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Recovery of the Metals Formed as Sludge in Acid Tanks During the Production of Stainless Steel

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Abstract

Stainless steels are widely used in various sectors depending on their high corrosion-resistance, high heat conductivity, formability and visual appearance. Stainless steel sheets are produced by hot rolling, cold rolling, heat treatments followed by descaling and pickling processes in acid tanks, respectively. While cold rolled stainless steel sheets are subjected to continuous heat treatment in order to provide the desired mechanical properties, high temperature oxides are formed on the surface of the sheet. These high temperature oxides dissolve in the acid solution during the descaling and pickling processes. The oxides, which become saturated and mechanically dissolved, begin to accumulate in the form of sludge at the bottom of the acid solution. This accumulated sludge is considered harmful to the environment and is disposed in various ways and becomes a financial burden. However, there are valuable compounds in this sludge containing iron and nickel, depending on the alloy. The aim of this study includes the recovery of the metals in the sludge formed by the pickling process after the heat treatment of the cold rolled stainless steel sheet by a direct reduction process. In the present study, a composite pellet was produced by mixing varying amounts of sludge, fine mill scale, coke and reagents to adjust basicity. Then the pellets were reduced at 1400 °C for 30 minutes to produce iron nuggets the products were visually observed and reduction values were calculated and compared.

Keywords: Stainless steel, recovery, metals, pickling, heat treatment.

1. INTRODUCTION

Stainless steel flat production consists of casting, hot rolling, cold rolling and solution annealing stages, respectively. In solution annealing after cold rolling, firstly heat treatment is applied, and then the stainless-steel sheet gains its stainless feature through acid solutions as shown in Fig.1. The reason for applying heat treatment; solution annealing can take place and the desired mechanical properties are gained to the stainless-steel sheet [1]. Significant amounts of solid wastes are generated during iron and steelmaking. These wastes generally contain unreacted materials like coke or iron bearing minerals [2].

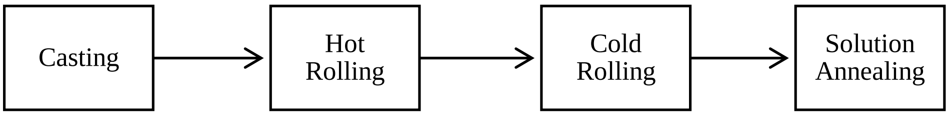

Fig. 1. Production Stages

The heat treatment process varies according to the alloy and thickness of the sheet. The heat treatment carried out under different conditions creates different oxide layers in different types of steel, depending on the alloy.

Solution annealing of stainless-steel production is carried out at different temperatures and times depending on the phase, alloy, thickness and deformation rates of the plate.

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In solution annealing, firstly heat treatment is applied in high temperature furnaces. The purpose of heat treatment is to ensure that the sheet comes to a temperature suitable for solution annealing and ensure the formation of high temperature iron oxide on the surface.

When the eutectoid temperature is exceeded in the iron-oxygen system, the thermal oxide scale formed typically consists of thick wustite. Magnetite overlies the wustite layer and the outermost hematite overlies the magnetite layer. In a study, it is stated that for iron oxides grown in air at 700-1250 °C, hematite is approximately 1%, magnetite is approximately 3.5-5% thick and chrome oxide layer is typically 1–3 nm thick [3, 4].

It has been reported that the dominant defects in wustite and magnetite are due to the iron void, while the dominant defect in hematite is the oxygen void [3, 5].

At the scale/gas interface, oxygen is adsorbed on the solid surface, resulting in the appearence of hematite. The oxygen vacancy forms at the magnetite - hematite interface. The resulting oxygen vacancy diffuses outwards to the hematite/gas interaction. The adsorbed oxygen jumps into the oxygen vacancy in the hematite [6, 7].

The layers on the stainless-steel surface are schematically drawn in Fig. 2.

