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RESEARCH ARTICLE

DETECTION AND CHARACTERIZATION OF SOME GLAZE FAULTS ENCOUNTERED IN SANITARYWARES

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ABSTRACT

The use of suitable glaze compositions, which enable ceramic sanitaryware (such as sink, toilet bowl, toilet bowl, etc.) to have better hygienic, aesthetic and technical properties, is of great importance as in other ceramic products. Glaze compositions, which provide durability to sanitaryware materials, reduce impact resistance and give ceramic material a hygienic appearance, are produced as ~97% white color depending on the preferences of the consumers, therefore, surface defects attract more attention in glazing and post-glazing process applications. When faults occurred during the different stages of manufacture detected on the final product, failure to detect faults on the final product by passing many production stages poses a problem in terms of intervention in the process. Faults that occur during glaze preparation are important in terms of cost. Since it is a stage in which many economic evaluations have been made in production, eliminating the faults caused from glaze preparation prevents further financial loss.

In this study, the appearance of the faults in the sanitaryware items and the change in their regions (occured as a result of the oils contaminations from the machinery and components used in the preparation of glaze, the pipes of the tanks used in the glaze transport tanks and the glaze transfer or the impurities contaminated from the environment, the splashing of the impurities by the colored glazes in the glazing cabinets etc.) were characterized by means of SEM (Scanning Electron Microscopy), XRF (X-ray fluorescence spectrometry), XRD (X-Ray Diffractometry) and color measurement (L a* b*) analyses. According to the data derived from the final defected products, the faulty products were imitated by using the same components and methods on the plates under the laboratory conditions. Finally, the solutions for the problems were determined on the basis of faulty products obtained in the laboratory.

Keywords: *Glaze Faults, Sanitaryware, Characterization*

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1. INTRODUCTION

The glaze covering the surfaces of ceramic products is among the main elements of ceramic production in terms of its visual effect on ceramic products, as well as in terms of protecting the product and ensuring its use for many years [1,2]. Moreover, since it is easy to clean and comes into contact with water, glaze becomes a more important production step in vitrified products with low water absorption (<1%) [2,3]. When the studies on sanitaryware production are examined in the literature, considering the problems experienced in the sector due to raw material supply, it is important to make seger calculations of different regional raw materials, to add them to the recipe or to reduce the ratio of high-cost raw materials in the recipe and to substitute alternative raw materials [4,5]. In addition, the precursor materials used in the glaze composition affect sintering temperature, microstructure, crystal development, energy costs, gas emissions and ultimately the effects on the final product properties [6,7]. However, the problems encountered in daily production in the factories currently working in the sector are solved by the R&D units, but these data remain individually within the industry. This study, unlike the literature, aims to create original and sectoral data in that it includes the examination of the problems encountered in production at the laboratory scale. As seen in Figure 1, since the sanitaryware products coming out of the kiln are large in size and the number of production is less than other ceramic products (such as porcelain, tile, etc.); therefore, the cost of the faults occurring in their production is relatively higher. Especially, it is more difficult to repair for the faults taking place in the products after firing, and this fault rate makes it as a waste product, because it disrupts the aesthetic and/or structure in use [8].

Figure 1. Kiln outlets of vitrified products [4].

In 2020, it is reported that in Italy, one of the important prominent ceramics manufacturers, the work done to reduce the costs by reducing the mass of the products produced in the industry has still not reached an adequate level [8,9]. The glaze, which is the most important factor in ensuring hygiene in such costly products, becomes even more important. While glazes are produced primarily from SiO_2, alkali metal oxides (Na_2O, K_2O, etc.), stabilizer alkaline earth metal oxides (CaO, BaO, MgO etc.), zircon silicate, opacifiers such as zircon oxide and crystallizing raw materials such as ZnO; it is a production stage where parameters such as compatibility with the body, melting and surface expansion are important [10]. When the ceramic defects occurring after glaze firing are examined, they can be grouped mainly under general headings such as cracking, pinholes, color changes, deformation, consolidation, pits or bumpy surfaces, spalling, etc. [11,12]. However, it has stages that cannot be produced by machine due to its very intricate and large size. This increases the manual processes in sanitaryware, and even requires manual touches in machine-made processes. These processes let the occurrence of pollution caused by external factors apart from general faults. Examples of some vitrified products are given in Figure 2.

