DEVELOPMENT OF MATT FLOOR TILE GLAZES WITH IMPROVED COLOUR PERCEPTION BY TAILORED CRYSTALLIZATION

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ABSTRACT

This study aims to investigate the correlation between digital colour performance and crystal phases formed in the matt glaze developed for porcelain tile. In addition to the standard glaze composition, seven different glaze compositions were designed and analysed. The colour perception was evaluated from the spectrophotometer and i1 profiler. The gamut volume was calculated by 2D CIE chromaticity diagrams of the ICC profiles. It was observed that the colour gamut volume increased with the formation of zircon crystal phase, while diopside phase formation decreased colour gamut volume and thus colour perception. The increasing anorthoclase phase with the addition of zinc oxide reduced the lightness of all colours and resulted in the darkest black colour.

1. INTRODUCTION

Ceramic materials are often chosen for their physical and chemical advantages, along with their aesthetic appeal, making them a sought-after option [1]. Economic, environmental, and aesthetic factors play a crucial role in the evolution of ceramic tile decoration techniques, resulting in significant recent changes. It's imperative to seamlessly adapt processes while upholding product quality standards, given the rapid technological advancements. Presently, the ceramic coating industry embraces state-of-the-art digital printing methods for pattern transfer [2-3]. A notable feature of these digital printing systems is ink composition, which consists of pigments and solvent solutions processed at a nano scale. Inks used in inkjet decoration are mostly pigment suspensions consisting of inorganic and complex metal oxides [4]. The use of pigment inks stands as the most effective solution for enhancing colour vibrancy and reproducibility on ceramic surfaces. The swift proliferation of inkjet technology can be attributed to its contactless decoration methods, enabling the printing of textured surfaces and high-resolution images, while also enhancing project management efficiency and reducing costs. With this method of production, it is easier and faster to switch to different products than with other decoration methods: it is possible to obtain all colours with only CMYK inks, less ink waste is formed and the need for less variety of ink is preferred because of its advantages. Consequently, digital printers have elevated inkjet printing to the forefront of ceramic tile decoration technology [4-10].

To profile a CMYK tile glaze coating, a test target designed and arranged in CMYK coordinate space is first printed on the tile surface. This target is used to create an ICC Profile, and the target printed on the tile surface is measured in CIELAB colour space and digitally matched to the specified colours. By measuring these graphs, it is possible to determine the colour gamut of a tile glaze coating, or we can use software to determine the colour gamut volume using an ICC profile [11-12]. Colour gamut matching plays an integral and important role in preventing colour casts caused by process variations in tile production [13]. For this reason, ongoing work is focused on improving gamut matching algorithms. Although it may seem that the wider the gamut, the more colours can be printed, gamuts of the same size are not always equal. One device may excel in reds, while another may perform better in blues. As a result, sometimes the same size gamut can produce very different results [14]. Traditionally, the way to visualize the gamut of a device is to outline it on a 2D xy chromaticity diagram [15]. However, the recent literature trend shows that image-dependent gamut mapping gives the best results [16]. Nevertheless, achieving acceptable print results requires pre-tuning the systems used and processing the image before printing, which necessitates calibrating each component. It is also crucial to create a profile to appropriately limit ink usage [15]. Excess ink use can lead to various problems, such as dot blurring and longer drying times, as well as higher costs [17].

Despite extensive recent research on digital inks, limited information is available on the glaze adaptations required for digital printing [18]. In this study, the effect of the raw materials of eight compositions was investigated to understand their influence on colour gamut volume and digital printing quality.

