XVI International Mineral Processing
and Recycling Conference
28-30 May 2025, Belgrade, Serbia

DOI: 10.5937/IMPRC25449K Original research article

# A PROPOSAL FOR ZERO WASTE IN THE IRON AND STEEL INDUSTRY: ZIRCONIA NOZZLE WASTE EVALUATION

**Semra Kurama[1#]**, 0000-0002-7554-3419,
**Hüseyin Boğaç Poyraz[1]**, 0000-0001-5351-6658,
**Zahide Bayer Öztürk[2]**, 0000-0001-8069-0694,
[1]Eskişehir Technical University, Department of Materials Science and Engineering, Eskişehir, Türkiye
[2]Nevşehir Hacı Bektaş Veli University, Department of Metallurgy and Materials Engineering, Nevşehir, Türkiye

**ABSTRACT** – With the increase in environmental awareness, it is seen that there are two focusing methods in industrial production. Therefore, the usability of one sector's waste as a potential raw material for another sector can play an important role in terms of energy and cost.
In the study, zirconia nozzles, used in the iron and steel industry, are consumed quickly. It is aimed at finding a solution to the accumulation of waste formed by the end of service life of them.
In the first part of the study, it was investigated the integrating waste zirconia nozzles from the Bilecik Iron and Steel Company (Bilecik, Turkey) into the production of ceramic floor tiles. After processing and firing in an industrial kiln, the formulated recipes are subjected to comprehensive physical and mechanical evaluations [19]. In the second part of the study, to aim for zero waste, existing waste was evaluated in the production of refractory bricks, and the use of alternative resources to zirconia, an expensive raw material, was examined. It showed the potential of waste zirconium nozzles as a sustainable alternative in ceramic tile/refractory production. It demonstrates its feasibility in reducing waste generation, lowering production costs, and promoting environmentally sound practices without compromising.

**Keywords:** Ceramic Tile, Refractory, Zirconia Nozzle, Waste, Recycling.

## INTRODUCTION

The iron and steel industry represents a strategically significant sector with substantial global production capacity [1]. However, its production processes inherently generate various waste materials, the complete elimination of which remains a considerable challenge. While waste management efforts predominantly focus on minimizing waste generation within a given sector, the cross-sectoral utilization of industrial by-products has gained prominence as a sustainable alternative. The ceramic industry not only produces waste during its own manufacturing processes but also presents a viable avenue for the valorization of waste materials originating from different industries. Numerous studies in literature have explored the incorporation of industrial waste into ceramic-based applications, including ceramic tiles, sanitaryware, and

[#] corresponding author: skurama@eskisehir.edu.tr

refractory materials. Notably, integrating industrial by-products into ceramic tile formulations has emerged as an effective and environmentally sustainable strategy for waste reduction [2]. Several studies have investigated the utilization of diverse industrial residues in ceramic tile production, including granite waste [3], glass shards [4], various slags [5-7], boron-related residues [8], waste clay [9], and different types of ashes [6, 10]. These research efforts highlight the potential of industrial waste repurpose within the ceramic sector, contributing to both environmental sustainability and resource efficiency.

In response to growing ecological concerns, research within the refractory sector, a subset of the broader ceramic industry, has increasingly focused on minimizing the reliance on virgin raw materials and reducing production costs, thereby promoting more sustainable practices. Ghonaim et al. [11] conducted a study on the preparation of traditional refractory concrete, incorporating 50% alumina grog or bauxite as key components. Similarly, Khalil et al. [12] investigated the production of mullite-based refractories using a composition of 40% recycled alumina-silicate waste and 60% bauxite, which was subsequently sintered through pressing at 1600℃. Their findings indicated significant improvements in the physical properties of the resulting materials. Furthermore, Mazzanti et al. [13] analyzed the mechanical and thermal performance of refractories by incorporating ceramic waste derived from alumina silicate. Their study demonstrated that the inclusion of ceramic waste effectively enhanced the modulus of rupture (MOR), thermal shock resistance, phase composition, and microstructural characteristics from ambient temperature up to 1500℃. Notably, their results indicated that refractory compositions containing 20% ceramic waste exhibited comparable performance to those produced using untreated alumina-silicate materials, underscoring the potential of recycled ceramic waste in refractory applications.

