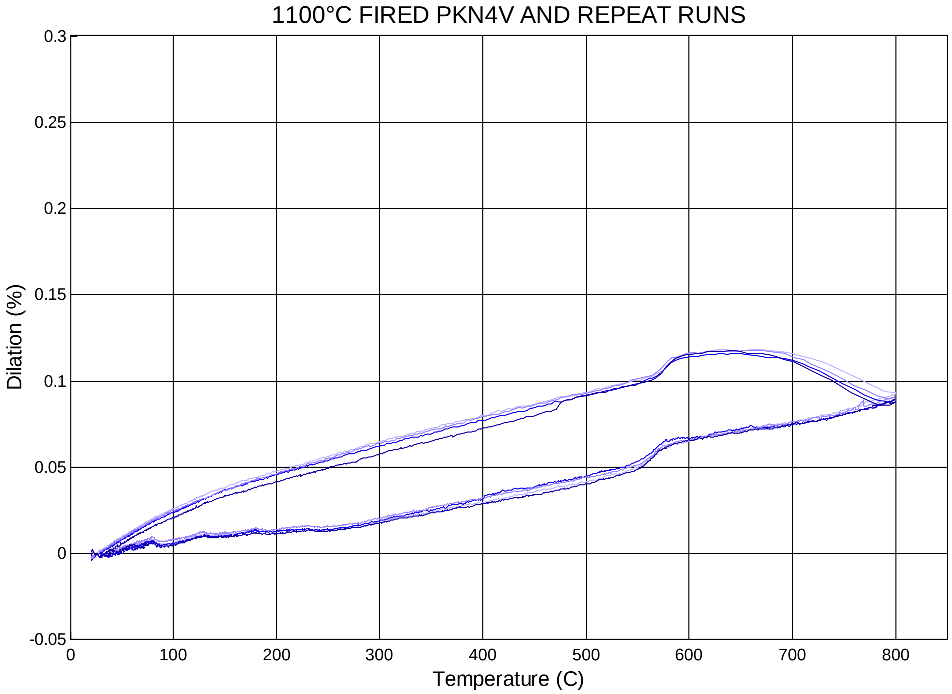


Figure 35: 1100°C Fired PKN4V and Repeats

Figure 36: Three Runs of 1100°C Fired PKN4X

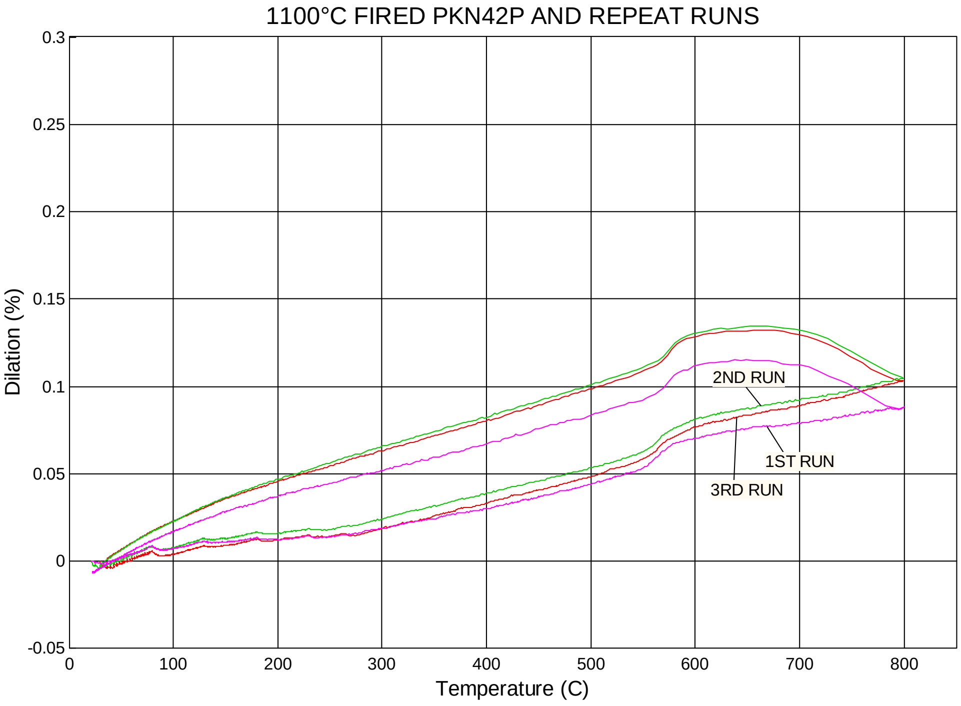


Figure 37: Three Runs of 1100°C Fired PKN42P

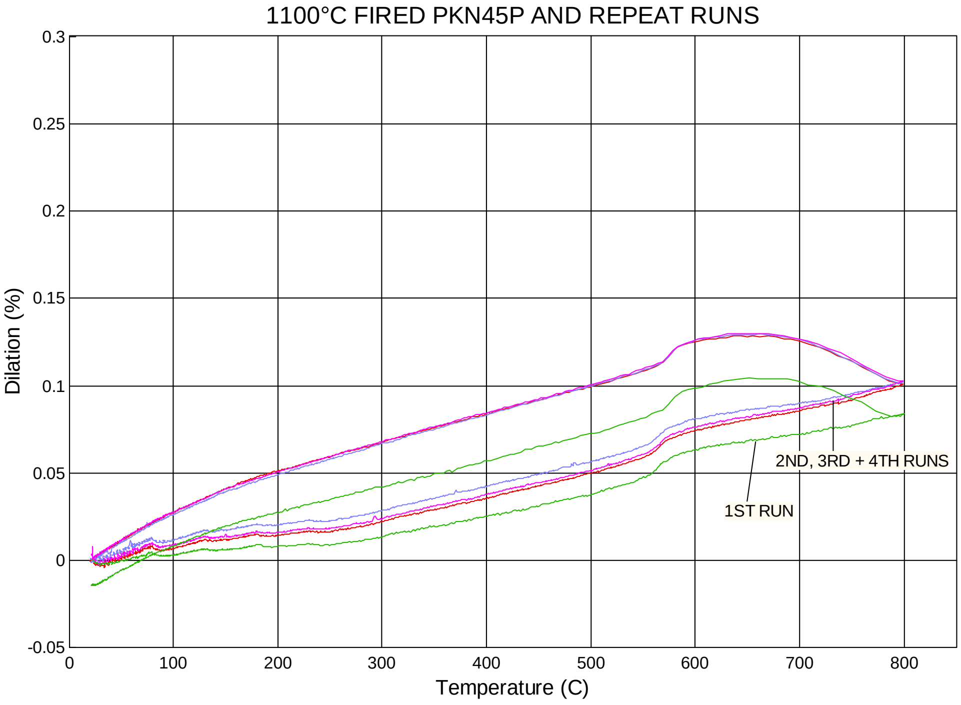


Figure 38: Four Runs of 1100°C Fired PKN45P

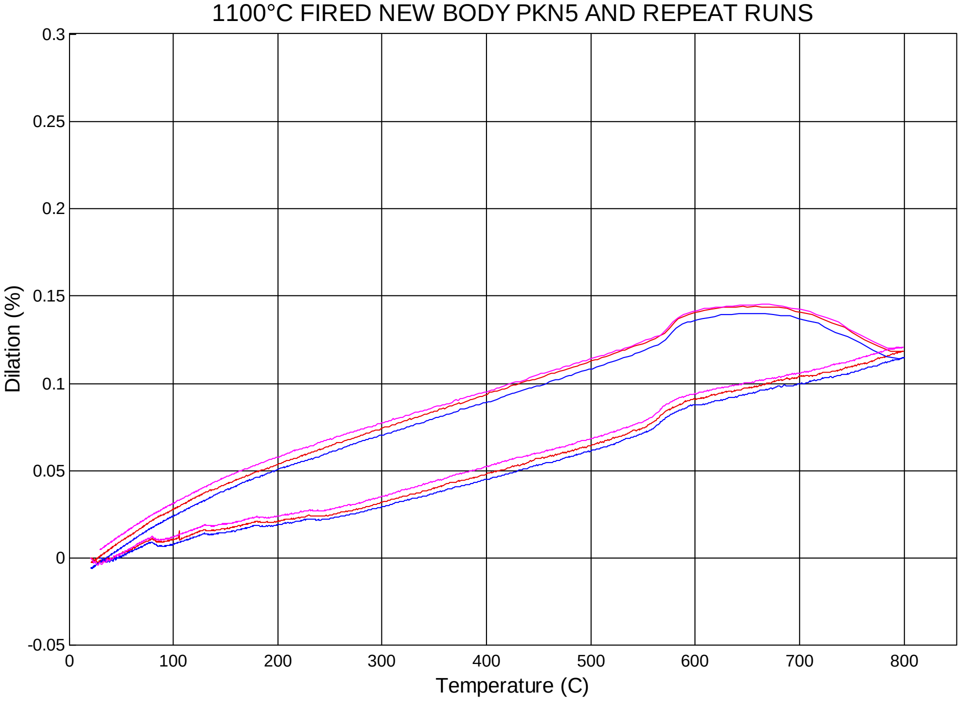


Figure 39: Three Runs of 1100°C Fired PKN5

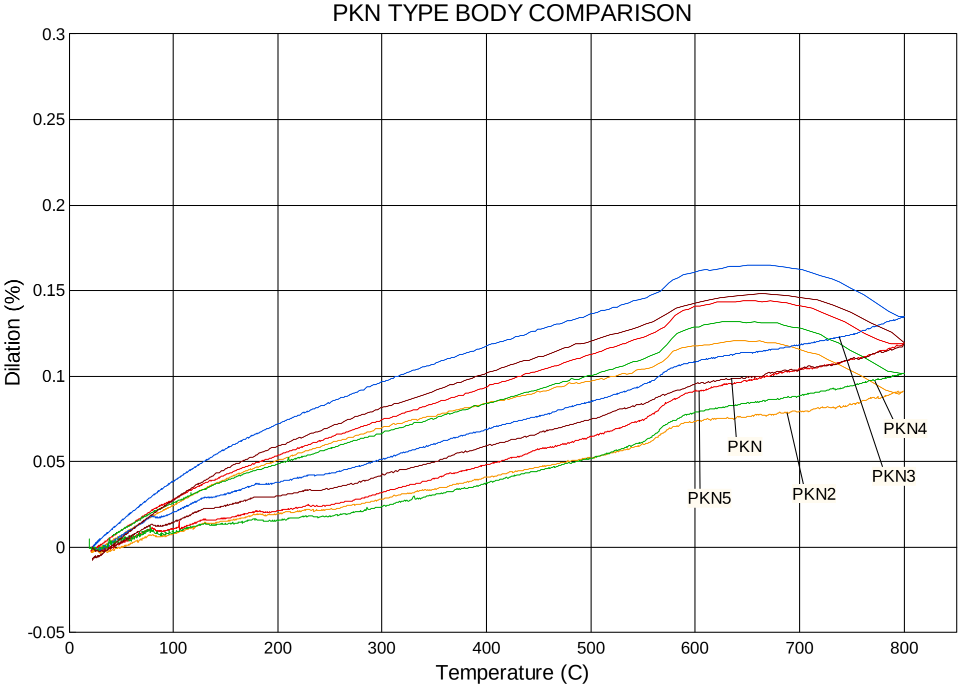


