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# Pilot Studies to Produce Steel from Mill Scale: Novel Approach to Recycle Waste Material

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Mill scale and ETP sludge have emerged as by-products rich in iron, originating from the steel production process within hot and cold rolling steel companies. Typically constituting 1% to 3% of the weight of the steel subjected to milling, this study focuses on transforming waste into Direct Reduced Iron (DRI) through an induction furnace, leveraging the reduction process. The research commenced with the design of a suitable induction furnace, exploring various process parameters related to processing, optimization, and characterization. The induction furnace underwent scrutiny involving different combinations of mill scale, reducing agents, time, and temperature. In the final step, the successful production of DRI from mill scale, a waste material, was confirmed by EDAX characterization. Even after iron is recovered from waste, the management of metallurgical waste is not fully resolved because slag is produced at the end of the steel recovery experiments. The obtained slag was characterized by employing SEM, EDAX, and XRD. Further, experiments were conducted to use waste slag in different proportions as a supplementary material in cement mortar. The results were promising, and it was observed that variation in proportion provides variation in the compressive strength of the cement block; therefore, slag can be utilized as needed with cement to produce cement blocks with desired compressive strength. This research sheds light on the creation of value-added products from waste. It contributes to preventing losses within the steel industry, reducing pollution loads, and opening avenues for environmentally sustainable practices in the stainless steel sector for a circular economy.

**Keywords:** circular economy, material recycling, induction furnace, direct reduced iron, sustainable steel.

## 1. Introduction

Stainless steel production is currently one of the fastest-growing sectors in the global manufacturing industry. The stainless steel manufacturing process generates significant amounts of waste. According to the literature, producing three tonnes of stainless steel produces approximately one tonne of waste [1]. This situation is critical due to the significant waste quantity and toxic substances, such as chromium, lead, nickel, and cadmium. These elements pose serious occupational and environmental health risks [2,3].

In 2019, global crude stainless steel production exceeded 50.7 million tons. India ranked the second-largest producer, boasting an impressive growth rate of over 7%. India is also the second-largest consumer of stainless steel worldwide, with apparent consumption reaching 3.2 million tons in 2018-19. Thus, India is a leading producer of stainless steel, with a significant portion of its production concentrated in Gujarat and the fastest-growing market in stainless steel production in 2019 [4]. Such growth has also resulted in large quantities of solid waste generated during steel processes. Solutions needed by the Industry sector. So, high-priority waste streams from such industries were identified and approximated, and the research work was planned accordingly. The steel processing may be generalized in the flowchart depicted in Figure 1.

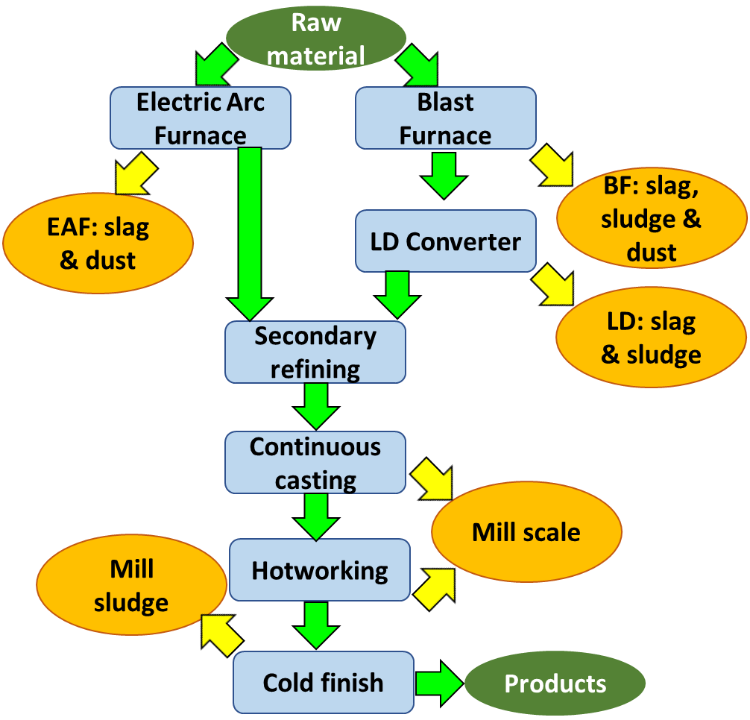



Figure 1: Flow sheet of the steel-making process and the primary solid wastes generated in each step

