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**ORIGINAL ARTICLE**

# Characterization and Management of Solid Wastes from Steel Mill Plant (Case Study: North of Iran)

**Zahra Zamiraei*, Mohammad Panahandeh, Mokarram Ravanbakhsh, HabibFathi-dokht**
Environmental Research Institute, Academic Center for Education, Culture & Research (ACECR), 4144635699, Rasht, Iran
*Corresponding author: E-mail: Zamiraei@gmail.com

**ABSTRACT**
*Signi cant quantities of wastes are generated as the waste materials or byproducts every day from steel processes. This paper described and analyzed the generation, characteristics and chemical composition of the most of wastes obtained from the Gilan steel mill plant, in north of Iran. According to the origins and characteristics, the Gilan steel mill plant can be mainly classi ed into two categories, mill scales and oily sludges. The characteristics and the formation mechanisms of mill scales and sludges in hot rolling and cold rolling are described in this paper. Based on chemical composition analysis, they usually contain considerable quantities of valuable metals and materials. These wastes are considered to be hazardous materials and if landfilled therefore need to be treated. It also reviews the present treatment processes of these wastes, and determined the best processes for the treatment of the Gilan mill scale, oily sludge and other wastes. It is very essential not only for recycling the valuable metals and mineral resources but also for protecting the environment.*
***Keywords:*** *Steel mill plant, Mill scale, Oily sludge, Waste management.*

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## INTRODUCTION

In recent years, the steel industry worldwide achieved remarkable growth rates. It is not only growing in Asia, but also in Europe and America.The iron and steel sector has a very substantial role in Iran's Economy. According to the statistics published by World Steel Association, Iran was the fifteenth crude steel producer in the world with the production of 15.4 million tones/year in 2013 [1].

Steel is an alloy of iron with varying amounts of carbon and some other elements such as Manganese, Chromium, Nickel, Molybdenum, Zirconium, Vanadium, Tungsten and so on. Currently there are more than 3000 catalogued grades of steel available.

Steel is manufactured from iron ore mostly using blast furnace (BF) and basic oxygen furnace (BOF) and using electric arc furnace (EAF) in case of manufacturing from scrap materials [2]. Molten iron is produced in BF in presence of coke and molten steel is produced in BOF in presence of oxygen [3]. Smelting and refining process involves carbon reduction in BF to produce molten iron and decarburization of molten iron to produce molten steel. After BF and BOF processes, molten steel is controlled to a target composition and temperature for processing into continuous casting machine to produce slabs, billets etc. Finally, the castings are rolled into the required dimensions in the rolling mill to get finished steel product [4].

One of the wastes generated in steel plants is the mill scale which represents about 2% of the steel produced [5,6]. It is formed during the continuous casting and rolling mill processes when steel is submitted to thermal gradients in oxidant atmospheres, which promotes the growth of iron oxides layer at the surface of steel. In the integrated plants, the mill scale is habitually used as a raw material at the sintering plants [7]. The recycling of this waste as briquettes used in BOF steelmaking as well as an addition to the iron ore pellets designated for blast furnace process was also reported.3,4,6) Finely, there are some attempts to use the scale for pure iron powder production [8-10].

The steel wastes consist of lots of hazardous element, such as Cr, Co, Ni and so on. Thus, the disposal of these industrial solid toxic wastes can cause environmental risk due to the mobility of toxic elements [11]. These materials are harmful to the environment, especially to the human health. How to handle thewastes and recover the valuable metals from them arevery important at the present period not only for the resource andeconomy but also for the environment. This paperwas described the physical and chemical characteristics of wastes of the Gilan steel rolling mill in north of Iran, and the methods of treating the wastes and recovering the valuable metals from them.

## MATERIALS AND METHODS

### Study area

The Gilan steel rolling mill is located in the industrial area of Rasht City in Guilan province, north of Iran. Current capacity of steel production equivalent to 2,000,000 tones of hot rolling sheet and 500,000 tonnes of cold rolling sheet per annum.

### Sampling and sample preparation

In order to wastes characterization, sampling was done by simple random sampling. The waste mass collected was fragmented and homogenized, then, random sampling was again conducted. This material was taken to laboratory and was prepared for analysis according to extraction procedure requirements.

### Chemical analyses

Solution samples were filtered through 0.22 µm membrane filters and acidified with HCl for cation analyses on a Perkin Elmer Aanalyst 100 Atomic Absorption Spectrophotometer (AAS) [12]. All solutions were kept at 4°C until analysis.

## RESULTS AND DISCUSSION

The treatment policy of waste is closely associated with the characteristics of the wastes. It is therefore important to know the physical and chemical properties of the wastes before a treatment method is developed or chosen.