2. EXPERIMENTAL PROCEDURE

Industrial grade kaolin (Kaolin, Bulgaria), wollastonite, dolomite, potassium feldspar, nepheline, and Na-feldspar (Straton, Türkiye), one commercial matt frit (containing zinc oxide and barium oxide) were used to produce matt glaze. The contents of the raw materials used in the preparation of glaze recipes are given in Table I. A floor tile matt glaze composition containing 35% matt frit was taken as the standard (STD) composition and new compositions were created by changing the ratios of the raw materials in the glaze. Glaze compositions and the Seger amount of matt frit used in the glaze recipe are given in Tables II and Tables III. Eight different matt glaze compositions were batched and arranged in a porcelain jar containing alumina balls. The total weight of the compositions prepared was weighed as 300 grams. The compositions were wet milled for 30 minutes. Matt glaze slurries were milled until a sieve residue of 45 µm was achieved between 1% and 1.5% for good sinterability. The density of the slurries was adjusted to 1650 g/cm^3 and 160 grams of glaze were applied to the floor tiles of 45x45 cm with a spray gun. The tile samples were dried at 200 °C for 10 min. in a laboratory-type drier.

	SiO_2	Al_2O_3	CaO	MgO	ZrO	K_2O	Na_2O	TiO_2	ZnO	BaO	LOI
Kaolin	52.4	32.6	0.15	0.22	0.00	1.09	0.22	0.19	0.00	0.00	13.2
Clay	51.8	26.6	0.27	0.00	0.00	1.49	0.15	1.17	0.00	0.00	18.4
Na-feldspar	70.3	17.5	0.88	0.00	0.00	0.00	10.9	0.00	0.00	0.00	0.41
Wollastonite	46.3	0.10	51.9	1.12	0.00	0.00	0.00	0.00	0.00	0.00	0.58
Dolomite	0.19	0.11	37.9	15.3	0.00	0.00	0.00	0.00	0.00	0.00	46.5
K-Feldspar	67.5	17.2	0.40	0.00	0.00	12.3	2.40	0.00	0.00	0.00	0.20
Nepheline	60.8	22.4	0.30	0.00	0.00	4.90	11.5	0.00	0.00	0.00	0.10
Zircon Silicate	30.7	3.00	0.00	0.00	62.6	0.00	0.24	0.00	0.00	0.00	3.46
Zinc Oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	99.7	0.00	0.30
Barium Carb.	0.00	0.00	0.00	0.00	0.00	0.00	0.30	0.00	0.00	76.9	22.8

Table I. *Oxide (wt.%) content for raw materials*

Acidic Oxide	Stabilizer	Basic Oxide				
SiO_2	Al_2O_3	K_2O	Na_2O	CaO	ZnO	BaO
1.80	0.43	0.11	0.04	0.39	0.36	0.10

Table II. *Seger oxide mole matt frit*

	STD	NA	AN	PA	AP	ZR	ZN	BC
Matt Frit	35	35	35	35	35	30	30	30
Wollastonite	10	10	10	10	10	10	10	10
Dolomite	10	10	10	10	10	10	10	10
Na-feldspar	10	0	20	0	20	10	10	10
K-feldspar	10	10	10	20	0	10	10	10
Nepheline	10	20	0	10	10	10	10	10
Kaolin	10	10	10	10	10	10	10	10
Clay	5	5	5	5	5	5	5	5
Zircon Silicate	0	0	0	0	0	5	0	0
Zinc Oxide	0	0	0	0	0	0	5	0
Barium Carbonate	0	0	0	0	0	0	0	5

Table III. *Glaze compositions (wt.%)*

The gamut scale was printed on the sample tiles by using a plotter (Kerajet). After drying the tile samples were fired in an industrial fast-firing kiln at 1190 °C for 45 min. The powder glaze was used to form cylinder tablets by a laboratory type press with a die size of 4 cm in diameter, 0.6 cm thick, fired in the same firing regime to perform XRD analyses. The colour values of the gamut scales on the tile surface were determined with i1 profiles and the data were transferred to the computer.

Colorimetric values: lightness (L*), redness (a*) and yellowness (b*) based on the CIELAB standard were determined by a spectrophotometer (Konica Minolta, CM 600d). Colour difference (ΔE) can be calculated according to the equation below [19].

$$\Delta E=[(\Delta L^2) + (\Delta a^2) + (\Delta b^2)]^{1/2}$$

The gamut volumes, which are unitless values, were determined using the Colour Think Pro 3.0.3 program to analyse the obtained data. Profiles were made using the Photoshop program from the data obtained from the gamut scales and a preview of the prints was created with these profiles. X-ray diffraction (XRD) analysis with CuKα radiation, scanning range (2θ) of 10°–70° (D8 Eco, Bruker), was performed on pelleted powders.

