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Review

Ascertaining and Optimizing the Water Footprint and Sludge Management Practice in Steel Industries

Atun Roy Choudhury [1,2,*], Neha Singh [3], Arutchelvan Veeraraghavan [4], Ayushi Gupta [5], Sankar Ganesh Palani [2,*], Mohammad Mehdizadeh [6,7], Anahita Omidi [8] and Duraid K. A. Al-Taey [9]

1 Cube Bio Energy Pvt. Ltd., Madhapur, Hyderabad 500081, India
2 Department of Biological Sciences, BITS Pilani Hyderabad Campus, Hyderabad 500078, India
3 Chadwick's FSM Laboratory, Banka BioLoo Limited, Shed no-37, Mallapur, Hyderabad 500076, India; neha.lab@bankabio.com
4 Department of Civil Engineering, Faculty of Engineering and Technology, Annamalai University, Annamalai Nagar, Chidambaram 608002, India; arul.au@gmail.com
5 Institute of Environment and Sustainable Development, Banaras Hindu University, Varanasi 221002, India; ayushi.gupta10@bhu.ac.in
6 Department of Agronomy and Plant Breeding, Faculty of Agriculture and Natural Resources, University of Mohaghegh Ardabili, Ardabil 5619911367, Iran; mehdizade.mohammad@gmail.com
7 Ilam Science and Technology Park, Ilam 6939177157, Iran
8 Department of GIS and Remote Sensing, Faculty of Geography, University of Tehran, Tehran 1417853933, Iran; omidiannahita@gmail.com
9 Department of Horticulture, AL-Qasim Green University, Babylon 964, Iraq; duraidaltaey@gmail.com
* Correspondence: atnroy10@gmail.com (A.R.C.); sangan@hyderabad.bits-pilani.ac.in (S.G.P.)

Abstract: Steelmaking is a water-intensive process. The mean water intake against each ton of steel manufactured is ascertained as between 2 and 20 m^3. Primarily, the stated requirement is in the form of make-up water to compensate for evaporation and mechanical losses and does not contribute to wastewater generation. Conversely, unit operations, such as rolling, continuous casting, pickling, etc., generate highly complex wastewater rich in polycyclic aromatic hydrocarbons (PAH), cyanide, ammonia, non-consumed acids, benzene, toluene, xylene, oil, grease, etc. Further, the conjugative wastewater contains a high concentration of metallic oxides, toxic elements, oil, nitrogen, and heavy metals such as zinc, nickel, chromium, etc. These contaminants are generally treated and neutralized using physicochemical and membrane-based systems. This also yields hazardous sludge, which is landfilled, thereby incurring an ancillary financial burden. However, sludge can be a frugal source of extracting multi-dimensional benefits. The present review investigated and identified the most water-intensive and wastewater/sludge-contributing unit operations and proposed a preferential combination of treatments to balance efficacy and economy. Further, the various global practices for sludge recycling and management documented in the existing literature are summarized and ranked with the help of the analytic hierarchy process (AHP). The findings revealed concrete making and nutrient recovery as the most- and least-preferred recycling alternatives.

Keywords: steel industry; sludge management; waste stabilization; analytic hierarchy process; landfilling; sludge recycling

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1. Introduction

Ironmaking and steel production are vital industrial processes that involve the transformation of iron ore into molten iron and its subsequent conversion into various grades of steel, supporting diverse sectors worldwide. The production process is complex and incorporates a series of operations in the following order: manufacturing of pig iron in the blast furnace (BF), steel manufacturing, shaping through rolling mills, finishing, and polishing [1]. The production of carbon steel involves a synergistic use of both BF and the basic oxygen furnace (BOF). In the BF, iron ore is melted and purified, yielding molten iron. Subsequently, the molten iron is carefully transferred to the basic oxygen furnace, where a controlled supply of oxygen is blown through it, eliminating the excess carbon and impurities. This meticulous process yields superior-quality carbon steel. The production of stainless steel using the electric arc furnace (EAF) process in conjunction with refining methods, such as argon oxygen decarburization (AOD) or vacuum oxygen decarburization (VOD), involves several key steps. Initially, a mixture of carbon steel and stainless steel scrap is charged into the EAF, where the electric arc generates high temperatures to melt the scrap into a molten state [1,2]. The other two primary alloying elements used in fusion with iron (Fe) are Chromium (Cr) and Nickel (Ni). The mix ratio varies between 7.8:1.6:0.6 and 5.2:2.6:2.2 for Fe, Cr, and Ni, respectively. The quality of the final output depends mainly on the optimal proportionate factor. Subsequently, the molten metal may undergo further refining in either an AOD or VOD vessel. In the AOD process, a mixture of argon gas and oxygen is injected to reduce the carbon and impurity content, while the VOD process utilizes a vacuum environment and oxygen to achieve decarburization. The refined stainless steel is then solidified through continuous casting, resulting in various shapes such as slabs, blooms, or billets, which can be further processed into sheets, bars, or coils. This integrated approach offers a comprehensive method for efficiently converting carbon steel or scrap stainless steel into high-quality stainless steel products with the desired composition and properties. The addition of iron yields better strength and durability but impacts it adversely through rusting and pitting [3]. Adding a significant amount of Cr and Ni hampers the strength but improves the ductility and corrosion resistance [2,3]. Based on the Fe, Cr, and Ni mixing ratio, stainless steel can be classified into three categories: austenitic, ferritic, and duplex. Austenitic stainless steel (face-centered cubic structure) with a higher percentage of Ni (8–12%) and low carbon iron provides enhanced corrosion resistance and ductility. The ferritic variant with a higher percentage of chromium (11–30%) and a minuscule portion of nickel (<0.5%) (body-centered cubic structure) stands better against stress but is tough to weld. Duplex, the equal combination of both, offers superior strength and resistance against corrosion and cracking [1,4]. The steel manufacturing process is subdivided into multiple operations, summarized in Figure 1 [1,2,5,6].

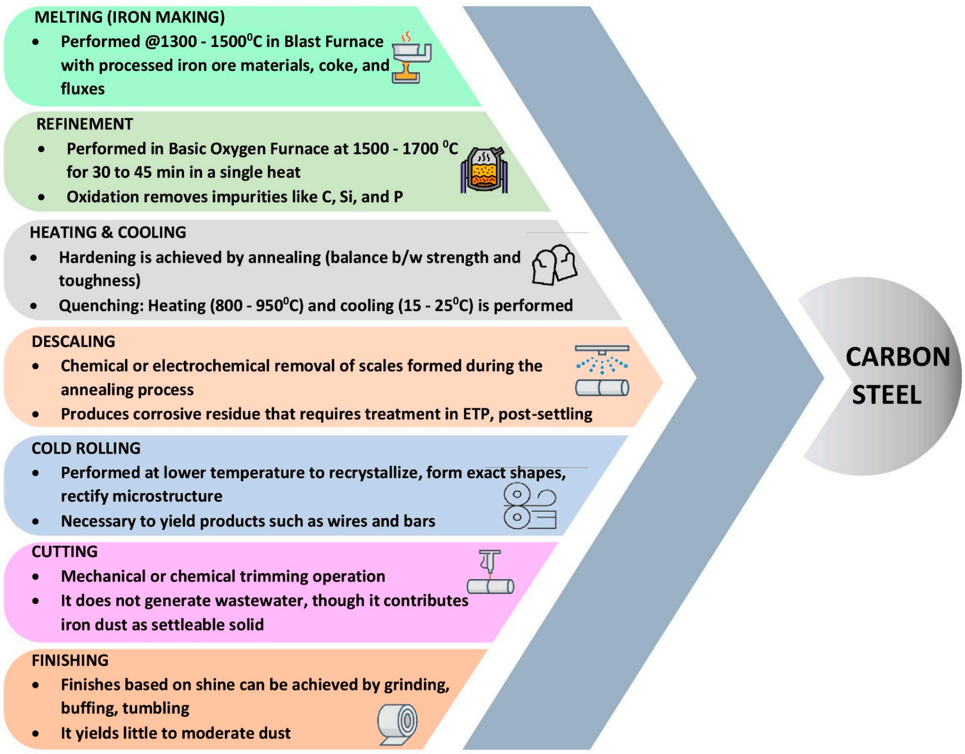

Figure 1. Process flow diagram for carbon steel manufacturing.