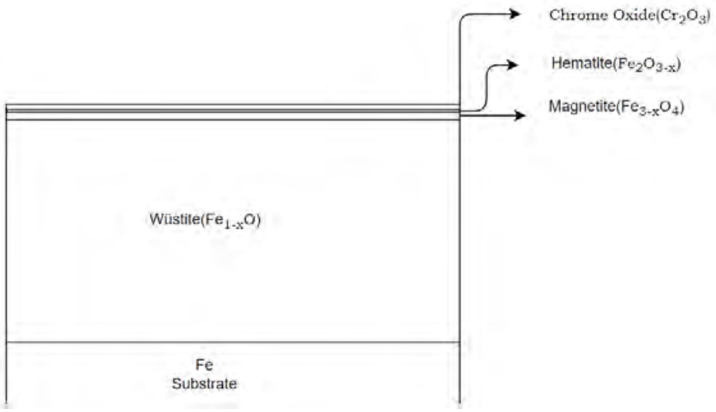


Fig. 2. Layers of Stainless Steel

After the heat treatment, the stainless-steel sheet is taken into the solution; The high temperature iron oxide layer on the surface is cleaned and the solution annealing ensures the formation of a chromium oxide layer on the surface. Thus, the plate gains the feature of being stainless.

The cleaned stainless steel high temperature oxide accumulates in the solution tanks in the form of sludge, which contains Fe, Cr, S and Ni. Rather than being disposed of in a landfill, these metals and other valuable components can be recovered from stainless steel pickling sludge, which not only provides economic benefits but also eliminates the harmful effects on human health and the environment [8].

The recycling of these metals, which has high energy use in production, high carbon emissions and the possibility of financial evaluation, is rapidly gaining importance in the world. [9]

Kobayashi, investigated the reduction and melting mechanism depending on the gas composition and pellet temperature at a constant furnace temperature of 1450 °C. In that study it was observed that the heat has increased rapidly up to 1100 °C and then it slows down. At 1370 °C the temperature showed a decrease and continued to rise again. Which was the point where the gas evolution was completed and the pellet has melted. The change in slope shows us that some endothermic reactions has occurred [10].

Carburization and melting can also be taken into account as reactions. It is understood from the analyzes that the following reaction steps occur:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2 \qquad (1.1)$$

$$Fe_3O_4 + 4CO = 4Fe + 4CO_2 \qquad (1.2)$$

$CO_2 + C = 2CO$ Which is an endothermic reaction and occurs above 1000^oC (1.3)

$C_{(aq)} = C_{(s)}$ Carburization (1.4)

$Fe_{(s)} = Fe_{(aq)}$ Melting (1.5)

If the reaction temperature is in balance with the heating rate of the furnace the pellet temperature can be kept constant. The heat transfer rate is faster than the chemical reaction and the pellet temperature increases rapidly, causing the melting to begin with the unreacted iron oxide content with the molten gangue [10].

$$FeO_{(aq)} + C = Fe_{(aq)} + CO \tag{1.6}$$

When composite pellets containing iron oxide and carbon are heated to high temperatures, the metallic iron formed after the reduction of iron oxides may melt partially or completely depending on the temperature and the degree of carburization of the product. The change of pellet structure during the process depends on many factors; eg furnace temperature, type and amount of reducing agent, pellet size, residence time in the furnace and amount of gangue, ash and binder in the mixture.[11][12].

In the present study, sludge containing stainless steel high temperature oxide was obtained from a stainless-steel production factory, Trinox Metal, and recycling possibilities through direct carbothermal reduction were investigated.

2. MATERIALS AND METHOD

The $CaCO_3$ neutralized sludge containing high temperature oxides was obtained from the acid tank used for pickling. After dewatering and drying 105°C for 2 hours, the sludge was ground in a ball mill for 10 minutes to dispense the flocculated sludge powder. Then, the ground sludge powder was characterized by dimensional analysis, XRD and XRF analyzes as given in Fig.3, Fig.4 and Table 1, respectively.