The utilization of high-temperature-resistant materials is crucial in the iron and steel industry, particularly for applications requiring durability under extreme thermal and chemical conditions. In this regard, zirconia ($ZrO_2$) nozzles are extensively employed for regulating liquid metal flow due to their exceptional thermal resistance and chemical stability. These ceramic nozzles are widely used across various industrial sectors and can be manufactured through different advanced fabrication techniques, including additive manufacturing and direct ink writing [14]. The production process typically begins with high-purity zirconia powder, which is shaped into the desired nozzle form and subsequently subjected to high-temperature sintering to attain the necessary mechanical and thermal properties [15]. One of the most significant applications of zirconia nozzles is in the continuous casting of steel, where they serve as critical components in tundish refractory systems, ensuring controlled metal flow and operational efficiency [16, 17].

In the iron and steel industry, molten metal is transported using ladles and subjected to various metallurgical treatments at different processing stations, such as ladle furnaces and converters. Following these processes, the liquid metal is transferred to the continuous casting system, where it is shaped into semi-finished or finished products. During this stage, the molten metal passes through a tundish and is subsequently directed into open-bottomed copper molds. Precise control of metal flow from the tundish to the mold is critical for regulating casting speed, optimizing production planning, and ensuring product quality. To achieve this, flow control systems are installed beneath the tundish, consisting of a fixed zirconia nozzle and a replaceable zirconia nozzle. These nozzles are periodically replaced through a waste removal and disposal system to maintain production efficiency in accordance with operational parameters [18].

Despite their widespread application, limited research has focused on the reuse of zirconia nozzle waste generated in steel production facilities. However, some studies have investigated the potential of repurposing this waste as a zircon substitute in ceramic applications, such as wall tile glazes and ceramic tile formulations [18, 19].

In this study, the reuse potential of zirconia-based nozzle materials, which serve as pouring outlets in crucibles within the iron and steel industry, was investigated. These nozzle components become inoperative after casting due to wear-induced deformation and thermal expansion. Currently, they are not recyclable within the iron and steel sector and are instead disposed of as industrial waste. However, given their high zirconia content, these materials present a promising opportunity for repurposing in both the ceramic tile and refractory industries. The potential applications of these waste materials include enhancing surface whiteness in ceramic tile formulations and serving as raw materials for the production of alumina-zirconia refractory components. To explore these possibilities, experimental studies were conducted to assess the feasibility of incorporating waste zirconia nozzles into ceramic and refractory applications, thereby contributing to resource efficiency and sustainable waste management.

## MATERIALS AND METHODS

The waste zirconia nozzles (WZ) utilized in this study were obtained from Bilecik Iron and Steel Company (Bilecik, Turkey) and subjected to a purification process to eliminate any residual iron components. This was achieved through the precise removal of iron fragments using a diamond cutter, ensuring the purity of the base material. Following mechanical separation, the purified WZ underwent further processing, wherein they were crushed using a jaw crusher to reduce their particle size. The complete preparation procedure for the waste zirconia nozzles is illustrated in Figure 1.

Subsequent chemical characterization of WZ was performed using X-ray fluorescence (XRF) spectroscopy (Rigaku ZSX Primus model), and the results are presented in Table 1. Additionally, the crystalline phase composition of WZ was analysed through X-ray diffraction (XRD) using a Rigaku Miniflex 600 series diffractometer. The analysis was conducted over a 2θ range of 5° to 70° at a scanning speed of 2°/min, employing Cu Kα radiation at 40 kV and 30 mA. The results, depicted in Figure 2, confirmed the presence of both baddeleyite ($ZrO_2$) and hafnium dioxide ($HfO_2$) phases in the WZ samples.

