Physicochem. Probl. Miner. Process., 61(3), 2025, 203933

http://www.journalssystem.com/ppmp

Physicochemical Problems of Mineral Processing

ISSN 1643-1049
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Prevention of black core formation in ceramic bodies

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Abstract: Ceramics Industry is the major consumer of industrial raw materials including various types of clay minerals. The existence of impurities in ceramic raw materials is a challenging issue to produce high quality ceramics. Coloring impurities such as Fe and Ti cause discoloration within the ceramic bodies and they have to be kept below certain limits. Organic carbon present in clay rocks leads to another aesthetic problem within fired ceramic bodies referred to as "black core". During biscuit firing process organic carbon in the body composition slowly burns out. Burning requires oxygen and that oxygen is robbed out of Fe_2O_3, which is another impurity, reducing it to FeO. During the ongoing burning process FeO then melts, interacts penetrates within the surrounding matrix creating the so-called black core structures. Black core formation is undesirable both aesthetically and in terms of mechanical durability. In this investigation experimental studies have been conducted to reduce the black core formation in the ceramic bodies where organic carbon rich clay sources are used in the recipe. Test results have proven that black core formation could be greatly reduced to negligible levels by the chemical treatment of the clay raw material containing organic carbon as the impurity.

Keywords: black core, ceramic bodies, hydrogen peroxide leaching

1. Introduction

Ceramic tile production is a complex process where aesthetics and structural durability must be optimized together. In this process, production parameters must be managed precisely in order to obtain high-quality products. However, various defects encountered during the production process can seriously affect the quality of the products. One of these defects is the "Black Core" that causes both aesthetic and structural weaknesses because of a dark core formed the inside the ceramic tiles. It has been stated in the literature that the "Black Core" defect accounts for 15% to 20% of ceramic tile production flaws worldwide (Johnson & Smith, 2020; Gupta & Rao, 2019).

The "Black Core" is usually caused by glitches in the firing process. Failure to provide adequate air circulation during firing causes a lack of oxygen in the interior of the tile, which leads to the accumulation of unburned carbon residues. This has been observed especially in ceramics fired at high temperatures (Martinez & Lopez, 2021). Additionally, improper firing time or temperature may cause the clay to not sinter fully, which may trigger the "Black Core" error (Chen & Lee, 2018).

Another important factor affecting the occurrence of defects is the quality of the raw materials used. Failure to mix raw materials homogeneously may result in the formation of carbon-rich areas in some areas. In this case, sufficient combustion does not occur in these zones during firing, resulting in a "Black Core" formation (Kim & Park, 2022). This risk increases particularly in clays with high organic matter content. Studies show that a 2% deviation from homogeneity in the clay mixture can increase the incidence of the "Black Core" by up to 12% (Chen & Lee, 2018). The effect of this defects on ceramic tiles is not limited to aesthetic deterioration; It also negatively affects the mechanical durability of the tiles. In a study by Martinez and Lopez (2021), it was reported that the mechanical durability of tiles with the "Black Core" defect can decrease by up to 10%. This situation emerges as a serious problem in the construction industry, which wants to provide a long-lasting and durable surface, especially in tile applications.

DOI: 10.37190/ppmp/203933

In this context, ceramic tile manufacturers need to establish a careful control mechanism in their production processes to minimize the "Black Core" defect. Optimizing firing parameters, meticulously monitoring the quality of the raw materials used and ensuring homogeneity in the production line are key factors in preventing this defect. In addition, continuous monitoring of production processes and making necessary improvements will contribute to both increasing product quality and reducing manufacturing costs.

2. Materials and methods

In this study, clay samples obtained from the Şile-Istanbul district were used. Hydrogen Peroxide (H_2O_2) was utilized as a chemical agent in leaching tests. A magnetic stirrer with heating capability was employed during the leaching experiments. Leach temperature was controlled around 55^0C using a thermocouple thermostat system connected to the stirrer. At the end of the leaching experiments the liquid phase was filtered off and the solid residue was dried for analysis. Carbon contents of the test samples were determined employing a carbon-sulfur analysis device.

The test samples were soaked for 24 hours and then screened off through appropriate sieve sizes and the undersize fraction was used in all leach experiments. 25 g of dry sample was used in all tests where agitation speed and duration were 400 rpm and 3 hours respectively.

Chemical and mineralogical analyses of the samples were carried out using Axios Maxmodel X-ray Spectrophotometer device (XRF, PANalytical) and X'pert Pro MPD X-ray Diffractometer (XRD, PANalytical). Rietveld method was used to determine the quantitative XRD results.

Prior to the firing tests the test sample was dried using an infrared lamp, milled to eliminate coarse particles and the ground powder was added water to achieve a moisture content of 5.5 wt% and pressed at a pressure of 300 kg/cm². Cylindrical tablet samples, measuring 40 mm in diameter and approximately 5 mm in thickness, were then sintered using in a fast-firing industrial roller porcelain kiln at a temperature of 1185^0C.

