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RESEARCH ARTICLE

A Case Study on "Reuse of Stainless Steel Finishing Wastewater"

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Abstract

Steel pickling is part of the finishing process in the production of stainless steel, in which oxide and scale are removed from the surface of stainless steel, by dissolution in acid. Steel pickling process produced large quantity of diluted acid which further treated by individual industry or as combined effluent treatment. During the pickling process pickled liquor/s applied on steel surface and due to that metal oxide and scale is removed from the surface of steel and mixed or suspended in the acid solution. When the strength of pickle liquor reduced, it is discarded and is drain out from pickling tanks. This liquid waste is called spent picking liquor (SPL). The pH of SPL is around 1.5 to 2. SPL is hazardous waste as per Environment Protection Act 1986 Government of India. SPL sample was mixed with the concentrated H_2SO_4 of a particular amount, and this solution was added in the particular amount of iron scrap powder. Then mixture was heated around 100°C and in this heated mixture small amount of concentrated HNO_3 was mixed. The solution was put in the furnace for cretin duration at temperature about 900°C. At this temperature all iron oxide converted into α-Fe_2O_3 which commercially known as red oxide. The use of SPL to make red oxide not only solves the problem of safe disposal of SPL but also gives the value added product.

INTRODUCTION

Mankind has utilized iron for thousands of years, but it was not until the early decades of the 1900's that the first stainless steel was patented and manufactured. An industry that has, over the past 100 years, made a significant contribution to the development of our world.[10] India is the world's second-largest consumer and third-largest producer of stainless steel, the nation's average per capita consumption of stainless steel is only about 2 kilos, whereas the global average is 5 kg.[11] India has been outpacing global stainless steel growth rates consistently over the last several years. During the last 15 years, Indian stainless steel production has grown at an average of 16% per annum against the world average growth rate of 6%. The Indian stainless steel market is expected to grow by 11% annually during the next decade.[12] Stainless steel doesn't stain, corrode, or rust as easily as ordinary steel, but it is not stain-proof. Standard mill finishes can be applied to flat rolled stainless steel directly by the rollers and by mechanical abrasives. Steel is first rolled to size and thickness and then annealed to change the properties of the final material. Any oxidation that forms on the surface (scale) is removed by pickling, and a passivation layer is created on the surface. A final finish can then be applied to achieve the desired aesthetic appearance.[1]-[8] The discharge from the pickling area generally includes spent strong liquor and acidic rinse water. In addition, there may

be effluents from degreasing, fume scrubbers, passivating plants, and other ancillary processes together with floor washings and spillages. The liquors may also be contaminated with oil and grease from rolling mills and by leakages from hydraulic equipment. The spent pickle liquor may contain anything from 5 to 15 percent free acid and 2 to 10 percent ferrous iron. The volume of water used for rinsing is in the range of about 250 to 450 liters/ton of steel pickled.[13] One of the most troublesome wastes from the steel plant is the pickle liquor. The most common method of treating pickle liquor is to add lime to neutralize the acid. Extensive lagoons are required to dispose of the voluminous watery sludge. It is usually impractical to dewater this sludge in a vacuum filter.[13] The most severe environmental and health problems associated with waste water from the steel industry originate from high levels of metals such as chromium and nickel. Iron exists naturally in the water and has low toxicity. Nitrates have over the last decades gained more attention since it causes indirect effects of the environment.[9] The finishing of steel generally carries out with various techniques, but in developing countries like India acid pickling is generally used. The various acids are used but mostly the sulfuric acid, nitric acid and hydrofluoric acid are utilized.[1] Particularly in Jodhpur several steel finishing industries exist for numerous utilities like different kitchenware or domestic items. Around 50 industries exist and they produce around 150 – 200 TPD and before moulding the final shape, steel is pickled with the help of Sulfuric, Hydrofluoric and Nitric acid. Due to this complete process almost 20T per day spent acid have been drain to Common Effluent Treatment Plant (CETP) for treatment.

