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Ceramic Products from Waste

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1. Introduction

The industrial revolution changed the world; it generated the great humanity progress. But, the industrialization is accompanied by the generation of wastes, which could be negative to the natural environment. Unfortunately, environmental issues were not remembered, as should be.

One general conclusion from Gungor and Gupta (1999) in their literature review is: environmental issues are gaining justifiable popularity among society, governments and industry due to negative environmental developments.

The current state of manufacturing processes consume enormous tons of different forms of natural resources like raw materials, energy, water, etc.

The giant amount of waste generated is still far from being used in its totality as a product or by-product, making technological alternatives needed in order to reduce its possible environmental impact; where, the major potential impacts of its disposal on terrestrial ecosystems include: leaching of potentially toxic substances into soils and groundwater; reductions in plant establishment and growth due primarily to adverse chemical characteristics of the waste; changes in the elemental composition of vegetation growing on the waste; and increased mobility and accumulation of potentially toxic elements throughout the food chain.

There are many reasons to increase the amount of waste being utilized or re-utilized. Firstly, disposal costs are minimized; secondly, less area is reserved for disposal, thus enabling other uses of the land and decreasing disposal permitting requirements; thirdly, there may be financial returns from the sale of the by-product or at least an offset of the processing and disposal costs; and fourthly, the by-products can replace some scarce or expensive natural resources (Ahmaruzzaman, 2010).

Waste such ashes from: coal, municipal solid waste, wood, and so on, have good potential for use in ceramic products. Various ceramics systems have been shown to be suitable for producing products that are thermally and mechanically stable and exhibit good chemical durability. Palomo et al. (1999) activate fly ash for applications in building sites. The studies of Barbieri et al. (1999) and Leroy et al. (2001) are examples of the glass-ceramics obtained using fly ash. The results obtained by Zimmer & Bergmann (2007) indicate that fly ash, when mixed with traditional raw materials, has the necessary requirements to be used as a raw material for production of ceramic tiles.

Ceramic products have the largest range of functions of all known materials. Despite the already existing variety of compounds, the number of processing techniques, and the known diversity of properties and applications of the materials, ceramics are synthesized into glasses, polycrystals, and single crystals, and many forms dictated by their use, including fine powders, fibres, thin films, thick films, coatings, monoliths, and composites. Polycrystalline components are conventionally produced by powder synthesis and forming processes followed by sintering at high temperature compared to polymers processing temperature.

The main advantages of the ceramic processing route include the fact that ceramics can be processed at reasonably low temperatures; a large number of ceramics product is tolerant of variations in waste composition; ceramics exhibits reasonable chemical durability - ceramics are radiation resistant and can suffer changes occurring at different environments as humidity, temperature, sun, salt, wind, and so on.

However, the main concern in the use of a waste as secondary raw material in the formulation of a ceramic product is its immobilization inside the ceramic body after transformations occurred during the ceramic process, at the thermal treatment; which, depending of the ceramic product could fuse, partially fuse or sinter the ceramic formulation.

Ceramics product could be considered interesting in the immobilization of hazardous wastes, because they are able to retain heavy metals in their structure with a significant reduction of volume.

The positive aspects of waste inertization technology in ceramic products are process flexibility since various types of wastes such as sediment and ashes can sometimes be used without preliminary preparation.

There are several ways to start a formulation of one ceramic product, which the easiest form is evaluate the effects of waste additions in a ceramic formulation.

The properties of ceramic products depend of its composition. Calculating oxide composition of an intended formulation containing waste is a profit compared with simple waste additions. However, relative calculations of compositions are not the only think that influences the manufacture of a ceramic product, it is important too: loss of ignition (outlet material), particle friction (influences the particle mobility), particle size (thinner are more reactive), etc.

There are a number of measurements to determine the nature of the waste besides its compositions. A good characterization is primordial to starts a formulation of a ceramic product using waste. Chemical composition, mineralogical composition, granulometric size distribution and morphologic aspect are important things to be analyzed. But, a good waste characterization is accompanied of thermo-gravimetric analysis (TGA), differential thermal analysis (DTA), and refractoriness and so on to understand the properties that each waste could give to a specifically ceramic product.

The aim of this chapter was to study the use of waste in ceramic formulations with or without traditional raw materials that would result in ceramic products with satisfactory technological properties, allowing its utilization.

It will be discussed the requisites that one waste must have to be added in a ceramic formulation and when ceramics products not support waste.

2. Overview of Researches in Ceramic Waste

The ceramic heat treatment process has been demonstrated as one valid technologies for the inertization and volume reduction of different categories of wastes. The produced ceramic product can in fact subsequently be disposed in landfill sites reducing environmental hazard.