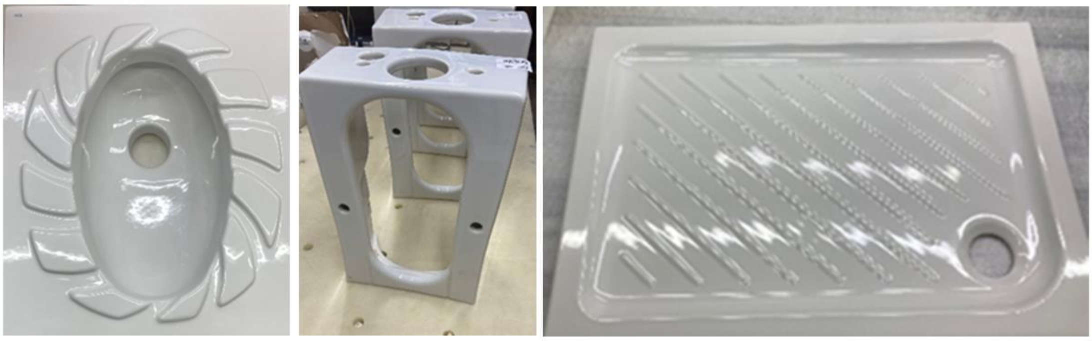

Figure 2. Some vitrified products.

In the study, after the detection of defects, which are generally included in the concept of pollution, but whose exact cause is unknown, these faults are imitated on a laboratory basis and the stages that need to be controlled in production in this direction are examined. The data obtained through the study are an addition to the main glaze, raw materials, precursors and energy etc. problems studies in the literatüre also it will contribute to production problems in terms of solution methods in industry.

2. METHOD

In the study, slip and glaze of the product called as vitreous china (VC), which is used in production in Isvea Sanitaryware factories, was used. The sources of faults in production line have been identified. The faulted samples obtained by applying them on specimen of 10x10 cm under the laboratory conditions were characterized. Scanning electron microscope (SEM) and chemical composition analyses (EDX) images were obtained with Zeiss Supra 50VP Brand device. The faults detected at this stage are classified as follows.

2.1. Faults Originated From Glaze Preparation

2.1.1. Tank pipe end

In order for the glaze suspension prepared in glaze preparation to be used in the process, it must be transported via tanks [3]. Although the inner parts of the tanks are made of plastic material, metallic pipes made of chrome-plated steel materials are generally used to transfer the glaze to the robot or

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glazing cabinets. The inner parts of these pipes are caused by the friction of the glaze suspension, the upper parts are worn by the removal and installation of the clamps, and the abraded metallic particles mix into the glaze and cause staining on the glaze. The tank pipe end and its stain fault are given in Figure 3.

A B

Figure 3. Tank pipe end (A) and faults due to tank pipe end (B).

2.1.2. Glaze preparation mixers

There are mixers used in glaze preparation and mixing glazes. These mixers are generally used in rheological adjustments of glaze suspension. Meanwhile, dried machine oil contaminations in the chain and bearing parts of these mixers, which have up and down moving parts, mix into the glaze. The glaze preparation mixer and its stain defects are given in Figure 4.

(A) (B)

Figure 4. Faults caused by glaze mixers (A) and glaze preparation mixer (B).

2.1.3. Colored glaze splashing

In the recent years, many colored sanitaryware products have been manufactured by ceramic companies. Although these production rates do not usually exceed 2%, there are some production difficulties in manufacturing them. In cases where the colored glaze needs to be changed, the system is completely washed with water. However, if the washing is not done properly, the glazes of different colors remaining in the system smear on the other colors and cause staining defects. Colored glaze splash stain defects is given in Figure 5.

Figure 5. Faults due to splash of colored glaze.

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2.1.4. Funnel for raw material addition

The raw materials that make up the glaze suspension are loaded into the mill from the weighing silo. Such faults can be prevented by using automatic systems while dosing to the mill. However, some glaze suspensions cannot be made with an automatic system in line with glaze consumption. The reason for this is that the glaze suspension cannot be passed through the system as tonnage or some raw materials that are not in the system are thrown manually. Some raw materials, which are proportionally less in glaze suspensions, are dosed manually. The raw material funnel, which is placed in the mouth of the mill when the workers do the dosing manually, is a metallic material made throughout the enterprise. Abrasions occur over time due to the contact of the metallic material with the raw materials, and these worn parts cause stain defects. The raw material chamber (funnel) and its stains faults are given in Figure 6.