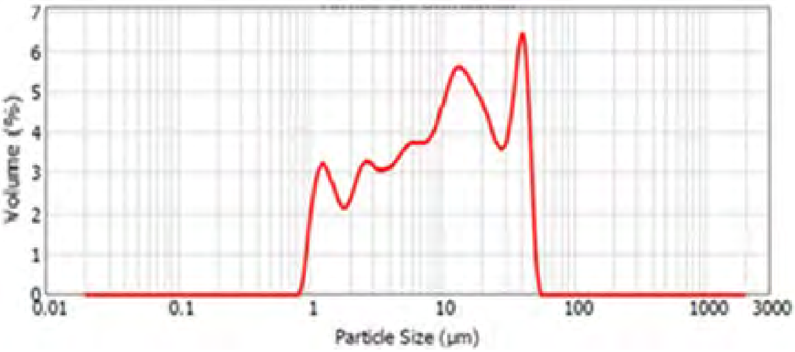


Fig. 3. Size Distribution of Dried Pickling Sludge

According to Fig.3 it was observed that particle size of the powder is less than 50 µm and its average particle is calculated to be 11.50 µm.

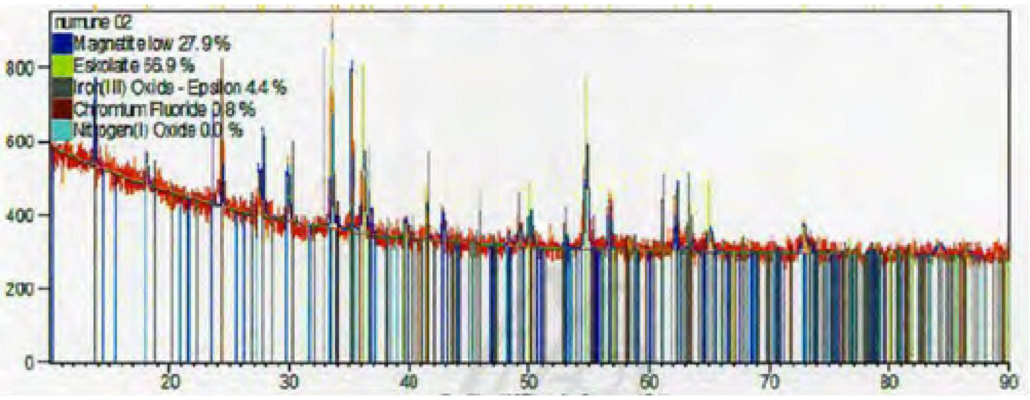


Fig. 4. XRD Patterns of Dried Pickling Sludge

Both XRD and XRF results reveal that the nearly half of the sludge is composed CaO, due to the neutralization by $CaCO_3$, 31 % of magnetite and 6 % of Cr_2O_3, 3.5% of NiO.

Table 1. Chemical Compositions of the Raw Materials.

Raw Material	Fe_2O_3	Fe_3O_4	*FeO*	SiO_2	Al_2O_3	*CaO*	*MgO*	*NiO*	Cr_2O_3	*MnO*	*S*	C_f	*VM*	*Ash*
Steel Sludge	30.98	-	-	-	-	56.21	-	3.44	6.26	0.30	2.80	-	-	-
Mill Scale	-	91.48	6.36	0.56	0.21	0.11	0.13	-	-	0.85	0.01	-	-	-
Coke	-	-	-	-	-	-	-	-	-	-	-	88.17	0.44	11.39
Coke Ash	10.28	-	47.00	-	31.50	4.00	1.50	-	-	-	0.44	94.72	-	-

For the reduction of sludge, coke is used as carbon source. Additionally due to the relatively low iron oxide content of the sludge mill scale was added in order to obtain a better metal – slag separation. Their chemical analyzes are also given in Table 1.

