ON THE USE OF TURKISH CLAYS TO REPLACE UKRAINIAN CLAYS IN PORCELAIN TILE COMPOSITIONS

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ABSTRACT

The search for alternatives to Ukrainian ball clays has become a strategic issue in the European ceramic tile industry as a result of supply shortages due to the war. In relation to this, Türkiye may be a country of interest because, apart from being well known for its sodium feldspar mines, the country also has important deposits of white clays of different plasticity.

This paper revises some of the most important Turkish sites where ball clays with potential application in porcelain tile manufacture occur. Commercially available clays were selected from deposits in different regions of Türkiye, including the Şile (Istanbul), Konya (Doğanhisar and Ilgın regions) and Afyon (Alanyurt) areas. All these clay deposits are Oligo-Miocene, Neogene to Pliocene of age and the first two occurrences deposited in the continental lacustrine environments, while the latter developed by the hydrothermal alteration of the felsic ignimbrites. The clays were characterised on the basis of their technological behaviour, i.e., plasticity index, milling residue, pressing compaction, fusibility (water absorption) and fired body whiteness. For comparison purposes, two commercial Ukrainian samples were also characterised.

The results obtained show that there are clays in Türkiye with complementary characteristics that allow them to be used as plastic components in porcelain tile compositions. However, none of the clays alone can be considered as an alternative to Ukrainian clays. Thus, very different mineralogy composition gave rise to a wide range of particle size distributions, plasticity index, bulk density and fusibility, enabling clay mixtures to be formulated. For the design of mixtures, a simple methodology is proposed based on the definition of the trinomial of properties to be optimised, plasticity/fusibility/whiteness, and on the normalisation of the most common variation range of these properties. Using this methodology, two mixtures are proposed, one binary (with Afyon and Istanbul clays) and the other ternary (with the three Turkish clays), which, to a great extent, allow optimisation of the trinomial of properties and therefore, for their use as substitutes for Ukrainian clays in most porcelain tile compositions.

1 INTRODUCTION

The consumption of white plastic clay ("ball clay") from Ukraine has become very important in the ceramic tile industry in Europe, mainly in the manufacture of porcelain tile. The interest in Ukrainian clays lies in the appropriate combination of properties they possess, in particular the trinomial whiteness-plasticity-fusibility, which is difficult to find in ball clays from other sources [1]. These excellent technological properties are a result of their mineralogical composition and grain size distribution, with a high content in fine clay minerals (mainly kaolinitic in nature) and a reduced amount of iron oxide. Basically, two qualities are marketed with alumina contents of 23-24% and 27-28% [2], although there are many variants, which differ in plasticity and clay mineral content.

Until 2022, consumption of Ukrainian clays was estimated at over 3 Mt per year, destined for the main European ceramic tile producers, such as Italy and Spain. However, the conflict in Ukraine has led to an unexpected cut in supply. For this reason, the search for alternative clays to Ukrainian clay with high degrees of plasticity and whiteness has become an important issue for the tile industry.

In this respect, it should be noted that Türkiye has an abundance of natural resources and its mining industry is one of the sectors showing steady growth. The country is well known in the ceramic industry as supplier of high-quality raw materials such as sodium feldspar or boron compounds, however, it is less well known for its clay deposits. This paper therefore describes different types of clays that could be used in porcelain tiles.

One of these clays come from the Afyon region. This material appears around Alanyurt village, in Afyonkarahisar City. The Afyon clay is an ignimbrite type pyroclastic rock that is variously altered and in which there are basically 3 types of clay zones: 1- white-coloured zones: illitic parts, 2- beige and creamy levels: kaolinite-dominated parts, 3- green-pale or green zones: contain smectitic clays [3]. However, all the different zones of the Afyon clay cannot be operated separately, due to the complex alteration events.

Thus, supply companies usually operate all clay groups together, marketing them as a single product under the name Afyon clay.