3. Results and discussion

In this investigation two different clay samples were used in the leaching tests. The XRD pattern of the #1 test sample and corresponding mineralogical distribution are presented in Fig. 1 and Table 1 respectively.

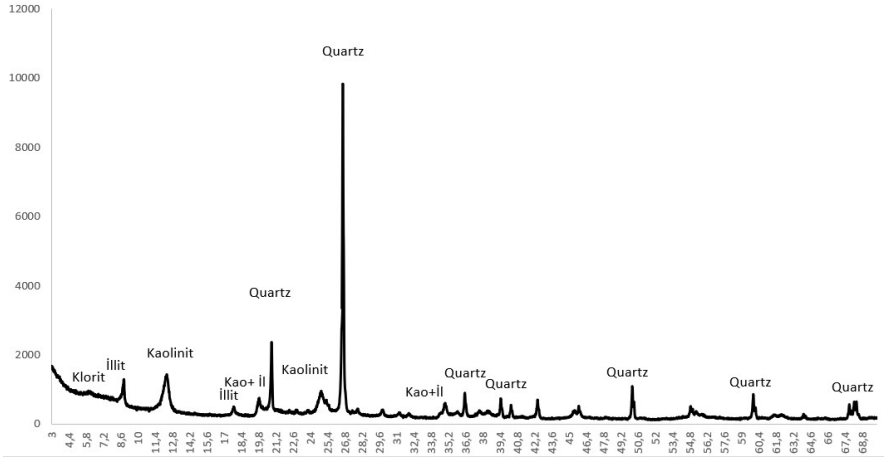


Fig. 1. XRD Pattern of the #1 test sample

Table 1. The mineralogical composition of #1 clay sample

Mineral	Weight, %
Quartz	33.33
Chlorite	2.24
Illite	23.58
Kaolinite	40.85

The XRD analysis of #1 clay sample shows that the sample is mainly composed of quartz, illite and kaolinite minerals and chlorite existence is observed to some extent. The results of chemical analyses of the test sample are presented in Table 2. The particles size distribution and the respective C contents regarding #1 clay sample is presented in Table 3.

The findings seen in Table 3 show that C content below 53 □m considerable reduces. Therefore, leach tests were carried out using -53 μm size fraction.

In the leaching tests varying amounts hydrogen peroxide was added yet keeping the total liquid volume constant so that the solids ratio by weight was 50%. Experimental conditions are given in Table 4. The H_2O_2 additions seen in Table 4 were arbitrarily chosen since there was not a reference value to be taken in the literature.

C content below 53 μm size fraction is seen to be around 0.57%. In order to check the black core formation within the untreated sample a biscuit was prepared using the -53 μm size fraction and fired at 1185°C. The black core formation inside the test sample is clearly seen in Fig. 2.

Table 2. Results of the chemical analysis of #1 clay sample

Element	%
L.O.I.	6.79
SiO_2	64.45
Al_2O_3	21.27
TiO_2	1.23
Fe_2O_3	2.62
CaO	0.27
MgO	0.61
Na_2O	0.11
K_2O	2.37
C	1.56

Table 3. The particle size distribution and the C contents of #1 clay sample

Size Fraction μm	Weight %	Cumulative Undersize %	Carbon %
+1000	3.72	100.00	18.91
-1000 +500	5.12	96.28	4.15
-500 +212	7.91	91.16	1.76
-212 +106	5.12	83.26	1.19
-106 +53	6.51	78.14	0.65
-53 +38	4.19	71.63	0.52
-38	67.44	67.44	0.57
Feed	100		1.56

Table 4. Leach conditions adopted in the tests

Test Number	H_2O_2 addition % by solids weight
1	5
2	10
3	20
4	30
5	40

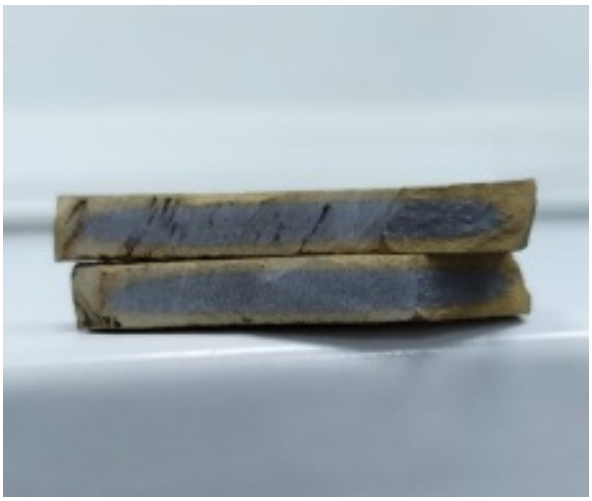


Fig. 2. Black core formation inside the untreated -53 μm size fraction test sample

Following the leach tests the samples were dried and analyzed for C and the results are presented in Table 5. The results of carbon analyses conducted on the samples show that C contents in all tests do not vary a lot and remains around 0.26 %. However, some amount of decrease in the carbon content from 0.57% is clear. In order to see the effect of reduction in carbon on the black core formation, firing test was performed using the sample of test 1 assaying 0.26% C. The result of firing test is presented in Fig. 3.