This study is structured in two parts, each focusing on the valorization of waste zirconia nozzles (WZ) in different industrial applications. The first part, which has already been published, investigated the use of WZ in ceramic tile production. This phase involved a comprehensive experimental analysis, including a comparative evaluation of the color properties of standard zirconium raw materials and waste zirconium. The results demonstrated that replacing 2% by weight of conventional zircon raw materials with WZ in white ceramic floor tile bodies led to improvements in both body whiteness and firing strength [19].

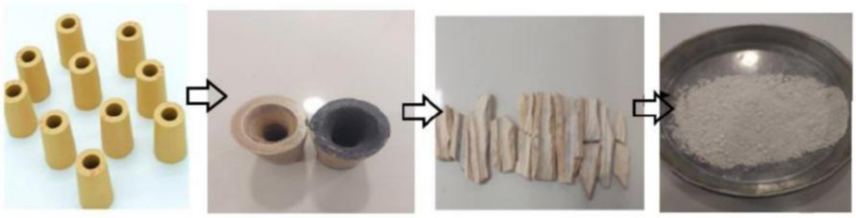

**Figure 1** The preparation of zirconia nozzles for applications [19]

**Table 1** The chemical analysis of WZ (wt.%)

| Oxides | $Na_2O$ | MgO | $SiO_2$ | $Al_2O_3$ | $P_2O_5$ | $K_2O$ | CaO | $TiO_2$ | $Fe_2O_3$ | $ZrO_2$ | $Hf_2O$ | LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| WZ | 0.01 | 1.72 | 1.57 | 1.22 | 0.01 | 0.01 | 0.08 | 0.19 | 0.01 | 93.34 | 1.71 | 0.12 |

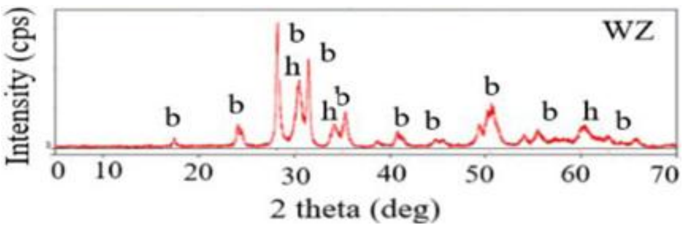


**Figure 2** XRD phases of the WZ (**b**: baddeleyite, **h**: $HfO_2$) [19]

Building upon these findings, the present study focuses on the second part, which explores the potential utilization of WZ in refractory applications. While the first part established the feasibility of WZ in the ceramic sector, this study extends the research by investigating its suitability for the refractory industry. By addressing both ceramic and refractory applications, the overall research aims to contribute to a more comprehensive waste management strategy, promoting circular economy principles in industrial processes.

In the second phase of the study, the waste zirconia nozzles (WZ) were ground to a particle size of less than 100 µm using a ball mill and subsequently incorporated into refractory formulations. The ground WZ was blended with zircon silicate brick raw material at varying proportions of 0%, 10%, 20%, and 30% by mass. Calcium aluminate cement and organic binders were added to the mixture to enhance its binding properties and workability. The consistency of the mixture was adjusted to ensure suitability for the shaping process.

To form test specimens, the prepared mixture was subjected to uniaxial pressing at a pressure of 50 MPa, resulting in cylindrical and prismatic samples. These pressed specimens were initially dried in a low-temperature oven at 110°C to remove residual moisture. Subsequently, they underwent a sintering process at 1550°C for 2 hours to achieve the desired phase development and densification. The raw materials and their respective proportions used in the refractory formulations are presented in Table 2.

