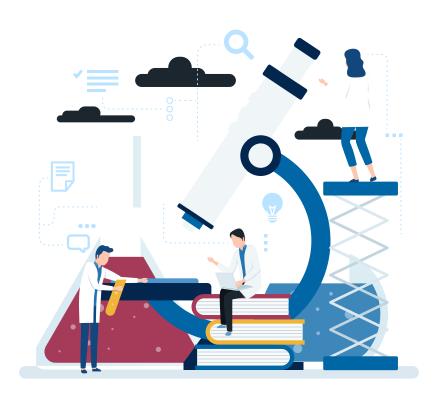
# REPORT HIGH QUALITY TILES WITHOUT EXPENSIVE CLAYS: EASIER THAN YOU THINK





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## HISTORY

Many centuries ago when the first Porcelain Stoneware formulas were developed, no Ukrainian Clay was present in the market. Whiteness and plasticity required for low water absorption and low porosity had been provided by high quality ball clays.

The main sources for these ball clays were UK and Germany. The clays from the UK were of higher quality and purity, whilst the German ones had the advantage of their cost, quite significantly lower compared to British ones.

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Loss upon firing %	Mechanical resistance N/ mm²
Vesko Granitik	59.0	1.4	25.0	0.8	2.2	0.5	9	9.0
Ceraterra TSMA	60.0	0.5	26.0	1.3	0.8	0.11	10	8.0
Fuchs FT-A	63.0	1.4	25.0	1.0	2.2	0.2	7	6.0
Fuchs FT-S	65.0	1.4	23.0	1.0	2.2	0.1	7	6.0
Fuchs Pím	63.0	1.3	25.0	1.7	2.4	0.2	7	6.0
Sarcal KSG	50.0	1.3	33.0	1.3	0.6	0.1	12	-
Sarcal BS3	46.0	1.4	36.0	1.3	0.5	0.1	14	-
Damrec RC 593	-	1.3	27.0	1.2	-	-	10	5.0
Damrec RC 784	-	1.5	26.0	1.4	-	-	10	6.0
EuroArce 951	56.0	0.8	29.0	1.4	2.1	0.2	9	-
EuroArce 952	61.0	0.8	25.0	1.4	2.1	0.2	9	-
EuroArce 960	51.0	0.2	32.0	1.2	1.2	0.8	12	-
ECC Hyplas 67	65.0	1.7	23.0	1.0	2.0	0.4	6	7.0
ECC Hyplas 71	69.0	1.7	20.0	0.9	1.9	0.4	5	7.0
Stephan Schmidt 301	63.0	1.5	24.0	1.0	1.9	0.2	7	4.0
Stephan Schmidt 1033	65.0	1.6	22.0	1.1	1.9	0.2	7	4.0
Stephan Schmidt 0747	71.3	1.5	22.1	1.4	2.4	0.3	6.6	3.3
TGA 7023	74.9	1.4	19.2	1.1	2.1	0.1	5.2	3.5
TGA 7036	73.5	1.3	22.0	1.3	2.1	0.2	5	4.5

From "PORCELAIN STONEWARE. Production manual and method of use" Dr. Giovanni Biffi (1999)

Looking for alternatives to these sources, Ukrainian clays came to the main Western European countries, where Porcelain Stoneware formulas were developed. High  ${\rm Al_2O_3}$  content and high purity were the main advantages of these clays which could allow for "Superwhite" formulations. Overtime these formulas were exported to other countries, specifically to Italy, Spain and Germany where the machinery producers promoted these new formulations.

The political crisis in the Ukraine made supply unstable and the necessity to find a replacement became something vital. Although it was not the case for all the tile manufacturers, some countries really struggled with the existing situation of the market, hence some new approaches were demanded by the industry.