2. The Requirement for Water

The comprehensive water demand in steel plants is the summation of the individual requirements for activities such as cooling (make-up water to compensate for evaporation and mechanical loss in operations such as quenching, BF shell, continuous casting, and hot rolling), cleaning (BF, basic oxygen furnace (BOF), coke oven, etc.) descaling (hot rolling and continuous casting), chemical and electrochemical treatments (tin-plating and galvanization), and scrubbing (particulate suppression). Further, the micro-scale water demand can be dissected as direct and indirect cooling (BF oven and other machinery) related requirements, gas washing related requirements in BF, and combined requirements for chemical operations, such as degreasing, pickling, rinsing, etc. Figure 2 delineates water demand, and possible wastewater characteristics contributed to the sequence of each unit operation [7].

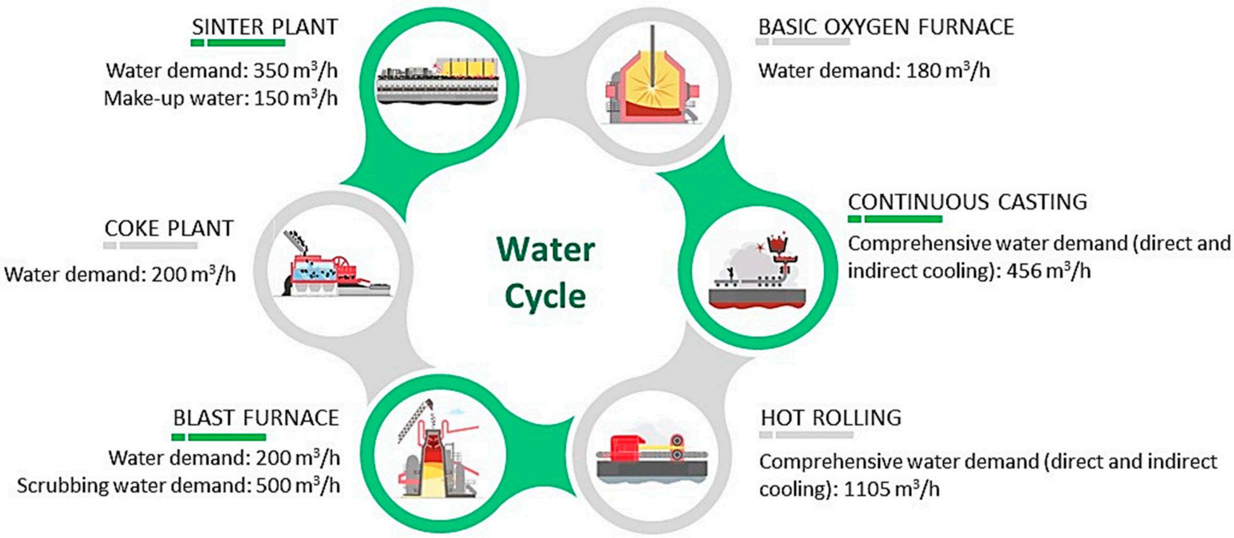

Figure 2. Qualitative and quantitative assessment of water requirements for unit operations involved in carbon steel manufacturing.

2.1. Water Cycle

Water consumption is a crucial aspect of iron and carbon steelmaking processes, playing a fundamental role in their production. The utilization of cooling systems is of paramount importance as they rely on water to regulate temperatures in equipment and machinery, including blast furnaces, converters, and continuous casting machines. Water is efficiently circulated through cooling jackets and spray systems to effectively absorb heat and prevent overheating. An essential operation in BF operations is stave cooling, where water-cooled staves act as protective barriers against the elevated temperatures and chemical reactions occurring within the furnace's inner walls. Furthermore, water is instrumental in gas cleaning systems, which purify hot gases by effectively removing impurities. Within the steelmaking processes, water serves the critical purpose of cooling during operations such as those performed in the basic oxygen furnace and electric arc furnace. Water-cooled panels and systems successfully disperse the heat generated during these reactions. Continuous casting also relies on water, as it solidifies molten steel by guiding it through water-cooled molds and spray cooling systems. Consequently, these water-consuming operations are indispensable for ensuring the integrity and efficiency of carbon steel- and ironmaking processes. The water footprint and associated information of major unit operations related to iron and carbon steelmaking are delineated below [7,8].

Sinter plant: Freshwater is essential for serving as a coolant in the sinter machines, ignition hood, and fan within the sinter plant. The intake demand consists of 350 m^3/h of raw water and 150 m^3/h of make-up water. In a sinter plant, water serves multiple functions, primarily encompassing the cooling of the sinter machines, the ignition hood, and the fan. During these operations, the water inevitably interfaces with the sintering process, thereby exposing it to potential impurities, such as suspended solids, iron oxides, and chemicals employed in the overall procedure. As a consequence, the cooling and cleaning activities produce wastewater as an inevitable by-product.

Coke plant: Freshwater is required to function as a coolant for wet quenching, as well as direct and indirect cooling in the coke plant. The intake demand for the plant is 200 m^3/h of freshwater, which compensates for mechanical losses, evaporation, and blowdown. As the coking process generates intense heat, the resulting hot gases undergo a cooling phase, leading to condensation and the generation of wastewater. This wastewater encompasses a range of impurities, including ammonia, phenol, and cyanide compounds. Moreover, in order to mitigate air pollution, the gases released from the coke ovens undergo a series of scrubbing and cleaning procedures. Water serves as a medium to effectively eliminate particulate matter, sulfur compounds, and various other pollutants from the gases.

Blast furnace: The blast furnace operation necessitates 200 m^3/h of freshwater for the indirect cooling of the BF body, valve, and tuyere. A small quantity of wastewater is generated from the direct cooling of BF slag. Additionally, 500 m^3/h of water is indispensable for the wet scrubbing of BF gas, although the resulting hot wastewater contains a high concentration of suspended solids.

Basic oxygen furnace: Water plays a crucial role in the indirect cooling of lances, hoods, and side tuyere in the steelmaking process. Additionally, a raw water intake demand of 180 m^3/h is necessary for the wet scrubbers used in BOF gas cleaning.

Continuous casting: The casting process requires a total water supply of 456 m^3/h for effective cooling. This includes 6 m^3/h of demineralized water for the indirect cooling of the casting mold, along with 300 m^3/h of coolant water. Additionally, there is a need for 150 m^3/h of water supply to directly cool the continuous casting machines, resulting in the generation of wastewater containing high concentrations of hydrocarbon and metal oxides.

Hot rolling: In the hot rolling process, efficient cooling is crucial, and it involves three distinct water requirements.

Firstly, for the indirect cooling of the furnace, a continuous supply of 5 m^3/h of softened mixed water is necessary. This water aids in maintaining the optimal temperature and preventing overheating.

Secondly, to compensate for various losses and ensure effective cooling tower operation, approximately 100 m^3/h of mixed water is required. The cooling towers play a vital role in dissipating the excess heat and maintaining the overall efficiency of the system.

Lastly, mitigating direct cooling losses is essential for the hot rolling operation. To achieve this, a substantial supply of approximately 1000 m^3/h of mixed water is needed. This water is utilized to cool hot run out tables, steel products, and to facilitate scale breaking, among other related processes.

Most of the unit operations associated with steelmaking are water-intensive, and the total water requirement per hour of steel manufactured is around 180 m^3 for BOF at a rate of 0.6 to 0.9 m^3/t. Mostly the water in direct and indirect cooling applications in steel plants records thermal losses and seeks make-up water. The heat-intensive application requires demineralized water to evade corrosion-related issues, and pasteurization of the coolant is mandatory after certain cycles in the semi-closed circuit. Disinfection is generally performed using a combination of sodium hypochlorite and biocide. For a few occasions, pH adjustment is also required prior to the recirculation. However, the blowdown can primarily be reused within the loop as make-up water without any prominent treatment. The comprehensive water consumption stands at nearly 10% against the intake volume, including evaporation loss, mechanical loss, and other miscellaneous losses in the ETP.

Presently, most steel plants across the globe operate on the zero liquid discharge ideology. Usually, a combination of electrolytic precipitation, biological digestion, and membrane filtration yields more than 90% of the recovery. Recovery and reuse of treated wastewater are ideal options from both environmental and economic perspectives. However, the hazardous sludge generated from the treatment process has to be handled according to regulatory norms [1,7,9–11].