3. RESULT AND DISCUSSION

The XRD analysis performed on the matt glaze samples in Figure 1 shows the crystal structures of porcelain tile matt samples. The Zircon phase occurs in ZR and the other glazes do not contain this phase. The lowest albite amount is in BC and the highest albite phase is in AP. The cristobalite phase peak is highest at PA. While the orthoclase phase peak is highest in BC, it is not seen in AP, ZR, and ZN. The quartz peak, which is higher in AN, is lower in AP, ZN and BC. The anorthoclase phase peak is lowest in BC and highest in ZN. The Akermanite phase is lowest in ZR and highest in BC. The diopside phase peak is lowest in ZR and highest in AN.

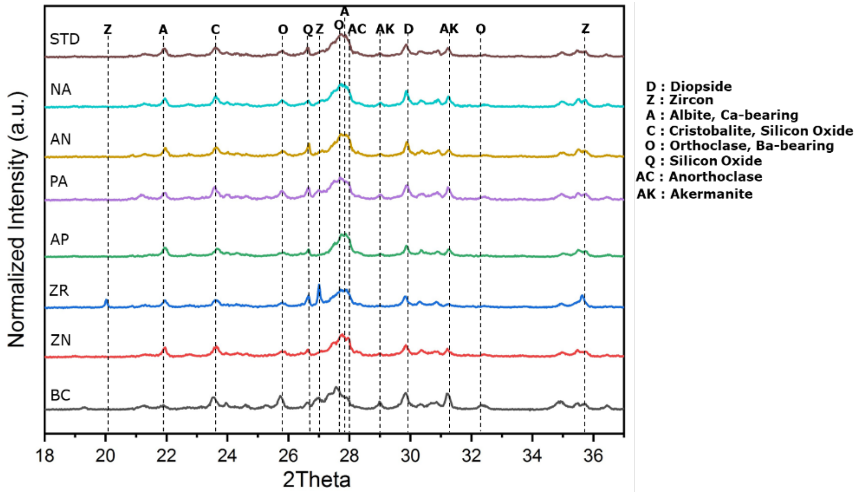

Figure 1. *XRD patterns of investigated porcelain tile matt samples*

The L* a* b* colour values of the CMYK colours printed on the tile were measured and are shown in Figure 2. When the blue colour is examined, the ZR composition has the highest b* and a* value. The AP composition has the lowest b* and a* value for the blue colour. When the magenta colour is examined, all compositions are close to each other in general. When the a* value for the magenta colour is examined, the ZR composition has the highest a* value and the AP composition has the lowest a* value. It is seen that the AP composition is more bluish than the other compositions in the magenta colour. When the b* value for the yellow colour is examined, the ZR composition has the highest b* value and the NA composition has the lowest b* colour value. When L* values for the black colour are examined, the ZN composition has the darkest colour perception and the highest a* value. The AP composition, whose a* and b* values are closest to zero, has the lowest L* value.