As an example of application with the worst waste (radioactive waste) in its reducing environmental hazard was related by Donald et al. (1997) work, where one solution could be the waste form, in other words, the rationale behind the immobilization of radioactive waste materials in glass or ceramic hosts is to provide a solid, stable and durable material that can be more easily stored or disposed of than the current liquid wastes. Immobilization may be accomplished either by dissolution of the waste elements on an atomic scale within the host lattice, or by encapsulation of the waste within an inert matrix. Wasteforms can be temporarily stored at the solidification processing plant (during which time the heat generated by the decay of the fission products decreases), but the longer term strategy is to dispose of them permanently in an underground repository as part of a multibarrier approach. The immobilized waste would therefore form only one part of an engineered system designed to prevent contamination of the biosphere with radioactive elements.

There are many wastes and kind of wastes disposed in landfills that could be used as a ceramic raw material. There are many kinds of ceramic products, it is thus necessary, for the utilization of civil or industrial wastes, to look for ceramic technologies in order to generate components in cementitious, glass or traditional ceramics.

Incineration is a commonly accepted solution throughout the world for managing the increasing production of Municipal Solid Waste (MSW). In the Ferreira et al. (2003) work, three main factors were considered relevant to evaluate fly ash suitability for each application: suitability for processing, technical performance and environmental impact:

- the first factor, suitability for processing, depends on physical-chemical characteristics of the fly ash, such as particle size and chemical properties, that may constitute a limitation for a specific process (although in some cases these characteristics can be adjusted so as to comply to processing requirements);
- technical performance is the second factor considered. Even if fly ash can be easily processed, the final product cannot be used unless it presents good technical properties;
- finally, the third factor considered is environmental impact. Toxicity does not necessarily disappear with fly ash valorisation. The risks imposed on the environment by each possible application must be carefully weighed against creating new pollution sources elsewhere.

Colombo et. al (2003) reviewed waste vitrification technologies and related that analysis of different methods of vitrification, according to physical state and composition of the waste, can offer a guideline for process selection. The vitrification process, initially proposed for high level radioactive waste management, has been demonstrated as one of the most valid technologies for the inertization and volume reduction of different categories of wastes, as testified by a large and growing scientific literature devoted to the topic. The produced glass can in fact subsequently be disposed in landfill sites without posing any environmental hazard.

According to Colombo et. al (2003), the main advantages of the vitrification process are:

- inorganic glasses can incorporate large amounts of heavy metal ions, chemically bonding them inside their inorganic amorphous network;

- the obtained glasses are inert towards most chemical or biological agents, so they can be disposed of in landfills without problems or used for roads, pavements, embankments, etc.;
- the vitrification process can accept wastes of different composition and form, such as liquids, muds, solids or their mixtures. Therefore, a well designed vitrification plant can be flexible enough to treat wastes of various type, without or with a minimal pre-treatment;
- vitrification is a mature technology, and glass-forming systems have been extensively investigated in the academia, so their properties are well known;
- vitrification results in a large reduction in volume of the waste.

In one method for the immobilization of high level radioactive waste (HLW) as reviewed by Donald et al. (1997) a suitable glass host is used to dissolve the HLW to form a glassy (vitreous) homogeneous product that can be cast into suitable forms, including large glass blocks. Under suitable conditions, it is possible to incorporate up to 25-30 wt% HLW into a glass. The choice of glass composition is a compromise between high HLW solubility, manageable glass formation temperature, and low leachability in repository environments. Various glass systems have been shown to be suitable for producing waste glass forms that are thermally and mechanically stable and exhibit good chemical durability. The main advantages of the vitrification route include the fact that glass is a good solvent for HLW; glass can be processed at reasonably low temperatures; glass is very tolerant of variations in waste composition; glass exhibits reasonable chemical durability; and glass is radiation resistant and can accommodate changes occurring during radioactive decay of HLW constituents (Donald et al., 1997).

3. Ceramic Processing

Usually, the ceramic products are manufactured from materials which are solid state, which most often is in powder form. The consolidation of a part can occur with or without fusion of the employed raw material. Even the ceramic products that are manufactured at room temperature or close to it, such as cement and gypsum, its raw materials have undergone a prior heat treatment at high temperatures – more than half melting temperature. During the heat treatment that the material has suffered, a thermal activated atomic diffusion leads to the formation of phases which act as a trapping against the leaching of these elements in their operating life.

However, mostly of time is cost impeditive the use of the class of ceramics called "advanced ceramics", these kind of products are distinguished by their high chemical purity, careful processing and high values of the useful properties.

Advanced ceramics are materials systems more refined, sometimes with special compounds and the processes were developed for high structural performance: biocompatibility, magnetic and electronic applications, among other special application – with specific property from high technological demand.

Ceramic processing is used to produce commercial products that are very diverse in size, shape, detail, complexity, and material composition, structure, and cost. Ceramics are typically produced by the application of heat upon processed natural raw materials (minerals) to form a rigid product.

Ceramic products that use naturally occurring minerals as a starting material most of time undergo special processing in order to control purity, particle size, particle size distribution, and heterogeneity. These attributes have an important character in the final properties of the

finished ceramic. Chemically prepared powders also are used as starting materials for some ceramic products. These synthetic materials can be controlled to produce powders with precise chemical compositions and particle size.