Ukrainian clay quarry in Donetsk

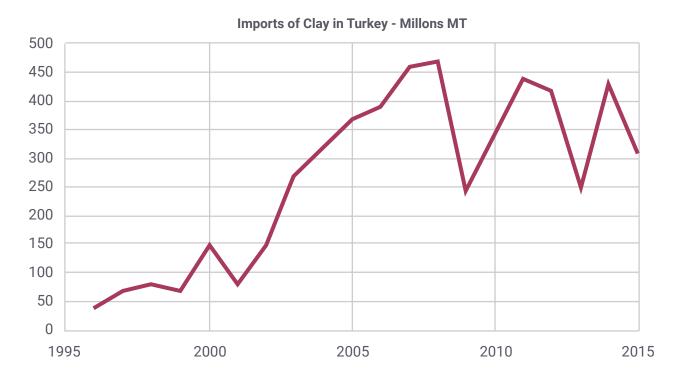
## **ALTERNATIVE SOURCES**

#### LOCAL CLAYS

This is the best solution if the local clays present the required quality.

Some countries, especially those who had seen reduced high quality clay availability, started exploring the possibilities of the local clays, being aware of their limitations, but also of their advantages, especially considering price and availability.

In order to bring some actual data of such potential replacement, we will use a case study we performed in one of the countries that were severely affected by that situation: Turkey.



Both 2009 and 2013 represent two moments where political tensions made supply become very tight.

Most of the Turkish manufacturers already had a solution for this particular problem, as the clay from Istanbul and its surrounding areas showed very good quality and was as close a match as possible to the Ukrainian clays.

	SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	Na <sub>2</sub> O	Na <sub>2</sub> O	LOI
Clay 1	62.1	23.2	2.35	1.14	0.14	0.58	0.17	2.13	8.2
Clay 2	78.4	11.6	1.72	0.52	0.77	0.72	0.25	1.57	4.9

Taking a deep look to those figures, it's quite logical to think about a potential replacement. But then politicians and governments decided to close down those clay quarries extracting and producing the above mentioned high quality clay. Deadline was fixed on 2015, hence urgency for finding a solution was even higher.

Luckily for the tile producers, the deadline was extended to 2020, reducing the urgency but all of them were aware of the need of switching their Istanbul clay-based formulations to some variations based on existing formulas. We will review this further when we talk about "New Formulations".

In some other countries, like in South America or some South East Asia regions, although high quality clays have been present in the formulas, they are not its main component hence they try to use local sourced clays when available.

#### CHEAPER SOURCES

Another alternative to the use of high quality and/or local clays is to source cheaper clays. Those clays will not present the same properties as the expensive high quality ones, though it may be enough for a low-end product market.

We will talk about the different options in the following countries:

- **Spain:** Some high quality clays are present in this country, although in most of the cases its impurities limit its implementation and usage in the industry. A number of clays from the Teruel Province present high organic matter content along with some TiOx and FeOx in its composition. Both of these oxides will lead to lower brightness and higher yellow and red coordinates in LAB color profiles. There are also some clays in the northern provinces but their processing and logistic costs together with their Kaolinitic composition, hinder its implementation in the market.
- **Portugal:** The clays in Portugal typically are of a higher quality than the Spanish ones. Some of them will present analogue performance to some high quality German/British ball clays. Although whiteness is one of their main characteristics its plasticity is below the required levels exhibited by the alternative high quality clays. This may allow ceramists to develop some very white formulations, but will still require further improvement of their plasticity, demanding the presence of some additives.
- **Brazil:** The majority of the high quality clays in Brazil are located in the northern provinces of Amazonas river. Their performance are equivalent to the Portuguese clays so they will also need to use some additives to enhance their efficiency
- **USA:** Clays from the Tennessee area although of good quality, their Kaolinitic composition limits their direct application without making some adjustments to the formulas.
- Others: Due to high diversity of clays all around the world, we can say that most of the countries will have some clay sources that may be suitable for being used in Ceramic Tile production. However, like the ones mentioned earlier, they will most probably need some adjustments in order to achieve the highest performance.

### **NEW FORMULATIONS**

Though it can be seen in some cases as a step-back, due to the similarity with older formulations, there are some new trends, based on different raw materials, like Kaolin, where plasticity is recovered when using some additives.

Several research projects have been carried out, focused on reducing the presence of plastic materials, reducing the costs involved and the variability of raw materials in the ceramic tile body formulations..

