VALORIZATION OF BOILER WOOD ASHES IN THE CERAMIC INDUSTRY

Author: Laurent Soum

Research Engineer

Manager: Gérard Pillet

Head of R&D Department

Société Française de Céramique (SFC), Les Ulis, France.

1. ABSTRACT

The development of biomass energy in France generates a consequent increase in the production of combustion residues whose current valorization is limited to agricultural spreading. Given the mineral nature of the biomass boiler ashes, SFC has initiated in 2012, with the support of ADEME - the French Agency for Environment Development and Energy Efficiency - , a study on the valorization of boiler wood ashes in the ceramic industry.

This article refers to this work and presents the results obtained in the laboratory and in the pilot test realized in partnership with a manufacturer of the clay sector.

2. INTRODUCTION

Since 2000, with the aim of developing the use of biomass as a privileged path for the control of energy resources consumption in France, ADEME launched the Wood Energy [1] program for the implementation of boilers in the territory. With the growing accumulation of combustion residues, the Société Française de Céramique (SFC) has initiated in 2012 the CERACENDRES project to study the terms of use of wood ashes in the different masses of the ceramic industry as auxiliary fluxes or colouring compounds.

3. WOOD ASHES, A POTENTIAL CERAMIC RAW MATERIAL

There are several types of combustion stokers which are dependent of the power of the installation; the most common being the inclined grate stoker. The combustion leads to two types of ashes:

- Powdery ashes called "flying ashes" which are driven to the chimney and recovered through the use of bag filters and/or electrostatic precipitators.
- Coarse ashes called "sub-hearth" which are extracted directly below the combustion grate (ash pit).

Two ash extractor ways exist for sub-hearth ashes: a dry process where the ash pit is emptied using a scraper; and a wet process where the ashes drop into a pool of water to agglomerate the particles and avoid dust. As will be shown below, the significant presence of lime in the ashes makes the extraction method important for the stabilization of CaO, as this is generally unstable in the dry ashes and tends to rehydrate easily. This feature must be specifically studied for the ceramic shaping processes systematically made by the wet method, and beyond for the casting processes which are carried out in the liquid path.

Indeed, it is understood that the process of extracting sub-earth ashes has a significant impact on their implementation in a ceramic mass.

3.1. CERAMIC INDUSTRY AND DEPOSITS OF WOOD ASHES IN FRANCE

In order to verify the adequacy between the amounts of ashes available in France and the ceramic productions, a regional mapping was compiled based on ADEME data as shown in Figure 1.

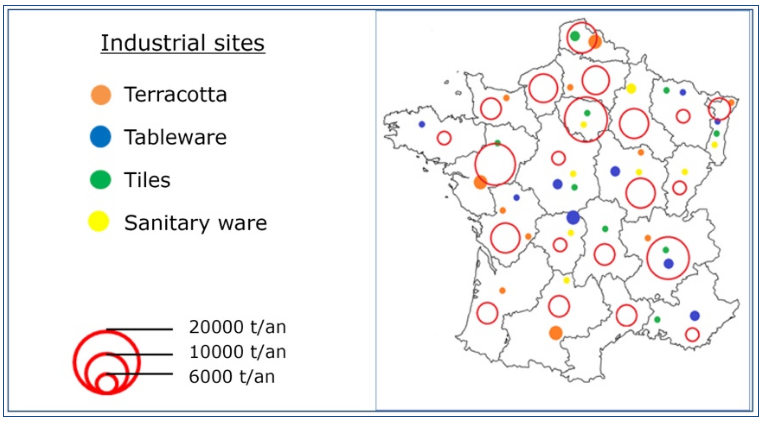

Figure 1: *Mapping of ceramic sites and deposits of ashes by region in 2013 [2].*

On the one hand, the ceramic industry (excluding terracotta) in France represents 730kt of products in 2012 [3]; this volume reaching 4,7Mt taking into account the tiles and bricks industry [4]. On the other side, from 2009 to 2013, ADEME has identified more than 2,400 wood boiler installations for a consumption of over 1.5Mtoe with over 700kt of ashes produced.