### Chemical composition of the Gilan steel rolling mill wastes

### Iron oxide millscale

One of the wastes generated in steel plants is the mill scale. Figure 1 shows the scale of the Gilan steel rolling mill. The steel scales mainly include the iron oxide and some other metal oxides. The compositions of the scales from various steps were approximately similar. The scale appearance is gangue and dark gray color.

**Figure 1** The sample of the Gilan steel rolling mill scale

The chemical analysis of thescale from the Gilan steel rolling mill is shown in Table 1. From this table, the Gilan steel rolling mill contained much more iron oxides. The Gilan steel rolling mill routinely measure scale output. Typically, the scale of the Gilan steel rolling mill production is about 15 kilograms per tonne of rolling steel.Therefore, actual annual scale production data is approximately 30 thousand tons.

**Table 1** Total concentration of heavy metals in Wastes (mg/L)

| Heavy metals / Total concentration | Fe | Mn | Cu | Zn | Ni | Cr | Co | Cd | Pb | As | Oil & Grease |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Mill Scale | 65% | 2984 | 312 | 2230 | 325 | 103 | 65 | 3.96 | 48.13 | 0.1 | - |
| Oily Sludge | 60.3% | 3523 | 130 | 1541 | 298 | 101 | 88.62 | 2.9 | 4.46 | 0.13 | 30.69% |

### Oily Sludge

Significant quantities of sludge are generated as waste material or byproduct every day from steel industries. Oily cold rolling mill sludge is a kind of by-product of steel making in the process of cold rolled strip production and is basically composed of metallic iron and iron oxides (60 wt%) with variable oil and grease (30 wt%). Figure 2 shows the oily sludge of the Gilan steel rolling mill. Since the sludge contains lots of iron and alloying elements along with plenty of hazardous organic components, it is considered as both an attractive secondary source and an environmental contaminant. The sludge is mainly reutilized as a raw material in secondary smelt furnaces [13-15]. Table 1 shows the chemical analyses of oily sludge from the Gilan rolling mill. The rate of oily sludge production of the Gilan steel rolling mill is about 1.5 liter per tonne of steel produced. Therefore, actual annual scale production data is approximately 25 thousand tons.

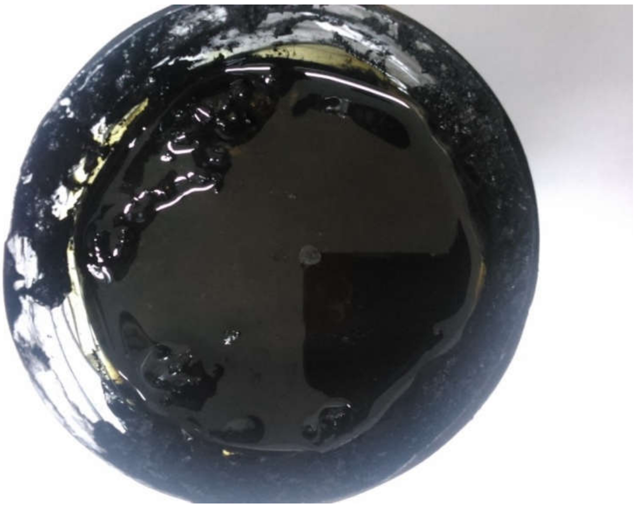

**Figure 2** The sample of the oily sludge of the Gilan steel rolling mill

**Other wastes**

The other wastes of the Gilan steel rolling mill are used rolls, dust, used oil and grease and spent refractories. The quantity of the formation of these wastes is modicum per tonne of steel. The quantity of the Gilan steel rolling mill wastes per tonne of steel production and per annum are given in Table 2.

**Table 2** The quantity of the Gilan steel rolling mill wastes

| Waste | quantity per tonne of steel product | quantity per annum (ton) |
|---|---|---|
| Millscale | 1.5 % | 30,000 |
| Oily sludge | 1.5 Lit | 25,000 |
| Used refractories | 0.2 % | 4,000 |
| Dust | 20 g | 40 |
| Used rolls | Depending of reparation | - |
| Oil and grease | Indeterminate | - |

**Formation mechanisms**

Reducing the formation of wastes and deciding on treatmentmethod requires an understanding of the formation mechanisms of the wastes.

**Functional description of a descaling unit in the Gilan rolling mill plant**

The below described descaling units serve to remove the primary scale forming on metallic surfaces during furnace treatment in the Gilan steel rolling mill. The scale layer is removed by water being sprayed onto the metal surface at high pressure while the material is passing through a dedicated descaling cabin. Primary scale is removed essentially by three physical processes. The individual contribution of each of these processes to the descaling result depends on the type of scale forming in the furnace, which in turn is determined by the type of material heated in the furnace. The following three physical mechanisms can be distinguished:

1. Generation of heat stress in the scale layer due to cooling
2. Explosive energy as a result of the increasing volume of water when it evaporates
3. Mechanical forces caused by the impact of the water jet and rolls

Materials tending to form a relatively thick and porous scale mainly benefit from the first two physical mechanisms. By contrast, the third mechanism is more effective with materials forming a thin, coherent and adhesive layer of scale. The latter type of scale is called sticky scale and it is much more difficult to remove than scale of the first category.