As presented in Figure 1, the following waste streams were identified in steel processing [5,6]:

- Mill Sludge: Primarily generated during the water treatment of rolling mill processes.
- Mill Scale: Formed on the surface of the metal during hot-working processes. Mill scale typically does not contain hazardous or flammable materials.
- EAF Slag & Dust: By-products of the steel melting process in an electric arc furnace.
- BF Slag, Sludge & Dust: Residual materials produced from the iron-making process in the blast furnace.

- LD Slag & Sludge: Waste products from the steel-making process in the LD converter.

With increased environmental awareness, global steel producers are compelled to adopt environmentally sustainable business models proactively. The steel industry is an integral part of a circular economy model, which promotes zero waste by reusing and recycling by-product materials. The steel industry has made significant progress in finding new markets and applications for steel by-products and wastes such as process slags, sludges, and mill scale [7]. Further, researchers have made various attempts to convert stainless steel oxides back into reduced steel, focusing on the reduction of iron oxides using hydrogen as a reducing agent, microwave heating, exploring the surface modification of stainless steel to improve its properties, and examining the kinetics of reduction processes [6,8].

Spreitzer and Schenk [9] discussed the potential of using hydrogen, a carbon-free reducing agent produced via renewable energies, to reduce iron oxides, thus avoiding the emission of greenhouse gases during the steel reduction process [9]. In addition, the research on the coatings and surface modifications of stainless steel, specifically for solid oxide fuel cell interconnect applications, has been reviewed to overcome issues like corrosion and degradation, which could potentially apply to the reduction of stainless steel oxides as well [10]. It is also reported that studies on the kinetics of iron oxide reduction have been crucial in understanding the reduction behavior and mechanisms applicable to stainless steel oxides. The effects of various factors, such as grain size and impurities, on the reduction rates have been investigated and reported [11].

Thus, the research trends suggest a multidisciplinary approach to the conversion of stainless steel oxides, with a significant focus on environmentally friendly reduction agents, an understanding of the kinetics of reduction, and the application of surface treatments to enhance the properties of reduced stainless steel. Research into converting stainless steel oxides back into reduced steel within an electric arc furnace (EAF) has explored several pyrometallurgical processes, focusing on recovering valuable metals and efficiently treating wastes like EAF dust. Wang et al. [12] reviewed the physical and chemical properties of EAF dust and various pyrometallurgical processes like rotary kiln and rotary hearth furnace, which are used for the recovery of metals such as zinc, lead, and iron, as well as the production of high-value alloys from low-zinc EAF dust [12]. Most of the research was observed to focus on waste generated from EAF or recycling waste employing EAF. Whatever method is used for the recovery of iron, slag is generated at the end of the process.

Therefore, even after iron is recovered from waste, the management of metallurgical waste is not fully resolved. This issue has motivated another research objective, which is essential about using waste slag as a supplementary material in cement mortar. Steel slag, which could be a severe environmental threat due to its release into nature in the past, is currently under investigation by several researchers. The use of slag in cement mortar has gained significant interest due to its potential to improve the mortar's mechanical properties while contributing to environmental sustainability. Usually, the slag is primarily composed of silicates and aluminosilicates, which are beneficial for cementitious applications. Using steel slag as fine aggregate replacement while considering size distribution increases compressive strength [13,14,15,16].

However, extensive research on reducing stainless steel oxides by employing induction furnaces is not evident. Further, Micro, Small, and Medium Enterprises (MSME) in the Steel sector in India rely on induction furnaces for steel processing, and waste produced from induction furnaces or waste recycling with the use of induction furnaces is not extensively reported in the literature. Therefore, the research gap needs to be filled with specific experiments. Hence, this research was initiated with this background and followed scientific protocols described in the following sections. Thus, the main objective of the research was to check the possibility of iron recovery from steel processing waste. Then the remaining material after the process was to be tested for different combinations in cement mortar to benefit the environment.

