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TREATMENT OF SPENT PICKLING LIQUOR

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ABSTRACT

Spent pickle liquor is pertinent to hazardous waste. Several cases of recovery and regeneration methods are employed to recover and regenerate the acid and metals from the spent pickling liquor. But these methods are sumptuous, and not amenable for small scale manufactures. There are severe problems in its disposal to lined sites (landfills). A survey has been guaranteed to minimize the generation of the pickling sludge by different neutralizing agents and their compounding.

Keywords: Pickling Liquor, Hazardous Waste, Sludge, Precipitation, sludge characterization

I. INTRODUCTION

Rapid industrialization brings a great deal of pollution, whether it is air, land, water or noise. One of the major business organizations in India is the increasing degree of land pollution largely due to the uncontrolled administration of industrial solids and hazardous waste. Hazardous waste can be delineated as a wasteland if it shows any of the following: corrosivity, ignitability, reactivity or toxicity [1].

One of the major environmental problems for the steel industries comes from pickling plant waste. Steel finishing operations, such as pickling, galvanizing, plating, etc., involve a surface cleaning process to winnow out the scale, rust and dust. This procedure is held out by immersion of steel in hot, acidic solution either Hydrochloric acid or Sulfuric acid. Hydrochloric acid (HCl) is a preferred used acid in the pickling process because following advantages over Sulfuric acid:

a) Faster cleaning rate at room temperatures with lower doses

b) Less chances of over pickling

c) Safer to handle than chemical oxidizers

In an industrial pickling process, iron oxide dissolves in HCl acid, the ferrous salt and water are formed according to the following reactions:

$$Fe_2O_3 + Fe + 6HCl \longrightarrow 3\,FeCl_2 + 3H_2O \quad (1)$$

$$Fe_3O_4 + Fe + 8HCl \longrightarrow 4\,FeCl_2 + 4H_2O \quad (2)$$

$$FeO + 2\,HCl \longrightarrow FeCl_2 + H_2O \quad (3)$$

The HCl acid also reacts with the base steel by the following mechanism:

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2 \quad (4)$$

Spent baths must be disposed because the efficiency of pickling decreases with increasing content of dissolved metals in the bath. Waste pickling liquors (WPL) are regarded as hazardous waste and specifically listed in Hazardous Waste (Management & Handling) Amendment Rules 2002 [2] due to its corrosive nature and presence of residual acid as well as high metal content.

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In parliamentary law to prevent the contamination of the surroundings and to achieve the permissible effluent discharge limit, many techniques have been tried for WPL treatment The literature reported various processes for regeneration of acid and recovery of metals from waste pickling liquor. Metals (Fe, Cr and Ni) can be recovered from spendstainless steel pickling liquor by membrane electrolysis method. For higher nickel content recovery iron has to be slain from the waste solution prior to electro deposition [3]. Pyrometallurgical process has been analyzed for total regeneration of both, acid and metals in the form of oxide [4]. Inorganic acids regenerated by diffusion dialysis and effects of metals have been considered on its regeneration efficiency [5]. Fe is recovered from spent pickling by ultra filtration [6] and solvent extraction method [7]. Iron and chromium are recovered as Iron and Chromium Fluoride hydrates form, from mixed hydrofluoric and nitric acid solution by crystallization method [8]. Acid regeneration and metal recovery from diverse sources of pickling liquor by different methods have been discussed by [9-10]. But these methods are sumptuous, and not amenable for small scale manufactures. Sometimes the generated products such as iron salts and iron oxide offer little promise as a universal answer to the problem because of a limited market of the compound [11].

The convenient and economical treatment method for waste pickling liquor in developing country like India, where approximately 30 million's Micro, Small & Medium Enterprises (MSMEs) exist is precipitation/ neutralization, under appropriate pH conditions [12-13]. The drawback of this treatment process is that it gets a huge quantity of slime. Thus, it requires vast land to dispose the precipitate and it will increase the handling price. In the normal practice, sludge is disposed of at the side of roads and railway track to fill low lying regions. This may induce severe health risk. To take out these drawbacks a study has been guaranteed to minimize the generation of the pickling sludge by using different neutralizing agents and their compounding.

II. MATERIAL AND METHODS

The pickling effluent samples were gathered up from steel industry where Hydrochloric acid (HCl) is used for pickling of mild steel. Waste pickling acid (WPL) was chosen for the subject area. Pickling effluent was characterized as per the standard methods [14] and the results obtained are given in Table 1. In normal practice, lime is used for discussion of the WPL and generates tons of slime. Therefore, calcium oxide is used as a basis for comparing the generation of sludge and treatment cost.