According to Reed (1995), ceramics processing commonly begins with one or more ceramic materials, one or more liquids, and one or more special additives called processing aids. The starting materials or the batched system may be beneficiated chemically and physically using operations such as crushing, milling, washing, chemical dissolving, settling, flotation, magnetic separation, dispersion, mixing, classification, de-airing, filtration, and spray-drying.

Before the development of scientific insights of ceramics processing, the properties of the product were often correlated with changes in a processing operation to identify the more important superficial variables. This empirical approach is still used. However, empirical correlations such as these do not provide a scientific understanding of the fundamental causes of behavior during processing and forming. The probability that adjustments based on empirical correlations alone will produce significant advances is small, because the potential number of unsuccessful combinations of variables is always relatively coarse. Also, empirical correlations may be of little heuristic value when the processing engineer is faced with a lack of reproducibility in manufacturing, an insufficient reliability in the performance of nominally identical products, or when developing new products (Reed, 1995).

Viewed as a science, ceramics processing is the sequence of operations that purposefully and systematically changes the chemical and physical aspects of structure, which we call the characteristics of the system (Reed, 1995).

The objectives of the science of ceramics processing are to identify the important characteristics of the system and understand the effects of processing variables on the evolution of these characteristics. The objectives in process engineering should be to change these characteristics purposefully to improve product quality. Because of the key dependence on controlling characteristics, an understanding of techniques for characterizing the starting materials and the process system at each stage is an integral part of any discussion of ceramics processing (Reed, 1995).

3.1. Characterization of Ceramic Raw Materials

As a starting point for the use of waste as ceramic raw material is the knowledge of the whole environment generator of this waste to be aware of the possible constituents of this waste, including small proportion. It is also necessary to assess whether the process can produce different wastes in different periods. One think should be careful if there is a possibility that the residue present or release corrosive gases when thermally processed (COS, H₂S, HCl, SO₂, NO_x etc.), which can cause problems in the equipment with which it will contact.

The next step is to characterize morphological and dimensional waste constituents with microscopy technique and could supplement with granulometry. In general, smaller dimensions of the components from residue, higher will be the reactivity and the lower will be the fluidity. Likewise, morphology with low aspect ratio is less favourable fluidity and also to its packaging.

The chemical analysis is essential, but it is not easy without knowing beforehand what they may contain the residue and the possible elements of which it consists.

From the knowledge of the chemical composition, it is promising to have an idea of what are the possible applications that a waste may have. Besides the chemical composition, identification and quantitative estimation of the proportions of the various mineral species in a system such as waste polycompost provide important information to get an idea of what the behavior of the residue of an application as ceramic product.

An important factor of mineralogical knowledge is its crystallinity, which could indicate the possible isomorphous replacements, which are more intense in materials of lower crystallinity in comparison to their relative high crystallinity.

However, before proceeding with a possible test of this residue is important to know their loss to fire (LOI), which is more appropriately accomplished by a thermogravimetric analysis (TGA).

Figure 1 shows a TGA analysis of a hypothetical waste, this mass loss is concentrated between 200 and 300 °C and corresponds to approximately 90% until a temperature of 1000 °C. If this residue were used, it will result in their almost total escape into the atmosphere.

The loss is linked to the output of volatiles during thermal processing and in some ways is a component that acts against the consolidation of the ceramic material, which can be bad for a dense ceramic or good for a refractory insulating material of low density. In the study of Bragança, Zimmer and Bergmann (2008), for example, is employed wood waste (sawdust) to form the porosity of a refractory insulator. The sawdust can generate output for its porosity and also contributes exothermically to the firing process due to its oxidation reaction - combustion.

It is noteworthy that the volume reduction due to material output is far superior to weight reduction, because the gases that go out have lower density compared with the remains, the latter is usually inorganic.

