

A Review on Regeneration Process of Waste Pickling Acid at Steel Industries

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Abstract: In steel industries the hot rolled steel coil requires pre-treatment before undergoing various other processes like cold rolling, galvanising etc. This pre-treatment is aimed to remove various oxide layers, rust or scale and other impurities from the steel surface by passing the workpiece through the vat of pickle liquor. The pickling process generates large amount of pickling sludge which contains acidic rinse water, dissolved metal salts of iron, iron chloride, zinc and waste acid. The spent pickle liquor is considered a hazardous waste as per Indian Standards. In this paper we have completely reviewed the treatment of stainless steel, also discussed about the traditional methods for treatment of spent pickle liquor, regeneration of acid and utilization of waste sludge.

Keywords: Pickling process, acid regeneration, traditional treatment methods, pyrohydrolysis, neutralization, diffusion dialysis.

1. INTRODUCTION

Steel manufacturing includes many hot working processes at an elevated temperature which leaves a layer of oxides or scale on steel surface, thus, to remove these impurities and stains from the surface of steel it goes through a unit process called pickling. The pickling process was reviewed at ESSAR STEEL INDIA LIMITED. PUNE FACILITY (Maharashtra) in which the hot rolled coil is placed on the uncoiler and the strip is pulled through the acid bath section (four tanks in a row containing hydrochloric acid) at a speed of 540 feet per minute and the rubber scrubber scrubs the surface to remove the impurities easily. The strip is then passed to the water tank where it is rinsed with water sprays and air-dried, leaving with a dull silver luster. At the end of pickling line the strips are recoiled and passed for other processes like cold rolling and galvanizing. During pickling process large amount of pickling acid is wasted whose direct dispose cause great impact on an environment, therefore, this waste acid is regenerated by Acid Regeneration Plant (ARP) which consists of four tanks, namely, waste acid tank, water tank, alkaline solution tank, and oxygen tank. By using conventional methods in this ARP line we can regenerate the pickling acid upto 99.9%, this acid is regenerated till it is removing the impurities from the surface of steel.

This research paper includes brief introduction of production of stainless steel, pickling process, methods of regenerating the waste pickling acid.

2. STAINLESS STEEL PRODUCTION

Stainless steels are alloys of iron which contain minimum 10.5% of chromium so as to increase the resistance against corrosion. Chromium protects the steel surface from rust and corrosion by forming a layer of chromium oxide on it. Various other alloying metals like nickel, nitrogen and molybdenum are added to enhance the structure of the steel and also to improve its properties like toughness, formability and strength.

2.1 Treatment of Steel

Steel treatment is a complicated process in which steel goes through different kinds of unit operations to gain the improved surface qualities. Examples of such operations are hot rolling, pickling, cold rolling, galvanization and colour coating.

2.1.1 Rolling process

There are two types of rolling processes which to be performed after the casting of steel.

A. Hot Rolling: It is a process in which steel is treated above its recrystallization temperature around 600-700 degree Celsius.

B. Cold Rolling: It is a process which is carried out under recrystallization temperature in which thickness of steel is reduced by using the two rotating cylinders. The rolling mill consists basically of rolls, bearings, housing to accommodate these parts, and a drive for power supply.

Rolling Mills are classified as:

1. Two - high mills
2. Two- high reversing mills
3. three-high mills
4. Four- high mills

The figure shown below is depicting the rolling process of 4 HI mill.