2.2. Wastewater Scenario

The quantity of wastewater discharge is estimated to be 25–26 m^3/ton of steel produced, which signifies the quantity of water consumption is not more than 3–4 m^3/ton and the rest is lost due to evaporation (Table 1). The discharge water has a diverse range of pollutants based on the point of generation. The wastewater and effluent generated from hot rolling and coking operations tend to have higher concentrations compared to those generated from cold rolling and scrubbing. In hot rolling, the wastewater contains elevated levels of scale particles, oil, acids, and various contaminants. Similarly, wastewater from coke plants includes pollutants, such as ammonia, phenols, cyanides, PAHs, sulfides, and heavy metals. On the other hand, cold rolling operations typically utilize water-based lubricants or emulsions that have lower environmental impacts. In scrubbing processes, the wastewater is less concerning but still carries a higher concentration of particulate matter and sulfur compounds [7,8,11–13]. Source segregation and separate pre-treatment are mandatory for each category mentioned above.

2.3. Sources and Characteristics

The major sources of wastewater generation in the steel processing industry include BF, Electrostatic Precipitator (ESP), and rolling mills. Wastewater generated from the BF is primarily from the washing activity, which includes the washing of gas containers. Thus, the primary pollutant existing in the waste stream is suspended solids. The concentration varies between 1000 and 8000 mg/L, based on factors such as furnace size, mode of operation, blast rate, and optimum pressure exerted. Further, a slip in the furnace can cause an additional solid burden of up to 25,000 mg/L. Further, sometimes semi-colloidal ferromanganese particles can be generated from the furnace that are to be co-flocculated and removed, impinging on additional operational cost. Additionally, washing flue gas containers contributes to the finest dust (particle size: 8–10 microns), adding color to the waste stream [8,11,12]. The activated carbon filter is widely used to mitigate the above issue. ESP generates a lesser volume of wastewater with higher concentrations of hard-to-settle finer particles, which can only be removed by advanced filtration.

The rolling mill's operation causes scale (higher oxides of iron) formation, and water is used to remove the same from the surface of the steel. Further, water is used as a coolant and transport media for rolled items and scales, respectively. The freshwater consumption usually varies between 450 and 1600 m^3/h, depending upon factors such as the rolling process (hot rolling consumes more water than cold rolling) and operational design [7,14]. The characteristics of the wastewater that contains scales vary significantly with the rolled products. Production of slabs and blooms yields scales of coarser nature. Most particles are more than 200 mm and can easily be removed by a coarse screen, followed by sedimentation. Manufacturing billets, tube rolls, and rods contribute to finer scales, complicating the wastewater treatment. The specific gravity of the scale is approximately 4, and the same can easily cause clogging of physical treatment units. If the scales are not effectively removed from the wastewater, they settle at the base of the receiving streams, leading to a decrement in depth and volume [8,11].

Milling operation also involves processes such as pickling and rinsing. The processes are primarily descaling- and finishing-oriented mechanisms which involve extensive acid usage at elevated temperature (~70 °C) [13,15], which generates a corrosive process residue. Though both the effluents have a similar ratio of raw acid and ferrous salt, the pickling water is highly concentrated (four to five times greater than rinse water). The quality of pickling water further varies based on the mode of operation. The continuous mode of stripping operation constitutes about 15% of ferrous salt and 7% of raw acid (H_2SO_4, HCL, HNO_3, H_3PO_4, and HF) [16]. Contrarily, acid concentration is reduced drastically to ~1% and salt percentage increases to 20% for batch operation, which is relevant from a salt recovery perspective. Despite encountering higher temperatures (75–95 °C), the wastewater stream generated from rinsing does not carry any combined acids, so the treatment is hassle-free [11].

Other prominent contaminants from the rolling operations are soluble and insoluble oils, grease, and other lubricants. The presence of oil both in free and emulsified forms is non-tolerable. Even the smallest volume may cause elevation of the COD level, the formation of film, and anoxic conditions, leading to the failure of the biological treatment unit. The operations of cold rolling, electrolytic lining, and mechanical workshops are the primary sources of soluble oils. These oils are a complex amalgamation of palm oil and synthetic substances, which at higher temperatures can cause emulsion. The treatment becomes challenging when the emulsion blends with detergents and kerosene. The degree of pollution varies proportionally with the recirculation count of the process water. A typical single-used effluent comprises around 150 mg/L of mixed oil with >30% solubility. A significant proportion (~40%) of ETP influent load comes from the cold rolling mill, and the elevated temperature (~120 °C) of it further makes it difficult to treat [5,8,12,13].

Table 1. Glimpse of steel production and wastewater generation in India [17].

No.	Plant Name and Location	Steel Production (Tons/Annum)	Water Consumption *		Wastewater Generation (m^3/Day)
			Overall (m^3/Day)	For Production (m^3/Ton of Product)	
1	Bhilai Steel Plant, Durg, Chhattisgarh	3,153,000	24,215	2.772	19,616
2	JSW steel Ltd., Vijayanagar, Karnataka	12,000,000	27,382	0.83	23,274
3	JSW Steel Ltd., Salem, Tamil Nadu	1,000,000	7230	2.62	5997
4	Bokaro Steel Plant, Bokaro, Jharkhand	4,000,000	38,466	3.5	30,301
5	Rashtriya Ispat Nigam Ltd., Visakhapatnam, Andhra Pradesh	4,400,000	139,506	11.47	118,580
6	Jindal Steel and Power Plant, Raigarh, Chhattisgarh	3,600,000	27,328	2.770	23,229
7	Jindal Steel and Power Plant, Angul, Odisha	2,700,000	11,023	1.48	8488
8	Jindal Steel and Power Plant, Patratu, Jharkhand	1,600,000	6809	1.55	5372
9	Arcelor Mittal Nippon Steel Ltd., Hazira, Gujarat	1,000,000	3230	1.16	2746
10	Durgapur Steel Plant, Durgapur, West Bengal	2,120,000	119,008	19.80	118,157
11	Rourkela Steel Plant, Rourkela, Odisha	4,200,000	43,983	3.89	37,386

Table 1. *Cont.*

No.	Plant Name and Location	Steel Production (Tons/Annum)	Water Consumption *		Wastewater Generation (m^3/Day)
			Overall (m^3/Day)	For Production (m^3/Ton of Product)	
12	IISCO, Burnpur, West Bengal	4,260,000	87,065	7.38	74,005
13	Chandrapur Ferro Alloy Steel Plant, Chandrapur, Maharashtra.	100,000	260	0.91	221
14	Salem Steel Plant, Salem, Tamil Nadu	339,200	13,249	14.15	11,261
15	JSW Steel Ltd., Dolvi, Maharashtra	5,000,000	140,774	10.11	111,657
16	TATA Steel Ltd., Ferro Alloy Plant, Bamanipal, Odisha	61,000	3002	17.89	2553
17	TATA Steel Ltd., Kalinganagar, Odisha	6,000,000	36,041	2.13	30,635
18	Ferro Manganese Plant, TATA Steel Ltd., Keonjhar, Odisha	50,400	655	4.67	560
19	TATA steel ltd., Jamshedpur, Jharkhand.	10,220,000	102,220	3.27	86,887

Note: * Water consumed depicts the total intake, including water consumed for domestic purposes. Typically, the requirement of freshwater varies between 4 and 15 m^3/ton of liquid steel yielded [18].

Steelmaking is a water-intensive process. Non-intermittent supply of freshwater is a mandate for direct and indirect cooling, scrubbing, and washing. The cooling process generally does not contribute to wastewater generation and only seeks make-up water regularly. Scrubbing and washing yields effluent rich in suspended solids, oils, metals, and other hazardous chemical compounds. The present study identified coke oven (CO) processing as the most hydro-intensive operation with the highest wastewater generation. Further, BF, quenching, chilling and scrubbing of CO gas, and separation of the by-products are identified as the unit operations with ample water and wastewater footprint. An old BF can consume up to 7.6 m^3 of freshwater to yield 1 mg of ingot steel. The ingot steel is further processed in the steel-melting shop through the continuous casting mechanism that generates hot wastewater with elevated concentrations of suspended and emulsified solids, oils, and grease. In addition, subsequent rolling operations contribute to effluent rich in scales (100–200 mg/L) and oils (10–25 mg/L). Finally, the spent pickle liquor (SPL) generated from the pickling process with a higher concentration of ferrous salts, heavy metals such as Zn, Ni, Cu, Cr, etc., and highly acidic waters impact the overall effluent quality. The composite process effluent is toxic and carries critical impurities, such as cyanides, heavy metals, phenol, oil and grease, ammonia, etc. SPL is primarily responsible for metal-rich sludge generation from steel mill ETPs. Figure 3 summarizes the wastewater cycle of the steel industry [8].