The mixtures were prepared by using 50% of mill scale and 50% of sludge. Coke amount in the mixture was determined by utilizing a Fe/C ratio of 3.5. Additionally, to change the basicity ratio and to obtain a low melting point slag, SiO_2 and Al_2O_3 were added. The mixture compositions of the samples are given in Table 2.

Table 2. Composition of the Samples.

Sample No.	Scale %	Sludge %	Coke %	Molasses (ml)	SiO_2 %	Al_2O_3 %	Basicity Value
1	42.5	42.5	15	1	-	-	6.29
2	41	41	18	1	-	-	5.47
3	37.5	37.5	16	1	9	-	1.71
4	35.6	35.6	15.6	1	10.4	2.6	1.23
5	33.1	33.1	14.5	1	14.1	5.0	0.82

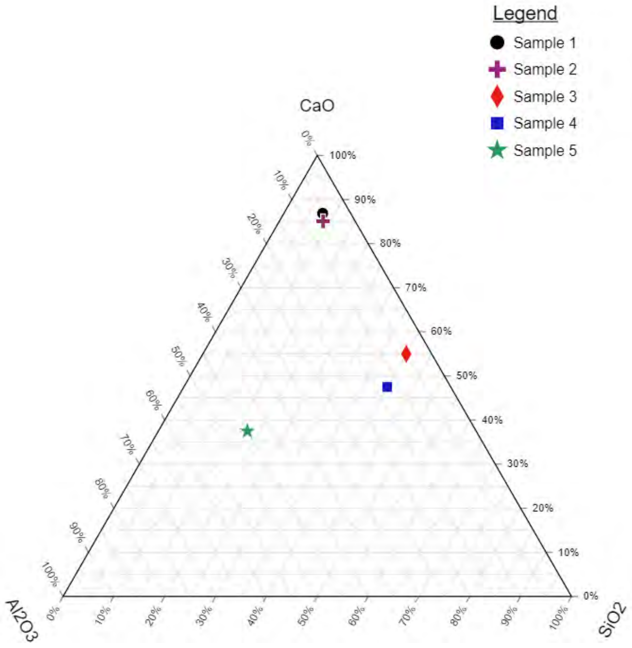


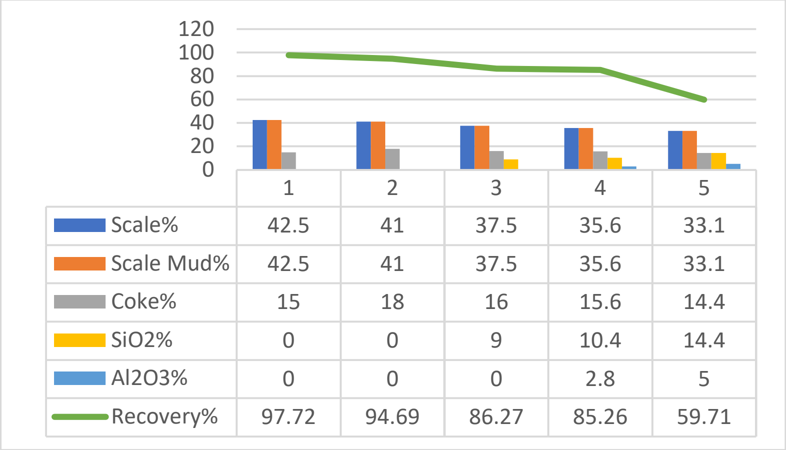
Fig. 5. The Locations of the Samples in the Triple Phase Diagram

1ml of molasses were added to strengthen the homogenized mixtures. The mixtures were pressed to produce pellets with a height of about 20 mm and a diameter of 20 mm at a weight of 2 tons for 30 seconds. The prepared pellets were initially dried at 105 °C for 2 hours then reduced at 1400 °C for 30 minutes in a Protherm PTF 15/50/250 tube furnace.