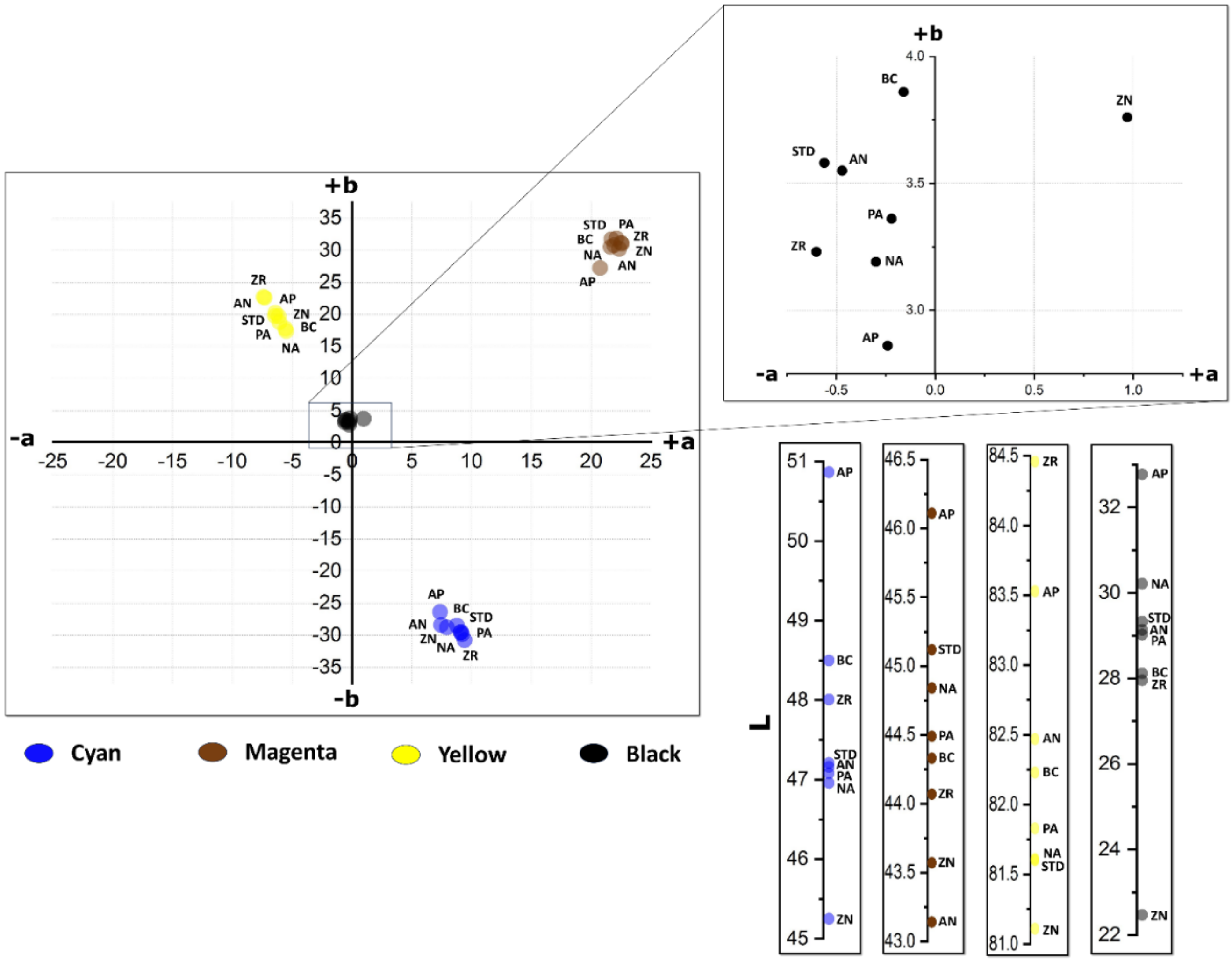

Figure 2. *Colour values of porcelain tile matt surface compositions*

Colour gamut volume data obtained from the tile surface is given in Figure 3. The gamut volume of ZR is 12123 and NA has the lowest volume with 8022. ZR has the biggest gamut volume amongst all the samples and is 24.4% larger than the STD composition. BC and ZN exhibit slightly lower gamut volumes compared to STD. With the use of albite instead of nepheline in AN, the gamut volume increased by 21.7%. When albite is used instead of potassium feldspar in AP, the gamut volume decreased by 11%.