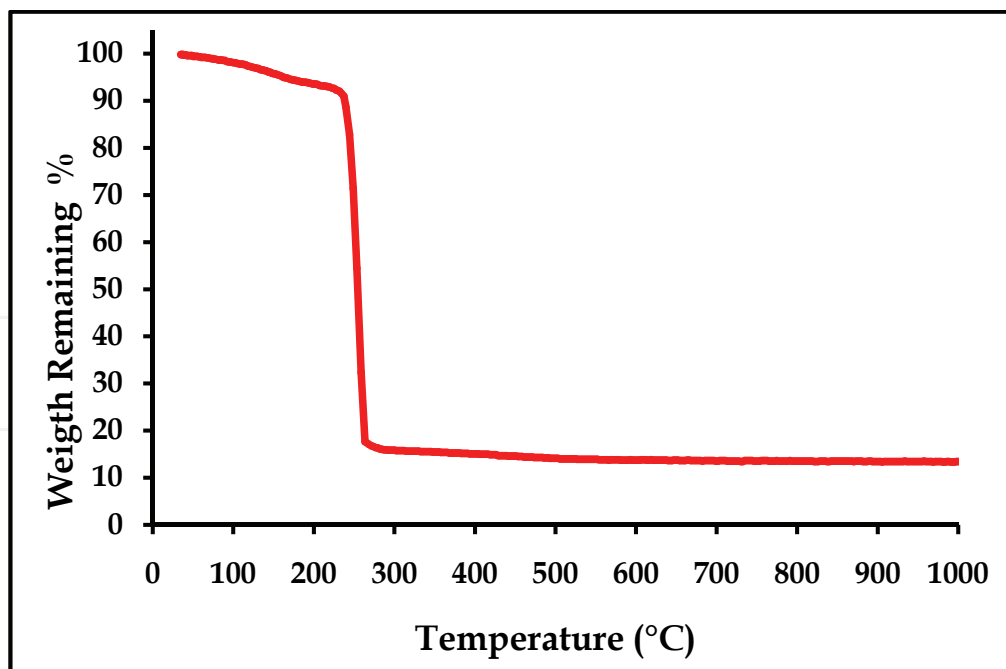


Fig. 1. Thermogravimetric annalysis from a hipotetical waste.

Concerning the size of the particles that form the residue or the grain size, can have sizes either coarse or small (bellow 50 micrometers). There are applications in ceramic products

for a wide range of particle size and if the particle size is very large for an application, it can be milled. The grind is a costly step and demand time, then should be avoided or very well rated for not making its use financially unfeasible.

Another property that can be easily assessed is the pyrometric cone equivalent (PCE). The PCE is a measurement of refractoriness given according to tests made with material in a cone pattern.

The deformation and softening due to the temperature rise are compared to material standards. Cones are designed to deform at certain times during firing, simply to record what happened during the firing (control). The exact moment when the cone is deformed mainly depends on two factors: time and temperature. With this concept in mind, it is necessary take care that PCE and temperature is not the same thing.

Like the PCE, the piroplasticity index (*PI*) could be applied to know firing details of ceramic products. The *PI* is a deformation of a specimen of certain size subjected to the action of gravity during firing under specific conditions. The procedure used to determine the rate of piroplasticity during the firing process consists of measuring the deflection of curvature of a specimen on two supports, separated by a distance determined, as shown in Figure 2.

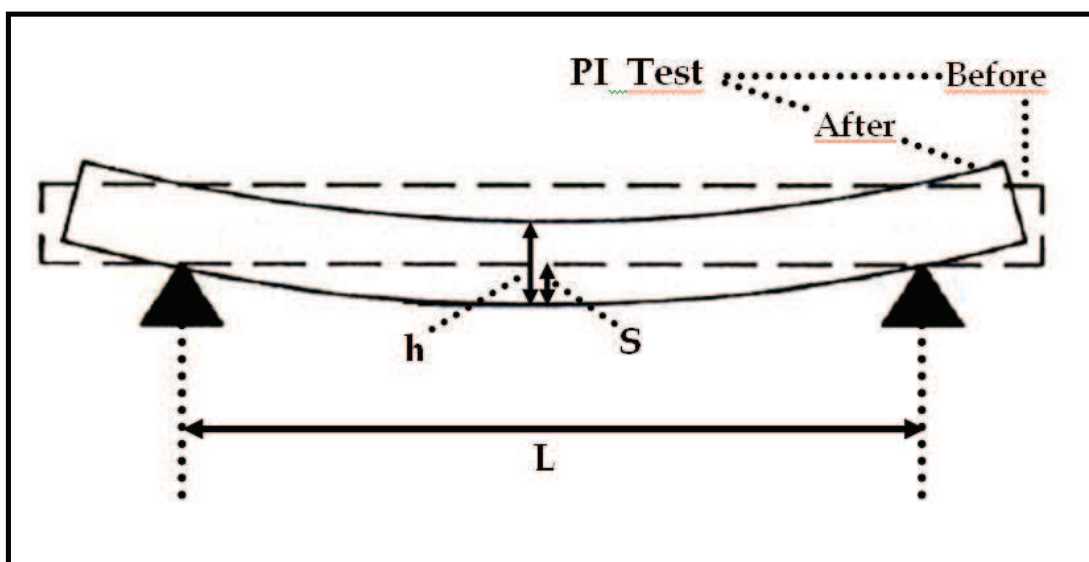


Fig. 2. Scheme of *PI* test.

The equation below (1) is applied for determine the *PI*, where h is the thickness of the body, S is the deflection of deformation measured by the deflection of the specimen and L is the distance between the on two supports.

$$PI = \frac{4k^1S}{3L^4} \quad (1)$$

Finally, an evaluation by a dilatometry curve can provide information about which temperature begins sinter and other information as the phase transformations and coefficients of thermal expansion. However, this analysis should be undertaken only after knowing the temperature where the material begins to soft (PCE temperature), to avoid damage in the dilatometer due to melting of the waste inside the equipment.

Figure 3 shows the dilatometric curve of a hypothetical waste, this at a temperature slightly above 700 °C is the largest expansion of the waste due to increased atomic agitation. However above this temperature, the thermal expansion is suppressed by the beginning of sintering, a phenomenon which is stronger as the temperature increases.