Figure 40: Comparison of all PKN-type bodies

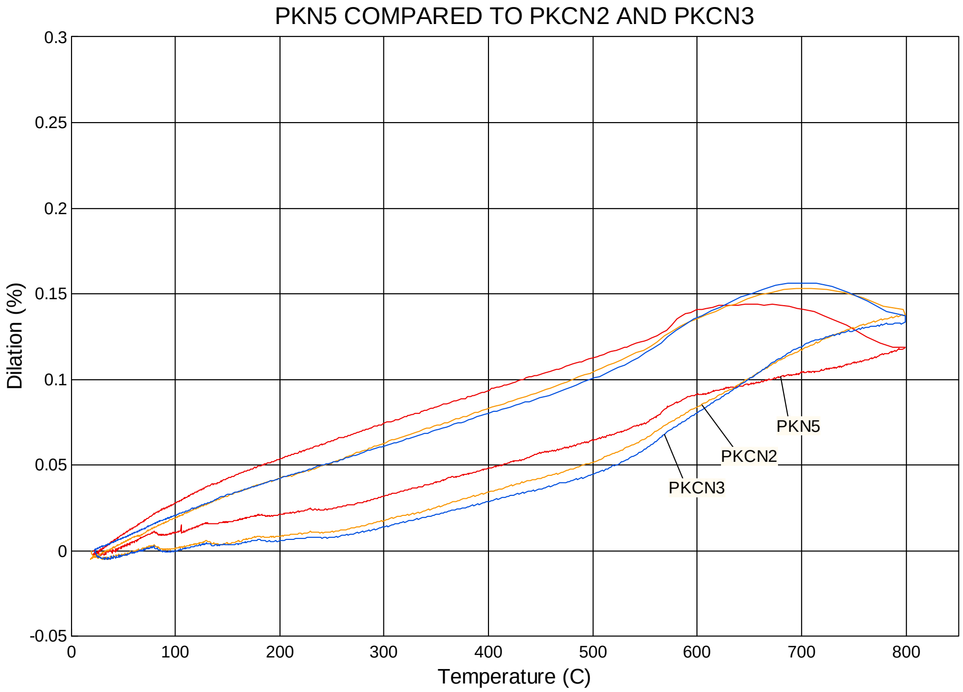


Figure 41: Comparison PKN5 with PKCN2 and PKCN3

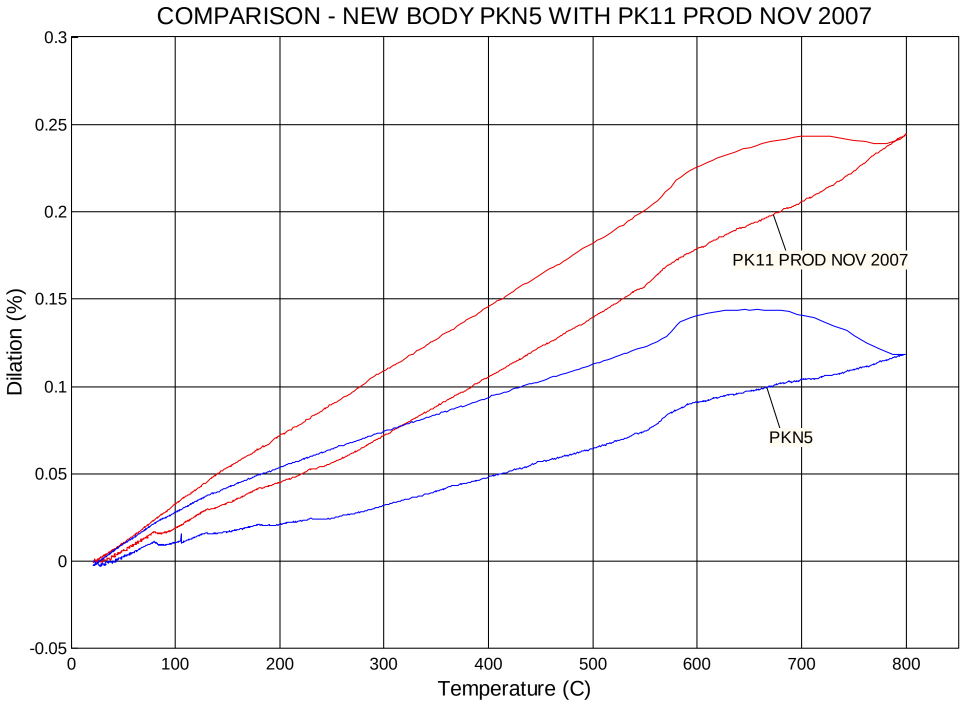


Figure 42: Comparison PKN5 with PK11 from Production

DISCUSSION OF THERMAL EXPANSION RESULTS[1]

- Figure [26] shows an 800°C thermal expansion comparison of 1100°C Fired PKN, of the same sample repeated, and of 1150 °C Fired PKN. The 1100°C Fired and repeat runs exhibit reversible thermal expansion behaviour because the top cooling curve returns to the starting (0% expansion) point, and also because the repeat curve is very close to that of the first run. The 1150°C Fired PKN has a higher thermal expansion coefficient (slope) than the 1100°C Fired PKN, as has been reported previously. The 1150°C Fired PKN plot here shows thermal expansion during heating only, but it is believed that this also exhibits reversible thermal expansion behaviour.

- Figure [27] shows an 800°C thermal expansion comparison between four PKN2 samples fired to temperatures 1000°C, 1050°C, 1100°C and 1150°C. The 1000°C Fired PKN2 shows shrinkage after cooling of ~0.02%, while the others show reversible thermal expansion behaviour. The 1100°C Fired PKN2 shows the lowest thermal expansion coefficient of the four firing temperatures.