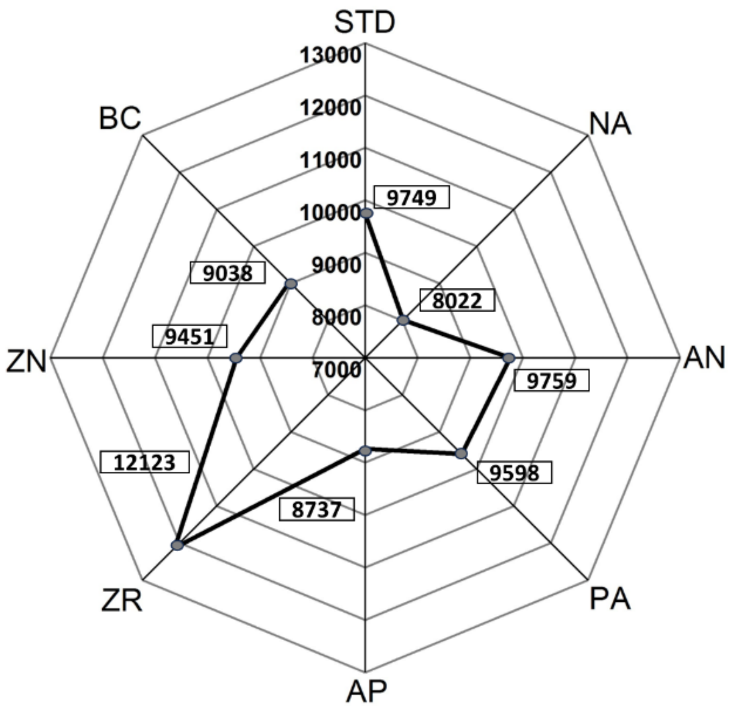

Figure 3. *Colour gamut values of porcelain tile matt surface compositions*

The graphical visuals of the colour gamut volumes compared with STD are given in Figure 4. All gamut volume graphs show a similar pattern. ZR shows an expansion in the yellow and blue areas compared to STD. ZN has a lower lightness value. PA shows more expansion in the green area. There is no growth in different areas in AN.

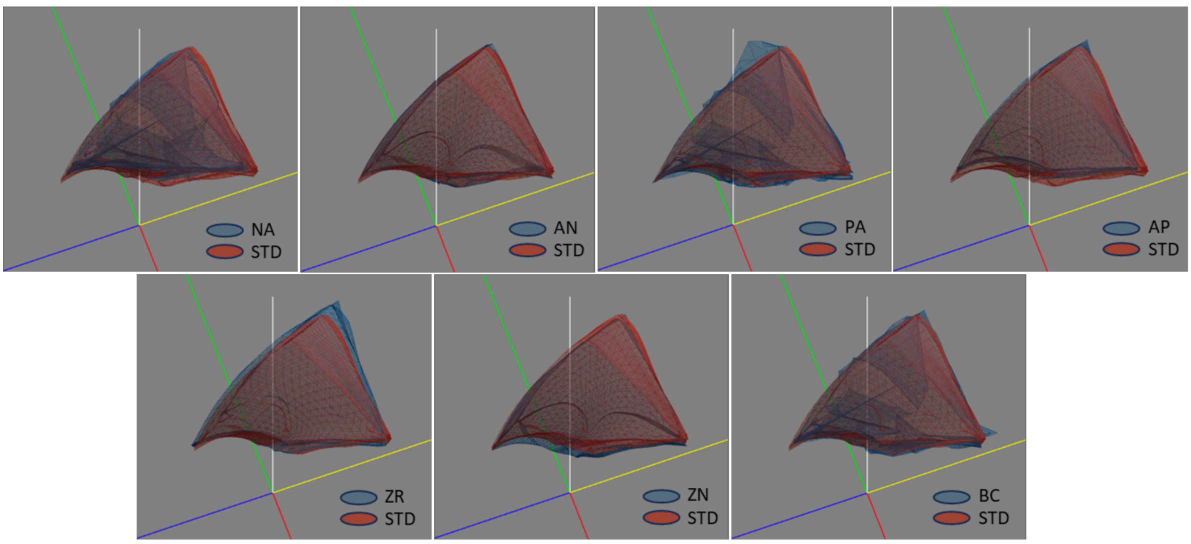

Figure 4. *Colour gamut values of porcelain tile matt surface compositions*

The same image converted with ICC profiles, made with the i1 profiler for all compositions, is given in Figure 5. The image appearance on the ZR composition is deeper, clearer and sharper. The colour saturation in recipe AN is weaker than in the other compositions.