These data clearly show the relevance of the use of wood ashes in ceramics with both a sufficient amount of ashes produced in the territory for industrial use and a geographic distribution of the ashes resources to the nearest ceramics production sites.

4. EXPERIMENTAL

4.1. CHEMICAL CHARACTERIZATION OF THE ASHES

A chemical characterization of the ashes was carried out based on 5 selected ashes representing the different types of existing boiler installations:

- 1 industrial boiler with sub-hearth ash extracted by dry method (SFC No. 47215)
- 2 industrial boiler with sub-hearth ashes extracted by wet method (SFC No. 46649-46654)
- 1 collective boiler with sub-hearth ash focus extracted by dry method (SFC No. 46647)
- 1 collective boiler with fly ash extracted by electrostatic (SFC No. 46648)

The Figure 2 shows the variations in chemical composition observed on the studied ashes. It is noted that the ashes are mainly composed of SiO_2 and CaO as well as of alkali elements providing a flux character. The impurity levels are relatively low particularly for iron (Fe_2O_3) because, in this study, only class A wood (wood chips and/or related to the wood industry) were selected to avoid all possible contamination by the presence of paint, nails, etc.

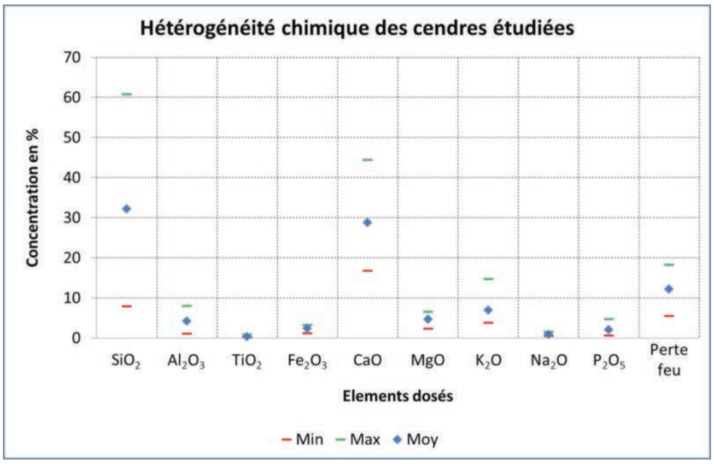

Figure 2: *Ashes' chemical heterogeneity.*

A mineralogical analysis of the ashes showed that most CaO was in its free form or as hemihydrates; a portion being also associated with silicates in the form of wollastonite or anorthite. The significant presence of free CaO raises the problem of the increasing amount of water during the shaping extrusion process. An ash obtained by the wet method extraction has the advantage of already being hydrated, avoiding rheological disturbances (increase of the shaping water) and avoiding the phenomena of swelling or the appearance of lime points after firing the samples.

Note that the significant presence of SiO_2 in some ashes also enables the stabilization of CaO by creating silicate phases within the combustion chamber.

4.1.1. RHEOLOGY – CASE STUDY

In order to observe the influence of the ash incorporation in such suspensions, viscosity measurements were carried out to compare the behaviour of different slurries. Figure 3 shows the preparation of a suspension to be cast for a sanitary application whose rheogram is presented here:

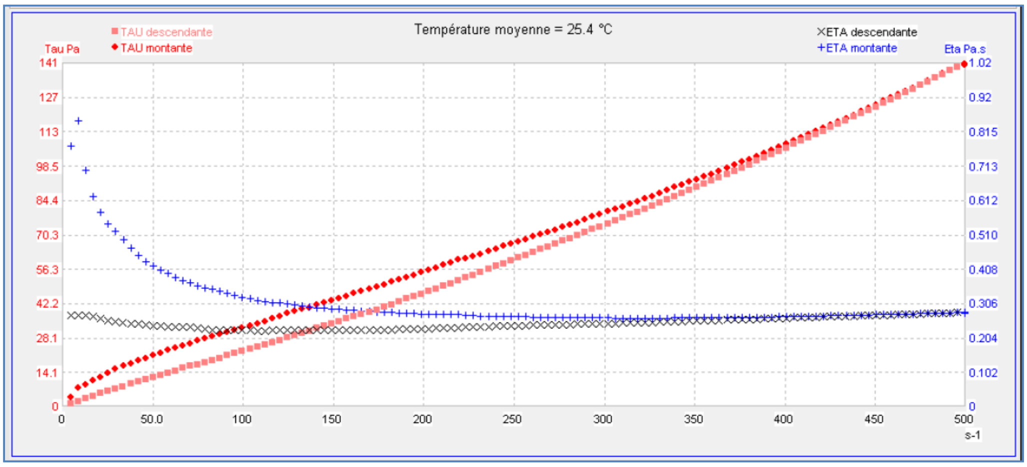

Figure 3: *Rheogram of a reference sanitary slip.*

The red dots in Figure 3 show the variation of the shear stress τ as a function of the velocity gradient. The blue dots show the apparent viscosity η. It appears that the higher the shear stress increases the more the apparent viscosity decreases, justifying the shear thinning behaviour of the slurry. This is a normal behaviour allowing correct shaping by casting (liquid method), for a typical thixotropic fluid. In the second case (Figure 4), the rheogram shows a suspension for the dry shaping of pressed porcelain stoneware tiles. The addition of ashes No. 47215 was carried out at 1 wt%.

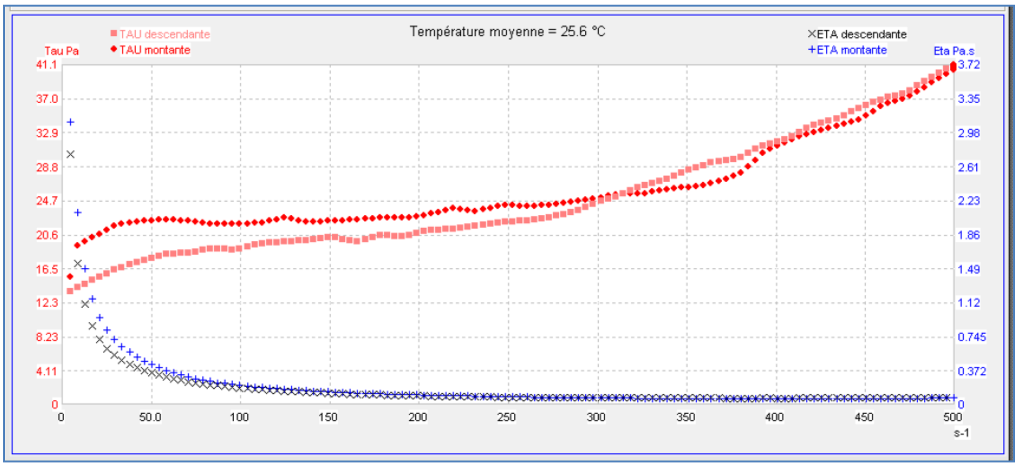

Figure 4: *Rheogram of the preparation 47215M1.*

Unlike the previous curve, the red dots don't pass through the origin which means that a minimum stress is necessary to allow the fluid to flow. It also appears that all of the points describe neither a curve nor a straight line. The behaviour of this suspension reveals difficulties for the development of samples for further study.

The results obtained can be explained by a number of parameters inherent to the preparation of slurries such as the particle concentration and the particle size distribution. Furthermore, associated with very high pH values, the ashes are heavily loaded with soluble salts (in particular $Ca(OH)_2$ induced by the presence of free lime which rehydrates) which will tend to disrupt the electrical neutrality of the suspension and therefore lead to the agglomeration or the flocculation of the particles

The slip presents a thinning rheological behaviour. However, even after an important addition of water and by applying sufficiently strong shear stress, the time during which the slurry becomes fluid is insufficient to successfully run test pieces which then have defects

Furthermore, it also represents an excessive addition of water which necessarily would involve a much longer shaping phase and drying time and therefore a higher energy consumption and an expensive process. Whether with sub-hearth or flying ashes, extracted by dry or wet method, the disruptions that they entail in these ceramic systems are very violent and fast. At this stage, without further research on an amendment of the deflocculating system or on a technology to allow the ashes to be inert, their inclusion in aqueous systems does not allow usable slips to be obtained.