Figure 6. Hopper for raw material addition.

2.1.5. Glaze preparation ceiling, glazing ceiling coating materials

Insulations are made in some places so that the production units are less affected by the weather conditions in summer and winter months. The materials from which these insulations are made are porous materials such as rock wool. Ceramic powders in the process can also accumulate in such porous materials and cause stains such as spilling after a long time. In addition, when the ceilings are not properly insulated or when cleaning is done on an upper floor, the water leaking from the gaps between the metal plates or the concrete flooring causes the metal parts to rust and the paint on the metal to spill. The images of the rust defects caused by the ceiling coating material of the glaze preparation line and glazing and the moisture on the ceiling are given in Figure 7.

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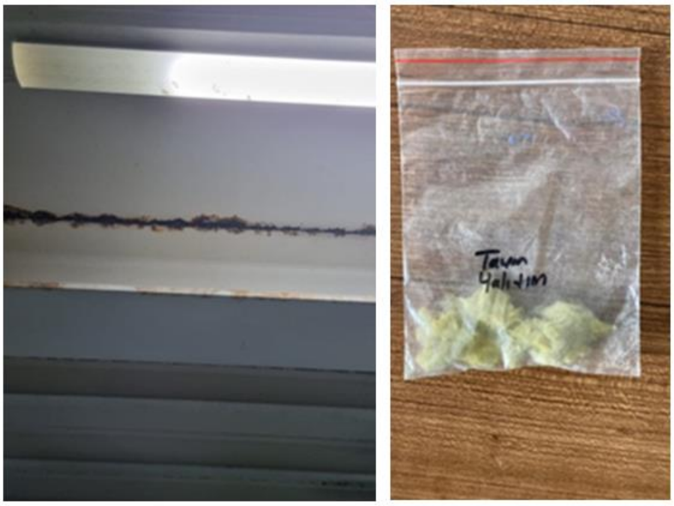

A B

Figure 7. Ceiling of glaze preparation (A) and defects originated from glaze ceiling coating materials (B).

3. RESULTS AND DISCUSSION

3.1. SEM/EDX Analysis of Tank Pipe End Faults

The pipes of the tanks are made of metallic materials. Since these materials are iron in their content, it is seen that there are iron stains when these materials are worn. When SEM analyses are examined, it is observed that a layered structure is formed in a hollow form in the region of iron stains. As seen in Figures 8 and 9, Fe^{+2} in the structure causes a regional deterioration by damaging the area around it as a result of melting with heat, as well as the place where it is poured. The iron region formed in the crystal phase disrupts the crystal formation in the structure. In the regional SEM analyses, it was determined that there are Fe_2O_3 phases on the crystal structure.

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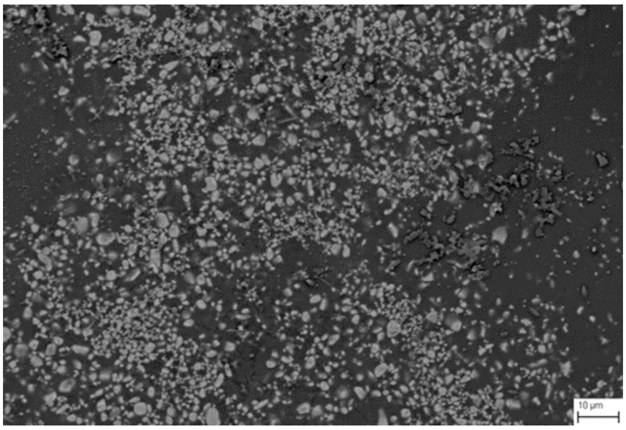

Figure 8. SEM image of the faults caused by the end of the glaze tank pipe.

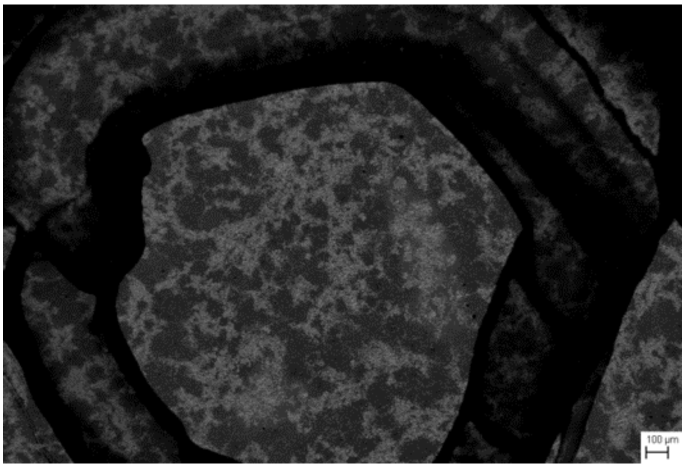

Figure 9. Sem image of iron phase fault caused by glaze tank pipe end defect.