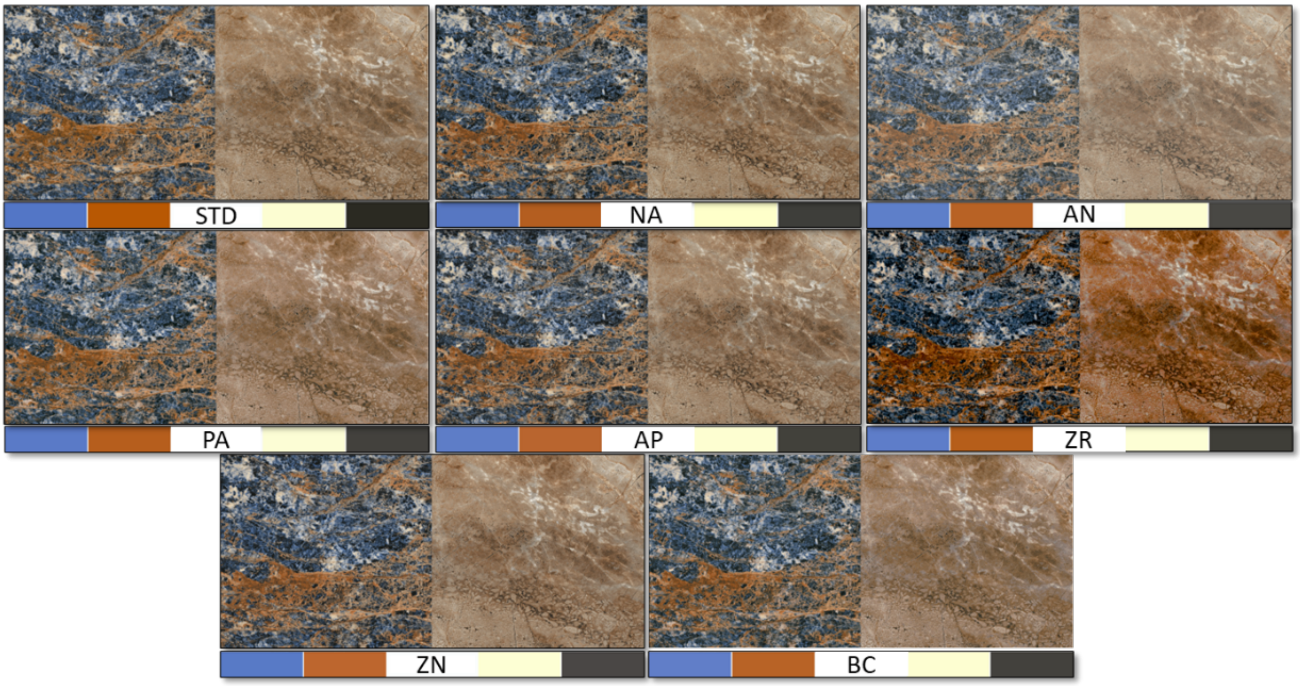

Figure 5. *Designs obtained from profile files*

4. CONCLUSION

It was observed that raw material changes in glaze recipes affected the colour values on the printing surface. The study showed that the gamut volume of the standard recipe decreased and increased depending on the raw material changes.

- The zircon phase increases the saturation of cyan, yellow and magenta colours and expands the colour gamut volume.
- With the addition of barium carbonate, the orthoclase and akermanite phases increased and the albite phase decreased.
- Due to the increase in the albite phase, the a* value of cyan and magenta colours decreased and the L* value increased.
- The increasing anorthoclase phase with the addition of zinc oxide reduced the lightness of all colours and resulted in the darkest black colour.
- By using albite instead of nepheline, there is an increase in the diopside phase and this reduces the gamut volume.

Thanks to the improvements in floor tile mat glaze recipes, it was learned that glazes with better colour perception can be made.

5. REFERENCES

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