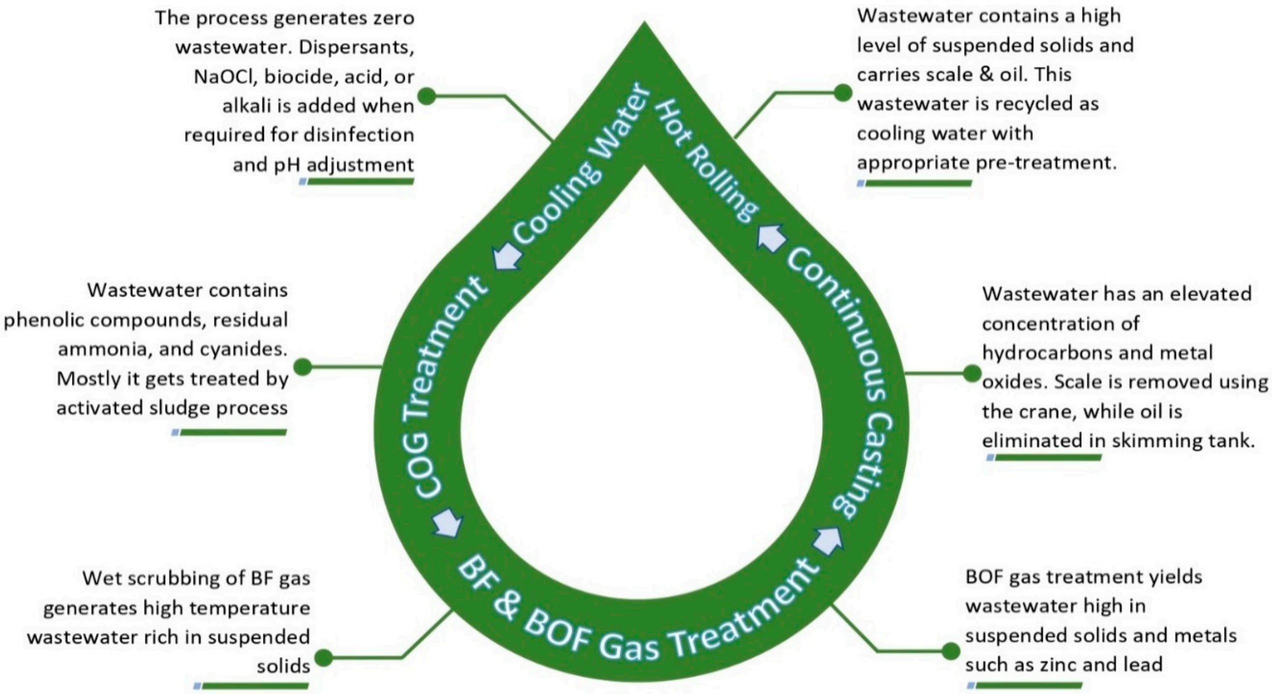

Figure 3. Steel industry wastewater characteristics cycle.

2.4. Treatment of Wastewater

The wash water from the flue gas chamber primarily contains settleable solids of higher specific gravity. Rectangular or circular settling tanks can easily eliminate the same with a retention period of around 12 h. Comparatively, fresher establishments prefer circular vortex flow clarifiers or tube settlers for rapid settling with minimal retention period (1–2 h). The effluent from the basin is separated using the overflow method, and it may contain suspended solids up to 100 mg/L. If feasible, the sludge is mechanically removed and sent to the filter press for further dewatering and recovery of essential salts (Fe_2O_3 and CaO) [12,13].

The scales generated from rinsing and pickling operations are of higher specific gravity and tend to settle quickly and easily. The scales are hazardous and thus should be stabilized and safely disposed of in secured landfills. The wastewater generated from the rolling operations carries free oil alongside the solids. The solids contributed from cold rolling are finer than that of hot rolling, hence the method of settling should be designed accordingly. A standard settling tank of dimensions $9 \times 5.5 \times 2.5$ m is recommended for effluent from hot rolling, whereas a tube settler is recommended for cold rolling mill effluent. The sludge contains higher concentrations of usable nitrates that can be retracted through resource recovery. The oil issue should be addressed by a skimming tank, and its concentration should be lowered below 10 mg/L before releasing/reusing. Recently, industries have started utilizing cleansing solutions of an alkaline nature, such as NaOH, Na_2CO_3, phosphates, and silicates, to remove oils before the effluent enters the ETP, thereby eliminating the need for skimming. Therefore, additional FOG removal need not be performed to avoid membrane fouling in the advanced treatment systems [8,11,13].

2.5. Effluent Treatment Plant

Irrespective of its quantity, the steel industry generates highly complex wastewater rich in toxic aromatic solvents, such as benzene, toluene, xylene (BTX), cresol, and phenol. Laterally, the wastewater streams from rolling and pickling operations contribute to ammonia, non-consumed acids, PAH, oil, and grease. The amalgamation of such critical pollutants makes it extremely difficult for a standalone system to yield the desired output. Thus, combining primary, secondary, and tertiary treatment is always recommended to tackle the whole gamut of pollution at different stages. A high load of scales, suspended solids, oil, and grease is primarily addressed by physical separation systems, such as screening chambers, sedimentation tanks, tube settlers, and skimming tanks. Post-gravity-settling, finer particles are chemically settled in coagulation and flocculation basins. In most cases, the permeate is subjected to advanced oxidation processes, such as photo-Fenton's oxidation, ozonation, UV photolysis, etc. [19]. Oxidation and subsequent adsorption ensure the removal of PAHs, cyanide, phenols, etc. Sometimes, biological systems, such as activated sludge process, moving bed biofilm bioreactor, sequential batch reactor, etc., are employed to eliminate the organic impurities, but owing to the longer treatment period, incapability of handling shock loads, the requirement of specific microbial species etc., adaptability of these systems remains as a stigma [20]. Presently, membrane-based separation technologies are highly preferred in steel industries, as they yield the highest treatment efficacy and recovery, as presented in Figure 4 [18].

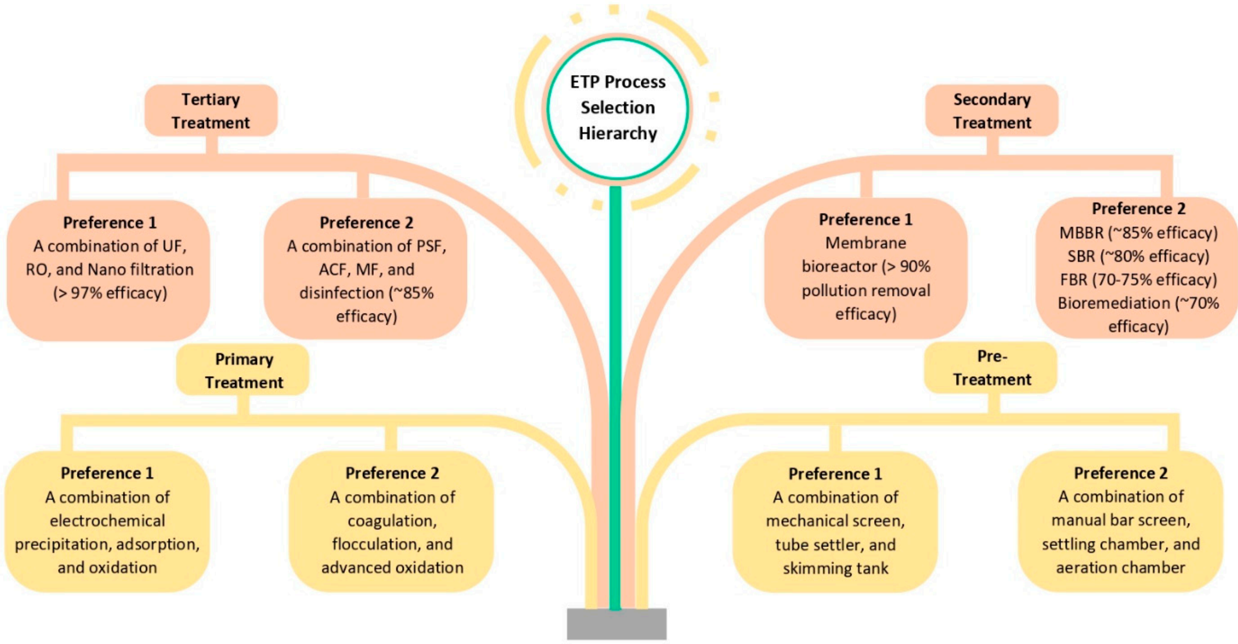

Figure 4. Hierarchy of wastewater recycling process selection cycle.