1. CASE STUDY:

Steel finishing industries of Jodhpur generally adopted several activities like hot rolling, pickling, rinsing with water, packing, etc. As shown in flow diagram (Figure 2). When iron and steel products are pickled with sulfuric acid, they are immersed in an acid bath. As a result, iron dissolves in sulfuric acid and forms solution of a ferrous sulfate. After continuous pickling, ferrous ions concentration increases while free sulfuric acid content decreases to a point where the pickling process is no longer effective. This acid is considered as spent and replacement is required for new batch. The specific data of two different capacity of local plant are shown in table 1.

The spent pickling liquors as shown in table 1 are of two types and in this study these are designated as SPL1 and SPL2:

1. Spent Sulfuric acid and rinse water (SPL1)
2. Spent mixed acid (H_2SO_4, HNO_3 & HF) and rinse water (SPL2)

These SPLs are useless for these industries. But actually both SPLs have diluted acid whose strength is already been reduced. So they may be utilized in other processes also. In the red oxide production iron sulfate is generally utilized which is oxidized and converted into the red oxide which is nothing but iron oxide There are 16 known iron oxides These compounds are either oxides (Hematite, Magnetite, Maghemite, β-Fe_2O_3, ε-Fe_2O_3, Wüstite), or hydroxides and oxide-hydroxides (Goethite, Lepidocrocite, Akageneite, Schwertmannite, Feroxyhyte, δ-FeOOH, high pressure FeOOH, Ferrihydrite, Bernalite, $Fe(OH)_2$, green rusts). At high temperature these oxides finally oxidized to α–Fe_2O_3 at temperature 900°C which is commercially known as red oxide.[1]-[8]

$$\text{All Iron Oxide} \xrightarrow{\text{Temperature } 900^{O}C} \alpha - Fe_2O_3 \ (\text{Red Oxide})$$

The general estimated amount of Spent Pickling Liquor (SPL) produced from Jodhpur local industries is around 20T per day (This data is collected from Common Effluent Treatment Plant (CETP) Salawas, Jodhpur). Now in Jodhpur this SPL is mixed with alkaline waste of other industries (to reduce the strength of SPL) and collected at CETP storage tank where this waste treated with lime or quick lime for neutralization. Due to neutralization reaction various salts are formed which are precipitated in the tank then these precipitated salts are further transported to landfill site for land filling purpose.

2. SAMPLE COLLECTION:

Various samples have been collected from the pickling units of Jodhpur. Both SPL1 and SPL2 samples are collected separately and then treated individually as well as treated after mixing of them.

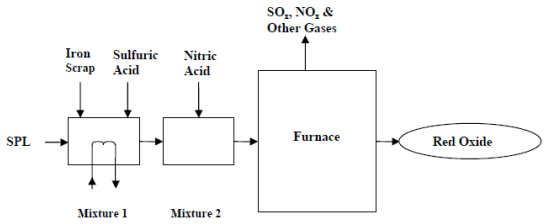

Figure 1: Flow diagram of laboratory setup for treatment of SPL

3. METHODOLOGY:

(a) Various observations have been taken with varying amount of acids during treatment. The three type of sample have been adopted namely:

- Sample SPL1: This is diluted sulfuric acid and rinse waste water from pickling
- Sample SPL2: This is diluted mixed acid and rinse waste water from pickling
- Sample Mix SPL: This is the mixture diluted sulfuric acid, rinse waste water of diluted sulfuric acid, diluted mixed acid and rinse waste water diluted mixed acid from pickling from pickling

(b) (i) A particular amount of iron scrap powder and concentrated H_2SO_4 was mixed in the collected SPL's and mixture heated about 100°C.

(ii) A small amount of concerted HNO_3 was mixed in SPL's.

(iii) SPL's mixture was heated in furnace at temperature of 900°C for certain duration and then cooled to ambient temperature.

(c) Spectrophotometer was used for analysis of color of crystals which was obtained from the experiment in terms of wavelength.