The obtained reduced samples were observed and reduction ratio values were determined by the following equation;

Reduction ratio = (Removed oxygen from iron oxide / Initial oxygen of iron oxide) × 100% (2.1)

3. RESULTS AND DISCUSSION



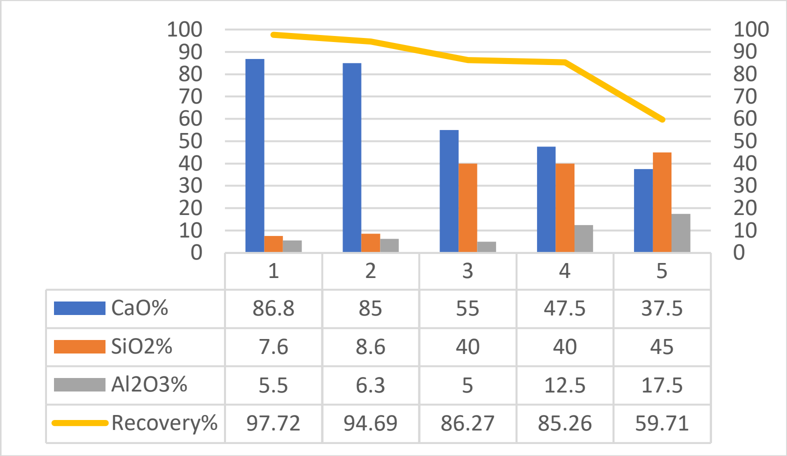
	1	2	3	4	5
Scale%	42.5	41	37.5	35.6	33.1
Scale Mud%	42.5	41	37.5	35.6	33.1
Coke%	15	18	16	15.6	14.4
SiO2%	0	0	9	10.4	14.4
Al2O3%	0	0	0	2.8	5
Recovery%	97.72	94.69	86.27	85.26	59.71

Fig. 6. Reduction Data of Samples 1-5

The highest efficiency was observed in the Sample 1 containing 42.5% scale, 42.5% scale sludge and 15% coal. The lowest efficiency was observed in Sample 5, which contains 33.1% scale, 33.1% scale sludge, 14.4% coal, 14.4% SiO_2 and 5% Al_2O_3.

It is thought that the reason for this is the chemical compounds in the scale obtained from the mud. In the slag analysis, it was observed that the reducers added from the outside decreased the CaO concentration and the reduction efficiency decreased as the CaO concentration decreased.

The slag composition of the prepared pellets after reduction was examined and shown in Figure 6.



	1	2	3	4	5
CaO%	86.8	85	55	47.5	37.5
SiO2%	7.6	8.6	40	40	45
Al2O3%	5.5	6.3	5	12.5	17.5
Recovery%	97.72	94.69	86.27	85.26	59.71

Fig. 7. Slag Compositions of Samples 1-5

As the amount of CaO in the slag composition decreased, the amount of SiO_2 and Al_2O_3 increased, and it was observed that the reduction efficiency decreased with the decrease in the amount of CaO despite the increase in other reducers.

The relationship between the basicity value, which decreases with the decrease of CaO concentration, and the metal recovery after reduction was examined and it was observed that the trends were the same.

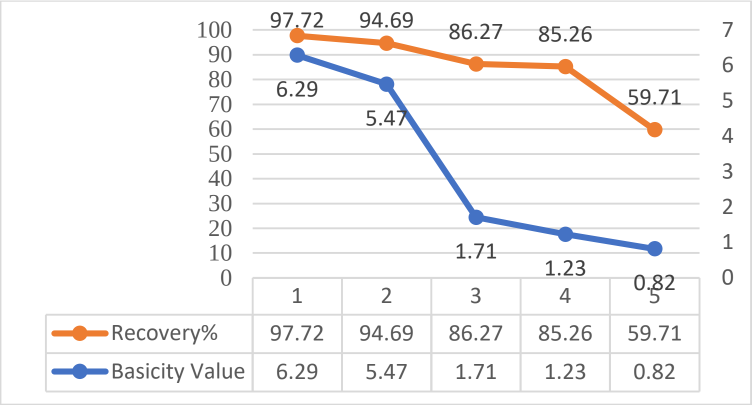


Fig. 8. Relation Between Recovery% and Basicity Value of Samples 1-5

As other indicators show, the reduction efficiency decreased as the basicity value decreased (Figure 7).