## 2. Methods and Methodology

The mill scale and sludge were obtained from a local steel rolling mill in Ahmedabad, Gujarat, India. It is reported in the literature that the mill scale is the flaky surface of hot rolled steel, consisting of iron oxides such as iron(II) oxide (FeO), iron(III) oxide ($Fe_2O_3$), and iron(II, III) oxide ($Fe_3O_4$). The appearance of the collected samples matched the scientific description. The sample was formed during steel processing in rolling mills, and it's colour is bluish-black. Mill scale is initially protective against corrosion but becomes problematic when steel needs further processing, as it hinders painting and welding. Therefore, it has to be removed from steel surfaces before further processing in rolling mill.

The experimental method followed for this research to produce DRI or sponge iron, utilizing waste streams from stainless steel/iron oxide, including mill scales and mill sludge, is depicted below.

a) Waste Stream Mixing: Combining fluxes with the waste stream and charging into an induction melting furnace (100KW-3200Hz, 100Kg).

b) Reduction Process: Conducting reduction in the prototype at temperatures ranging from 1000 to 1200°C, as outlined in our patented process.

c) Sample Analysis: Drawing and cooling of samples for X-ray fluorescence (XRF) analysis to determine composition. If results are unsatisfactory, the reduction step is repeated.

d) Temperature Adjustment: Raising the temperature to the liquidus point, approximately 1600°C, to facilitate the melting process.

e) Pouring and Cooling: Transferring the liquid metal out of the furnace and allowing it to cool.

f) Quality Assurance: Performing XRF analysis on the cooled metal to ensure quality standards are met.

g) Recycling of Waste Stream: Utilizing the waste stream and using fluxes after recovery to produce various building materials such as bricks and blocks.

h) Further Analysis: Conducting thorough analysis on recycled materials for potential further utilization.

The entire process is summarized in Figure 2.