In recent times, the incorporation of tertiary treatment units, such as pressure sand filter (PSF), activated carbon filter (ACF), micron filter (MF), ultra-filtration (UF), reverse osmosis (RO), etc., extended the liberty of reusing the treated effluent. The assorted combination of these processes yields more than 95% of pollutant removal. Additionally, membrane bioreactor (MBR) application is also gaining popularity among steel industry professionals. The system promises a consistent efficacy of 90% or above and addresses most pollutants, including BOD, COD, total solids, heavy metals, oil and grease, etc. Havoc initial investment, membrane fouling and flux deterioration, and lack of availability of trained manpower are the critical hindrances against the large-scale adaptation of MBR.

The process also generates harmful by-products, such as sludge and salt from secondary treatment units and ATFD. Both products are hazardous and have an elevated concentration of certain heavy metals [8,12,13]. Salt with no recovery potential needs to be landfilled safely. Contrarily, sludge can be a promising source of nitrogen for various applications in agriculture, once treated and stabilized properly [21,22]. Figure 5 showcases the process flow from generation to the ultimate disposal of steel mill effluent.

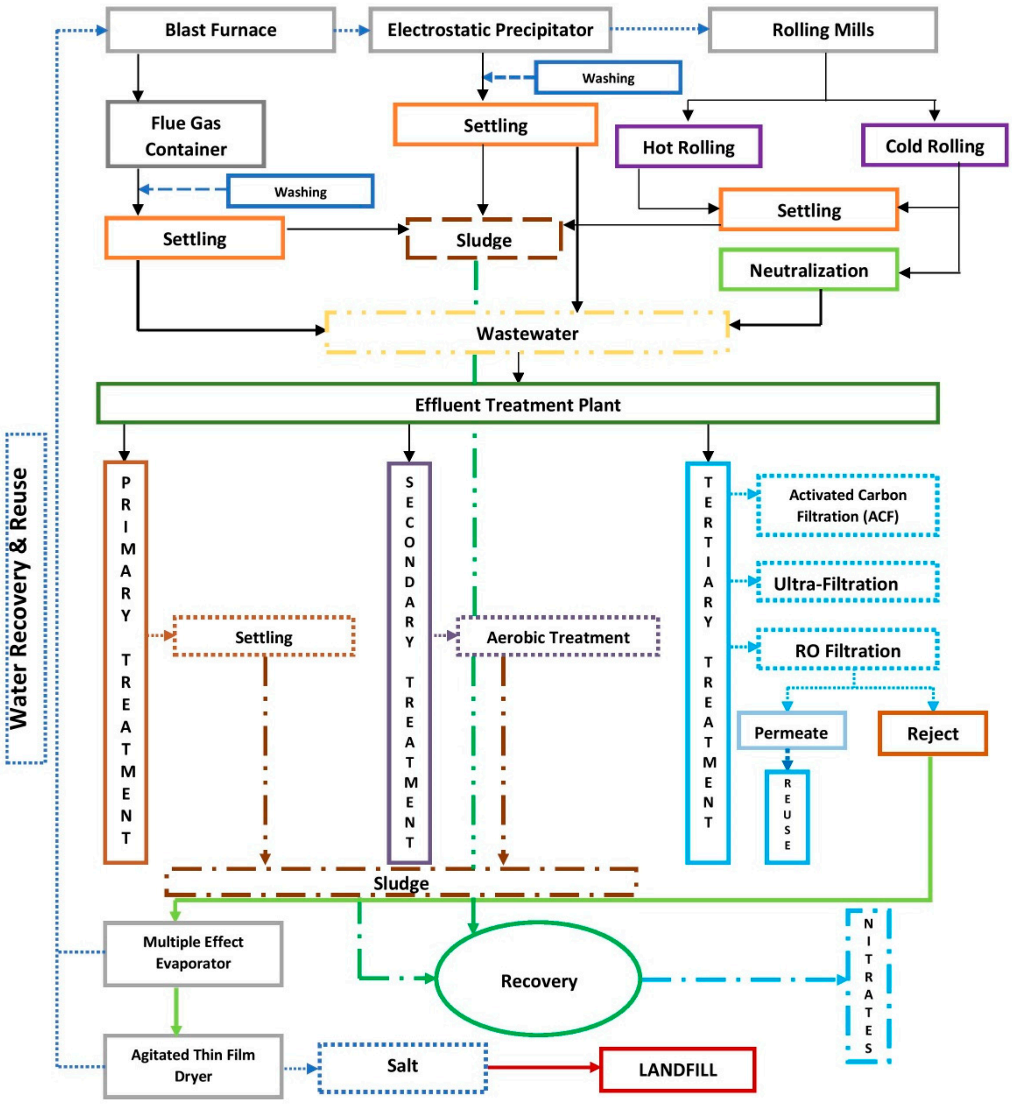

Figure 5. Process flow diagram with possibility of recovery.

2.6. Characteristics of ETP Sludge

Separation and pre-treatment of primary effluent at the source is the key to ETP's success in steel mills. The heterogeneity in wastewater characteristics from different operational sources makes it difficult for the ETP to meet the expected treatment efficiency. After in situ pre-treatment, the wastewater streams should be collected in an equalization tank, in which an agitator can be introduced to ensure homogeneity. The solids that escaped from initial pre-treatment need to be removed with the help of an advanced settling mechanism, such as a tube settler. Oil and other greasy substances can be conveniently removed by skimming operations before introducing them for organic removal. In the effluent, BOD, COD and VFA can be addressed in aerobic treatment systems (i.e., advanced oxidation process, rotating biological contactor, membrane bioreactor, etc.). The effluent can be further polished with an advanced unit, such as an activated carbon filter for color removal; UF and RO for the removal of TDS and COD; or a multiple-effect evaporator (MEE) and agitated thin film dryer (ATFD) to facilitate further recovery from RO reject and ensure zero liquid discharge (ZLD).

The secondary sludge from the ETPs and dried sludge from the forced evaporation system carry elevated concentrations of acids, oil and grease, heavy metals, etc., and are considered hazardous. Researchers have investigated the feasibility of recycling this sludge as a soil conditioner, alternate aggregates, raw material for brick and cement making, etc. [23–25]. However, the reported findings are mostly inadequate to arrive at any conclusion, as most of these studies did not provide much detail on the characterization of the sludge. Thus, a detailed analysis of the sludge and the end products is of utmost importance to ensure zero leachability and regulatory compliance. Tables 2 and 3 depict the physical and chemical characteristics, and Table 4 delineates the metal concentrations of steel mill ETP sludge [26].

Table 2. Physical characteristics of steel mill ETP sludge.

No.	Parameter	Unit	Method	Result	Remarks
1	Physical State	-	-	Solid	-
2	Color	-	-	Dark Brown	-
3	Texture	-	-	Wet Cake	-
4	Odor	-	-	No	-
5	Paint Filter Liquid Test	-	USEPA SW-846; 9095A	Pass	No infiltration through PFLT paper
6	Bulk Density	g/cc	ASTM D 5057-10	1.42	On wet basis
7	Is there any violent chemical change (in air) (Normally unstable) (Yes/No)	-	-	No	-
8	Reacts violently with water (Yes/No)	-	-	No	-
9	Generation of toxic fumes with water/acid/basic (Yes/No)	-	-	No	-
10	Forms potentially explosive mixture with water (Yes/No)	-	-	No	-
11	Explosion when subjected to a strong initiating force (Yes/No)	-	-	No	-
12	Explosion at normal temperature and pressure (Yes/No)	-	-	No	-

Table 3. Chemical characterization for steel mill ETP sludge.

