22nd WEDC Conference New Delhi, India, 1996

REACHING THE UNREACHED: CHALLENGES FOR THE 21ST CENTURY

Reuse of spent pickling liquor

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IRON AND STEEL parts are generally treated with acids viz hydrochloric acid of concentration 25 to 85 per cent (Vol.) or sulphuric acid of concentration 5 to 15 per cent (Vol.) in the metal processing industries to remove the oxide layer (Fe0) from their surface before any further processing such as electroplating, metal finishing etc. This process called pickling generates two types of wastes:

- Spent pickling liquor, because the pickling bath is discarded periodically on the accumulation of high concentration of iron (70 to 100 g / 1) in it.
- Rinse water containing 0.05 to 5.0 g / 1 ferrous iron and high acidity (pH less 3).

In order to prevent the pollution of environment and to achieve the permissible effluent discharge limit of 3 mg / 1 iron and pH of 6-9, such effluents have to be treated by a suitable technique before their disposal into river / water streams.

Effluent treatment

The spent pickling liquor containing 2-7 per cent free acid (pH less than 0.1) and 5-15 per cent ferrous iron is at present disposed off after neutralization with lime or caustic soda. But, it results in the production of large quantity of sludge, whose dewatering is difficult and disposal is a serious problem, because, it comes in the category of toxic / hazardous waste under the hazardous waste Act 1989. Moreover it is quite costly as large quantity of lime or alkali is required to precipitate the heavy metals of the effluent.

The steel producers and metal processing industries are now showing keen interest to install the units for the acid recovery from spent pickling liquor, because of the strict attitude of the Pollution Control Authorities. Besides that, pickling process becomes economical and non-polluting. With the recycling of recovered hydrochloric acid, the fresh acid requirement is reduced to a minimum.

Pickling liquor regeneration

The pickling acid bath contains mainly ferrous chloride ($FeCl_2$) produced on account of the following reaction and the unused hydrochloric acid (HCl).

$$Fe0 + 2\ HCl = FeCl_2 + H_20$$

The regeneration of spent pickling liquor is carried out by oxixdizing its dissolved iron chloride ($FeCl_2$) in a fluidized bed reactor at about 800°C. The valuable ferric oxide (Fe_20_3) is also produced as a by-product. For this, the reaction is reverse of pickling reaction, producing gaseous hydrochloric acid.

$$4\ FeCl_2 + 0_2 + 4\ H20 = 2\ Fe_20_3 + 8\ HCl$$

The hot reactor gases are first passed through the cyclone separator to recover the Fe203 granules and then passed through the pre-evaporator to concentrate the incoming spent pickling liquor. The hydrochloric acid is recovered by the absorption of gaseous HCl in water in the absorber. The details of the process are shown in Figure 1.

Table 1

Parameter	*Amount (Rs. in lacs)*	
	Expenditure	*Saving*
Electric power consumption per month, 8.0 x 10? kwh at Rs.3/kwh	2.40	-
Fuel consumption per month 25 MT at Rs.12,000.00/MT	3.00	-
Cost of recovered HCL acid of concentration 15 per cent (having 1.1 sp.gravity) 400 MT per month (of cost Rs.600.00/MT	-	2.40
Transportation charges saved as spent pickling liquor ay have to send to some other treatment plant in the absence of its own ARP to prevent environmental pollution, 400 kl/month at Rs.300/kl.	1.20	
Cost of fresh HCl acid (30 per cent) saved or pickling due to reuse of recovered acid.	-	2.00
Cost of about 65MT Fe_20_3 produced from spent pickling liquor having 120 g/l Fe^2 + and 40 g/l HCl at Rs.2000/MT.	-	1.30
Total annual charges of depreciation, interest and maintenance at 10, 15 and 4 per cent respectively of the capital cost of Rs.40 lacs	11.60	-
Annual salary of operating staff (One engineer and one helper)	1.60	-