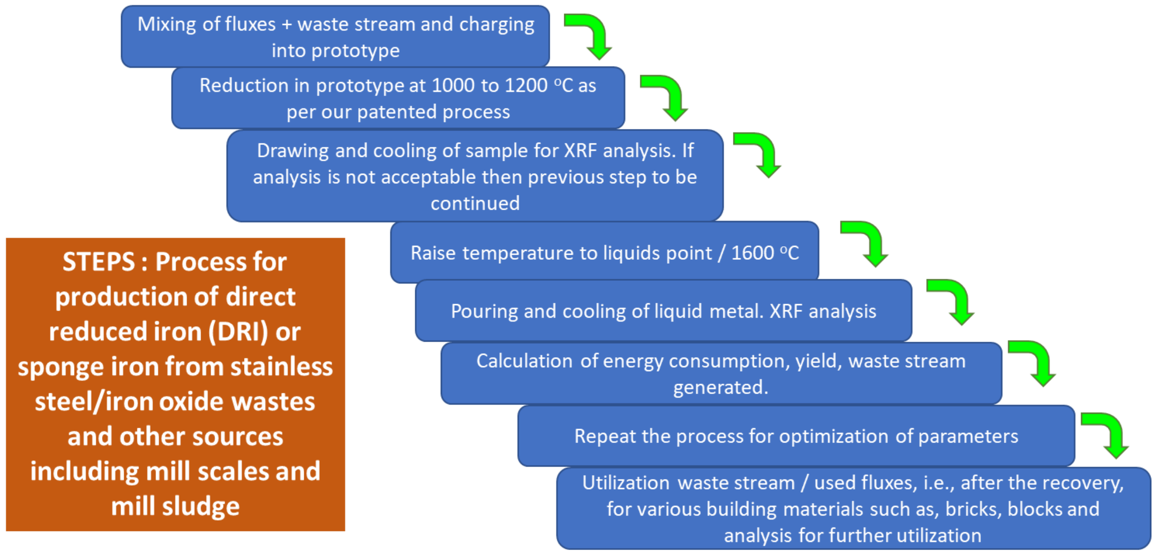



Figure 2 Protocol for steel production from Mill scale and ETP sludge

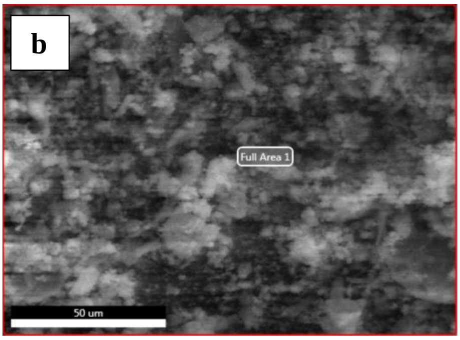
After experiments were conducted in an induction melting furnace as per the protocol stated above, the metal and slag were separated. Big lumps of slags were arduous in nature. Two big lumps S1 and S2 were chosen for further analysis. Slag samples S1 and S2 were big chunks and hence could not be used directly in the experimental work. Therefore, before carrying out, the experimental work the two slag lumps S1 and S2 were finely pulverized in a pulverizer to get the powder form. In order to evaluate the efficacy of waste slag with cement mortar, the two slag samples S1 and S2 were incorporated in cement paste and there performance was compared with ground granulated blast furnace slag which is used in the construction industry. Mix proportion of all the materials was calculated as per BIS 10,262:2009. The initial and final setting time of cement was determined according to BIS 4031: 1988 (Part-5).

## 3. Results and Discussion

In this studies, combination of carbonates of calcium and barium were added in an induction furnace along with ETP sludge and mill scale to produce carbon monoxide. The temperature in the induction furnace was kept as per the theoretical need obtained by the Ellingham diagram [17]. The results are depicted in Figure 3 for sludge and in Figure 4 for mill scale.

**a**

**b**



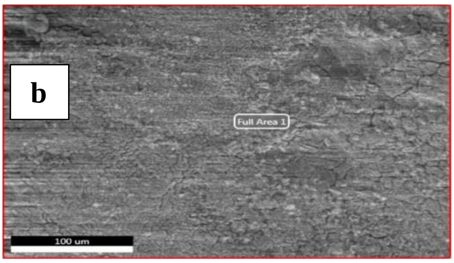

**c**

| Element | Weight % |
|---|---|
| C K | 8.71 |
| O K | 32.37 |
| NaK | 0.23 |
| MgK | 0.53 |
| AlK | 0.18 |
| SiK | 0.47 |
| S K | 5.03 |
| CaK | 16.27 |
| BaL | 0.54 |
| CrK | 5.03 |
| MnK | 1.56 |
| FeK | 23.46 |
| NiK | 4.87 |
| CuK | 0.77 |

Figure 3: Sludge (a) actual photo of sludge (b) SEM image of sludge (c) EDAX analyis of sludge

**a**

**b**




**c**

| Element | Weight % |
|---|---|
| C K | 8.53 |
| O K | 12.00 |
| NaK | 0.02 |
| MgK | 0.08 |
| AlK | 0.20 |
| SiK | 0.37 |
| S K | 0.07 |
| CaK | 0.14 |
| BaL | 0.13 |
| CrK | 2.08 |
| MnK | 2.64 |
| FeK | 70.99 |
| NiK | 2.01 |
| CuK | 0.74 |

**c**

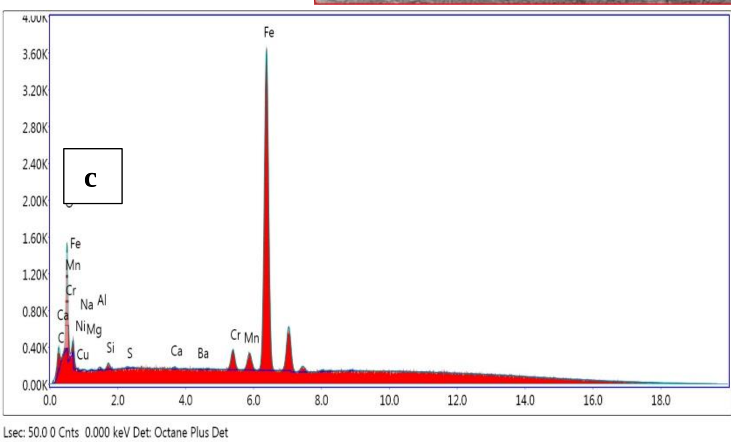



Figure 4: Mill scale (a) actual photo of mill scale (b) SEM image of mill scale (c) EDAX analyis of mill scale

Figures 3a and 4a represent photos of sludge and mill scale, respectively. It was observed that sludge was powder and brown, whereas the mill scale was like metal chips, very hard non, non-porous, and bluish-black in color. The EDAX analysis depicts that in both sludge and mill scale, the highest percentage is iron, i.e., 23.46% and 70.99%, respectively. Thus, both are potential candidates as raw materials for producing DRI.