- Figure [28] shows an 800°C thermal expansion comparison between four PKN3 samples fired to temperatures 1000°C, 1050°C, 1100°C and 1150°C. The 1000°C Fired PKN3 shows shrinkage after cooling of ~0.01%, while the others show reversible thermal expansion behaviour. The 1100°C Fired PKN3 shows the lowest thermal expansion coefficient of the four firing temperatures, but has a higher thermal expansion coefficient than both 1100°C Fired PKN and 1100°C Fired PKN2.

- Figure [29] shows an 800°C thermal expansion comparison between four PKCN3 (lithium carbonate containing PKN3) samples fired to temperatures 1000°C, 1050°C, 1100°C and 1150°C. These all show shrinkage after cooling of between 0.04% and 0.07%, which indicates that sintering is not complete with firing up to 1150°C and continues with reheating during thermal expansion runs to 800°C.

- Figure [30] shows an 800°C thermal expansion comparison between the first and two repeat runs of 1100°C Fired PKCN3. This shows shrinkage after cooling of ~0.06% for the first run, and higher reversible and virtually identical thermal expansion for the two repeat runs. The repeat thermal expansions track that of the first run up to ~600°C, and diverge above this temperature, which indicates that continued sintering of this lithium carbonate containing mix occurs above 600°C. Re-Firing to 800°C completes any residual sintering required of this body, and the resulting body has a higher thermal expansion coefficient than before.

- Figure [31] shows a similar 800°C thermal expansion comparison between the first and two repeat runs of 1100°C Fired PKCN2. This shows shrinkage after cooling for the first and second runs, and higher reversible thermal expansion for the third run. This shows the same behaviour as 1100°C Fired PKCN3, but requires two 800°C repeat firings to complete the residual sintering.

- Figure [32] shows an 800°C thermal expansion comparison between two samples of 1100°C Fired PKN3 from separate firings. This shows both reversible and consistent thermal expansion behaviour for this body.

- Figures [33, 34 and 35] show 800°C thermal expansion comparisons of first and repeat runs for 1100°C Fired PKN4 bodies with increasing charcoal content (0%, 5% and 10% respectively). The PKN4 body is as per the PKN3 body, but using red VRM clay instead of grey IAB clay. The lower thermal expansion of the second PKN40 run is not understood and will be investigated further,

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[1] The text is directly quoted from the Cermalab report. The figure numbers have been edited to reflect their place in this report.

but the thermal expansions of the others are all reversible and similar. These results show that charcoal content up to 10% does not affect thermal expansion coefficient of this body. These thermal expansions are lower than for 1100°C Fired PKN3 but are higher than for 1100°C Fired PKN2.

- Figures [36 and 37] show 800°C thermal expansion comparisons of first and repeat runs for 1100°C Fired PKN4 bodies without charcoal but with 2% and 5% paper fibre respectively. These show small sintering shrinkages for the first runs, but reversible thermal expansions for the repeat runs that are of similar coefficient to the charcoal containing types.

- Figure [38] shows 800°C thermal expansion comparisons of first and repeat runs for 1100°C Fired PKN5 body. The PKN5 body is as per the PKN4 body with 2% paper clay, but with bentonite added at the same level as before (to improve plasticity / workability and green strength). These thermal expansions are all reversible and similar, but are slightly higher than for the PKN4 series.

- Figure [39] shows a comparison 800°C thermal expansion plot of all 1100°C Fired PKN-type bodies using the last repeat run of each type. By comparing top temperature expansions, this shows that PKN5 with 0.12% is in the middle of the range (0.09% to 0.135%), and has repeatable thermal expansion very similar to the original PKN.

- Figure [40] shows a comparison 800°C thermal expansion plot of the last repeat runs of each of 1100°C Fired PKN5, PKCN2 and PKCN3. The PKCN-type bodies were originally considered to have much lower thermal expansion than the PKN-types, but this work shows that repeat runs increase this in the case of the former but not the latter. This comparison shows that PKN5 has lower 800°C expansion and higher 500°C expansion than the others, and indicates that PKN5 has less of a quartz transition effect than the PKCN-types (PKN5 has a thermal expansion difference between 500°C and 700°C of 0.039%, while PKCN2 has 0.065% and PKCN3 has 0.075%).

- Figure [41] shows a comparison 800°C thermal expansion plot of 1100°C Fired PKN5 with the Production PK11 sample of November 2007. The PKN5 body has thermal expansion coefficients 25°C to 500°C of 1.38 x10-6 and 25°C to 700°C of 1.56 x10-6, while the PK11 Production body has coefficients in the same temperature ranges of 2.95 x10-6 and 3.05 x10-6.