According to the EDX analyses, the values in the Fe_2O_3 are compatible the SEM analyses (Table 1). The zircon-based calcium alumina silicate structure, which forms the basic structure of the glaze, defines the formation of the glaze in all EDX studies. Apart from this, it is seen that the pieces that can break off from the pipe end are simulated in the experimental studies where the Fe_2O_3 ratio is relatively high. These defects cause brown iron stains after firing [11,13].

Table 1. The results of the SEM/ EDX analysis for Glaze Tank pipe end defects.

	MgO	**Al_2O_3**	**CaO**	**Fe_2O_3**	**SiO_2**	**Na_2O**	**ZrO_2**	**Total**
1	2.87	8.96	14.93	10.83	57.71	4.69	0	99.99
2	0	5.01	4.87	3.83	41.2	2.68	42.41	100

3	0	4.84	7.37	6.42	41.24	3.14	36.98	99.99
4	1.26	5.46	6.75	7.72	44.9	3.02	30.89	100
5	2.08	7.37	6.64	0	55.74	2.31	25.86	100

3.2. SEM / EDX Analysis of Glaze Preparation Mixers Based Faults

Since the need for production is continuous, glaze preparation tanks are changed frequently depending on the product manufactured. Glaze tanks, which are changed due to rheological changes, are mixed in production mixers after adding binders. In the meantime, impurities are mixed with the structure, and the staining that occurs as a result of this, as it is organic based, removes many components from the structure at ~450°C, thus causing black or dark staining in the structure. Although the mixer ends are made of chrome-plated steel material, the hard particles in the glaze (such as quartz and alumina, etc.) break the coating on the mixer blades and cause such staining. As seen in Figures 10 and 11, the particles are disseminated in the whole sample [14].

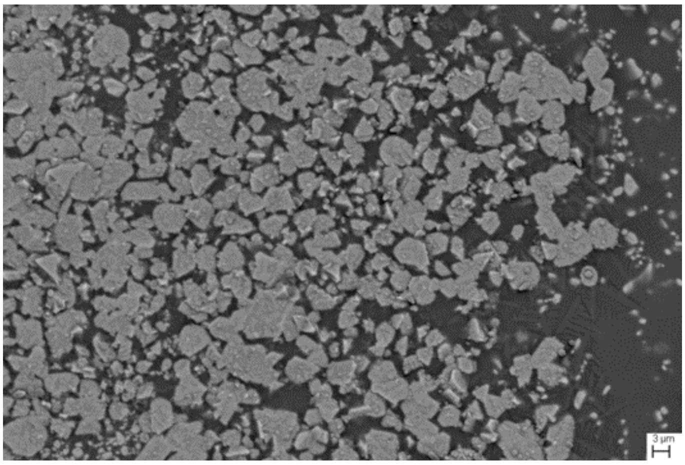

Figure 10. SEM image of the faults caused by the glaze mixer.

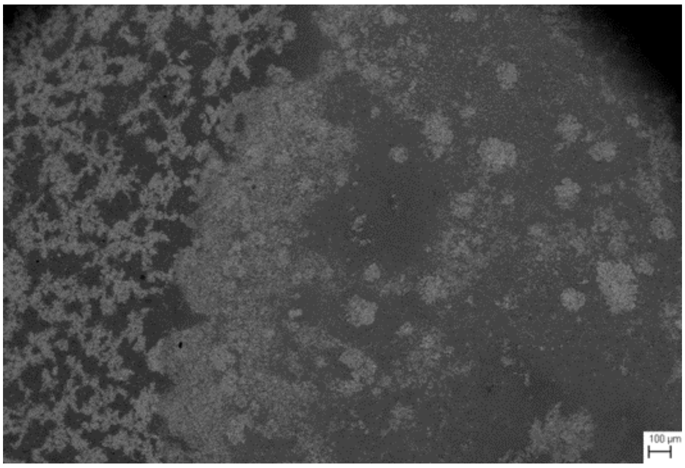

Figure 11. SEM image of the faults caused by the glaze mixer.