After the experiments as per the protocols described earlier, the steel and slag were separated. The steel samples were analyzed and depicted in Table 1.

Table 1: EDAX analysis of DRI produced from waste with different coke percentage

| Sample No. | SS metal sample | Mill scale Sample | Sample No.22 | Sample No 23 - | Sample No 24 | Sample No 25 |
|---|---|---|---|---|---|---|
| Description | Reference sample | Base Sample | Process sample | Process sample | Process Sample | Process Sample |
| C% | BDL | 8.53 | 0.87 | 9.37 | 10.66 | 9.24 |
| O2% | 2.86% | 12 | 1.34 | 18.34 | 20.42 | 20.24 |
| Cr% | 11.45* | 2.08 | 6.57 | 1.07 | 9.07 | 5.60 |
| Mn% | 8.87 | 2.64 | 4.16 | 7.59 | 22.61 | 4.12 |
| Fe% | 66.67 | 70.99 | 81.27 | 57.93 | 16.68 | 40.40 |
| Na% | 3.92* | 0.02 | 1.34 | 1.88 | 5.33 | 3.56 |
| Ni% | 1.62 | 2.01 | 1.86 | 0.66 | 0.42 | 0.50 |
| Cu% | 1.62 | 0.74 | 1.43 | 0.70 | 1.17 | 0.79 |
| Process parameter | - | - | Coke–20% | Coke–15% | Coke–10% | Coke–5% |
| Result | - | - | OK | Not OK | Not OK | Not OK |
| Remarks | Cr was14% but analysed as 11.45% No Na content in SS. Sodium contamination / analytical error | | O2 % can be taken as below 0.5% based on reference sample O2 analysis | | | |

Several DRI samples were produced with parameter variations and analyzed using EDAX. A few results of EDAX analysis were presented in Table 1 for quick understanding purposes. The critical parameter is the percentage of coke in flux along with sludge or mill scale. It can be easily deduced that the iron in DRI varies with increased coke percentage. With 20% coke in flux, the DRI produced is 81.27% of iron and O2 percentage, which also reduced significantly to 1.34%. Thus, these results depicts the success of producing DRI from sludge/mill scale by employing an induction melting furnace.

Afterwards, the slag was taken for further processing as per the described protocol. Figure 5 depicts the actual photographs of waste slag S1 and S2.

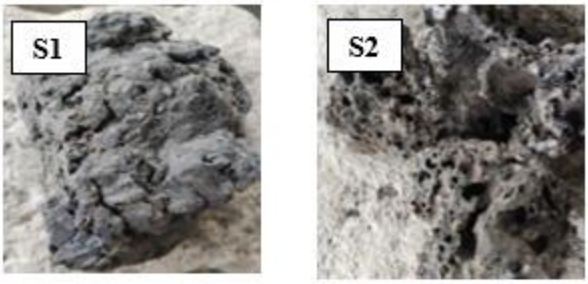



Figure 5: Photographs of slag produced after experiments

Slag lumps' morphology differed; slag 1 was non-porous, and slag 2 was highly porous. SEM, EDAX, and XRD instruments further characterized the slag samples.

The SEM and EDAX results of S1 and S2 slags are represented in Figure 6 and 7, respectively. The SEM images of slags are with a magnification of 100µm. The images show that S-2 type slag are denser and has closed packing efficiency as compared to the S-1 type slag.