No.	Parameter	Unit	Method	Result	Remarks
1	pH	-	USEPA SW-846; 9045C	6.9	-
2	Flash Point	°C	USEPA SW-846; 1020A	>200	Non-flammable
3	Loss on drying (LOD) at 105 °C	%	APHA 23rd 2540 B	48.2	-

Table 3. *Cont.*

No.	Parameter	Unit	Method	Result	Remarks
4	Total Solids	%	APHA 23rd 2540 B	51.8	-
5	Volatile Solids	%	APHA 2540 B and E	2.1	Non-biodegradable
6	Calorific Value	cal/g	IS: 1350 (Part-II)-1970	368	On dry basis
7	Water soluble inorganics (WSI)	%	APHA 2540 B and E	0.87	Non water soluble
8	Water soluble organics (WSO)	%	APHA 2540 B and E	0.36	Non water soluble
9	Reactive Cyanide	mg/Kg	SW-846 9014 B and APHA 4500CN-K	0.04	Not detected
10	Reactive Sulfide	mg/Kg	SW-846 9030B and 9034	<1.0	Not detected
11	Total Chloride as Cl	%	APHA 4500-Cl-B	<1.0	10% solution of dried sample
12	Total Nitrogen as N	%	CHNS analyzer	ND	-
13	Total Carbon as C	%	CHNS analyzer	ND	-
14	Total Hydrogen as H	%	CHNS analyzer	ND	-
15	Total Sulfur as S	%	CHNS analyze	ND	-
16	Ammonia as N ((Water leaching tests (WLT))	mg/L	APHA NH3 B, C	4.12	-
17	Total Phenols (WLT)	mg/L	APHA 5530B and D	ND	10% solution of dried sample
18	Cyanide in WLT	ppm	APHA 4500CN-K	ND	10% solution of dried sample
19	Hexavalent Chromium (WLT)	mg/L	APHA 3500 Cr B	<0.2	10% solution of dried sample
20	Fluoride as F-(WLT)	mg/L	APHA 4500 F-D	<1.0	10% solution of dried sample
21	Nitrate Nitrogen as N	mg/L	APHA 4500 NO3B	154.89	10% solution of dried sample

Table 4. Metal analysis of steel mill ETP sludge.

No.	Parameter	Unit	Method	Result	Remark
1	Zinc (Total)	mg/Kg	SW846; 3050 B and 7950/APHA 3120B	28.46	2% solution of dried sample
2	Zinc (WLT)	mg/L	SW846; 7950/APHA 3120B	<1.0	10% solution of dried sample
3	Copper (Total)	mg/Kg	SW846; 3050 B and 7210/APHA 3120B	284.9	2% solution of dried sample
4	Copper (WLT)	mg/L	SW846; 7210/APHA 3120B	<0.5	10% solution of dried sample
5	Arsenic as As (Total)	mg/Kg	APHA 3500 As B/APHA 3120B	<1.0	2% solution of dried sample
6	Arsenic as As (WLT)	mg/L	APHA 3500 As B/APHA 3120B	<1.0	10% solution of dried sample
7	Cadmium (Total)	mg/Kg	SW846; 3050 B and 7130/APHA 3120B	<0.1	2% solution of dried sample
8	Cadmium (WLT)	mg/L	SW846; 7130/APHA 3120B	<0.01	10% solution of dried sample
9	Total Chromium (Total)	mg/Kg	SW846; 3050 B and 7190/APHA 3120B	14,250	2% solution of dried sample
11	Lead (Total)	mg/Kg	SW846; 3050 B and 7420/APHA 3120B	<10	2% solution of dried sample
12	Lead (WLT)	mg/L	USEPA 1998, SW846; 7420/APHA 3120B	<0.1	10% solution of dried sample
13	Nickel (Total)	mg/Kg	SW846; 3050 B and 7520/APHA 3120B	2689	2% solution of dried sample
14	Nickel (WLT)	mg/L	USEPA 1998, SW846; 7520/APHA 3120B	<1	10% solution of dried sample
19	Mercury as Hg (Total)	mg/Kg	SW846; 7471A/APHA 3120B	<1.0	2% solution of dried sample
20	Mercury as Hg (WLT)	mg/L	SW846; 7470A/APHA 3120B	<0.01	10% solution of dried sample

Parallelly, the ETP sludge was characterized using gas chromatography for the presence of various organic substances, such as chloroform, carbon tetrachloride, benzene, chloro-benzene, cresols, 1,4-dichlorobenzene, 1,2-dichloroethane, pyridine, ethyl methyl ketone, nitrobenzene, tetrachloroethylene, trichloroethylene, 1,1-dichloroethylene, 2,4-dinitrotoluene, endrin, heptachlor (and its epoxide), hexachlorobenzene, hexachlorobutadiene, hexachloroethane, lindane, methoxychlor, pentachlorphenol, toxaphene, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 2,4,5-TP (Silvex), vinyl chloride, 2,4-D chlordane. However, the concentrations of all the organics mentioned above was below the detection limit.

Further, the sludge is characterized by its highly inorganic nature, containing significant amounts of metals, such as iron, chromium, nickel, and zinc, and other pollutants, such as acid, BTX, oil and grease, etc., as stated before. These pollutants are present due to the industrial processes involved in steel production. The high level of contamination in steel mill ETP sludge makes it challenging to apply biological treatment methods for sludge handling and management. Unlike sewage sludge, which mainly consists of organic matter, steel mill ETP sludge requires specialized treatment techniques, such as physical and chemical processes, to address the inorganic pollutants effectively. Its unique composition and properties necessitate tailored approaches, such as brick making, aggregate and concrete making, recovering nutrients, and landfilling, for its proper disposal or reuse in an environmentally responsible manner.

3. Possible Recycling Alternates for ETP Sludge

The common problem encountered in steel mill effluent's primary and secondary treatment is sludge generation. Due to the contamination with persistent pollutants, presently the majority of the steel industries pay little attention to facilitating scientific recycling and recovery of sludge. Contrarily, landfilling of the sludge causes enormous logistical and waste-disposal costs. Various possibilities of wholesale end-use are investigated and proposed by researchers across the globe. Table 5 comprehends the most promising and viable methods that have the potential to be replicated at a field/industrial scale.

Table 5. Comprehensive review of sludge handling and management techniques.

No.	Summary of the Study	Key Findings of the Study	Feasibility of the Method	Source
1	• American Society for Testing Materials (ASTM) compliant bio-bricks were developed from the wastewater sludge for severe climatic zones. • More than 50,000 bio-bricks were produced and utilized in the making of recreational structures and maintenance buildings.	• Synthesis of similar shape and form of bio-brick by replacing clay and shale up to 30% with wastewater sludge.	100% of sludge can be converted into bio-bricks using the cold pressing process. The process lefts zero residue	[27]
2	• Brick making and application as lightweight aggregate and cementitious material were the most promising recycling/reuse-related applications for dried wastewater sludge and incinerated sludge ash.	• Brick making delivered a successful outcome for replacing clay up to 40%. • Lightweight coarse and fine aggregates produced from the pelletized sludge ash showcased compromised mortar strength. • Incinerated dewatered sludge with limestone developed significant cementitious properties.	Entire sludge and ash can be recycled through aggregate, brick, and cement making applications	[25]

Table 5. *Cont.*

No.	Summary of the Study	Key Findings of the Study	Feasibility of the Method	Source
3	• Blast furnace slag was utilized as a flocculant for removing phosphorus from the wastewater in a constructed wetland. • The toxicity and economic feasibility were the two factors left to be investigated.	• Escalation in wastewater pH required higher dosage and contact time and inflated reduction efficacy.	Blast furnace slag is already widely used as a commercially viable material in the production of bricks and concrete. Consequently, it does not seem logical to apply it as a flocculant despite the obstacles involved.	[24]
4	• Recycling and reuse opportunities from each intermediate item of steelmaking, such as slag, dust, and process gases, were reviewed. • The scope of possible product recovery is comprehended as follows: cement, fertilizer, road stone, asphalt, metal recovery in the form of zinc and iron, electricity, heating, plastic products, and paints.	• Ammonium sulphate can be recovered from the ETP sludge and used as fertilizer. • Iron oxides in the dried sludge can be used in cement manufacturing as a raw material.	Recovering nutrients from sludge can be a challenging process due to its high contamination levels with heavy metals and other pollutants. Nevertheless, utilizing sludge in cement manufacturing has the potential to consume up to 20% of the generated sludge.	[28]
5	• The process involved a reduction of acid pickling and galvanization sludge into sponge iron in the short rotary kiln alongside iron ore dust and iron and steel dust. • The primary constituents of the sludge were identified as iron, nickel, and chromium. • The reducing environment was created by injecting the combustion gases into the kiln.	• Sponge iron was produced in a specially designed short-length rotary kiln with steel mill ETP sludge and other metal dust.	The reuse of 100% of the sludge in this process is feasible without any reservations. However, it should be noted that constructing a separate kiln with special dimensions is a costly endeavor.	[29]