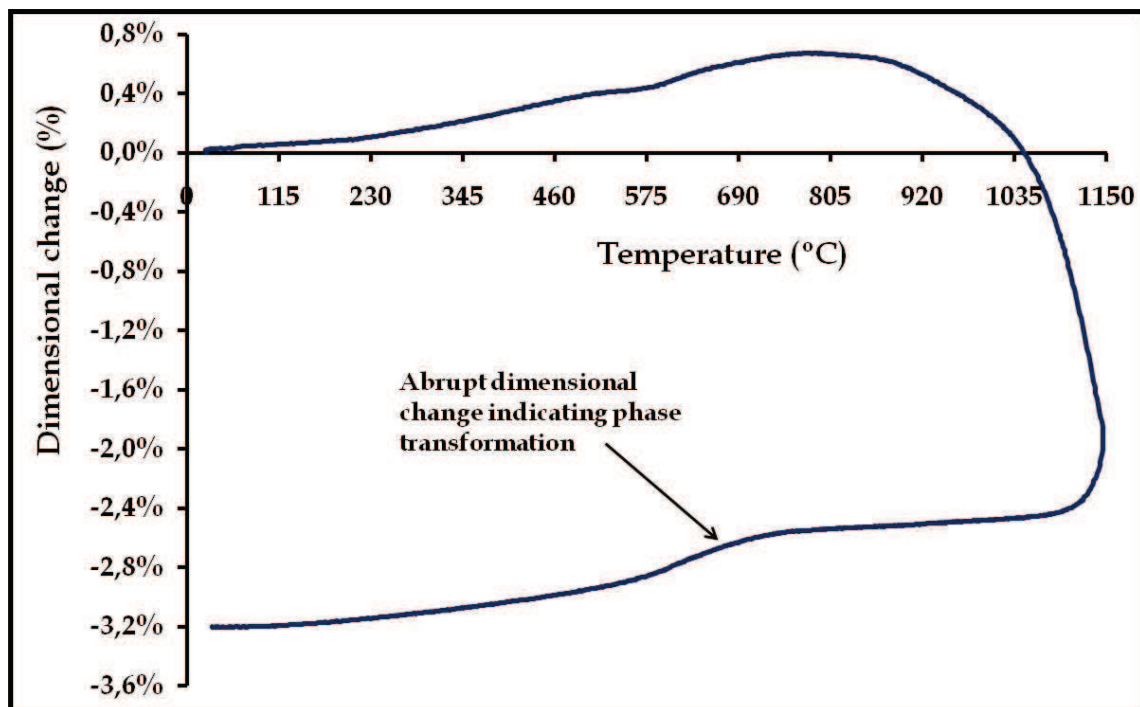


Fig. 3. Expansion/contraction of a hipotetic waste.

3.2. Preparation of Ceramics Formulations

The main types of ceramics products are based on aluminosilicate, potassium silicate ($K_2O-Al_2O_3-SiO_2$) or magnesium silicates ($MgO-Al_2O_3-SiO_2$).

The performances of ceramic materials are determined not only by the structure and composition, but also by defects (such as pores), second phases (which can be deliberately added to facilitate processing), and interfaces.

Special groups are zircon and mullite-based ceramics fine as well as low-thermal expansion ceramics in the system $Li_2O-Al_2O_3-SiO_2$ and borosilicates.

In Figure 4 is shown a schematic ternary diagram with the percentage mole of Al_2O_3 , SiO_2 and alkalis. This diagram shows in generic way the molar composition of silica-alumina refractories, glass and traditional ceramics. A diagram like this can be used to verify, for example, as would be the maximum residue, in terms of chemical composition, that could be added to a ceramic formulation, and also serve to show in what area of this graphic take place the formulation with the increasing of the waste amount.

A system graphically expressed in chemical form (generally in oxide form), which could be among others in form of weight too, allows delineate the composition of a formulation and its application as a ceramic product. Ceramic products containing in their chemical composition in the form of oxides Al_2O_3 , SiO_2 and alkali oxides and / or alkaline earth metals are widely used and a simplified manner are shown in Figure 4.

As can be seen in Figure 4, each class or type of material has a composition distinct from others and sometimes may have very similar compositions, but most often differ substantially from the heat treatment to which the material is submitted.