**Cold rolling**

 

The Gilan cold rolling mill stands for the production of sheet rolling products with smallest possible thickness tolerances and an excellent surface finish. With an entry thickness of 2-3.5 mm of hot rolling coil, the final thickness of the flat rolled sheet is achieved to0.4-0.6 mm.

Cold rolled steel is essentially hot rolled steel that has had further processing. The steel is processed further in cold reduction mills, where the material is cooled (at room temperature) followed by annealing and/or tempers rolling. This process will produce steel with closer dimensional tolerances and a wider range of surface finishes.

**The treatment of steel wastes**

Almost every output stream can be seen as an input to another process, instead of a costly waste disposal issue.

In some cases, the by-product may require reprocessing prior to input to another process; other times, the byproduct can be reused as is. Frequently, the components of a waste stream (metals, salts, etc.) which are thecause of costly hazardous disposal requirements are in fact valuable resources worth recovering. The below described the treatment options of the Gilan steel mill plant:

**Mill scale**

Mill scale refers to a form of by product that is mixed with oil in various steel-making processes. It is sold very inexpensively as an industrial waste in the form of iron oxide, rather than collected through a recycling process. Most of this material is reused either as a material in the manufacture of iron ore pellets for a melting furnace or as the coolant of a ladle converter. Recently, with respect to the development of a waste recycling method and the rise in raw material price of steel products, the recycling process that collects pig iron by producing direct reduction iron (DRI) [16,17] using high purity iron mill scale has become a subject of much interest.

The process byproduct of the Gilan mill scale from the rolling process containing > 65% Fe is generally recycled into the sintering plant. Generally, 70–100% mill scale containing high iron is being recycled through either briquetting or sintering route without any difficulties. In the Gilan mill scale, de-oiling of the material is required [14].

The oil in contaminated mill scale comprises about 10% of all the lubricants brought into a steel mill, and only about half of all oily sludge (contaminated and uncontaminated) can be processed by the sinter plant[18].

A process for de-oiling mill scale which comprises [19]:

(a) collecting mill scale and analyzing for oil content; and then

(b) slurrying the portion of mill scale containing more than 0.5 weight percent oil in water to achieve an aqueous mill scale slurry having at least 25 weight percent solids content; and then

(c) high shear agitating the aqueous mill scale slurry to form a reduced oil mill scale suspension in an oily water emulsion; and then

(d) phase separating the reduced oil mill scale from the oily water emulsion forming a reduced oil mill scale and an oily water emulsion; and then

(e) Fresh water rinsing the reduced oil mill scale to form an oil-free mill scale and a waste wash water; and then

(f) Recycling the waste wash water to form at least a portion of the aqueous mill scale slurry of step b; and then

(g) repeating steps (a) through (f) until the oil-free mill scale contains less than 0.5 weight percent oil; and then

(h) Drying the oil-free mill scale for use to form sinter plant feed in the steel making process.

**Rolling mill sludge**

The Gilan rolling mill sludge is the fine particles, which takes the oil portion along with the rolling cooling water. Recycling of these particles are challenging due to very high oil content (containing > 30 % Oil & grease).

The Gilan mill sludge contains considerable quantities of valuable metals and materials (containing > 60% Fe).

Recycling of high iron content of oily sludge to achieve reusable products is technically and economically feasible using the INMETCO direct reduction process.

During the INMETCO process, as was shown in Figure 3, annular furnace and electric arc furnace were respectively applied in the pre-reduction and melting stage.In this process, all oxidic dusts, sludges and oil-containing scale of occurring in iron and steelworks are processed to green, carbon-containing pellets and then reduced to a high iron and low tramp element containing sponge iron at temperatures of around 1250° C in a rotary hearth furnace. Zinc, lead and cadmium are expelled nearly completely and converted to a highly-concentrated heavy metal containing secondary dust. These heavy metals can be recovered from this dust without any further concentration in the appropriate metallurgical processes. The hot sponge iron can be melted directly in a submerged arc furnace in its specific slag to achieve a low-sulphur hot metal suitable for charging into the LD steelmaking plant [20].