Table 1: Characterization of pickling effluent

Parameter	Value	Parameter	Value
pH	0.9	Chemical Oxygen Demand (COD) mg/l	57
Electrical Conductivity (EC) mS/cm	20	Iron g/l	82
Temperature, ºC	32	Chloride g/l	92
Total Dissolved Solids (TDS) g/l	13		

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2.1 Chemicals used

Pickling effluent was treated with various neutralizing agents viz. Calcium oxide (CaO), sodium hydroxide (NaOH), potassium hydroxide (KOH) and their several combinations. Lime purity = 80% as CaO, NaOH = 97%, KOH = 84% have been taken. In the treatment of pickling effluent, first of all pH was raised up to 12-14 by lime, NaOH, KOH or their combination. After that alum was used to decrease pH up to 7. Free settling was allowed. Subprogram of the handling process is depicted in Fig.1.

Various combinations used for optimization of treatment and their appointments are presented in Table 2.

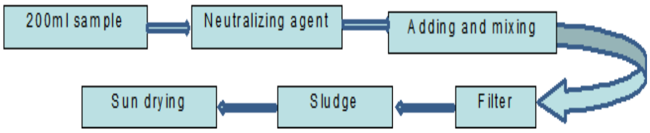

Fig1: Sequence of steps involved in the treatment process

III. RESULTS AND DISCUSSION

Treated effluent was analyzed as per standard methods [15] and the results are presented in Table 3 and Fig. 2. The values of physical and chemical properties of treated effluent were found inside the acceptable limits, after treatment with Lime, NaOH, KOH and their compounding. The color of treated sludge was fuller's earth color when WPL was treated with 100% lime only and brick red color when WPL was treated with 100% NaOH and 100% KOH. The pH and dissolved oxygen (DO) value of treated WPL lie in the orbit of 6.5 to 7.8 and 2 to 4.3 mg/l respectively as given in table 3. Graph of Conductivity and Total Dissolved solids (TDS) are presented in Fig. 2 and which confirms its linear relationship between them.

Treatment with neutralizing agent and their combination reduces TDS by 62-78%. Percentage reduction of TDS is given in Table 4. Highest reduction of TDS has been observed in treatment of lime only (78%) and lowest (62.31%) in KLH4 (80% KOH + 20% calcium oxide). 100% NaOH reduces TDS around 75% and 100% KOH reduces TDS approximately 68% in the treated effluent.

Table 2: Designation of samples with different combination for WPL treatment

Sample Code	Untreated Pickling effluent volume	Calcium hydroxide (10% solution)	Sodium Hydroxide (10% solution)	Potassium hydroxide (10% solution)
A	100 ml	-	100%	-
B	100 ml	-	-	100%
C	100 ml	100%	-	
KLH1	100 ml	80%	-	20%
KLH2	100 ml	60%	-	40%
KLH3	100 ml	40%	-	60%
KLH4	100 ml	20%	-	80%
NLH1	100 ml	80%	20%	-
NLH2	100 ml	60%	40%	-
NLH3	100 ml	40%	60%	-
NLH4	100 ml	20%	80%	-

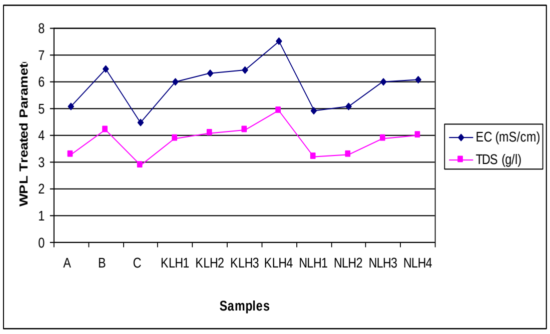

Fig 2: Graph showing the EC & TDS values vs Samples

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Table3: Percentage of Total Dissolved Solids removal

Sample Code	TDS in WPL (g/l)	TDS in treated WPL (g/l)	% TDS removal
A	13	3.3	74.62
B	13	4.2	67.69
C	13	2.9	77.69
KLH1	13	3.9	70.00
KLH2	13	4.1	68.46
KLH3	13	4.2	67.69
KLH4	13	4.9	62.31
NLH1	13	3.2	75.38
NLH2	13	3.3	74.62
NLH3	13	3.9	70.00
NLH4	13	4	69.23

3.1 Sludge Generation

Sludge generation quantity during treatment of WPL by various neutralizing agents and their combination results are given in Table 4. Sample C which is 100% lime, taken as a base for comparison of sludge generation and treatment cost. It can be observed from Table 5 that the minimum sludge quantity is generated when WPL is treated with 100% KOH and maximum with 100% lime. A 30% reduction of sludge generation quantity has been observed in comparison to lime only when WPL treated with NaOH only. 100% KOH reduces around 59.5% sludge generation quantity in comparison to 100% lime. Sludge reduction percentage increases from 11 to 56% in treatment of WPL, if the volume of KOH increases in combination of lime and KOH. In combination of lime and NaOH, sludge reduction increases from 25 to 33% by increasing the volume of NaOH.