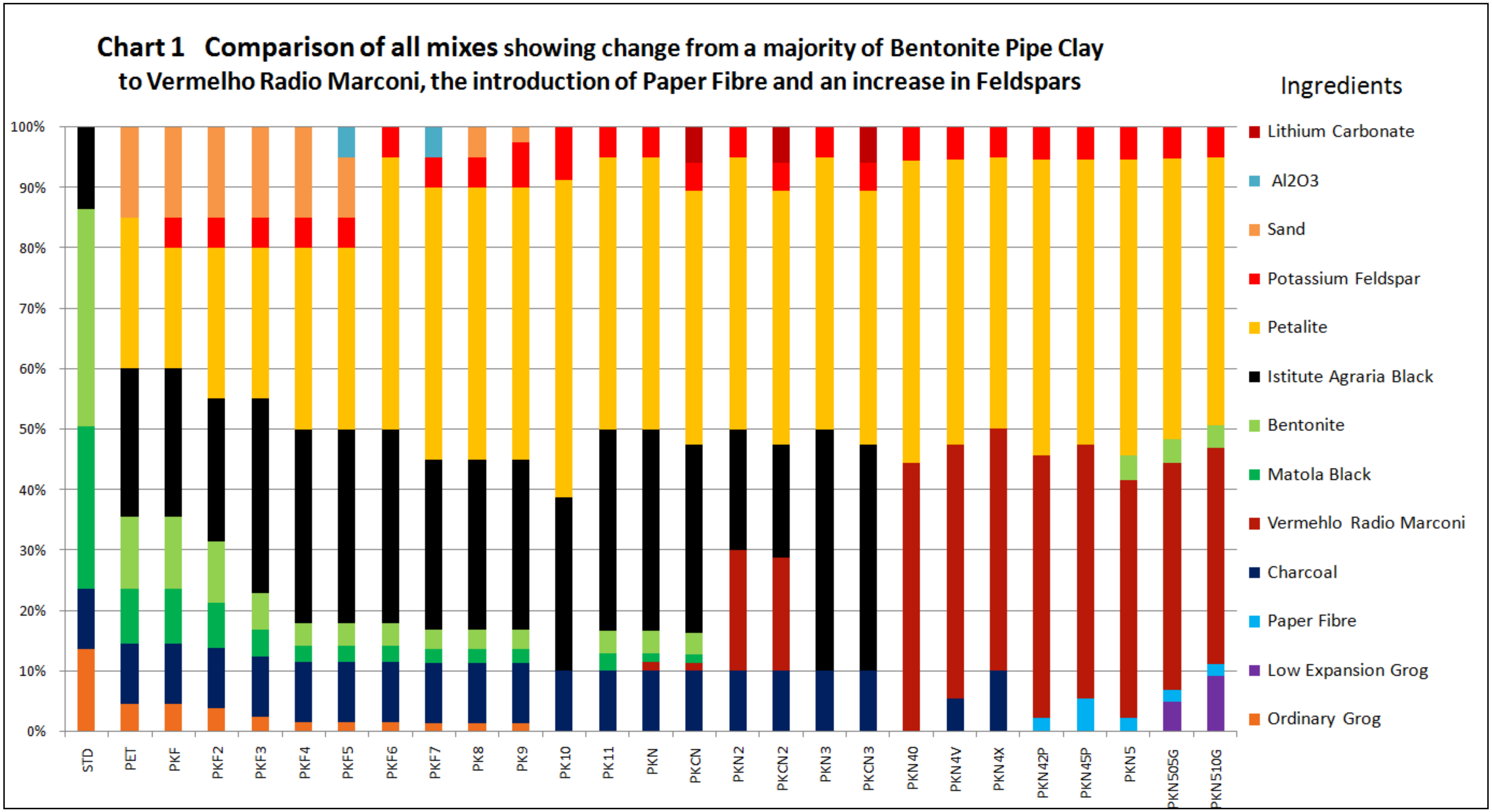

Chart 1 Comparison of all mixes showing change from a majority of Bentonite Pipe Clay to Vermelho Radio Marconi, the introduction of Paper Fibre and an increase in Feldspars