Various promising leads are emerging in order to try to facilitate the addition of ashes in the slips and thus reduce intakes of soluble salts including:

- A **washing of ashes** with water (formation of ash wafers by pressing filter method) or a hot extraction washing by Soxhlet; treatment to remove soluble salts responsible for rheological disturbances.
- A **heat treatment of ashes mixed with an excess of silica** to form stable calcium silicates and avoid rehydration of the lime contained in the ashes.

This rheological study, which induces severe constraints in achieving stable slips, has oriented the works on the extrusion processes for shaping clay products as shown in the tests presented below.

4.2. IMPLEMENTATION OF ASHES IN TERRACOTTA MASS

Once prepared, ashes were introduced into a clay mass in three separate rates, namely 3, 5 and 10 wt%. The ash was mixed and prepared in a kneader before strips extrusion, their dimensions being: 120x20x8mm. These strips were then dried at 110°C for 24h before being fired at 980°C in an electric furnace.

4.2.1. RESULTS AND DISCUSSION

4.2.1.1. COLOUR APPEARANCE OF THE SAMPLES OBTAINED IN THE SFC LABORATORY

After firing at 980°C, the samples have relatively homogeneous colours except for ashes No. 47215. The inclusion of this ash strongly modified the colour surface acting as efflorescence, the core of the strip remaining ochre.

Figure 5 : *Comparison between the reference and the 3 addition rates of ash No. 47215 (from top to bottom ref, 3, 5 and 10%).*

In the case of the other additions, Figure 5 shows the colours are well preserved and the final properties of the product will thus be studied.

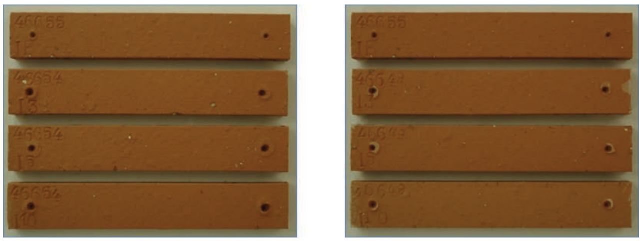

Figure 6: *Comparison between the reference and the 3 addition rates (from top to bottom ref, 3, 5 and 10%) – Left: ashes No. 46654 and right: ashes No. 44649.*

The colour chart shown in Figure 7 shows that it is almost impossible to detect differences with the naked eye without performing measurements.

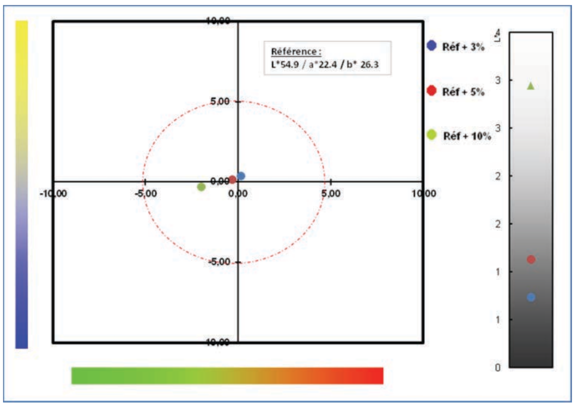

Figure 7: *Comparison of ash additions on colour in ashes No. 46649.*

The red circle shown in Figure 7 shows the acceptable limits of the colour changes corresponding to ΔE*=5. As measured points belong to this circle, it is considered that there is no major variation and that the final product is acceptable. This therefore reflects the first observations made with the naked eye.