As seen in the EDX analysis in Table 2, the stains transmitted from the bearing in the glaze preparation mixers are mainly chromium and iron content. Particularly iron-bearing particles were found. It is seen that the defect color is black and brown. As seen in Table 2, these rates increase due to the thinness of the chrome plating and the fact that the material at the bottom of the chromium plating consists of ferrous metallics.

Table 2. Sem/edx results of defects originating from glaze mixers.

	MgO	**Al_2O_3**	**CaO**	**Cr_2O_3**	**Fe_2O_3**	**ZnO**	**SiO_2**	**NiO**	**Na_2O**	**ZrO_2**	**Total**
1	8.04	4.12	0.95	1.58	64.29	21.03	0	0	0	0	100.01
2	12.36	6.9	3.21	1.42	50.01	17.44	8.65	0	0	0	99.99
3	7.07	0	0	1.53	66.47	24.2	0	0.73	0	0	100
4	1.68	6.35	8.54	0	4.36	1.88	46.16	0	2.78	28.25	100
5	0.86	7.85	5.47	0	0	1.38	59.89	0	4.11	20.44	100

3.3 SEM/EDX Analysis of Color Glaze based Splashes

Glaze spatter formation is the faults that may occur due to not washing the pumps used in the transfer of glazes in the process to the airbrush (pistole). Although the glazing colors are separated according to the production planning, sometimes colored and white glazes can be glazed in the same cabinets. In these cases, pumps and cabinets are washed. However, the particles remaining on the edges of the pumps or cabinets may appear on the glaze surfaces as a stain defect with the effect of compressed air. When the SEM analysis in Figures 12 and 13 are examined, it is seen that the impurities are in light gray tones and with less density compared to the SEM's of iron-bearing structures. It is seen that some pigments melt in the body, reducing the color formation in the glaze layer and there are small regional densities.[15]

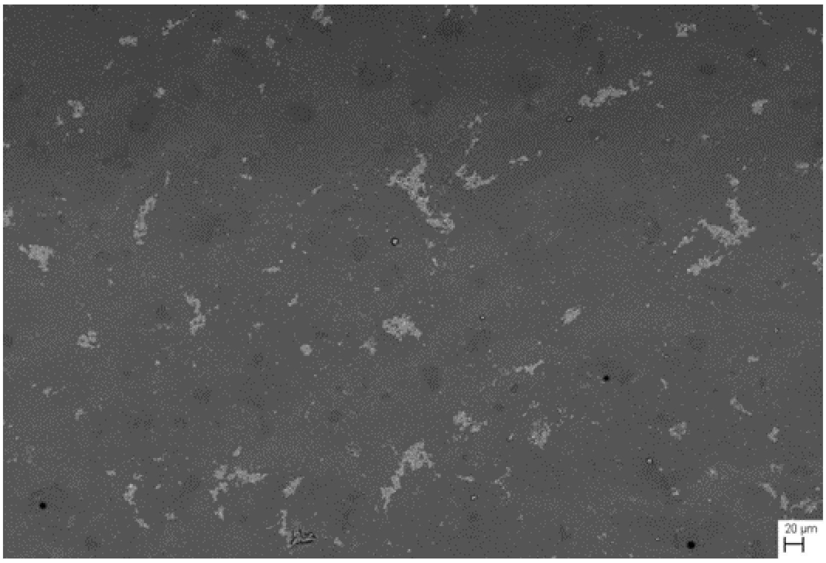

Figure 12. Sem image of the defects due to colored glaze splash.