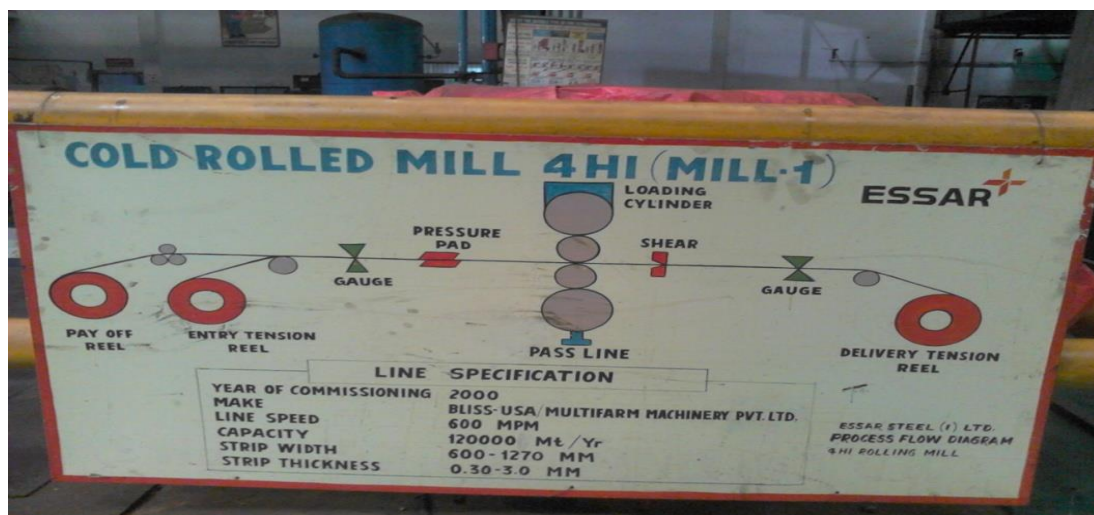


Fig. 1

2.1.2 Pickling Process

Pickling is a process in which thin layer of oxidized iron, or, scale is removed which are formed on the surface of the steel due to reaction of alloying metals with the oxygen of air at the high temperatures employed during hot rolling. To avoid that the oxide layers and other impurities is worked into the material matrix during the further processing of steel, it is essential to remove them and it is accomplished by a process known as pickling.

In this process the hot rolled coil is placed on the uncoiler and the strip is pulled through the acid bath section (four tanks in a row containing hydrochloric acid) at a speed of 540 feet per minute and the rubber scrubber scrubs the surface to remove the impurities easily. The strip is then passed to the water tank where it is rinsed with water sprays and air-dried, leaving with a dull silver luster. At the end of pickling line the strips are recoiled.

3. REGENERATION OF PICKLING ACID

During the pickling process large amount of hydrochloric acid is spent in order to remove the impurities. Direct disposing off the contaminated acid will have the huge impact on an environment and also depletes the quantity of fresh hydrochloric acid. Thus, to eliminate the need for and cost of disposal of spent acid and the cost of replacement of hydrochloric pickle liquor, we can regenerate spent acid from continuous pickling line up to 99.99% by using acid regeneration plant.

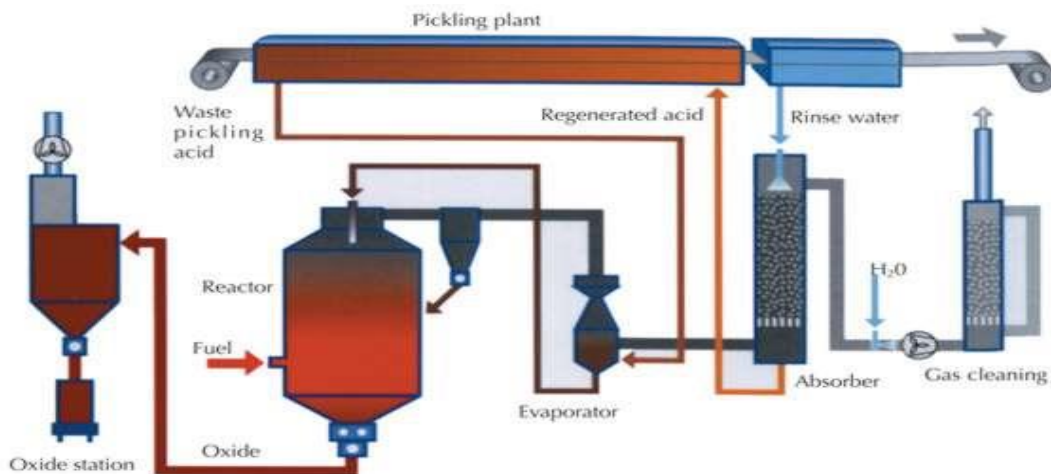
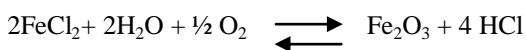