Another area of interest occurs in the Şile region, near Istanbul. These are Oligo-Miocene age clays, on the Late Cretaceous volcanic rocks as well as the Palaeozoic sedimentary rocks, a deposition in lacustrine environment. In general, these are highly plastic clays, although with amounts of iron oxide that exceed what is desirable [4].

Finally, a third zone of interest corresponds to the region of Doğanhisar near Konya. These are Neogene age deposits, with deposition within the fault-controlled basin in front of the metamorphic basement. As recently reported by Genç et al [5], these are clays with illitic-kaolinitic clay minerals, although generally with low plasticity.

Figure 1 details the location of the three selected contributing regions for ball clays on the map of Türkiye. There are different studies on the origin and geological structure of these deposits and also works that have addressed, separately, the possible use of clays from these regions in different types of ceramic products, including porcelain tiles [6,7]. However, there is no work that has raised in a more ambitious way the possible substitution of clay from Ukraine by mixtures of clays from Türkiye, something undoubtedly motivated by the urgent need to find alternatives to Ukrainian clays.

As a result of the above, the present work has a multiple purpose. Firstly, a physico-chemical and technological characterisation of commercially available samples of clays of the three selected Turkish regions is performed by comparing these with standard Ukrainian clays. After this characterisation, a methodology is proposed, based on property normalisation for the trinomial formed by plasticity/fusibility/whiteness, with a view to replicating as far as possible the characteristics of Ukrainian clays. Finally, the validation of some designed clay mixtures for optimisation of the trinomial properties will be carried out.

Figure 1. *Localization of the three selected clay deposits in Türkiye*

2 EXPERIMENTAL

2.1 CLAY SAMPLES USED

Commercial samples of Afyon, Istanbul and Konya clays (hereafter referenced A, I and K respectively) supplied by the R&D department of the Çanakkale Seramik company were used. For the sake of comparison, two samples of commercial Ukrainian clays, referenced U-25 and U-30, were also supplied and used due to their alumina content of approximately 25% and 30%, respectively. Table 1 shows the chemical composition obtained by XRF. With regard to the mineralogical composition, the main phases identified by XRD for all clays are kaolinite and illite as the main clay minerals, together with other non-plastic compounds such as quartz and feldspar, in variable amounts. In the case of the Afyon clay, an illite-smectite interstratification was also identified.

Ref	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Other	LOI
U-25	60.6	25.5	1.3	0.8	0.2	0.5	0.2	2.0	-	8.9
U-30	55.1	30.4	1.5	0.7	0.3	0.6	0.4	2.1	0.2	8.7
A	78.1	12.8	0.3	0.8	0.8	0.1	0.2	3.7	0.2	3.0
I	54.6	28.6	1.4	2.5	0.1	0.6	-	2.1	0.5	9.6
K	68.8	20.2	1.2	0.7	-	0.3	0.7	2.8	0.4	4.9

Table 1. *Chemical composition of the Ukrainian and Turkish clay samples used (in wt%)*

2.2 TECHNOLOGICAL CHARACTERISATION OF THE CLAY SAMPLES

A technological characterisation was performed, consisting of the determination of the Atterberg plastic index by the indentation method [8], as well as the assessment of clay behaviour in pressing and firing. For that purpose, a clay sample was subjected to primary grinding in a hammer mill and subsequent secondary aqueous wet grinding in a ball mill for 10 min, determining the residue on a 63 µm sieve. The resulting suspension was dried, crumbled and conditioned for subsequent pressing by spraying water until a powder moisture content of about 5.5% was obtained. The conditioned powder was pressed at a pressure of 300 kg/cm^2 to obtain cylindrical specimens of 4 cm in diameter and around 5 mm thick. The specimens were then dried and their bulk density was determined by the Archimedes method.

To evaluate the firing behaviour, the dried specimens were subjected to a heat treatment in a laboratory electric kiln, simulating industrial firing cycles. The cycle thus consisted of rapid heating and cooling with a residence time at maximum temperature of 6 minutes, resulting in a total firing cycle of about 50 minutes. The maximum firing temperature tested was 1220 ºC, which is a temperature slightly higher than that used in the industry for porcelain tile firing.