4. OBSERVATIONS AND ANALYSIS:

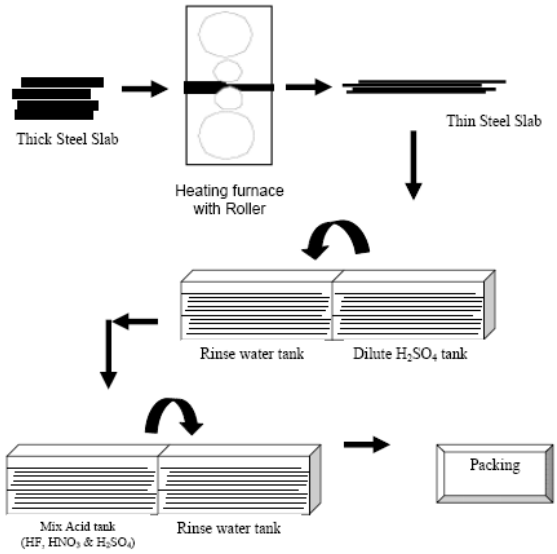

Figure 2: Flow diagram of typical pickling unit of steel finishing of Jodhpur local Industries

Table1: Statistical Data of various Jodhpur Local steel Industries

Unit	Processing		Chemical Consumption			Waste production		
	Maximum Capacity	Sample Collection day	H_2SO_4	HNO_3	HF	Sludge	SPL 1	SPL 2
One	100 T/D	16 T/D	1150 kg	1150 kg	150 kg	25 kg	1500 ℓ	1500 ℓ
Two	50 T/D	15 T/D	1060 kg	1060 kg	130 kg	22 kg	1400 ℓ	1400 ℓ

SPL's samples were treated as described in methodology to find out the optimum amount of concentrated H_2SO_4, amount of iron scrap, amount of concentrated HNO_3 and temperature and then analyze in spectrophotometer as these parameters were considered as the variables in this study.
Following combination of variables were used in the study

1. SPL1 20ml, iron scrap powder 10gm, H_2SO_4 2.0 ml and temperature 900°C. Amount of HNO_3 was varying from 1 ml to 7 ml. Results of experiment are given in table-2.

Table 2: Effect of amount of HNO_3 in SPL1

HNO_3 (in ml)	Wave length variation observed (in nm)
0.1	755
0.2	730
0.5	712
1.0	704
2.0	685
3.0	670
4.0	662
5.0	656
6.0	645
7.0	642

2. SPL1 20ml, iron scrap powder 10gm, HNO3 5.0 ml and temperature 900°C. Amount of H_2SO_4 was varying from 1 ml to 6 ml. Results of experiment are given in table-3.

Table 3: Effect of amount of H_2SO_4 in SPL1

H_2SO_4 (in ml)	Wave length variation observed (in nm)
0.1	757
0.2	735
0.5	715
1.0	698
2.0	687
3.0	666
4.0	652
5.0	641
6.0	636

3. SPL1 20ml, iron scrap powder 10gm, H_2SO_4 2.0ml, HNO_3 5.0 ml and varying from 100°C to 1000°C. Results of experiment are given in table-4.

Table 4: Effect of Temperature in SPL1

Temperature (°C)	Wave length variation observed (in nm)
100	759
200	718
300	696
400	691
500	683
600	670
700	661
800	645
900	636
1000	634

4. SPL2 20ml, iron scrap powder 10gm, H_2SO_4 4.0 ml and temperature 900°C. Amount of HNO_3 was varying from 1ml to 10ml. Results of experiment are given in table-5.

Table 5: Effect of amount of HNO_3 in SPL2

HNO_3 (in ml)	Wave length variation observed (in nm)
0.1	747
0.2	731
0.5	725
1.0	713
2.0	704
3.0	693
4.0	688
5.0	675
6.0	666
7.0	651
8.0	645
9.0	639
10.0	635

5. SPL2 20ml, iron scrap powder 10gm, HNO3 8.0 ml and temperature 900°C. Amount of H_2SO_4 was varying from 1 ml to 8 ml. Results of experiment are given in table-6.

Table 6: Effect of amount of H_2SO_4 in SPL2

H_2SO_4 (in ml)	Wave length variation observed (in nm)
0.1	749
0.2	734
0.5	723
1.0	714
2.0	701
3.0	689
4.0	674
5.0	650
6.0	644
7.0	636
8.0	634

6. SPL2 20ml, iron scrap powder 10gm, H_2SO_4 4.0ml, HNO_3 8.0 ml and varying from 100°C to 1000°C. Results of experiment are given in table-7.