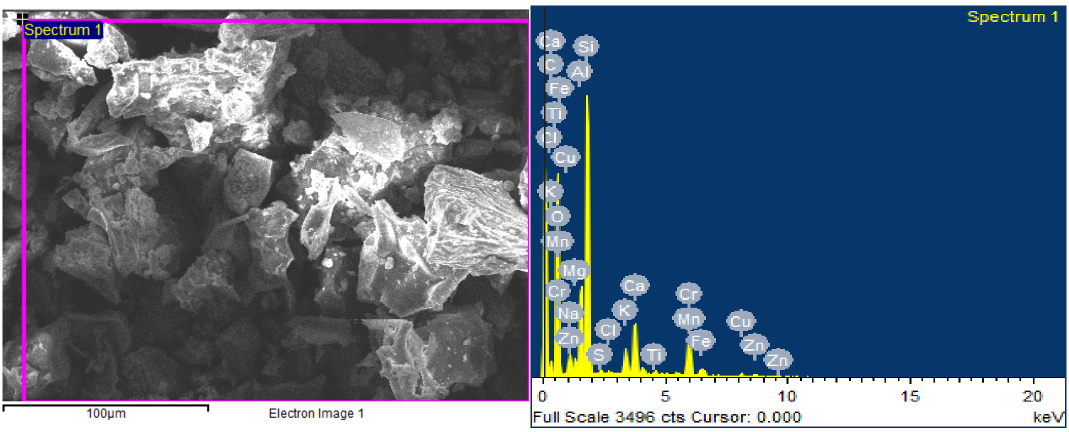



Figure 6: SEM and EDAX characterization of S-1

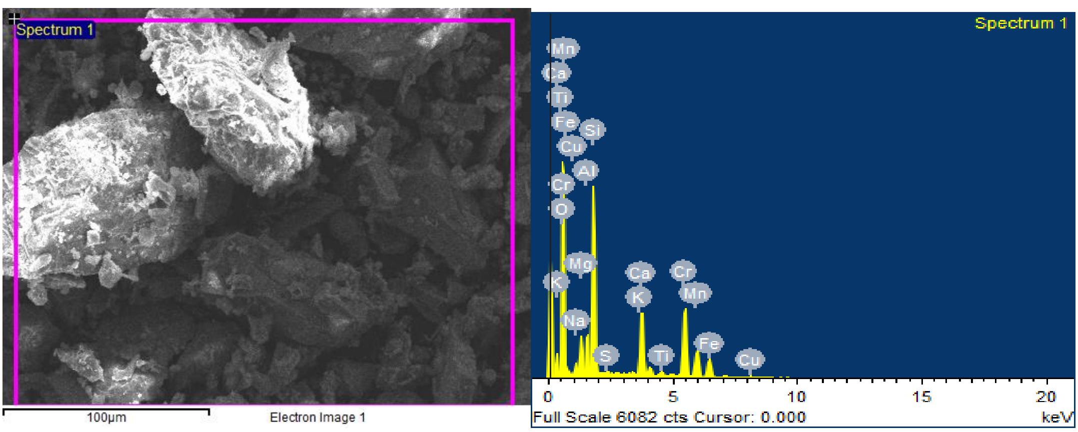
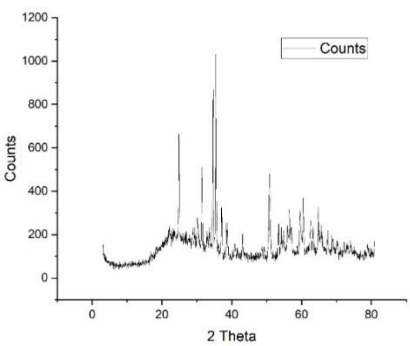



Figure 7: SEM and EDAX Characterization of S-2

EDAX of both the S-1 Slag and S-2 slag confirms the presence of Silica elements in the samples. The highest peak is shown for the Manganese element. The EDAX also indicates the presence of copper, calcium and potassium oxides as the secondary oxide, while the aluminium and ferrous oxides are primary oxides in S-1 slag.

The highest peak is shown for the silicon element. Other than silicon, calcium and carbon elements are shown to be a major element group of S-2 slag composites. The EDAX also indicates the presence of zinc, copper, and titanium oxides as the secondary oxide group, while aluminum and potassium are found to be the primary oxides present in S-2 slag.

The XRD patterns (Figure 8) for both the S-1 and S-2 shows similar characterization. The highest peaks were observed for S-1 slag. The peak count ranged between 750 to 800. This could be the diffraction due to the manganese element in S1. The second-highest peak was observed at an angle between 60 and 70 degrees, which could indicate the presence of silicon. Another 2 peaks ranged between 400-500 counts but at different angles, stating the presence of Calcium, Titanium, and other oxides.