**Table 2** Refractory samples and codes

| Samples | Cement (wt.%) | Organic binder (wt.%) | WZ (wt.%) |
|---|---|---|---|
| ***R0*** | 15 | 3.0 | 0 |
| ***R10*** | 15 | 3.0 | 10 |
| ***R20*** | 15 | 3.0 | 20 |
| ***R30*** | 15 | 3.0 | 30 |

**RESULTS AND DISCUSSION**

The physical and mechanical properties of the refractory samples incorporating waste zirconia nozzles (WZ) were evaluated by analyzing porosity, density, and flexural strength to assess their overall performance. An image of the prepared refractory samples is presented in Figure 3, while the detailed performance results are summarized in Table 3 and Figure 4.

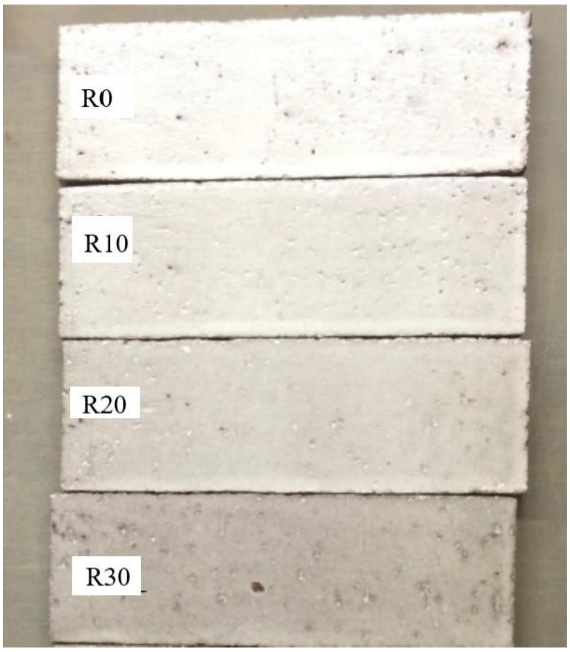


**Figure 3** Fired refractory samples

The findings indicate that increasing the WZ content up to 30% results in a notable enhancement in both density and mechanical strength, accompanied by a reduction in porosity. This trend suggests that the incorporation of WZ improves the packing efficiency of the refractory mixture, thereby minimizing void spaces and promoting a denser microstructure. The highest flexural strength and density values were recorded at 30% WZ addition, highlighting the positive impact of WZ on the overall refractory properties. Additionally, the observed decrease in porosity further supports the enhanced sintering behavior and structural integrity of the samples, reinforcing the potential of WZ as a valuable additive for optimizing refractory performance.

**Table 3** The properties of the prepared refractory samples.

| Waste ratio (wt.%) | Flexural strength (MPa) | Porosity (%) | Density (gr/cm$^3$) |
|---|---|---|---|
| R0 | 30 | 18 | 2.80 |
| R10 | 32 | 16 | 2.85 |
| R20 | 32 | 16 | 2.90 |
| R30 | 37 | 12 | 2.95 |

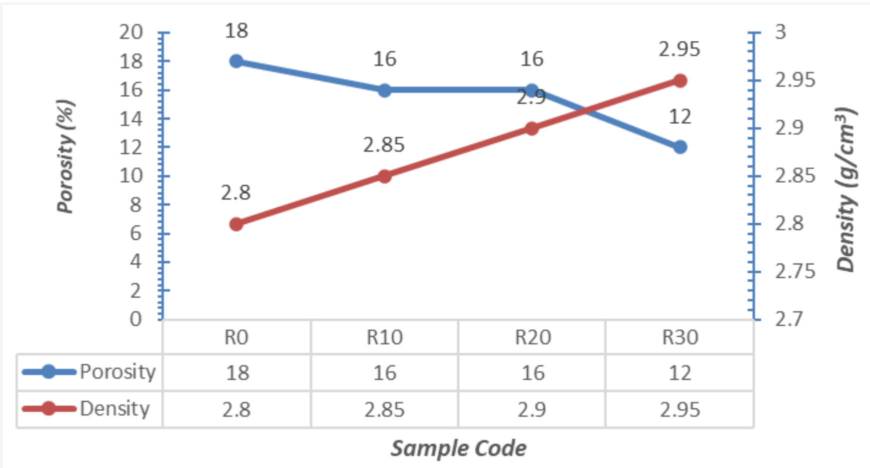


**Figure 4** Changing of porosity and density related with amount of Zirconia Waste amount (%WZ)

This study explored the potential reutilization of waste zirconia nozzles (WZ) in both ceramic tile production and refractory applications, demonstrating their effectiveness in enhancing material properties while contributing to sustainable waste management.