One of the main raw materials that has been used for replacing high quality clay is Kaolin. Although it is a clay its mineralogy is quite particular, as most of it is based on Kaolinite and as such the  $Al_2O_3$  content will be equivalent to standard high quality Ukrainian clay, which in turn offers a greater potential for replacement by Kaolin.

To overcome any potential problems with the introduction of kaolin a slight change to the body recipe, the addition of some other plastic materials or even additives may allow for its use at high levels in the formulation. Furthermore, its high purity and increased whiteness is another positive directing formulators towards its inclusion in new developments or improvements in existing ones.



Example of white Kaolinitic clay

## **ADDITIVES**

#### INORGANIC ADDITIVES

Changes in the formulations are introduced by changes in the main raw materials, but also in the minerals used in small proportions in the formulas.

**Kaolinites:** They are responsible for the formation of Mullite phases in the structure, bringing properties like mechanical strength, abrasion and low porosity.

**Bentonites:** They are used to keep stability in the formulas when being ground in the ball mill and later during storage in the tanks.

**Feldspars:** They were responsible for the main change in formulations during the 90's. They bring low absorption as they are adding some alkalinity to the formula, which has an impact on firing temperatures.

#### SYNTHETIC ORIGIN

The first products that were used as plasticity enhancers were based on Acrylic Acid derivatives. In most of the cases, performance was achieved with low dosages, though its price instability and the fact that they come from non-renewable sources is limiting its implementation.

### NATURAL ORIGIN - BIOPOLYMERS

Natural biopolymers represent the green alternative. They have been shown to give an equivalent or greater performance when being introduced into formulations. Biopolymers represent a very feasible option in the market to replace expensive high quality clays with lower cost ones, whilst keeping most of the properties, or even exceeding them.

There are several cases, especially in those countries where the abundance of high quality clay is not readily available, where Biopolymers allow ceramic tile producers to keep a quality standard which is good enough to compete with other manufacturers, while having a lower manufacturing cost.

Below is an example with two different formulations with and without Ukrainian clay, corresponding to standard formulations of both Porcelain Stoneware and Wall Tiles.

Raw materials	STD Porcelain Stoneware	New Porcelain Stoneware	STD Wall Tile	New Wall Tile	
Pegmatite	0	0	15	15	
Na Feldspar	50	50	0	0	
Clay 1	0	10	25	29	
Clay 2	0	10	20	26	
Kaolin	14	14	0	0	
Ukrainian Clay	30	0	10	0	
Marble	0	0	13	13	
Silica Sand	6	6	17	17	
Sodium Silicate	0.45	0.45	1	1	
Biopolymer	0	0.4	0	0.4	
Residue 45µm	3-4	3-4	0	0	
Residue 63 µm	0	0	5-6	5-6	
Dry Strength (Kg/cm²)	16.2	18.8	31.6	30.3	

Critical performance along the production line, mainly due to mechanical properties, is kept though Ukrainian Clay share has been replaced by local clays. This means that a much cheaper formulation is offering the required technical properties.

## CONCLUSIONS

We have looked into several ways of how to avoid using Ukrainian clay when producing high quality decorative tiles. Some may be more effective than others and several factors may influence the selection of one or another choice. However, we believe that additives are usually the easiest and cheapest solution.

Depending on the type of clay you use and your production process, you will have to decide which option may be more suitable for you. Borregaard has access to experts and laboratory facilities that can help you decide what is the best solution for you.

Additionally, more exhaustive information can be found in an extensive report carried out by the Ceramic Research Center (SAM) in Turkey and the Anadolu University.

If you prefer, you can also contact us to receive more information or ask any question!



## **ABOUT US**

Borregaard operates the world's most advanced and sustainable biorefinery. By using natural, sustainable raw materials, Borregaard produce advanced and environmentally friendly biochemicals and biomaterials that replace oil-based products. Our world-wide network of production facilities and sales offices assures the very best local service and competence where you need it. For us, providing our customers with the most dedicated technical assistance is key. Therefore, the company invests considerable resources in research and development. We continuously strive to develop wood based renewable products for new applications, and through that we contribute to delivering present alternatives to oil based synthetic products in a wide variety of industries.

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