4.2.1.2. SAMPLES CHARACTERIZATION

The following radar illustrations highlight the influence of ashes on the final properties of the samples and show the evolution of the main characteristics:

- Drying and firing shrinkages
- Evolution of the mechanical properties for the green-dry and fired products (determination of rupture modulus by 3-point bending test)
- Porous texture (bulk density and weight of absorbed water)
  - Case of No. 46654 ash:

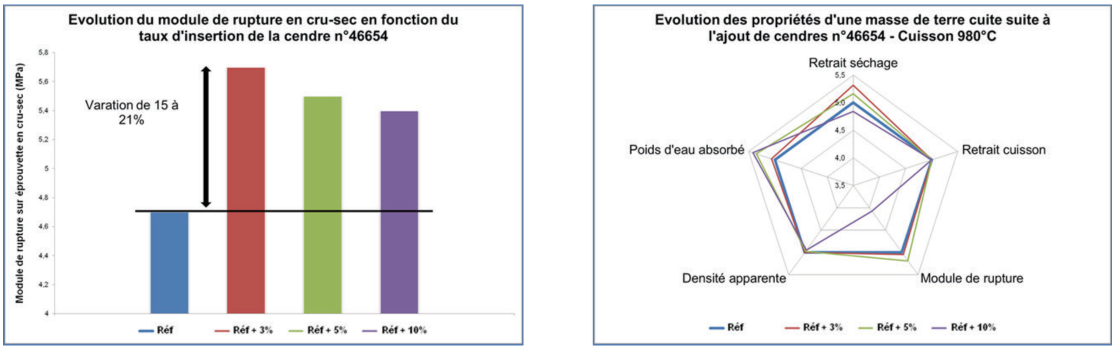

Figure 8: *Influence of ash No. 46654 on the clay product characteristics.*

The presentation of the green-dry modulus of rupture (Figure 8 left) shows that the ash acts as grog bringing a considerable gain in mechanical strength (15-21%) before firing. On the right of Figure 8, there is an increase in the drying shrinkage induced by a greater amount of water for shaping of the order of 5%. Apart from a higher water absorbed weight, the properties observed in terms of mechanical strength and bulk density are maintained or even improved for an addition of 5%. An addition of 10% shows a sharp drop in mechanical properties.

  - Special cases:

Figure 9 shows the influence of ashes No. 46649 and No. 47215, extracted by respectively the wet and dry method, on the clay mass. It appears that the results are similar for ashes No. 46649 and No. 46654 (wet method) with always a limit value addition that emerges in the vicinity of 5%.

Ash No. 47215 (extracted by dry method) raises the concern of the presence of lime mentioned above. This free CaO certainly brings a high mechanical strength in the dry raw products but will strongly disturb the clay mass after firing.