Water absorption as an estimate of clay fusibility was obtained by a vacuum method similar to that described in ISO 10545-3:2018. The whiteness of the fired specimens was estimated from the chromatic coordinate of the CieLab system, L*, using a visible light spectrophotometer model Color-Eye 7000A by Gretag Macbeth.

Finally, the same determinations were carried out with Ukrainian clays samples U-25 and U-30 for comparison purposes.

3 RESULTS AND DISCUSSION

3.1 TECHNOLOGICAL CHARACTERISATION OF THE SELECTED SAMPLES

Figure 2 represents, in the form of histogram diagrams, the plasticity index (from Atterberg limits), the percentage of residue on a 63 µm sieve (from standard lab milling) and the dry bulk density of the pressed specimens (from standard lab pressing conditions).

As can be seen, all clays, except clay K, show high plasticity values in line with those exhibited by the Ukrainian clay samples (sample U-30 is somewhat more plastic due to its higher clay content). With the exception of clay A, these values correspond to the high clay mineral content of these samples, judging by the high alumina content, the low silica content and the appreciable loss on ignition shown by their chemical composition (see Table 1). However, the high plasticity for clay A does not correspond to its chemical composition with a remarkable amount of silica and reduced alumina content. This plasticity should be attributed, to a large extent, to the presence of clay minerals of the smectite group, which exhibit extremely high plasticity as indicated in the literature [9].

The residue on a 63 µm sieve lies within the typical values for ball clays with variable amounts of quartz, since, in general, this mineral does not exhibit an excessively large particle size so that it cannot be reduced during the standard laboratory milling process. However, again an anomaly is observed in the case of clay A, since the residue reaches a value of almost 23%, which is much higher than usual and would confirm that Afyon clay contains a large amount of quartz with quite a coarse particle size [10].

Finally, the figure representing the bulk density confirms, in general, that the highest values of bulk density correspond to the clay samples that have a higher amount of free quartz, as is the case of the Afyon and Konya clays.