Fig. 2

3.1 Regeneration of Acid by Pyrohydrolysis

The waste pickling liquor is transferred to Acid Regeneration Plant (ARP) through high pressure pipelines and is stored in a tank of 20KL. Acid regeneration plant consists of four tanks, starting with the tank of waste pickling liquor and other three tanks consists of water, alkaline solution, oxygen in respective tanks. By using Pyrohydrolysis method we can regenerate hydrochloric acid and recover a metal-free acid solution. We also obtain high-quality iron oxide either as pellets, or, in fine powder which is strongly demanded by various industries.

In Pyrohydrolysis, there is chemical conversion of metallic salts using oxygen and steam at very high temperatures. Iron (II) chloride from the pickling line reacts according to following equations:



and ferric salts by:



The initial solution contains water and free acid which will rapidly evaporate at the temperature of reaction. The roasting gas contains the entire free and bonded acid in a form that can be absorbed. The spray roast process is performed at temperature well below the sintering temperature of iron oxide so that it can be obtained as red powder. The oxide product is either in granules in the size ranges 0.2 micro metres to 2 mm or as powder, depending upon the temperature of pyrohydrolysis.

4. NEUTRALISATION

It is one of the utilised method for treating the waste water from the pickling process. During pickling process large amount of water is used for rinsing of the acid from the surface of steel, the toxic acidic water is released directly to recipient with high metal concentration, therefore, neutralisation is used to reduce the metal concentration and rise in pH.

At present, the alkaline solution is circulated with waste pickling liquor to form a slurry which is fed continuously in the neutralising tank to make the pH 7.5 (approx.). This method increases the pH value, which leads to the precipitation of metal hydroxides due to their low solubility in water. The solubility of metal hydroxides directly depends on the pH value, the pH is usually increased using either slaked lime (Ca(OH)₂) or sodium hydroxide (NaOH).

5. SEPARATION BY USING MEMBRANE

It is simplest and cheapest method for separating the water and impurities by using a membrane which is a physical barrier that allows certain compounds to pass through, depending upon their physical and chemical properties. Membrane consists of porous layer with thin dense layer on top forming an actual membrane. Various other methods like reverse osmosis and nano-filtration can also recover metallic ions but they are still expensive due to high energy need.

5.1 Diffusion dialysis

It is also a membrane separation process. The spontaneous movement of a material from an area of high concentration to an area of lower concentration is known as diffusion. The movement of material is due the concentration difference. Dialysis is the common process of separating the molecules due to the rate of movement of molecules through semi-permeable membrane. In diffusion analysis process an ion exchange semi permeable membrane is placed between a flowing water stream and a flowing acid with dissolved metal solution. This membrane has positive charge on its surface which attracts the negatively charged anions in solution that come in close contact with the anion exchange membrane surface.

Some of the most common applications of this process include the recovery of mixed acids of stainless steel pickling baths, recovery of sulphuric acid/hydrochloric acid or sulphuric acid/nitric acid of pickling plants. Thus diffusion dialysis is very effective in recovering the mineral acids from the solutions of acid containing dissolved metals.

6. RESULT AND DISCUSSIONS

1. Approximately 36 KL of pickling acid is used in pickling line.
2. 25 KL (approx.) of pickling acid which comes out after removing the impurities contains ferric particles and rest is mixed with water.
3. Regeneration of 25 KL waste pickling liquor through Acid Regeneration Plant.
4. The remaining 9 KL acid which contains water is regenerated by evaporating the water from it.
5. Thus, approximately 35964 Litres of acid is regenerated from the above two processes.
6. Precipitated product from ARP line is used to form red oxide powder which is demanded by various paint industries and iron industries.

7. CONCLUSION

From our research we concluded that regeneration of waste pickling acid is environmentally friendly and also reduce the cost of using fresh acid again and again in pickling line. Regeneration process requires extra unit to be installed in a steel plant which provides job opportunities, but, this also increases the overall budget of the company. The extra budget can be overcome by selling the waste precipitated product i.e. iron oxide like red oxide powder at optimum price to various demanding industries.

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