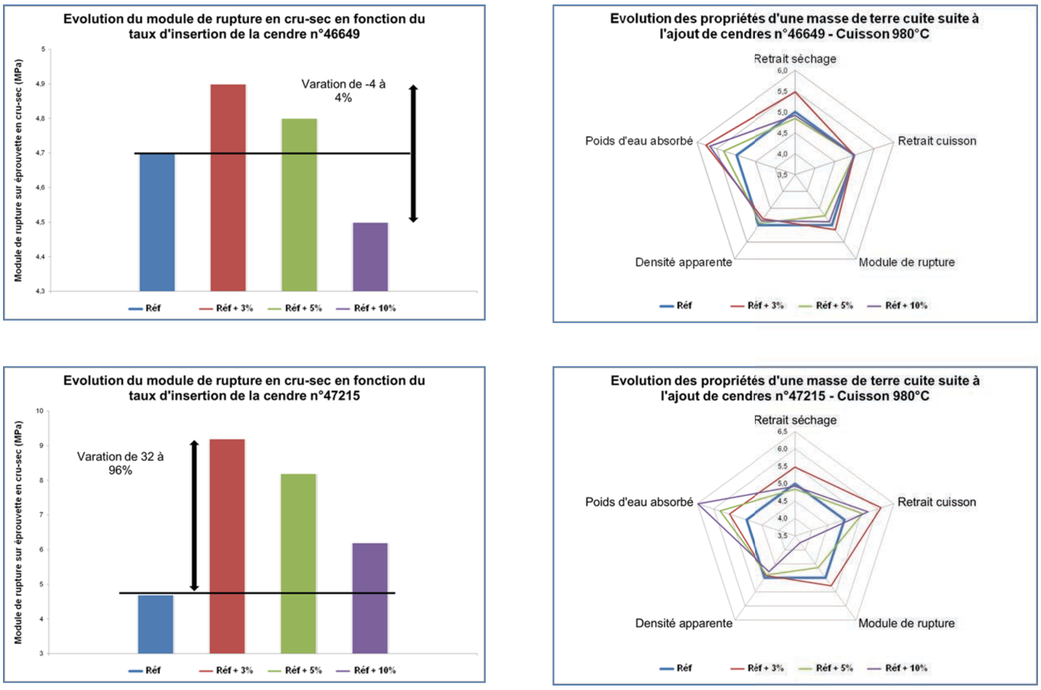

Figure 9: *Influence of ash No. 46649 (top) and ash No. 47215 (bottom).*

4.3. PILOT TESTS

With the encouraging results obtained in the laboratory, a pilot test was conducted in the company Rairies Montrieux. Located in Rairies (49) it is a representative French SME ceramic company, devoted to the production of clay products from onsite extracted raw materials to produce ceramic tiles and bricks for a global market.

The recovery of ashes from the actors in the timber industry required a preparation before addition into the different masses of study. The preparation of these ashes was entrusted to the technical centre GEO RESOURCES located in Vandoeuvre-lès-Nancy (54). This laboratory is part of the Scientific and Geological Association for Geology (ASGA) and is also linked to the CNRS and the University of Lorraine.

One of the first steps was to dry the ashes in order to work in good conditions and carry out the steps for screening, iron removal and grinding. Lots of ashes received by the contractor have significant differences in their behaviour and composition which forced the company to rethink and adapt the methods of treatment:

- Hammer milling
- Ceramic ball milling
- Impact milling
- Attrition
- Recovery of sludge screening
- Attrition of thickened sludge and drying

The packaging of ashes was carried in big-bags with a moisture forms not descending below 5% in order to limit the problems associated with the volatility and handling during tests.

4.3.1. MASS PREPARATION

The mixture was prepared in a secondary line of production, with its own clay stock. The supply of ash is carried via a small hopper at the side of the conveyor before being conveyed in the 2 worms located upstream of the extruder.

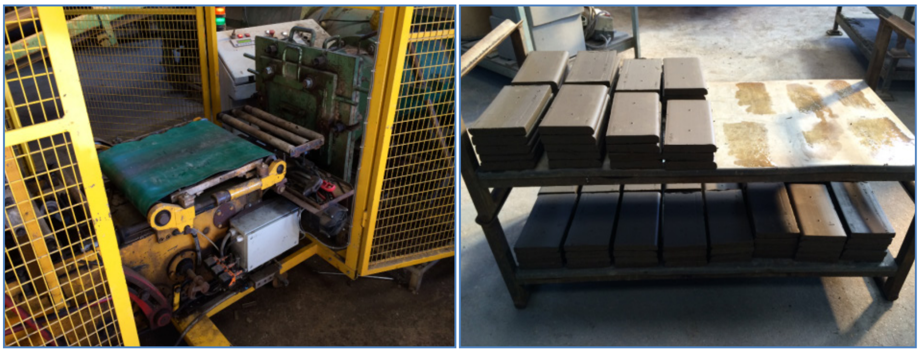

Figure 10: *Die of the extruder for splits output and extruded splits.*

Note: During extrusion, water is added during mixing in the twin worm. For addition with 10%, no change of water flow was executed due to the initiation of a machine sharing the same water network. This has had the effect of making drier extruded splits due to the presence of ashes which increases the amount of necessary shaping water.