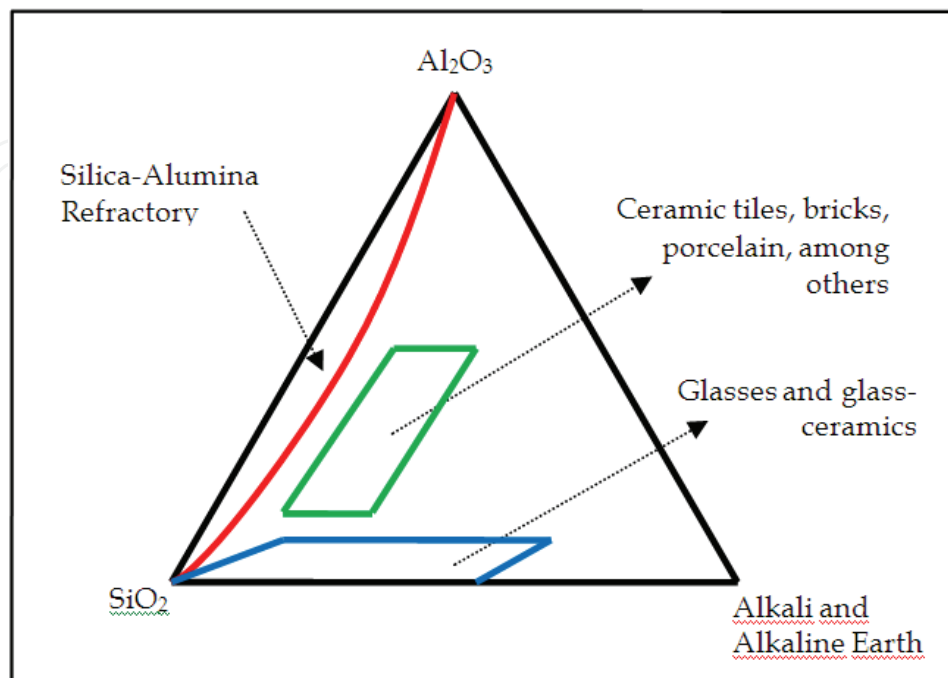


Fig. 4. Typical composition of common ceramic products.

The ceramic materials can be obtained from heat treatments that may be below or above its melting temperature. Among the main ceramic materials that are:

- i) Glass - inorganic product of fusion which has been cooled fast enough to pass through its glass transition to the solid state without crystallising;
- ii) Glass-ceramics - have an amorphous phase and one or more crystalline phases and could be produced by means of controlled devitrification (or controlled crystallization) of an already amorphous inorganic waste.
- iii) Sintered materials - produced from powder, by heating the material below its melting point (solid state sintering) until its particles unite to each other.

Once chosen the method for ceramic manufacture, the next step is to give form into a desired shape for the ceramic raw material. In the ceramic products that will be sintered or chemically bonded with hydration, this is accomplished by the addition of water and/or additives such as binders, followed by a shape forming process. Some of the most common forming methods for ceramics include pressing, extrusion, slip casting, tape casting and injection molding, among others.

The ceramic raw materials generally in small particles forms are sometimes agglomerated such an atomization to have a good fluidicity and compacticity, principally when will be pressed.

After ceramic shape forming, these material are "green" - they have form close to the final product and their properties are only to manipulate before next steps in the ceramics production. Then, a drying process is necessary to eliminate most of the additives according to the Bigot curve - Figure 5.

The drying process is important stage where there is appreciable shrinkage that needs to be faster enough to avoid defect because the rapid shrinkage.

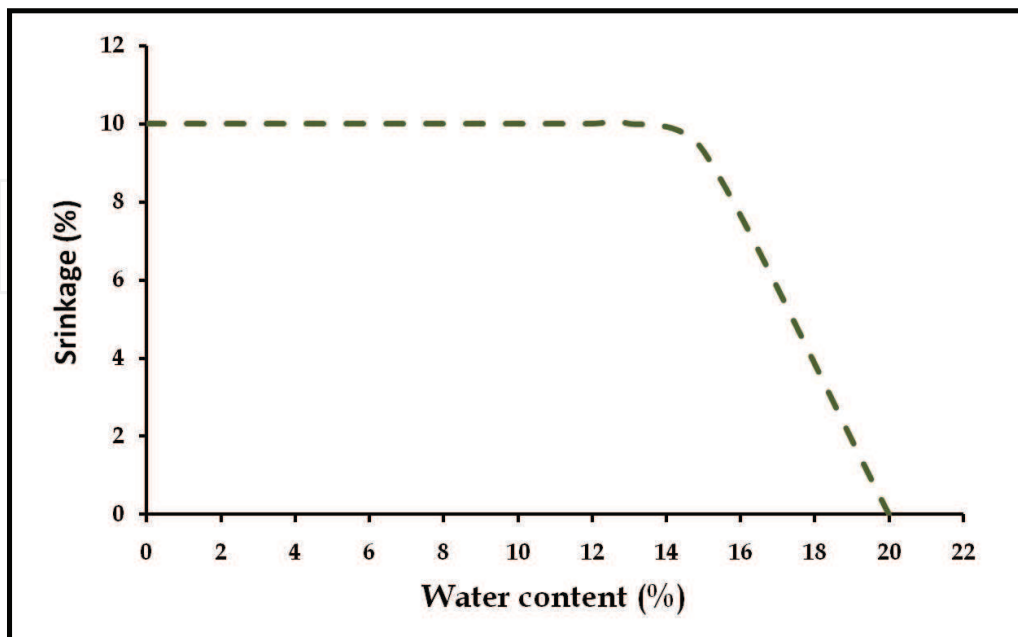


Fig. 5. The Bigot curve.