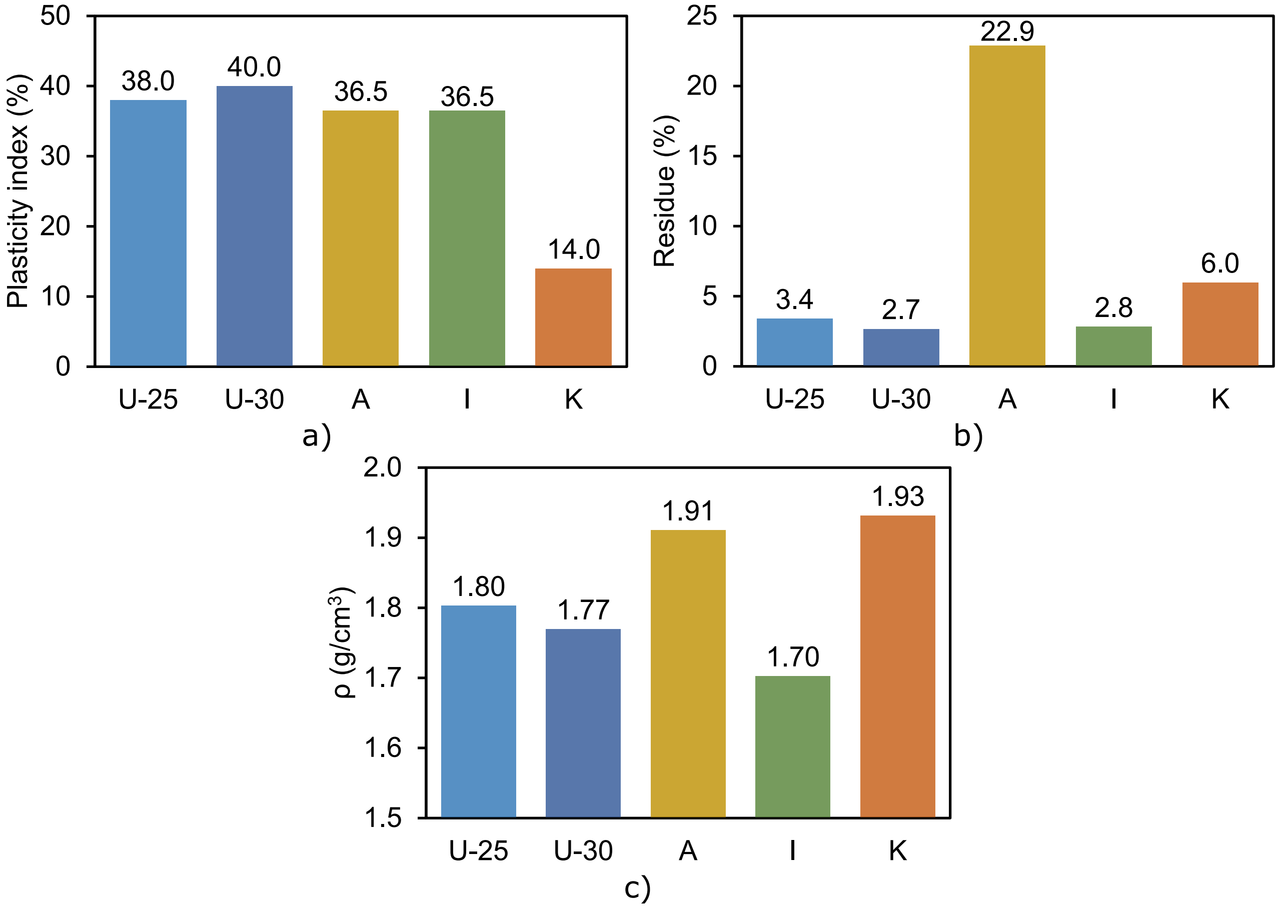

Figure 2. *a) Plasticity index, b) Residue at 63 μm sieve and c) Unfired bulk density (ρ) of pressed bodies made from the Ukrainian and Turkish clay samples*

In relation to the characteristics of the fired pieces, Figure 3 shows, also in the form of histograms, the water absorption and whiteness (chromatic coordinate L*) at a firing temperature of 1220 ºC.

In the case of water absorption, two groups of clays are clearly observed. On the one hand, the clays with a higher clay mineral content, of illitic-kaolinitic character, such as samples U-25, U-30 and I, show very low water absorption, close to zero. This is a result of the fusibility that the high presence of these minerals confers. They also have a relatively low free quartz content. On the other hand, in another category, there are clays with a higher amount of free quartz, such as A and K. Of these two clays, the high water absorption value of the Afyon clay stands out, which is not surprising, in view of its high amount of free quartz of coarse size.

Regarding whiteness, we would also obtain two groups, although different from the previous case. The first group would be made up of clays A and K with a low iron oxide content, which show whiteness values in line with those exhibited by the Ukrainian clays.

However, it should be noted that the high whiteness indexes presented by these clays have been obtained for considerably higher water absorption values (porosity) than those of the Ukrainian clays, so that the comparison is not entirely true. In any case, what is certain is the low contribution in iron oxide of these clays in a hypothetical composition of porcelain tile in which they could form part. On the contrary, as might be expected, the Istanbul clay shows a whiteness value very far from the group described above, because of the high amount of iron oxide in its composition (see Table 1).