The mixture is then extruded under vacuum to obtain 220 x 110 x 20 mm dimension splits (Figure 10 - left). Once extruded, the facing plates are labelled and placed on shelves before the drying step. At this critical step (Figure 10 - right), samples were taken and sealed in plastic bags to perform humidity measurements in laboratory and determine the mechanical behaviour after drying at 110°C.

Figure 11: *Drying (left) and firing (right).*

After the drying step, the parts are fired in a tunnel kiln at 1080°C (Figure 11). Final products are then sent by the plant to the SFC's laboratory to perform various characterization tests.

On receipt of the samples, some parts were damaged (Figure 12). After study, it looks like a drying defect appeared, probably caused by the problems encountered during the extrusion of green parts. This will be confirmed by laboratory measurements.

Figure 12: *Drying defects observed on the received splits.*

4.3.2. CHARACTERIZATION OF FACTORY-MADE PRODUCTS

4.3.2.1. ON GREEN PRODUCTS

Sample name	Shaping water (%)	Drying shrinkage (%)
Rairies Montrieux reference (RMU)	23.2	5.3
RM + 5% ash Millet (RMM5U)	21.3	4.9
RM+ 10% ash Millet (RMM10U)	19.7	4.3

Table 1. *Evolution of RM shaping conditions depending on Millet ashes.*

The lower values seen in Table 1, either in terms of the amount of shaping water or drying shrinkage of parts, are due partly to the presence of ash but also to the problem of initiation of a machine which decreased the flow in the extruder. A change in the water flow, as it is typically done during the shaping, would have avoided these variations in results.

Sample name	Rupture modulus (MPa)
Rairies Montrieux reference (RMU)	7.2
RM + 5% ash Millet (RMM5U)	7.6
RM+ 10% ash Millet (RMM10U)	7.2

Table 2: *Mechanical strength of green-dry products with Millet ashes.*

The Table 2 shows that the cohesion of the product in green-dry is maintained with an improvement in the addition up to 5% of ashes, confirming laboratory results.

4.3.2.2. ON FIRED PRODUCTS

No defects or deformations and no significant differences in colour to naked eye were observed on the final product.

Sample name	Total shrinkage (%)	Firing shrinkage (%)
Rairies Montrieux reference (RMU)	7.2	1.9
RM + 5% ash Millet (RMM5U)	7.2	2.3
RM+ 10% ash Millet (RMM10U)	6.6	2.3

Table 3: *Parts shrinkages depending on introduced ashes (Millet).*

Similarly to drying shrinkage, the firing shrinkage (Table 3) is stable and consistent with typical values of clay products.

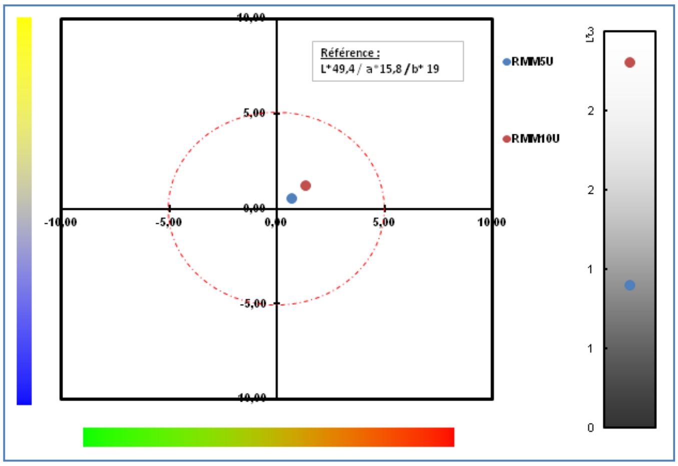

Figure 13: *Colour comparison between RMU and RMM5U, RMM10U at 1080°C.*

As it has been previously observed in laboratory tests, the colour changes induced by the presence of ashes are visible (Figure 13), but remain very close to the reference. This therefore validates the results obtained in the laboratory phase.