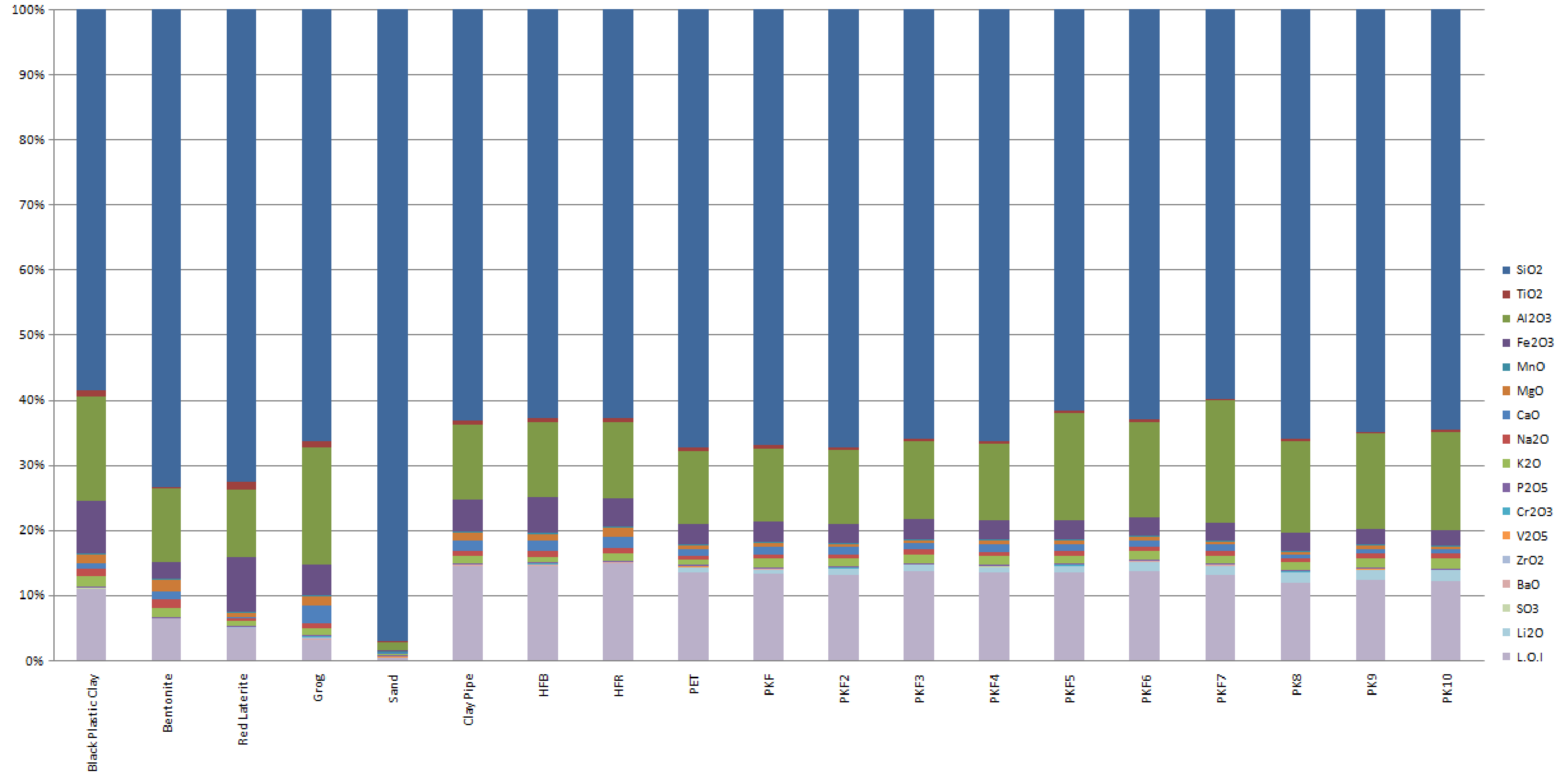

Chart 2 Comparison of all the oxides in various mixes

References

Documents prepared by Bruce Berger, CERMALAB et al, 2005-2008

C07-279 GTZ Baldosa Tile Rev1 180308
C07-286 GTZ XRD, XRF. TE
C08-016 GTZ Probec PKN5 Body Part 1 Thermal Expansions 020608
Fired Crushing Strength of Normal and Lithium Carbonate bodies
GTZ body development pkn5 with grog
GTZPKN4PKN5APBDS
MoRCCSGtz190508
PK11PK11MIXGRATECOMP
PKNPKCNBODYPLOTS
PKNSERIESRECIPES
Q8-009 GTZ further body development
REPcrispinplots1