Table 5. Carbon contents after leaching tests conducted with #1 clay sample

Test #	C, %
1	0.26
2	0.30
3	0.22
4	0.27
5	0.26



Fig. 3. Black core formation inside -53 μm test sample containing 0.26% C after H_2O_2 leaching

Firing test results seen in Figs. 2 and 3 show a remarkable decrease in the black core formation. This decrease in the black core formation is well correlated with the decrease in the C content as a result of H_2O_2 treatment. Following experiments were carried out using #2 clay sample collected from the same mine site as #1. Prior to the tests the clay sample was sieved through 150 μm aperture screen and the upper and lower size fractions were assayed.

Table 6. Results of the chemical analysis of #2 clay sample

Element	+150 mm, %	-150 mm, %
L.O.I.	3.31	7.04
SiO_2	82.69	62.94
Al_2O_3	4.92	22.1
TiO_2	0.29	1.33
Fe_2O_3	7.54	3.16
CaO	0.17	0.22
MgO	0.11	0.63
Na_2O	0.3	0.24
K_2O	0.49	2.11
C	0.45	0.047

Elemental analyses seen in Table 6 shows that clay fraction in the undersize considerable increases while C is reduced from 0.45 to around 0.047% and Fe content decreases more than half. Therefore, leaching tests to reduce the black core formation were carried out using the size fraction below 150 μm. The XRD pattern of the #2 test sample below 150 μm and corresponding mineralogical distribution are given in Table 7 and Fig. 4 respectively.

Table 7. The mineralogical composition of #2 clay sample

Mineral	Weight, %
Quartz	34.72
Illite	26.14
Kaolinite	39.14

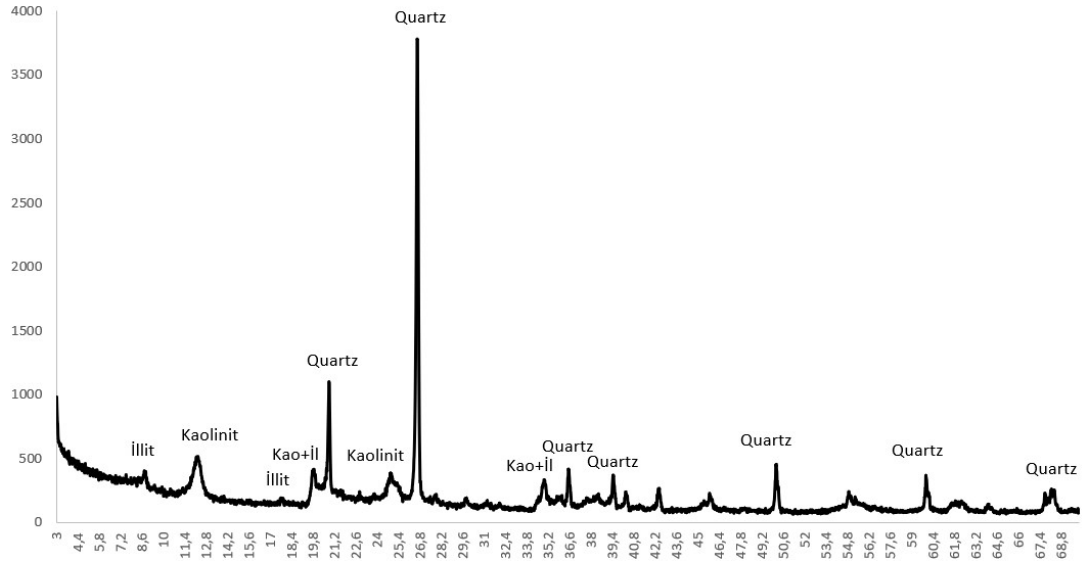


Fig. 4. XRD Pattern of the #2 test sample

According to the XRD analysis seen inf Fig. 7, the mineralogical composition of #2 tests sample is seen to be similar to that of #1 test sample. Test carried out using #1 clay sample showed that down to 5% H_2O_2 addition by weight of the solids clearly reduced black core formation. Hence lower H_2O_2 dosages were used in the tests conducted with #2 clay sample so as to reduce the potential operational costs. In Table 8 H_2O_2 additions are given. Table 9 presents the C contents of the samples treated with H_2O_2. The sample initially assays 470 ppm C, however, following the agitation tests adding H_2O_2, a gradual decrease in the carbon contents of the samples are seen.