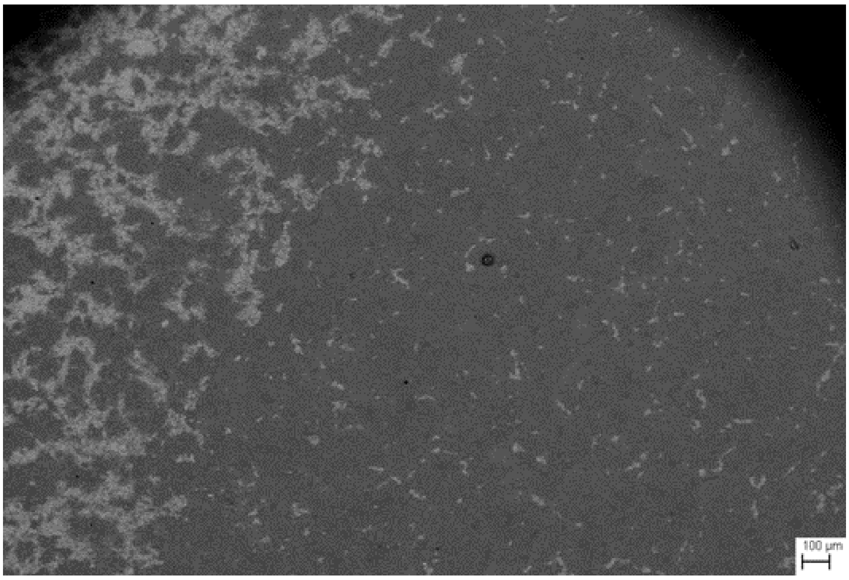

Figure 13. Sem image of the defects due to colored glaze splash.

It has been observed that the dulled glazes come in the same color as in the stained areas. Due to the dull of glazes, Al ratios are high. It was observed that the structure of glossy glazes was targeted in the regions with high zircon ratio, while the alumina ratios were high and the matte glazes stained when the faulty regions were targeted with a low ratio (Table 3).

Table 3. Sem/edx results of defects caused by colored glaze splash.

	MgO	Al_2O_3	CaO	ZnO	SiO_2	Na_2O	K_2O	ZrO_2	Total
1	3.5	6.78	5.32	0	42.92	3.15	1.69	36.64	100
2	2.72	14.72	5.29	0	70.53	4.41	2.23	0	99.9
3	2.5	14.19	5.09	2.1	67.37	4.39	2.65	1.7	99.99
4	0.82	9.25	5.85	1.16	61.6	3.51	0.7	17.11	100

3.3. SEM/EDX Analysis of Raw Material Adding Funnel Sourced Defects

Since this tool is made of metallic materials in the operating workshops, iron stains have been observed. The fact that it is less than the other raw materials given in the study causes the glassy phase to be observed predominantly in the SEM images, while the impurities can be clearly examined in dark black in Figure 15. It has been observed that there are iron stains in the light gray areas, micro pinhole defects occur in the SEM images of these spots, the iron particles formed in these areas are separated from the environment by burning out and they leave stains in the structure together with the pinhole defect. In Figures 14 and 15, SEM images of the defect originating from the raw material chamber are given.

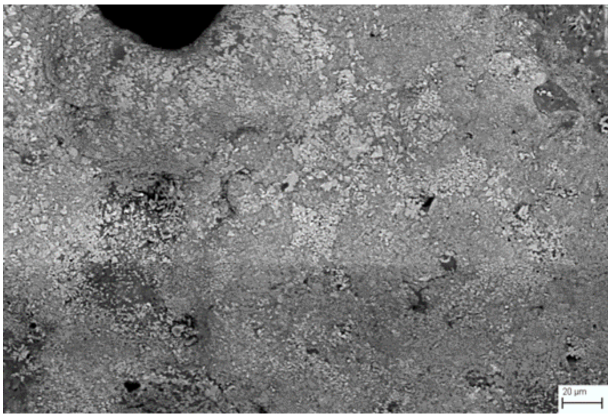

Figure 14. Sem image of the defect originated from the raw material hopper.

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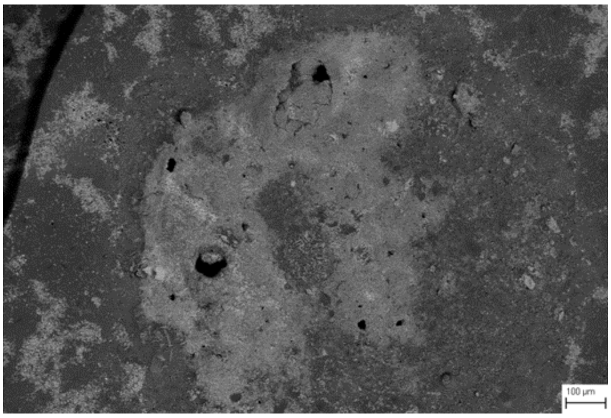

Figure 15. SEM image of the defect originated from the raw material hopper.

Since the iron rate is determined by the EDX analysis done for the black spots, the Fe_2O_3's rate can increase up to ~62% and these results are given in Table 4. The results obtained from the spot EDX analysis done for the iron points support this determination. The deterioration of the glassy structure in these regions is associated with relatively low SiO_2 ratios.