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Table4: Sludge generated

Sample Code	Sludge generation in treatment of pickling effluent (quantity 200ml)		% reduction in sludge generation
A	13	g	35.00
B	8.1	g	59.50
C	20	g	Base
KLH1	17.83	g	10.85
KLH2	13.68	g	31.60
KLH3	13.98	g	30.10
KLH4	8.85	g	55.75
NLH1	14.94	g	25.30
NLH2	14.35	g	28.25
NLH3	13.6	g	32.00
NLH4	13.44	g	32.80

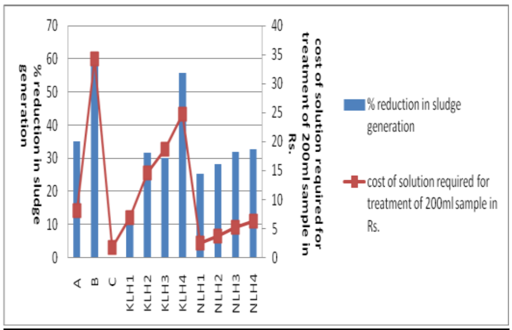

Fig 3: Graph between % reduction in sludge generation vs cost of solution required for treatment of 200ml sample

IV. CONCLUSIONS

Three different neutralizing agents viz. potassium hydroxide, sodium hydroxide and calcium hydroxide and their combinations have been used for study of the sludge generation quantity in waste pickling liquor treatment. Sludge characterization study has been done by XRD and XRF. The following conclusions can be drawn from the study:

a) 100% potassium hydroxide generated lowest sludge but the cost of potassium hydroxide pellets is much higher than the sodium hydroxide (the cost of potassium hydroxide pellets is approx. 3 times of sodium hydroxide pellets).

b) The economic solution is to use 20% calcium hydroxide and 80% sodium hydroxide for WPL treatment without much affecting the quality of treatment.

c) Lower sludge generation will result in lower cost of sludge handling i.e. sludge collection, transportation and disposal arrangement.

REFERENCES

[1] Wentz Charles A., Hazardous Waste Management, 2 ed., McGraw –Hill, Inc., New Delhi; 1995.

[2] The Gazette of India, Extraordinarily, Part 11, Section 3, Sub section (ii), May 20, 2003. Published by Authority No. 471, MoEF, Notification, New Delhi.

[3] Roemer Frank. Metal recovery from spent stainless steel pickling solution Resources, Conservation & Recycling 60. 2012. pp.72-77.

[4] Roemer F., Total regeneration of mixed pickling acid from stainless steel production-combination of nano-filtration and thermal processes, In: Preprints of the International conference and exhibition for filtration and separation technique. 2009. pp.529-33.

[5] Oh S.J., Moon S.H., Davis T., Effect of metal ion on diffusion dialysis of inorganic acids. Journal membrane science 169 (1). 2000. pp.95-105.

[6] Bern at Xavier, Recovery of Iron (III) from aqueous stream by ultra filtration, Desalination 221. 2008. pp. 413-418.

[7] Agarwal A., Sahu K.K., Kumar S., Studies on solvent extraction of Fe (III) as a step conversion of a waste effluent to a value added product 92. 2011. pp. 3105-3111.

[8] Forsberg M. K, Rasmuson C.K., Crystallization of metals fluoride hydrates from mixed hydrofluoric and nitric acid solution, Part 1, Fe (III) & Cr (III) 312 (16-170). 2010. pp. 2351-2357.

[9] Agarwal, A., Sahu, K.K., An overview of the recovery of acid from spent acidic solution from steel and electroplating industries. J. Hazardous. Material, 171 (1-3). 2009. pp. 61-75.

[10] Regal- Rostock M., A review on methods of regeneration of spent pickling solution from steel processing. Journal Hazardous Material 177. 2010. pp.57-69.

[11] Tang B., YuanL.J, Shi T.H., Yu L.F., Zhu Y.C., Preparation of nana-sized magnetic particles from spent pickling liquors by ultrasonic-assisted chemical co-precipitation. Journal Hazardous Material 163. 2009. pp. 1173-1178.

[12] Mughal S.T, Tahira S., Tayyaba A, Farzana B, Treatment of Electroplating effluent J. Chem. Soc. Pak. 30 (1). 2008. pp. 29-32.

[13] Galvez J.L., Javier D., Carlos N., Federico C.M. Hydrolysis of Iron and Chromium Fluorides: Mechanism and Kinetics, Journal of Hazardous Materials 154. 2008. pp.135-145.

[14] http://www.eisbc.org/Definition_of_Indian_SMEs.aspx :- Dated 23April 2013.

[15] Singhal A., Tewari V.K., Prakash S., A Study on Sludge Minimization during the Treatment of Pickling Effluent, Journal of Environment, Science and Engineering 48(2). 2006. pp. 109-112.

[16] Standard methods for the examination of water and wastewater, 20th ed., published by APHA, AWWA, WEF, Washington, DC 1998.