The heat-treatment called firing is applied to produce a rigid, finished product. Some ceramic products such as electrical insulators, dinnerware and tile may then undergo a glazing process. Some ceramics for advanced applications may undergo a machining and/or polishing step in order meet specific engineering design criteria.

3.3. Sintering temperature

Most of the known rules correspond to raw materials with simple compositions, ie, presenting few constituents. These rules had a margin of error, but provide information that can serve as a reference point.

The Tamman temperature is generally half of the melting temperature and is considered the point at which begins sintering in ceramics materials. The atoms mobility depends of atomic mobility and some factors such as texture, size and morphology. The following semi-empirical relations for Tamman temperatures (2) are more commonly used, where T_T is the Tamman temperature and T_m is the melting temperature.

$$T_T = 0.5T_m \quad (2)$$

Sintering requires the proper compromise of temperature, time and atmosphere to arrive at the desired porosity characteristics. With higher temperatures, longer times, or smaller particles, the bonds grow more rapidly and densification becomes more evident. Sometimes pressure could be additionally applied to increase the sintering effect.

The sintering temperature is selected by considering the material composition and the powder particle size distribution.

Temperature is the most important parameter in the sintering process since the temperature increase the atoms mobility – important factor in the sintering.

3.4. The Eutectic Point

The eutectic temperature shows the lowest possible melting point achievable in the phase diagram elements.

In combination with alumina and silica, eutectics for alkalis occur at significantly lower temperatures than eutectics for alkaline earths. This is one reason alkalis are considered stronger fluxes.

Alkali Eutectic Points:

- Sodica ($\text{Na}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$): 732°C
- Potassia ($\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$): 695°C
- Lithia ($\text{LiO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$): 975°C

Alkaline Earth Eutectic Points:

- Calcia ($\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$): 1170°C
- Baria ($\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$): 1250°C
- Magnesia ($\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$): 1355°C
- Strontia ($\text{SrO-Al}_2\text{O}_3\text{-SiO}_2$): 1400°C

Phase diagrams can seem like a map to navigate in the melting temperature for different compositions. Each map is developed for a specific group of chemical elements. Usual phase diagram may represent the melting of four materials, which is called a quaternary phase diagram.

No phase diagrams exist for most of the virtually infinite combinations of elements we could come up with. But, if it is known that eutectics exist, it is necessary to find a complex composition that will bring our refractory material into the melt.

3.5. Cementitious

The main cementitious materials are the same present in the Portland cement.

There are four principal minerals present in the grain Portland cement: tricalcium silicate (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4), tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_5$) and calcium aluminoferrite ($\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$). The formula of each of These minerals Can Be broken down into the basic calcium, silicon, aluminum and iron oxide (Table 1). Cement chemists use abbreviated nomenclature based on Oxides of Various elements to Indicate chemical formulas of Relevant species, ie C = CaO, S = SiO_2 , A = Al_2O_3 , Fe_2O_3 = F. Here, traditional cement nomenclature abbreviates the oxide and is shown in Table 1.

Mineral	Chemical Formula	Oxide Composition	Abbreviation
Dicalcium Silicate (belite)	Ca_2SiO_4	2CaO.SiO_2	C2S
Tricalcium silicate (alite)	Ca_3SiO_5	3CaO.SiO_2	C3S
Tricalcium Aluminate	$\text{Ca}_3\text{Al}_2\text{O}_4$	$3\text{CaO.Al}_2\text{O}_3$	C3A
Tetracalcium Aluminoferrite	$\text{Ca}_4\text{Al}_n\text{Fe}_{2-n}\text{O}_7$	$4\text{CaO.Al}_n\text{Fe}_{2-n}\text{O}_3$	C4AF

Table 1. Chemical formulae and cement nomenclature for major constituents of Portland cement. Abbreviation notation: C = CaO, S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3 .

The composition of cement is varied depending on the application. A typical example of cement contains 50-70% C3S, 15-30% C2S, 5-10% C3A, 5-15% C4AF, and 3-8% other

additives or minerals (such as oxides of calcium and magnesium). It is the hydration of the calcium silicate, aluminate, and aluminoferrite minerals that causes the hardening, or setting, of cement. The ratio of C3S to C2S helps to determine how fast the cement will set, with faster setting occurring with higher C3S contents. Lower C3A content promotes resistance to sulfates. Higher amounts of ferrite lead to slower hydration. The ferrite phase causes the brownish gray color in cements, so that “white cements” (i.e., those that are low in C4AF) are often used for aesthetic purposes.

The calcium aluminoferrite (C4AF) forms a continuous phase around the other mineral crystallites, as the iron containing species act as a fluxing agent in the rotary kiln during cement production and are the last to solidify around the others.