Sample name	Bulk density	Absorbed water weight (%)
Rairies Montrieux reference (RMU)	2.15	4.8
RM + 5% ash Millet (RMM5U)	2.17	4.9
RM+ 10% ash Millet (RMM10U)	2.15	5.9

Table 4: *Evolution of the porous texture depending on the introduced ashes (Millet).*

Table 4 shows that the introduction at 10% is transforming the PEA parts while the reference and the RMM5U composition have an identical firing state. On the RMM5U and RMM10U compositions, the presence of black cores as shown in the following Figure 14 was observed:

Figure 14: *Black core on the parts from RMM5U and RMM10U series.*

Sample name	Rupture modulus (MPa)
Rairies Montrieux reference (RMU)	16.0
RM + 5% ash Millet (RMM5U)	19.4
RM+ 10% ash Millet (RMM10U)	22.0

Table 5: *Mechanical strength of fired products with Millet ashes.*

With regard to mechanical strength (Table 5), for an identical state of firing there is a real improvement in properties. These properties are even more affected by the presence of 10% of ashes. Note that these strength increases are to be related to the presence of black cores (Figure 14) which strengthen the structure in the heart of the material without altering the outside appearance of the parts.

5. CONCLUSION

By their chemical composition, ashes are close to ceramic components allowing substitutions synonymous of raw materials savings. The strong development of biomass energy coupled with a homogeneous distribution on all the territory allows to consider a valorization in the ceramic sector. The study of a clay mass doped by adding ashes shows that real gains are possible without affecting the characteristics of the finished products. Based on the work of the first laboratory phase, an addition of ashes limited to 5 wt% seems to be acceptable in order not to alter the final product. The pilot test carried out confirms this trend.

The purpose of this study is also to show that implementation on an industrial scale is possible with results matching those obtained in the laboratory. The main challenge remains the preparation of the ashes. Indeed, because of their difference in composition and/or behaviour (relating to the extraction mode), it is necessary to use several preparation methods to guarantee the attainment of a raw material usable directly by the industry.

6. PROSPECTS

In 2012, France produced 4,5Mt of finished products on the terracotta market. This activity represented 80% of the ceramic industrial park in France and is very promising but only concerns the specific sector of building ceramic products.

The various contacts with industry in this study have yielded an overview of the ash preparation process in order to obtain a usable raw material. The different types of ashes (wood species used, type of boiler, etc.) and their extracting methods require a choice of treatment techniques that can vary from an ash to another. As part of a valorization study, it was seen in the study of two cases (terracotta sector and tile sector) that the ashes handling costs could vary from 20 to 120 EUR/t to be profitable depending on the ceramic sector concerned. Indeed, casting and pressing processes, addressing an area of higher added value, require passing through a slip preparation and, currently, there is a problem in terms of a rheological point of view that has to be resolved. These processes, although more complex to implement, represent over 75% of the whole existing production processes and thus generate a very important developing field for the valorization of ashes.

That said, a work performed closely with companies specialized in the installation and leading of the treatment line would allow defining more precisely the cost on each stage of the process. Indeed, the drying step requiring heat input seems to be the most energy-consuming station contrary to the screening step. It would also be interesting to determine a minimum tonnage of ashes from which a treatment line would fall within acceptable performance cycle.

The CERACENDRES project is a first step towards creating a path for ashes recovery in ceramic industry. The new requirements at the wood boilers construction level require a flue gas treatment system which results in increased production of flying ashes. Extremely fine and light, they pose many problems (handling, reactivity, etc.) which will be the subject of a more specific study, programmed by SFC and its partners with the support of ADEME on the use of ashes in the different existing ceramic processes. This project will reach the end of the validation process, integrating the visions of both industries with common solutions. These works will answer these points while exploring the valorization of fly ash that remain problematic from an environmental perspective.

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