Table 8. H_2O_2 additions implemented in the tests using #2 clay sample.

Test Number	H_2O_2 addition % by solids weight
1	0.5
2	1

Table 9. Carbon contents after leaching tests conducted with #2 clay sample.

Test #	C, ppm
1	306.8
2	210.1

Following chemical treatment trials carried out with #2 test sample at lower H_2O_2 additions compared to sample #1, firing tests were conducted to check the existence of black core formation. Firing test carried out with the untreated test sample and also treated with 0.5 and 1%H_2O_2 are presented in Figs. 5, 6 and 7 respectively.

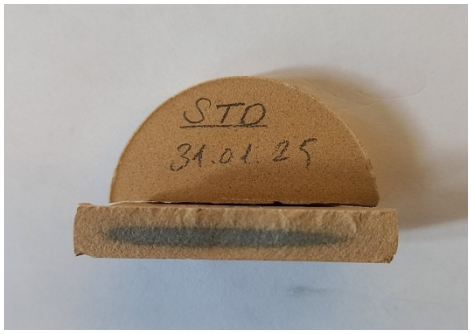


Fig. 5. Black core formation inside the #2 test sample without any treatment

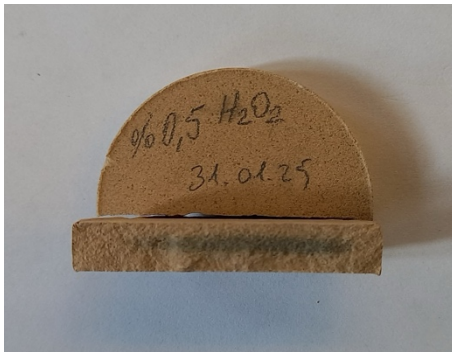


Fig. 6. Black core formation inside the #2 test sample treated with 0.5% H_2O_2 addition with respect to the solids weight

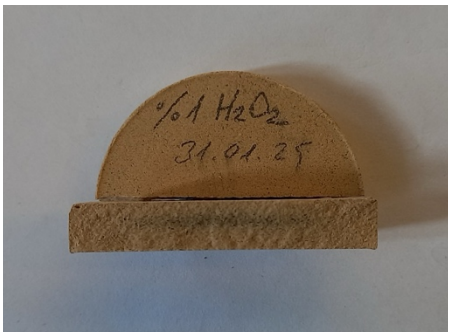


Fig. 7. Black core formation inside the #2 test sample treated with 1% H_2O_2 addition with respect to the solids weight

Firing tests using #2 clay sample showed a similar trend to those of #1 clay sample. Black core formation within the untreated sample is clearly visible though the C content was much lower compared to #1 test sample. The increase in H_2O_2 addition was clearly reflected as a gradual decrease in the black core formation.

4. Conclusions

In this investigation leach tests were carried out to reduce the effect of organic carbon that causes black core formation inside ceramics bodies. In the tests H_2O_2, which is a strong oxidizing agent, was employed. Leaching trials showed that the carbon content of the test sample #1 was reduced from about 0.57% to around 0.26%.

On the other hand, the initial C content of #2 sample was much lower compared to #1 test sample though there was still black core formation within the untreated fired sample. Following H_2O_2 treatment some amount of reduction in the C content with respect to the untreated sample was observed.

Some organic based chemicals may be used to avoid black core formation at industrial scales. The use of organic chemicals may be detrimental to human health at long term exposures. H_2O_2, on the other hand, may be costlier compared to the chemicals already used, however, there are many options to purchase H_2O_2 at lowest possible prices.

The reduction in the carbon content together with oxidizing conditions created by the addition of H_2O_2 prevented the formation of black core inside both fired test samples to a great extent.

It may be concluded that H_2O_2 addition will considerably reduce the black core formation in the fired ceramic bodies without any adverse effect on the recipe.

References

JOHNSON, L., SMITH, M. 2020. *Ceramic Tile Defects: Analysis and Mitigation*. Journal of Materials Processing Technology, 276, 116401.

GUPTA, P., RAO, K. 2019. *Thermal Behavior in Ceramic Manufacturing: A Study of Common Defects*. Journal of Ceramic Processing Research, 20(3), 294-300.

MARTINEZ, R., LOPEZ, A. 2021. *Mechanical Properties of Defected Ceramic Tiles: The Impact of Firing Errors*. Materials Science and Engineering: A, 789, 139589.

CHEN, Y., LEE, S. 2018. *Influence of Firing Conditions on Defects in Ceramic Tiles*. Journal of the European Ceramic Society, 38(14), 4825-4834.

KIM, J., PARK, H. 2022. *Material Homogeneity and Its Impact on Ceramic Tile Quality*. Ceramics International, 48(5), 6321-6328.