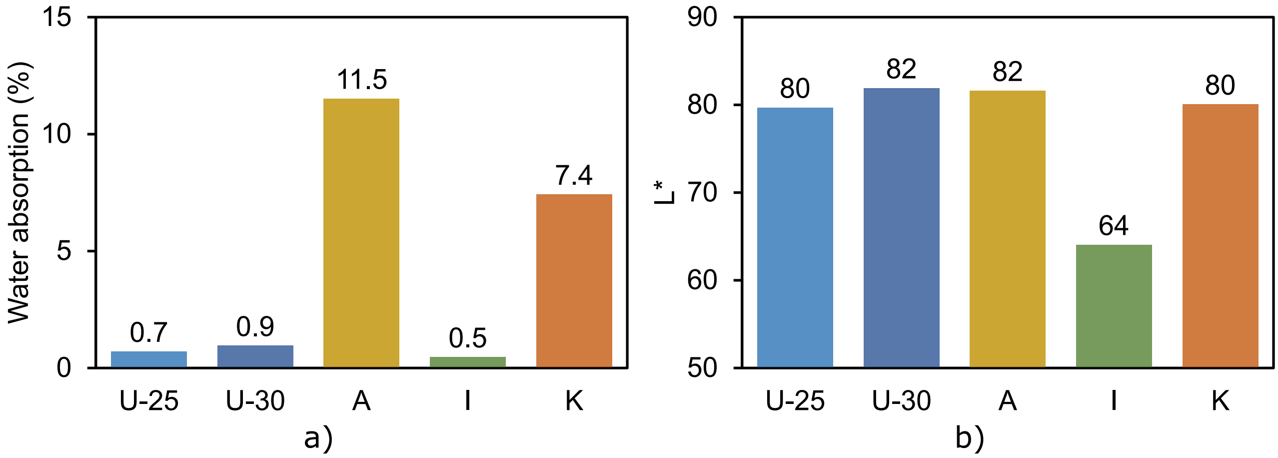

Figure 3. *a) Water absorption and b) Whiteness (chromatic coordinate L*) at 1220 ºC for the Ukrainian and Turkish clay samples*

3.2 COMPARISON WITH UKRAINIAN CLAYS BASED ON THE NORMALISATION OF THE TRINOMIAL OF PROPERTIES

As mentioned in the introduction, the success of Ukrainian clays in their application in porcelain tile compositions lies, apart from the economic aspect, in the excellent combination of what we could call the trinomial of properties: plasticity (P), fusibility (F) and whiteness (W). Based on the results described in the previous section, a simple methodology is proposed to evaluate how close or far a given clay may be from the optimum corresponding to this trinomial, as well as, in a second phase, the possible combinations between different clay samples that could allow this optimum to be approached. The methodology is based on the following two considerations:

1.- Defining the trinomial of properties that determine the quality of the clays and their suitability for use in the formulation of porcelain tile compositions. The properties to be optimised are plasticity (determined from the Atterberg limits), fusibility (estimated from water absorption at a temperature slightly higher than that of industrial practice, in this case 1220 ºC) and whiteness (determined from the chromatic coordinate L* at 1220 ºC).

2.- Normalising the trinomial of properties that allows a comparative value between clays to be established. This normalisation is performed based on experience, which allows assigning to each property a minimum and maximum value consistent with industrial practice. Thus, for plasticity, a value is assigned from a linear regression between 7% (minimum plasticity index value corresponding to a very low plastic clay) and 42% (maximum plasticity value for a highly plastic clay). For whiteness, a range is established between 55 (clay with poor whiteness) and 90 (very white clay).

For fusibility, these limits would be a water absorption of 14% (very low fusibility clay) and 0% (high fusibility clay). Table 2 shows the range (minimum and maximum values) used for the normalisation of the trinomial of properties.

Property	Parameter	Range
Plasticity (P)	Plasticity index (%)	7-42
Fusibility (F)	Water absorption (%)	0-14
Whiteness (W)	Chromatic coordinate, L*	55-90

Table 2. *Parameters and variation ranges for the normalisation of the property trinomial*

The graphical representation of the normalisation is shown in Figure 4, which greatly simplifies the comparison between the different clay samples. Thus, Istanbul clay shows high plasticity and fusibility but limited whiteness, Afyon clay is very plastic and white but not very fusible, while Konya clay stands out basically for its high whiteness. Ukrainian clays excel in all three properties, with higher whiteness for U-30 clay relative to U-25 clay. Thus, it can be clearly observed, as well as being obvious, that none of the three clays individually meet the combination of the trinomial of properties that would allow approach of the optimum represented by any of the Ukrainian clay samples. The same results show the excellent combination of the trinomial of properties for the Ukrainian clay samples.