Table 7: Effect of Temperature in SPL2

Temperature (°C)	Wave length variation observed (in nm)
100	761
200	745
300	727
400	701
500	691
600	677
700	661
800	645
900	636
1000	634

7. Mix SPL 20ml, iron scraps powder 10gm, H_2SO_4 3.0 ml and temperature 900°C. Amount of HNO_3 was varying from 1ml to 9ml. Results of experiment are given in table-8.

Table 8: Effect of amount of HNO_3 in SPL Mix

HNO_3 (in ml)	Wave length variation observed (in nm)
0.1	769
0.5	747
1.0	726
2.0	717
3.0	709
4.0	699
5.0	681
6.0	669
7.0	641
8.0	636
9.0	634

8. Mix SPL 20ml, iron scrap powder 10gm, HNO_3 7.0ml and temperature 900°C. Amount of H_2SO_4 was varying from 1 ml to 7 ml. Results of experiment are given in table-9.

Table 9: Effect of amount of H_2SO_4 in SPL Mix

H_2SO_4 (in ml)	Wave length variation observed (in nm)
0.1	767
0.2	749
0.5	731
1.0	717
2.0	703
3.0	691
4.0	674
5.0	650
6.0	635
7.0	634

9. Mix SPL 20ml, iron scrap powder 10gm, H_2SO_4 3.0ml, HNO_3 7.0 ml and varying from 100°C to 1000°C. Results of experiment are given in table-10.

Table 10: Effect of Temperature in SPL Mix

Temperature (°C)	Wave length variation observed (in nm)
100	766
200	751
300	740
400	725
500	707
600	691
700	672
800	655
900	640
1000	636

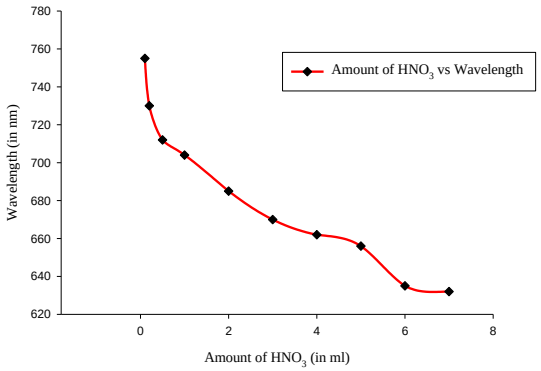

Figure 3: Graphical presentation of color of crystal on changing of amount of HNO_3 (where SPL1was 20ml, Iron scrap 10gm, H_2SO_4 2.0 ml and temperature 900˚C)

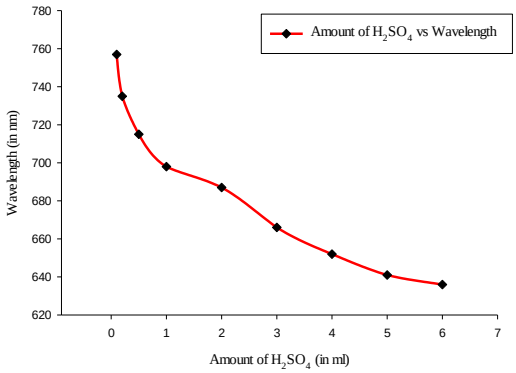

Figure 4: Graphical presentation of color of crystal on changing of amount of H_2SO_4 (where SPL1 20ml, Iron 10gm, HNO_3 5.0 ml and temperature of 900˚C)

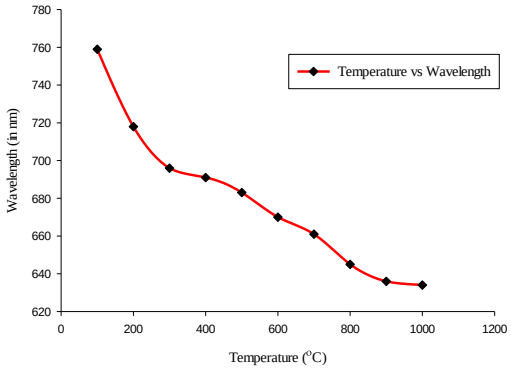

Figure 5: Graphical presentation of color of crystal on changing of temperature (where SPL1 20ml, Iron 10gm, HNO_3 5.0ml and H_2SO_4 2.0ml)