In the first phase of the study, experimental analyses indicated that incorporating 2%wt. WZ into ceramic floor tile formulations improved both body whiteness and firing strength. These findings suggest that WZ can be effectively utilized as a substitute for conventional zircon raw materials in ceramic tile production without compromising product quality [19].

In the second phase, WZ was ground and integrated into zircon silicate refractory mixtures at varying proportions (as in wt. 0%, 10%, 20%, and 30%). The performance evaluation of the refractory samples revealed that increasing WZ content led to enhanced density and mechanical strength while simultaneously reducing porosity. Notably, the highest flexural strength and density values were achieved at a 30% WZ addition, indicating improved structural integrity and optimized sintering behavior. These results underscore the potential of WZ as a valuable additive in refractory manufacturing.

Overall, the study confirms that waste zirconia nozzles can be successfully repurposed in both ceramic tile and refractory industries. Their incorporation not only enhances material performance but also supports resource efficiency and sustainable manufacturing practices, thereby contributing to the circular economy in industrial processes.

## CONCLUSION

This study explored the potential reutilization of waste zirconia nozzles (WZ) in both ceramic tile production and refractory applications, demonstrating their effectiveness in enhancing material properties while contributing to sustainable waste management.

In the first phase of the study, experimental analyses indicated that incorporating 2%wt. WZ into ceramic floor tile formulations improved both body whiteness and firing strength. These findings suggest that WZ can be effectively utilized as a substitute for conventional zircon raw materials in ceramic tile production without compromising product quality.

In the second phase, WZ was ground and integrated into zircon silicate refractory mixtures at varying proportions (0%, 10%, 20%, and 30%). The performance evaluation of the refractory samples revealed that increasing WZ content led to enhanced density and mechanical strength while simultaneously reducing porosity. Notably, the highest flexural strength and density values were achieved at a 30% WZ addition, indicating improved structural integrity and optimized sintering behavior. These results underscore the potential of WZ as a valuable additive in refractory manufacturing.

Overall, the study confirms that waste zirconia nozzles can be successfully repurposed in both ceramic tile and refractory industries. Their incorporation not only enhances material performance but also supports resource efficiency and sustainable manufacturing practices, thereby contributing to the circular economy in industrial processes.

## ACKNOWLEDGEMENT

*This study was supported by Eskişehir Technical University Scientific Research Program (BAP), 102 Research Support Project (102ADP) under Grant Number:24ADP143. The authors would like to thank Eskisehir Technical University Ceramic Research Center for supporting the X-ray analyses included in the study.*

## REFERENCES

1. Sakarya, O.H. (2022) Investigation of the Effect of Metallurgical Digital Twin Application on Production in an Iron and Steel Plant, 2022-August (ESTÜ-Graduate Thesis- Materials Science and Engineering).