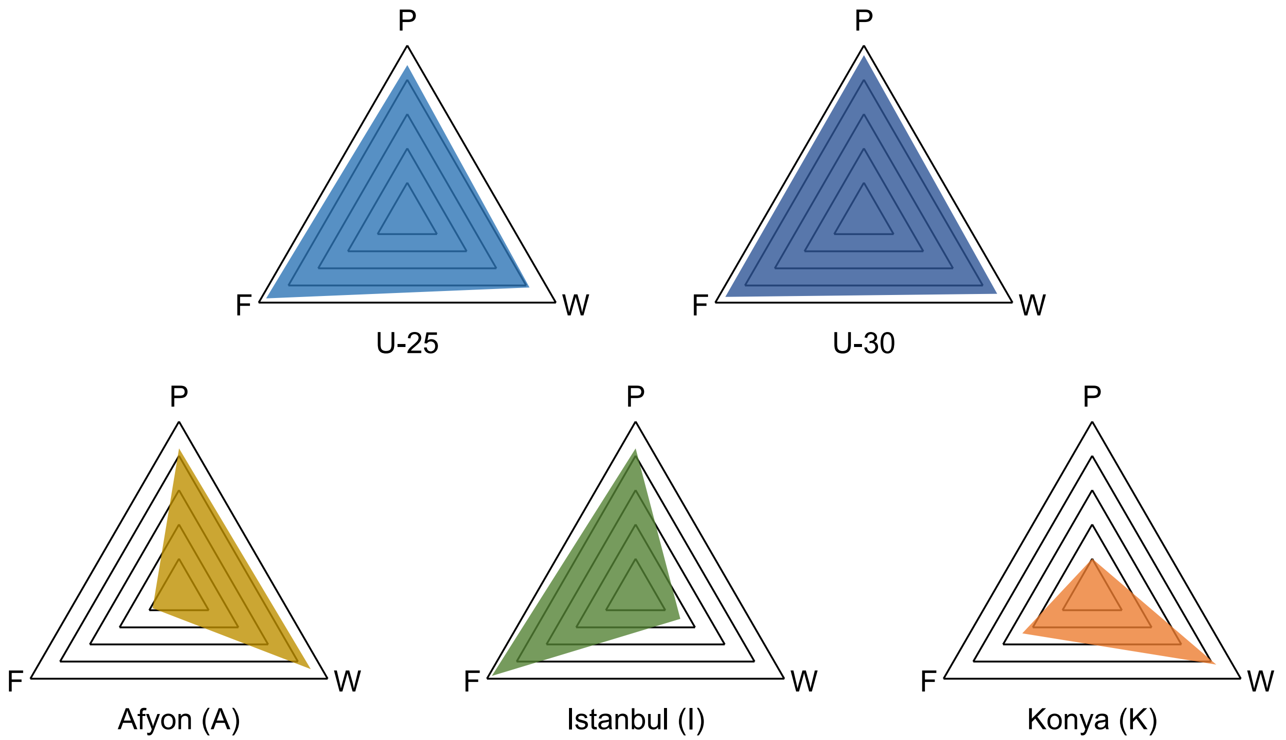

Figure 4. *Visualisation of the properties of clays, in comparison with Ukrainian clays, based on the normalisation of the trinomial of properties*

3.3 CLAY MIXTURE DESIGN FOR OPTIMISATION OF THE TRINOMIAL OF PROPERTIES

The above methodology allows, in a simple way, clay mixtures to be designed with the aim of optimising the properties, while approaching the optimum represented by the Ukrainian clays. The premise applied is that the mixture properties are additive, based on the properties of each individual clay, without there being any interactions, which translates into the following equation:

$$P_m = \sum_{i=1}^{n} (x_i \cdot P_i)$$

where:

P_m: estimated property for the mixture

x_i: mass fraction of each clay in the mixture

P_i: property for each individual clay

As optimisation criteria for the mixtures, a minimum plasticity index of 30% and a L* value of at least 75 as whiteness are established, allowing fusibility to be free since this property can be easily corrected by small adjustments in the formulation, such as the introduction of feldspars or other fluxing materials. Under these premises, Table 3 shows the optimum percentage of each clay in the final mixture. These percentages ensure the minimum plasticity and whiteness established and the highest fusibility in accordance with the normalisation. A binary combination, with clays A and I, and a ternary combination, with the three Turkish clays, are proposed.

Clay	Binary mix (%)	Ternary mix (%)
Afyon (A)	62	36
Istanbul (I)	38	35
Konya (K)	-	29

Table 3. *Design of binary and ternary mixtures from the clays studied for the optimisation of the property trinomial*

The mixtures detailed in Table 2 were processed in accordance with the procedure described for the individual clays and the parameters involved in the trinomial of properties were determined in the same way as for the clays. Figure 5 shows the estimated representation for the properties of the optimised mixtures (dashed line) together with the experimental representation obtained from their preparation and characterisation (coloured area). The figure shows the good correlation between the estimates and the experimental results, validating the methodology followed in the design of mixtures. Moreover, it is observed that both the binary mixture and, above all, the ternary mixture allow considerable improvement in the trinomial of properties to be obtained, which, although it does not reach the optimum values of the Ukrainian clays, could be considered a good alternative for a large part of the products currently manufactured from porcelain tile compositions.

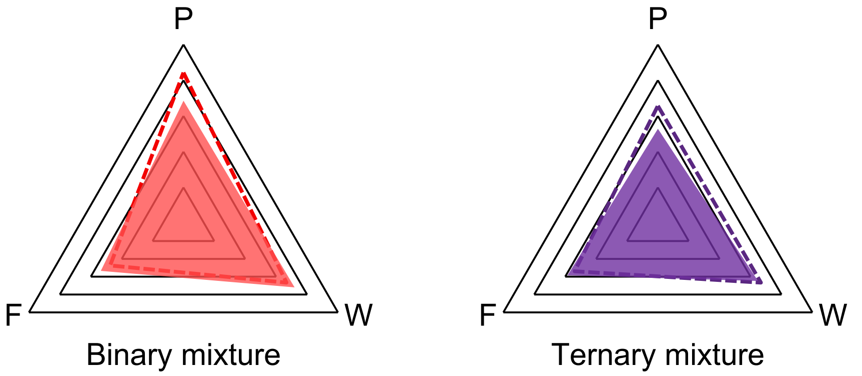

Figure 5. *Comparison between the estimation of the trinomial of properties from the mixture design (in dashed line) and the experimental values obtained with the mixtures (in solid colour)*

4 CONCLUSIONS

In this work, three areas in Türkiye with commercial availability of ball clays have been selected to be used in porcelain tile compositions, replacing Ukrainian clays. Specifically, the selected areas were Afyon, Istanbul and Konya. A technological characterisation has been carried out with a view to analysing their potential use in porcelain tile compositions, for which plasticity, milling residue, pressing compaction, fusibility and whiteness have been determined. The characterisation has been compared with two commercial samples of Ukrainian clay with different alumina content.

For a better comparison with the Ukrainian clays, a simple methodology has been proposed based on the normalisation of the most common range of variability of what could be called the trinomial of properties: plasticity, fusibility and whiteness. From this normalisation, it has been possible to verify, as the results of the technological characterisation had already anticipated, that none of the clays separately could work as an alternative to the Ukrainian clay. However, the great variability presented by the samples of the three clays regarding the different properties makes it possible to mix them. Based on the proposed methodology, two mixtures have been designed, a binary mixture (with Afyon and Istanbul clays) and a ternary mixture (with the three Turkish clays), which have been confirmed and validated at an experimental level to be a good alternative to Ukrainian clays for many of the current porcelain tile products.

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