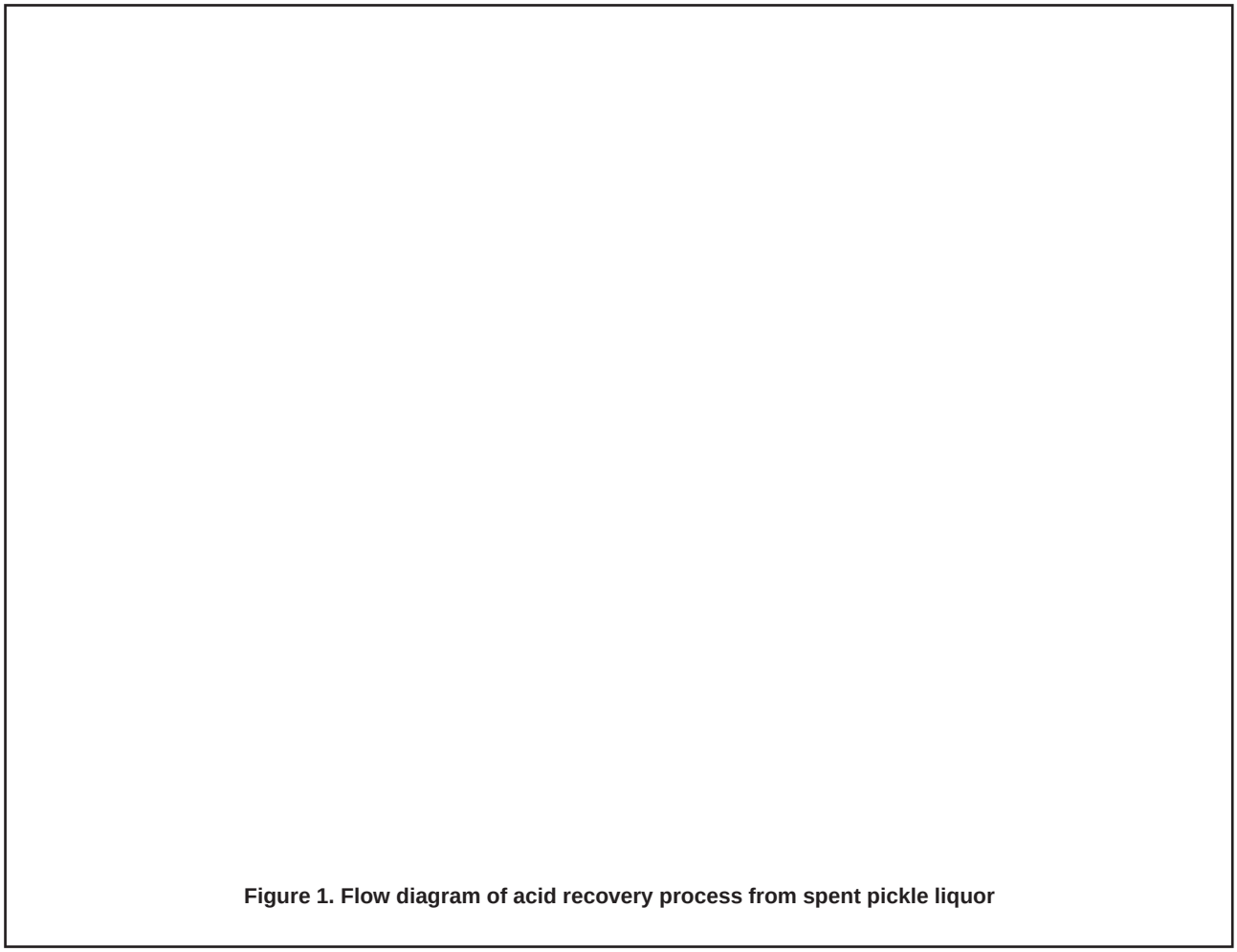

Figure 1. Flow diagram of acid recovery process from spent pickle liquor

Cost analysis

Hydrochloric acid requirement for pickling production of 1.5 x 10 MT (metric tonne) per month is 600 MT (of 20 per cent concentration) or 540 kl (kilolitre) per month (of 1.12 g / cm^3 density). But spent pickling liquor available for acid recovery in the acid recovery plant (ARP) will be about 80per cent of the acid used for pickling. (i.e. about 400 kl / month) due to carryover of the pickling liquor by the pickled articles and also due to the leakage from the pickling tanks.

The various components of expenditure for running ARP and of savings due to the recovery of HCl and Fe_20_3 (a by-product) are shown in Table 1.

Conclusions

It is observed that for the acid recovery plant of such a capacity, the total annual expenditure will be about Rs.78 lacs and the savings from it will be of the order of Rs.83 lacs. Thus there will be a net saving of Rs.5 lacs per year. Hence, it is a most cost effective technique. Moreover the serious problem of environmental pollution will also be solved.