Table 4. SEM/EDX results of raw material hopper defects (% by weigh).

	MgO	Al_2O_3	CaO	Cr_2O_3	Fe_2O_3	ZnO	SiO_2	Na_2O	K_2O	ZrO_2	TiO_2	Total
1	5.66	15.74	4.16	0	45	7.32	18.74	0	0	0	3.38	100
2	6.33	10.28	0	1	62.39	4.39	8.67	0	0	0	6.94	100
3	0	33.23	0	0	44.23	0	22.54	0	0	0	0	100
4	6.04	21.68	2.2	0.33	29.36	9.16	26.83	0	0.57	0	3.84	100.01
5	4.9	22.04	4.35	0	21.14	6.36	36.62	0	0	0	4.59	100
6	2.8	7.37	6.64	0	0	0	55.74	2.31	0	25.86	0	100

3.4. SEM /EDX Analysis of faults originated Glaze Preparation Ceiling and Glaze Ceiling Coating Materials

Ece Banyo factory operates as a two-story production facility. Glaze preparation and glazing sections are located at the bottom of the drying kilns. Since this platform is metal, stone wool materials are used in the interstices of the ceiling. These materials can deform over time with the effect of temperature and humidity, and they can break off from the structure and mix into the glaze tanks. It was determined that the materials used for insulation, other than iron, were poured in the particles poured from the ceiling due to the changes in ambient temperature, and Ca ions were high in these materials. In SEM analyses, this ratio is observed to be scattered regionally. Compared to the SEM analyses of the previous faults, it is observed that there is a more homogeneous structure and dark colored glaze structures are deteriorated, although it is not as effective as iron in the glassy phase. SEM images of the defects caused by glaze preparation ceiling and ceiling insulation materials are given in Figures 16 and 17.

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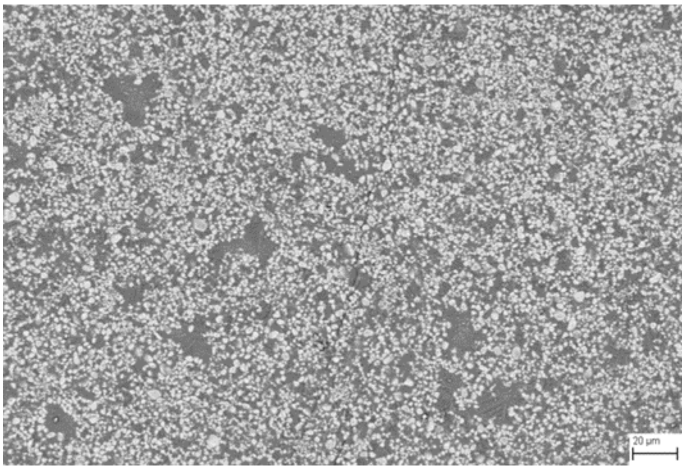

Figure 16. Sem image of defects caused by glaze preparation ceiling insulation material.

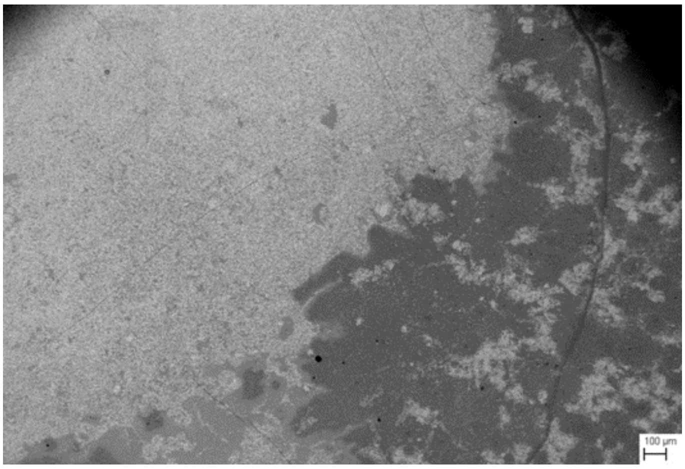

Figure 17. Sem image of defects caused by glaze preparation ceiling insulation material.

The fact that CaO in the EDX analyses varies between ~22% and 3% in the structure shows that this is due to different spills. The SiO_2 ratio, which indicates the glassy phase, also varies due to the mixed material, and this change can be examined proportionally in both the impurities and the main building raw materials in Table 5.