As shown in figure (3, 4 &5) with SPL1, as the amount of HNO_3 varying from 0.1 ml to 7.0 ml, obtained crystals were analyzed and found that wavelength varies from 755nm to 642nm. When amount of H_2SO_4 varying from 0.1 ml to 6.0 ml, obtained crystals were analyzed and found that wavelength varies from 757nm to 636nm, and when varying the temperature from 100°C to 1000°C, obtained crystals were analyzed and found that wavelength varies from 759nm to 634nm.

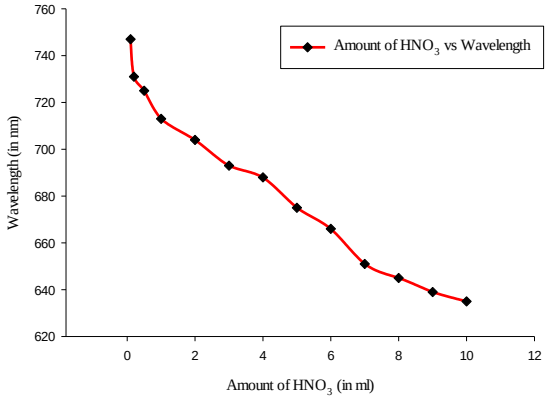

Figure 6: Graphical presentation of color of crystal on changing in amount of HNO_3 (where SPL2 20ml, Iron 10gm, H_2SO_4 4.0ml and temperature 900˚C)

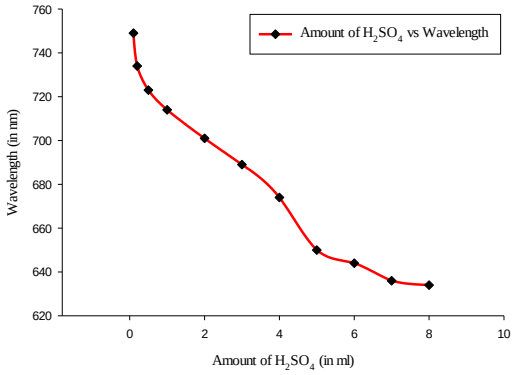

Figure 7: Graphical presentation of color of crystal on changing in amount of H_2SO_4 (Where SPL2 20ml, Iron 10gm, HNO_3 8.0ml and temperature 900˚C)

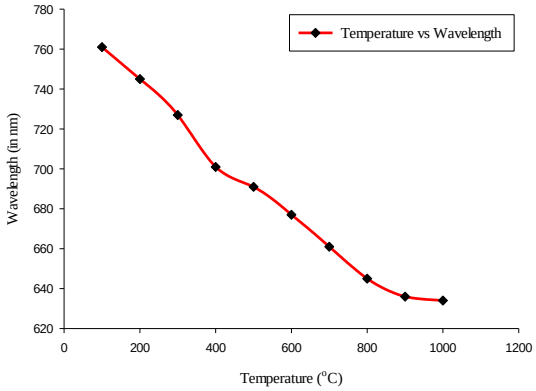

Figure 8: Graphical presentation of color of crystal on changing in temperature (where SPL2 20ml, Iron 10gm, HNO_3 8.0ml and H_2SO_4 4.0ml)

As shown in figure (6, 7&8) with SPL2, as the amount of HNO_3 varying from 0.1 ml to 10.0 ml obtained crystals were analyzed and found that wavelength varies from 747nm to 635nm. When amount of H_2SO_4 varying from 0.1 ml to 8.0 ml obtained crystals were analyze and found that wavelength varies from 749nm to 634nm, and when varying the temperature from 100°C to 1000°C, obtained crystals were analyzed and found that wavelength varies from 761nm to 634nm.