Table 5. *Cont.*

No.	Summary of the Study	Key Findings of the Study	Feasibility of the Method	Source
6	• Ferrous oxide (Wustite) and its micaceous pigment were produced from oily hot rolling mill sludge by the direct reduced iron (DRI) method supported by thermal decomposition. • Enhanced efficacy was observed with reducing agents, such as coke dust and blast furnace slag. • The yield of metallization was also reported to vary parallelly with a rise in temperature between 900 and 1150 °C.	• The yield of metallization depends on factors such as temperature, DRI time, and coke dust and sludge mix ratio. The optimum values were 1100 °C, 30 min, and >3.6, respectively.	The generation of hot rolling mill sludge is trivial and the consumption process is highly sophisticated. It can only be achieved by collecting the specific sludge directly at its source.	[30]
7	• The hot CO gas was recycled as the energy source for sludge drying and recovery of iron oxides and dust. • The dried sludge was screened (<5 mm), demetallized, and compacted to yield a lime sludge briquette. • Sludge drying was achieved in the dolomite sludge mix process by conjugating sludge with the hot dolomites from the rotary kiln. • The amalgam was later utilized as iron ore fines for sinter making process. • The above-delineated process resulted in the reduction of 15pprox. 10 USD operation cost against per ton of steel produced.	• Primary oxygen furnace sludge has been recycled as lime sludge briquette and dolomite sludge mix. • The former was used as a steelmaking coolant while the latter was absorbed for sinter production.	By eliminating BOF sludge from the wastewater stream and recycling it as a raw material for ironmaking, a reduction of up to 15–20% in the overall sludge burden can be achieved. Hence, this approach can be considered a partial solution when implemented at the source.	[31]
8	• The settled sludge from the collection and the pre-settling tank was withdrawn and partially dehydrated in the sludge thickening process. The same was reused as the partial replacement of coal in the coke plant.	• Primary wastewater sludge was collected, thickened, and reused as the fragmental replacement of coal in the coke plant.	Mechanical sludge drying is a costly process that comes with its own set of drawbacks. Additionally, the dried sludge does not possess a significant calorific value and largely contributes to ash generation.	[32]

Table 5. *Cont.*

No.	Summary of the Study	Key Findings of the Study	Feasibility of the Method	Source
9	• The researchers have reviewed the reuse of waterworks sludge in 4 broad categories, which consist of 11 possible ways: as a coagulant, absorbent, co-conditioner in the wastewater treatment, soil amendment, raw material for cement and concrete manufacturing, etc.	• Iron-containing steel mill wastewater sludge can be reused in the steel and iron industry as raw material	While reusing the entire sludge as a raw material in ironmaking may have an adverse effect on quality, it is worth noting that the metal-bearing portion of the sludge can be efficiently recycled if properly segregated.	[33]
10	• Incineration is the most promising method for handling sludge generated from continuous casting and hot and cold rolling mills. • Fluidized bed incinerators or rotary kilns are the preferred types for the above operation. • The significant advantage includes volume reduction, while problems such as the generation of Sox, Nox, particulate matter, polychlorinated dibenzo-p-dioxins (PCDD), and dibenzofurans (PCDF) remained the primary challenge. • The study further identified spent anion exchange resin as the novel inhibitor of pollution-causing gases.	• Incineration of hot rolling mill sludge followed by flue gas cleaning using anion exchange resins and other air pollution control devices.	Thermal methods for handling wet sludge can be an expensive endeavor and are not sustainable without energy recovery. Moreover, this process generates fly ash and bottom ash, which must be disposed of in secure landfills.	[34]

Table 5. *Cont.*

No.	Summary of the Study	Key Findings of the Study	Feasibility of the Method	Source
11	• The article explored the possibilities of hardening and reusing wastewater slurry as the partial replacement of coal in combustion engines or for forming concrete structures. • A combination of water: bentonite: ash: cement (49.5:1:24.8:24.8) delivered the best end product. • The by-product was analyzed for density, viscosity, water separation, compressive and tensile strength, and hydraulic conductivity (little excess value of $k_{10} = 1.54 \times 10^{-8}$) and found to be satisfactory.	• Thermal power plant fly ash and cement or ground granulated blast furnace slag is a great binding agent for the wastewater sludge.	Combining sludge with other cementitious elements shows promise as a raw material for concrete production. However, it is not advisable to utilize sludge as a direct substitute for coal due to its lower heating value and associated issues with ash generation.	[23]
12	• Steel mill sludge primarily includes ferrous oxide, fine coke dust, and a traceable amount of zinc, aluminum, calcium, nickel, silica, magnesium, etc. There is a sheer possibility of recovery of the above metals from the consortium.	• Recovery of precious metals from the steel mill sludge to minimize raw material consumption or synthesize new products for other industries.	Currently, the economic and technical feasibility of metal recovery from sludge is limited. Additionally, only a small portion of metal dust can be effectively recovered, while the remaining portion necessitates alternative disposal methods.	[35]
13	• BOF sludge was characterized, and the values were evaluated against a fixed set of questionnaires (radioactivity, hazardous properties, physicochemical state, pathogenicity, etc.) to identify the best-suited recycling, reuse, and treatment techniques for the prior-mentioned item.	• In situ vitrification, phytoremediation, bioremediation, disposal in hazardous waste management facilities, ceramization are the preferred method for steel mill sludge handling and management.	Biological methods are not particularly effective in addressing sludge issues due to the high concentration of inorganic constituents. However, for small-scale applications with appropriate precautions, ceramization can be considered as a viable option.	[36]

Table 5. *Cont.*

No.	Summary of the Study	Key Findings of the Study	Feasibility of the Method	Source
14	• The wet gas cleaning process in steel industries yields the sludges, namely, Linz-Donawitz sludge and BF sludge. • Those have iron oxide up to 70 and 40%, respectively. • The study identified the best practices for the reuse of sludge in steelmaking, consumption in the ceramic manufacturing process, and use as an adsorbent.	• The coarse fraction of sludge contains minute fractions of heavy metals, such as zinc and lead. Thus, the same can be reused in steelmaking process. • Up to 5% of sludge can be reused as raw material in the ceramic-making process. • Also, the sludge has proven its potential as an adsorbent for removing heavy metals from the aqueous solution.	Collecting source-specific sludge is a laborious task, and ceramization only utilizes a small fraction of the sludge. The remaining portion requires parallel recycling or disposal methods to be implemented.	[37]
15	• The study profoundly reviewed the scope of removal/stabilization of heavy metals and facilitating recovery of nitrogen from the cold rolling mill wastewater sludge as a soil conditioner. • Researchers suggested that the sludge can be used for reclamation of the degraded lands post stabilization for heavy metal leachability.	• Elevated conjugation of sewage sludge with degraded soils helped regain its total organic carbon value compared to the non-contaminated lands.	The process of sludge stabilization and decontamination is extremely laborious, and attempting to recover nutrients from it afterwards is technically and financially impractical.	[38]
16	• The tornado process obtained low zinc blast furnace sludge (LZBFS) from a furnace operating on a ferrous burden of 100% pellets. • Up to 10% replacement of LZBFS in regular briquettes does not impact the reducibility and strength.	• Low zinc cold-bonded briquettes were synthesized in a lab-scale study in a blast furnace shaft simulator.	The metal removal process is complex and requires advanced techniques. However, using only a small percentage (10%) of the sludge as a replacement for raw material in the briquette-making process may not be a practical or meaningful approach.	[39]