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Table 5. Sem/edx results of the defects caused by glaze preparation ceiling insulation material (% by weight).

	MgO	Al_2O_3	CaO	Fe_2O_3	ZnO	SiO_2	Na_2O	K_2O	ZrO_2	Total
1	0	9.66	22.11	8.04	0	55.32	4.88	0	0	100.01
2	0	0	2.85	0	0	34.56	0	0	62.59	100
3	0.99	4.92	9.46	5.84	0	38.53	2.21	0	38.06	100.01
4	2.28	8.97	16.23	9.64	0.83	52.46	5.48	0.35	3.77	100.01
5	2.08	7.37	6.64	0	0	55.74	2.31	0	25.86	100

3.5. XRD Analysis

As seen from the XRD analyses below, the analyses of the samples listed as 3.1-3.5 from bottom to top show that the quartz peak is seen apart from the defects caused by the ceiling covering materials, but the structure is deteriorated due to the Zr content of the ceiling material. XRD analysis are given in Figure 18.

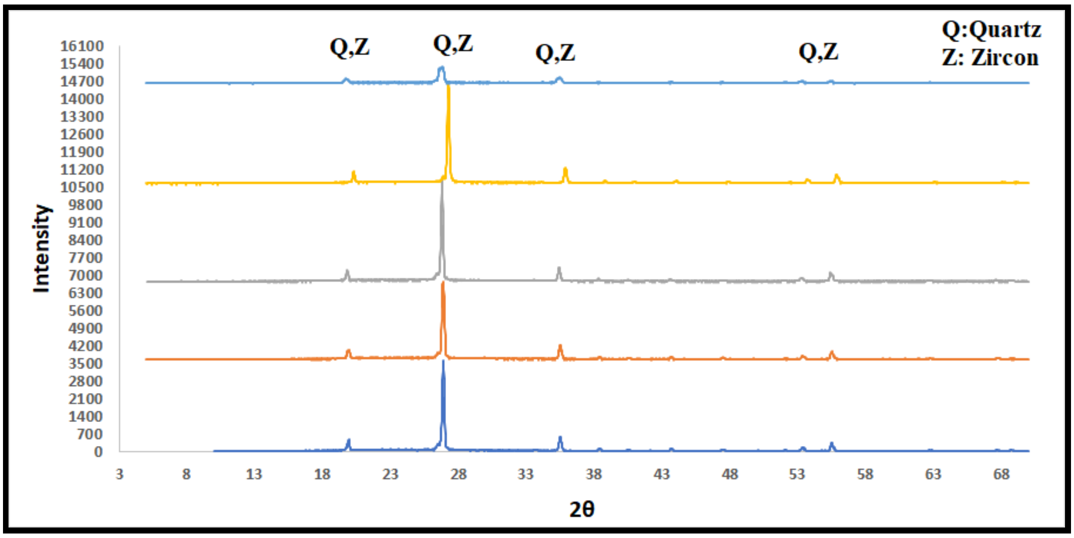

Figure 18. Xrd analysis results of the defects.

4. CONCLUSIONS

According to the results of the analysis, it was observed that Fe_2O_3 ratios were generally high in EDX spot analysis due to the iron content of the materials used in the process. In addition, it was observed that the crystal structure of the glaze was deteriorated in the point analysis where the Fe_2O_3 ratio was high, and the ZrO_2 ratio was low or not found at all in the SEM/EDX analysis. As known, vitrified glazes are mostly opaque glazes-based Zircon Silicate. There are very few studies in the literature in the field of vitrified ceramic materials. Especially glaze studies are carried out on products with high visual effects such as wall tiles, floor tiles and porcelain products. In addition, the main glaze defects are emphasized. With this study, scientific explanations of faults caused by different process components were made and some deficiencies in the field of vitreous ware were tried to be solved. The fact that R&D studies are not adequate in the sanitary ware industry causes engineers to not find answers to the defects. These causes time and product losses in the process. By focusing on the main cause of the problem, it will show a scientific way to understand the numerical analyses used in production more clearly and to make the right interventions in production by carrying out such studies in order to offer a solution and make the chief cause analysis right. The intense observation of Fe-containing point analysis in the findings is due to the fact that the materials used in the production units are metallic-based. In these regions, it was observed that the crystal structures of the glazes were also deteriorated with stain defects. For this reason, in the processes where these defects occurred, the sources of fault were eliminated and the products were recycled.

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