2. Goyal, R.K., Agarwal, V., Gupta, R., Rathore, K., Somani, P. (2022) Optimum utilization of ceramic tile waste for enhancing concrete properties, Mater. Today Proceedings, 49: 1769-1775. https://doi.org/10.1016/j.matpr.2021.08.011
3. Dino, G.A., Fornaro, M.A. (2012) Trentin Quarry waste: chances of a possible economic and environmental valorisation of the Montorfano and Baveno granite disposal sites, Journal of Geological Research, 452950: 1-11. https://doi.org./10.1155/2012/45295.
4. Luz, A.P., Ribeiro, S. (2007) Use of glass waste as a raw material in porcelain stoneware tile mixtures, Ceramics International, 33: 761-765.https://doi.org/ 10.1016/j.ceramint.2006.01.001
5. Liu, M., Ma, G., Zhang, X., Liu, J., Wang, Q. (2020) Preparation of black ceramic tiles using waste copper slag and stainless steel slag of electric arc furnace, Materials, 13: 776. https://doi.org/10.3390/ma13030776
6. Bayer Ozturk, Z. and Eren Gultekin, E. (2015) Preparation of ceramic wall tiling derived from blast furnace slag, Ceramics International, 41: 12020-12026. https://doi.org/10.1016/j.ceramint.2015.06.014
7. Bayer Ozturk, Z., Pekkan, K., Tasci, E., Yilmaz, S. (2020) The effect of granulated lead–zinc slag on aesthetic and microstructural properties of single-fired wall tile glazes, J Aust Ceram Soc., 56:609-617. https://doi.org/10.1007/s41779-019-00372-0
8. Ozkan, I. (2017) Utilization of Bigadiç boron works waste clay in wall tile production, Acta Physica Polonica A, 132: 427-429. https://doi.org/10.12693/APhysPolA.132.427
9. Ozkan, I., Çolak, M., Oyman, R.E. (2010) Characterization of waste clay from the Sardes (Salihli) placer gold mine and its utilization in floor-tile manufacture, Applied Clay Science, 49: 420–425. https://doi.org/10.1016/j.clay.2009.08.021
10. Zanelli, C., Conte, S., Molinari, C., Soldati, R., Dondi, M. (2021) Waste recycling in ceramic tiles: a technological Outlook, Resources Conservation and Recycling, 168: 105289. https://doi.org/10.1016/j.resconrec.2020.105289
11. Ghonaim, S.A., Ghazal, H.B.G., Abadir, M.F. (2010) Effect of type of aggregate on the properties of refractory concrete, Jour. of. Ameri. Scie., 6 (12):1025–1027.
12. Khalil, N.M. and Algamal, Y. (2019) Recycling of ceramic wastes for the production of high performance mullite refractories, Siliconindia, 1–9. https://doi.org.10.1007/s12633-019-00248-9
13. Mazzanti, F., Brentari, A., Burresi, E., Coglitore, A., Labanti, M., Martelli, S., Mingazzini, C., Ricci, A., Sangiorgi, S., Scafe, M., Villa, M. (2013) Exploitation of ceramic wastes by recycling in alumina-mullite refractories, Adv. Sci. Technol., 70:9–14. https://doi.org/10.4028/www.scientific.net/AST.70.9
14. Khanlar LN, Rios AS, Tahmaseb A, Zandinejad A. (2021) Additive Manufacturing of Zirconia Ceramic and Its Application in Clinical Dentistry: A Review, Dent J (Basel). 9: 104.
15. Web site 1: https://www.zen-ceramic.com/zirconiaceramics/zirconia-ceramic-nozzles-and-rods.html (Accessed 1 December 2023)
16. Web site 2: http://www.zirconianozzle.com/en/product.html (Accessed 1 December 2023)
17. Web site 3: https://www.earthwaterfire.com/products/zirconia-ceramics/ (Accessed 1 December 2023)
18. Karakedi Sakarya G., Berberoğlu A.O, Sakarya OH, Cengiz U, Ubay E. (2022) Investigation of The Usability of Zirconia Nozzle Waste Instead of Zircon In Wall Tile Glaze Composition, J Sci. Kocaeli University 5(1): (2022) 25-31 https://doi.org/10.53410/koufbd.1114530
19. Z.Bayer Ozturk, Y.Karaca, S.Kurama, E.Ubay, U.Cengiz. (2025) Utilizing waste zirconia nozzles for eco-friendly ceramic tile production, Journal of Ceramic Processing Research. Vol. 26, No. 1, pp. 43~50.