Table 5. *Cont.*

No.	Summary of the Study	Key Findings of the Study	Feasibility of the Method	Source
17	• Oxides of zinc and iron trigger metallic leachability from steel industry sludge. • This was stabilized using desilicated fly ash (DFA) and lime mixed at a ratio of 70:30. • The solidified specimens of 10%, 20%, 30%, 40%, and 50% binders were cured for 7 days and resulted in unconfined compressive strength of 0.49 N/mm^2 at 40% of DFA and lime at the pH of 12.88.	• The addition of 40% DFA and lime in a 7:3 ratio resulted in solidification of the specimen with a reduction in leachability up to 94 and 98.6% for Fe and Zn, respectively.	After successfully mitigating the leachability of metals, the resulting product can be utilized for brick making or similar applications. However, the financial feasibility of this approach remains uncertain and requires further evaluation.	[40]
18	• Sludge constitutes valued compounds such as SiO_2, Al_2O_3, CaO, and Fe_2O_3. • These are the primary raw materials for manufacturing ordinary Portland cement (OPC). • OPC was produced using an amalgamation of clinker, and raw sludge and parameters such as burnability index, compressive strength, hydration characteristics, etc., were examined. • The burnability index of the mixture improved upon adding steel sludge up to 2% dosage.	• Steel industry sludge was utilized (up to 2%) as a raw material in OPC manufacturing as the source of CaO and Fe_2O_3 without compromising on the quality.	The addition of steel sludge in cement manufacturing offers advantages. However, the main challenge lies in the dosage limitation of 2% by the weight of raw material, which poses a significant obstacle to its reuse potential.	[41]
19	• The study investigated the feasibility of using wastewater sludge as an alternate fuel for the cement industry. • The primary challenges highlighted are as follows: high moisture content, expensive drying process, high fly ash generation, etc. • Researchers depicted an optimum calorific value of 2828 cal/gm @ 17pprox. 73% dry solid content with the generation of around 49% of fly ash as residue.	• Dried and pelletized wastewater sludge was converted into alternate fuel for the cement industry.	Drying the sludge to the reported extent is an enormous undertaking, which directly impacts its calorific value (CV). Moreover, the substantial generation of ash, as reported, poses a significant financial burden for its disposal.	[42]

Sustainable Sludge Management and Hierarchy

Steel mill ETP sludge has been a neglected waste for decades, requiring immediate attention. The sludge consists of valuable minerals, nutrients, and compounds that can be recycled as raw materials for various applications. Contrarily, the presence of heavy metals in the sludge hinders the recycling and recovery process. The unresolved issues and economic non-viability make it challenging to opt for the most befitting alternate. This led to the idea of using an analytical hierarchy process for prioritizing the various available alternates, as depicted in Figure 6. Table 6 delineates a pairwise comparison to arrive at the priority-based ranking. The decision matrix was formulated based on the resulting weight from the principal eigenvalue of 6.20 against a consistency ratio of 3.7% (Table 7). The comprehensive findings for the sequential ranking are summarized in Figure 7.

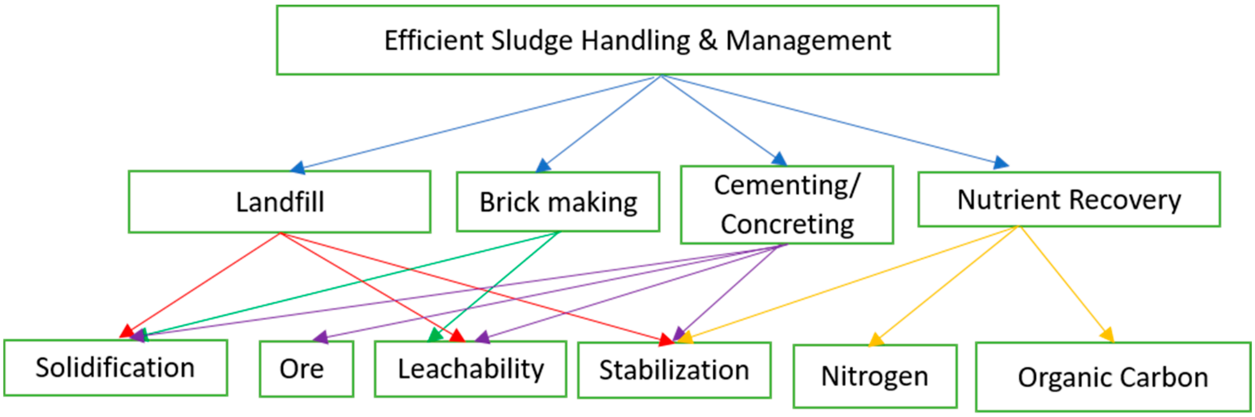

Figure 6. AHP hierarchies for prioritizing the effective handling and management of steel mill ETP sludge.

Table 6. Pairwise comparison using AHP analysis.

	Category	Priority	Rank	+	−
1	Land fill	10.1%	3	4.2%	4.2%
2	Brick manufacturing	30.1%	2	11.7%	11.7%
3	Concrete manufacturing	51.4%	1	23.7%	23.7%
4	Alternative fuel	5.4%	4	2.1%	2.1%
5	Nutrient recovery	2.9%	5	1.4%	1.4%

Note: The + and − values in the priority percentage indicate the direction of preference by the user.

Table 7. Decision matrix using AHP Analysis.

	1	2	3	4	5
1	1	0.20	0.14	3.00	5.00
2	5.00	1	0.33	7.00	9.00
3	7.00	3.00	1	7.00	9.00
4	0.33	0.14	0.14	1	3.00
5	0.20	0.11	0.11	0.33	1

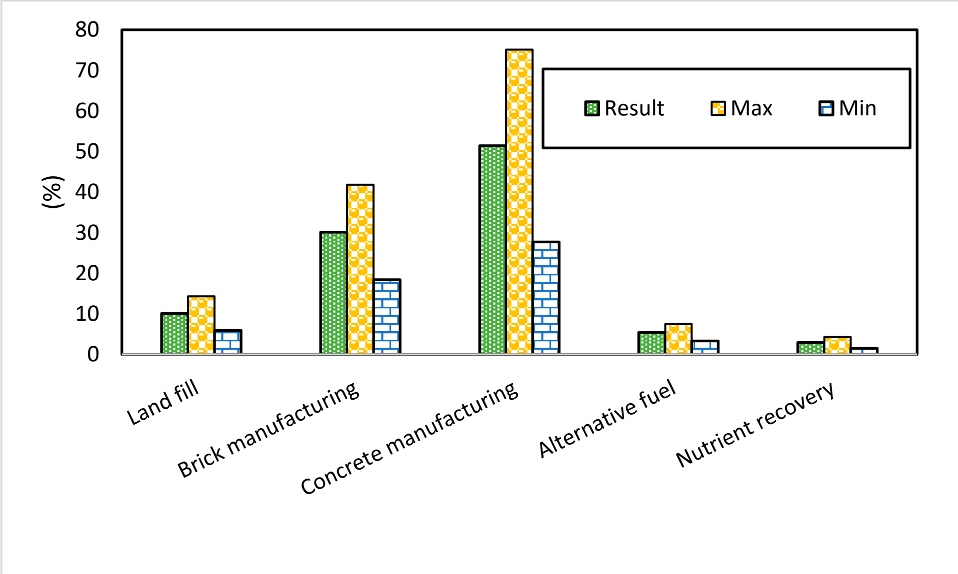

Figure 7. Consolidated AHP evaluation report for steel mill ETP sludge.

Based on the various evaluation criteria, such as economic and environmental feasibility, societal acceptance of the by-product(s), and ease of processing, the AHP model ranked concrete making as the top preferred option, followed by brick manufacturing, landfilling, recovery of alternate fuel, and nutrients.

The surprising placement of recovery alternates below the landfilling in the preference table is driven by economic hindrances. The above ranking (Figure 7) is time-bound and may vary once the product's acceptability improves with elevated awareness among the end-users.

4. Conclusions

Steelmaking requires between 2 and 20 m^3 of fresh water against each ton of steel produced. Blast furnaces, sinter plants, and coke plants have the most prominent individual water footprint among all the steelmaking unit operations. Fresh water requirements in a few of these operations sometimes goes as high as 500 m^3/h. A significant proportion of the freshwater used in these operations as a coolant requires no treatment, while operations such as rolling, continuous casting, pickling, etc., yield wastewater rich in PAH, cyanide, ammonia, non-consumed acids, BTX, oil and grease, etc. The study identified a combination of electrochemical precipitation, adsorption, oxidation, and membrane bioreactor facilities provide the best water recovery at a viable price point. The recovered water goes back to the system as make-up water, while the wastewater sludge is presently disposed of in secured landfills. The sludge contains Fe_2O_3, CaO, Nitrogen, Zn, Ni and Cr. Constituents such as Fe_2O_3 and CaO are valuable and used as raw materials for steel and cement industries. Nitrogen, an essential plant nutrient, can be extracted from the sludge and used as fertilizer. However, the abundance of leachable heavy metals makes recycling and reusing the sludge challenging. The pairwise comparison process in AHP showed that concrete making is the most feasible alternative, with a priority value of 51.4%, while nutrient recovery ranked the least-preferred alternate, with a priority value of 2.9%. The above ranking is a time-dependent and conclusive output of the multi-factorial statistical analysis.

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