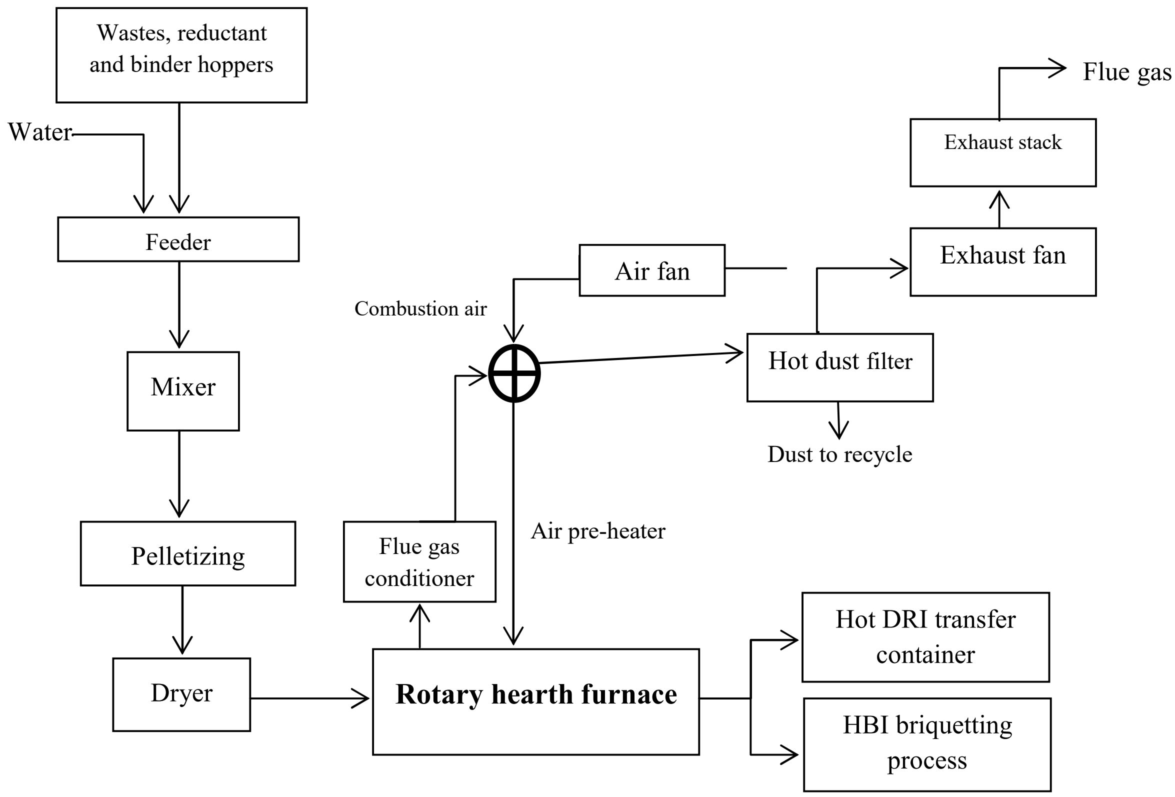


**Figure 3** The flow chart of INMETCO process

**Used oil and grease**

The treatment of aqueous or oily effluents is one of the most serious environmental issues faced by the minerals and metallurgy industries. Main pollutants are residual reagents, powders, chemicals, metal ions, oils, organic and some may be valuable (Au, Pt, Ag). The use of flotation is showing a great potential due to the high throughput of modern equipment, low sludge generation and the high efficiency of the separation schemes already available. So, it suggested that this process has been used to recycle process used oil[21].

**Recycling of Refractories**

Refractory reuse is increasingly prevalent as manufacturers realize that it is an economically and environmentally sound alterative to landfilling. In 1990, less than 45,000 tonnes of refractories were recycled by metals producers, representing less than 2 percent of total production [22].Refractories with high raw materials costs such as silicon carbide, zirconium oxide and chrome oxide can be economically recycled.To recycle Mag-Chrome bricks the product is separated into two products after the crushing and grinding stages. The first product is the high iron containing (and thus magnetic) chromite, which is separated by a magnetic separation line. The remaining material is MgO-rich and is then employed as a sand substitute in concrete. Both streams are washed to remove impurities. The separated chromite is recycled for use in the Mag-Chrome brick [23,24].

**CONCLUSION**

The Gilan steel mill wastes can be mainly classi ed into two categories, mill scales and oily sludges, according to the origins and characteristics. The scales and sludges were mainly present in the form of iron oxide and the most important metal elements, such as Zn, Mn, Cr and Ni. The scale and sludge from the Gilan steel mill plant are regulated as a hazardous waste because they contain considerable amounts of heavy metals and hazardous. Since mill scale and oily sludge containing > 70% and > 65% Fe respectively are iron sources and can be recycled. Generally, 70–100% mill scale containing high iron is being recycled through either briquetting or sintering route without any difficulties. Recycling of high iron content of oily sludge to achieve reusable products is technically and economically feasible using the INMETCO direct reduction process

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