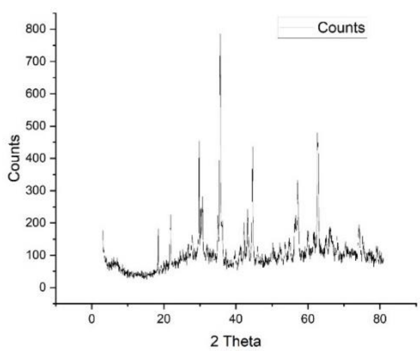




Figure 8. XRD Pattern of S-1 and S-2 slag.

The highest peaks were observed at 35-40 degrees at a count of 1000, which may be attributed to the presence of silicon element. The second highest peak was also observed between the same range, but its count was nearly 800, indicating the presence of calcium oxides. The lower peak band was observed between 60-80 degrees, showing the secondary oxides groups of Zinc, manganese, iron, etc.

In the present investigation, four trial mixes for each slag were carried out to determine the performance of industrial waste-based slag S1 and S2, and a set of 6 cubes were prepared for each trial mix. The cement replacement was done at 5,10,15, and 20% based on the weight of the cement. The cement pastes were cast using a mortar mixing machine into cube moulds of 50mm x 50mm x 50mm (Figure 9).

The water required was 30% of the total cementitious material, keeping the consistency of cement in mind. The cubes were demoulded with the help of a pressure pump and kept for curing. Figure 6 shows test cubes of S1 and S2. The test of compression of cubes was done at 7 days.

Figure 9: Cubes made with S1 and S2 Slag at different cement replacement percentage

The compressive strength of all the cubes was done with Amil's Compression testing machine and reported in Table 2.

Table 2: Compressive strength for various replacement levels of cement with slag S1 and S2

| | | |
|---|---|---|
| Slag_1(S1) | | |
| Replacement with OPC | | |
| Mix-1 (5% Replacement) | | |
| Material | Qty | 7day strength |
| Cement | 190gm | 48 |
| Slag | 10gm | |
| Water | 60gm | |
| Mix-2 (10% Replacement) | | |
| Material | Qty | 7day strength |
| Cement | 180gm | 22.4 |
| Slag | 20gm | |
| Water | 60gm | |
| Mix-3 (15% Replacement) | | |
| Material | Qty | 7day strength |
| Cement | 170gm | 35.4 |
| Slag | 30gm | |
| Water | 60gm | |
| Mix-4 (20% Replacement) | | |
| Material | Qty | 7day strength |
| Cement | 160gm | 28.4 |
| Slag | 40gm | |
| Water | 60gm | |
| Slag_2(S2) | | |
| Replacement with OPC | | |
| Mix-1 (5% Replacement) | | |
| Material | Qty | 7day strength |
| Cement | 190gm | 29.6 |
| Slag | 10gm | |
| Water | 60gm | |

| Mix-2 (10% Replacement) | | |
|---|---|---|
| Material | Qty | 7day strength |
| Cement | 180gm | 33.6 |
| Slag | 20gm | |
| Water | 60gm | |
| Mix-3 (15% Replacement) | | |
| Material | Qty | 7day strength |
| Cement | 170gm | 33.7 |
| Slag | 30gm | |
| Water | 60gm | |
| Mix-4 (20% Replacement) | | |
| Material | Qty | 7day strength |
| Cement | 160gm | 41.4 |
| Slag | 40gm | |
| Water | 60gm | |

From 7 days compressive strength results in can be noted that cement replacement can be done depending upon the required compressive strength. However, more studies are required to study the effect of the mixing of slag S1 and S2 in concrete.

## 4. Conclusion

The study was initiated to produce direct reduced iron (DRI) from mill scale and ETP sludge in an induction furnace. This study successfully demonstrates the feasibility of transforming mill scale and ETP sludge, by-products rich in iron from the steel production process, into Direct Reduced Iron (DRI) using an induction furnace. The successful production of DRI was confirmed through XRD and EDAX characterization, highlighting the potential of this method to create value-added products from waste materials. This research offers a viable solution to managing waste in the steel industry and contributes to reducing pollution loads and promoting environmentally sustainable practices within the stainless steel sector.

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conflict of interest

The authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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