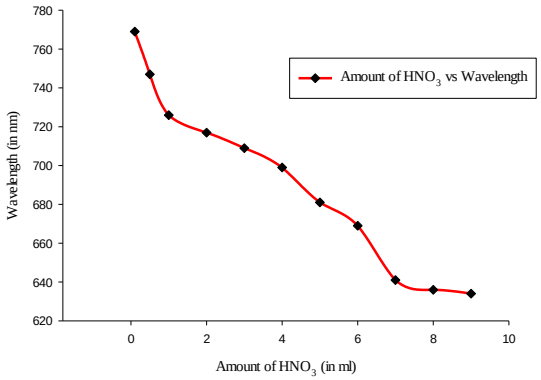

Figure 9: Graphical presentation of color of crystal on changing in amount of HNO_3 (where Mixture of SPL1 & 2 was taken 20ml, Iron 10gm, H_2SO_4 3.0ml and temperature of 900˚C)

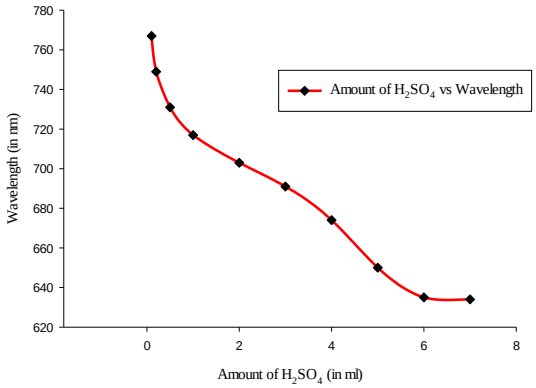

Figure 10: Graphical presentation of color of crystal on changing in amount of H_2SO_4 (where Mixture of SPL1 & 2 was 20ml, Iron 10gm, HNO_3 7.0ml and temperature 900˚C)

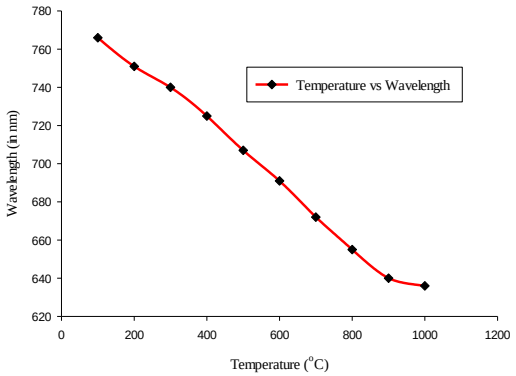

Figure 11: Graphical presentation of color of crystal on changing in temperature (Where mixture of SPL1 & 2 was 20ml, Iron 10gm, HNO_3 7.0ml and H_2SO_4 3.0ml

As shown in figure (9, 10 &11) with mix SPL, as the amount of HNO_3 varying from 0.1 ml to 9.0 ml obtained crystals were analyzed and found that wavelength varies from 769nm to 634nm. When amount of H_2SO_4 varying from 0.1 ml to 7.0 ml, obtained crystals were analyzed and found that wavelength varies from 767nm to 634nm, and when varying the temperature from 100°C to 1000°C, obtained crystals were analyzed and found that wavelength varies from 766nm to 636nm.

5. CONCLUSIONS:

(a) When SPL1 treated from the variation of amount of HNO_3, H_2SO_4 and temperature the optimum values for conversion into red oxide are 25%, 10% (V/V of SPL1) and 900°C respectively
(b) When SPL2 treated from the variation of amount of HNO_3, H_2SO_4 and temperature the optimum values for conversion into red oxide are 39%, 21% (V/V of SPL2) and 900°C respectively
(c) When mix SPL treated from the variation of amount of HNO_3, H_2SO_4 and temperature the optimum values for conversion into red oxide are 36%, 17% (V/V of Mix SPL) and 900°C respectively

This study indicates that SPL waste can be used to produce red oxide by adding of small quantity of concentrated HNO_3 and H_2SO_4. The red crystals obtained in this study was due to conversion of iron oxide at 900°C into α-Fe_2O_3 which commercially known as red oxide and is a value added product. The use of SPL to make red oxide not only solves the problem of safe disposal of SPL but also gives the value added product.

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