Although the precise mechanism of C3S hydration is unclear, the kinetics of hydration is well known. The hydration of the calcium silicates proceeds via four distinct phases. The first 15-20 minutes, termed the pre-induction period, is marked by rapid heat evolution. During this period calcium and hydroxyl ions are released into the solution. The next, and perhaps most important, phase is the induction period, which is characterized by very slow reactivity. During this phase, calcium oxide continues to dissolve producing a pH near 12.5. The chemical reactions that cause the induction period are not precisely known; however, it is clear that some form of an activation barrier must be overcome before hydration can continue. It has been suggested that in pure C3S, the induction period may be the length of time it takes for C-S-H to begin nucleation, which may be linked to the amount of time required for calcium ions to become supersaturated in solution. Alternatively, the induction period may be caused by the development of a small amount of an impermeable calcium-silicon-hydrate (C-S-H) gel at the surface of the particles, which slows down the migration of water to the inorganic oxides. The initial Ca/Si ratio at the surface of the particles is near 3. As calcium ions dissolve out of this C-S-H gel, the Ca/Si ratio in the gel becomes 0.8-1.5. This change in Ca/Si ratio corresponds to a change in gel permeability, and may indicate an entirely new mechanism for C-S-H formation. As the initial C-S-H gel is transformed into the more permeable layer, hydration continues and the induction period gives way to the third phase of hydration, the acceleratory period.

After ca. 3 hours of hydration, the rate of C-S-H formation increases with the amount of C-S-H formed. Solidification of the paste, called setting, occurs near the end of the third period. The fourth stage is the deceleratory period in which hydration slowly continues hardening the solid cement until the reaction is complete. The rate of hydration in this phase is determined either by the slow migration of water through C-S-H to the inner, unhydrated regions of the particles, or by the migration of H^+ through the C-S-H to the anhydrous CaO and SiO_2 , and the migration of Ca^{2+} and Si^{4+} to the OH^- ions left in solution.

3.6. Oxide Glasses

Oxide glasses can be made from many compositions of silicates, aluminates, borates, phosphates, halides and chalcogenides.

Commercially glasses do not have fixed compositions, but there are many thousands of glasses, every one with a different composition.

It should be emphasised that the ability of a material to form a glass also depends on the cooling rate from the melted glass. This cooling rate is below that the minimum cooling rate sufficiently to crystallization and the final temperature is below transition temperature.

There are three classes of components for oxide glasses: network formers, intermediates, and modifiers.

The network formers (for example: SiO_2 , B_2O_3 , GeO_2) form a continuous three-dimensional random network by themselves. The intermediates (for example: TiO_2 , Al_2O_3 , ZrO_2 , Be_2O_3 , MgO , ZnO) are that the cation can enter the network substitutionally, but which cannot by themselves normally form a network. The modifiers (for example: CaO , PbO , LiO , NaO , K_2O) alter the network structure; the cation can enter the network interstitially. Some elements can play multiple roles; e.g. lead can act both as a network former (Pb^{4+} replacing Si^{4+}), or as a modifier.

One possible disadvantage of waste use as a glass raw material is the coloring that could be obtained by the presence of ions in glasses materials that change colour when exposed to light. Frequently wastes present ions that result in a coloured glass, which is sometimes undesirable. Oxides of iron, titanium, chromium, cobalt, cadmium, nickel and cadmium are examples of components that could colour glasses.

4. Future Research

The characterization methods of materials have greatly improved its efficiency due to new technology that simplify its manufacture and also make easier the development of new methods of characterization.

Proper waste characterization is crucial, which will define the applications of each residue. The waste, because its intrinsic characteristics, can hardly be used for advanced applications without prior treatment because the highly costly involved in purification such as: electronic, electrical, and magnetic, among others.

Another aspect to be observed is if the use of waste may be dominantly negative to natural environment than its disposal in a landfill. In some cases, if the residue use requires a different process than a product without waste, which may require much more equipment and energy factors that have more environmental impact.

And not less important, independent of the method employed to conform a ceramic product, it is necessary take in account the pore volume of them, if not different things are being compared. Different ceramic processes and/or equipments employed generally produce different volume of pores in one product that strongly influences its properties. Sometimes some parameters need to be adjusted to the new raw material (waste in this case) develop similar porosities and then similar properties.

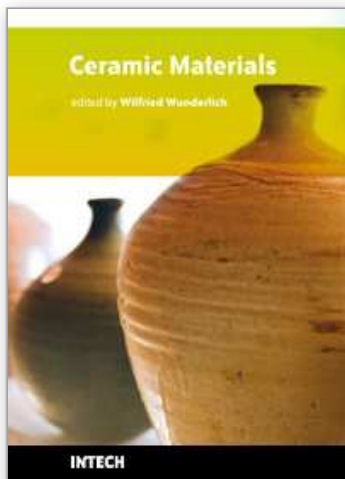
As an example, if a waste particles that has appreciable friction between other particles like the fly ash is employed substituting some part of a raw material with low friction between particles, then it will be necessary a lubricant additive and/or more strength to consolidate the ceramic product.

The negative environmental advance due to the industrialization must decrease to avoid the surging of untenable world. Therefore, new alternatives and known alternatives must be booth employed to minimize the waste generation and for the total usage of the waste generated.

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