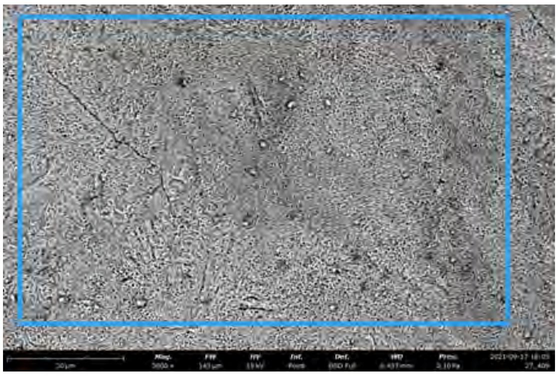


Fig. 9. SEM Analysis Image of Metal after Reduction

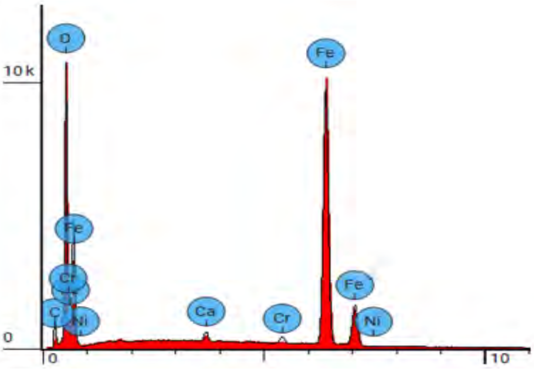


Fig. 10. Ingredient Peaks of Reduced Metal According to SEM Analysis

Table 3. Elemental Distribution of Metal after Reduction According to SEM Analysis.

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	18.782	7.000
8	O	Oxygen	38.266	19.000
20	Ca	Calcium	0.724	0.900
24	Cr	Chromium	0.744	1.200
26	Fe	Iron	41.485	71.900

In the analyzes performed it was observed that the metal concentration increased after reduction and reached the level of approximately 72% in weight concentration(Table 3.).

4. CONCLUSIONS

It is possible to recover the scale sludge consisting of stainless steel high temperature oxides by reduction.

It can be said by looking at the slag composition of the samples after reduction; $CaCO_3$, which is used for neutralization, acts as a good reducer during reduction.

The locations of the prepared pellets in the CaO, SiO_2, Al_2O_3 triple diagram are given in figure 5. The metal recovery efficiency order between the pellets was observed as Sample 1 > Sample 2 > Sample 3 > Sample 4 > Sample 5.

The sample with the highest recovery shows us that; There is a linear relationship between the CaO in the slag composition and the recovery percentage. It was observed that the recovery percentage decreased with the decreasing CaO concentration and basicity ratio, respectively, in the pellets.

Based on this, it can be said that in the recycling of scale sludge consisting of stainless steel high-temperature oxides, the percentage of CaO compound made by the element Ca from $CaCO_3$ added during neutralization affected the degree of reduction more and positively rather than other reducers.

While it was expected that the reducers added externally to the pellets would increase the reduction efficiency, they decreased it in the opposite direction. When the relationship between CaO concentration and metal recovery percentages is examined, it can be said that; Since externally added reducers reduced the CaO concentration, their effects on metal recovery were negative.

When the slag composition and metal recovery percentages were examined, a correct relationship was observed between both the basicity value and the metal recovery percentages. Because CaO not only provides the highest efficiency but also increases the basicity value.

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