EFFLUENT TREATMENT AND POLLUTION CONTROL IN METAL FINISHING

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Environmental pollution is the major and most serious ecological problem faced by the industrially developed countries. in the past 15 to 20 years, we have seen the transition from a total neglect of the effects of industrial pollution through to a major realisation of its serious effects, the recovery of valuable metals from wastes, and more recently to 'Zero discharge concept'. The main objectives of the pollution control are the prevention of physical damage to property, the elimination of health and safety hazards to plant personnel, the minimisation of economic losses through the reduction of plant maintenance, the disposal of wastes, the recovery of valuable waste products and the improvement of product quality.

There are two types of effluents from the metal finishing industry—those to be discharged to the open surface and those to be discharged to the open atmosphere. The former include treated waste water which contains cyanides, chromates, sulphides, fluorides etc. Cyanide vapours, nitrogen and sulphur oxide fumes, smoke and dispersed particles are some of the effluents discharged to the atmosphere.

Sources of air pollution

The contribution of effluents to air pollution by the metal finishing industry are as follows :

1. Vapours coming mostly from heat treating, scale removal, Carburising and chemical cleaning of castings. Most of the processes use salt bath and the gases coming out are mostly CO, CO_2, nitrogen oxides and cyanide[1-3].

2. Emission of nitrogen oxide fumes, that are coming out of the scale removal, metal cleaning operation, bright acid dipping and pickling with HNO_3[2].

3. Large amounts of nitrogen monoxide gases are produced in photoengraving in reclaiming metal when composite materials are stripped[2].

4. The gaseous fumes generated by salt bath processing in organic stripping. Due to the intense heat of the salt bath, the volatile components are formed of acrylic or epoxy paint, plastisol or organisol. The volatiles are usually in the form of complex hydrocarbon, ketones, aldehydes etc. As they leave the organic structure, they ignite at the surface of the molten salt. The combustion products form a mixture of CO_2, CO, water vapour and unburned hydrocarbons.

5. The hydrocarbon gases coming out of the ovens in the paint and coating industry[4].

6. SO_2, HF, and chlorine gases that are produced due to reaction with the metal surfaces during plating, pickling, cleaning etc.

Health hazards

Effluent gases in the air are in the form of solid or liquid particles consisting of a wide range of sizes from large particles over 20μ in dia. to aerosals or suspensions of fine particles extending into the submicron region less than 0.5μ. SO_2, nitrogen oxides and cyanide vapours are poisonous and obnoxious gases. Fine particles of water vapour combined with carbonates, nitrates, hydroxides and other caustic salts placed in the atmospheric suspension can give rise to eye and respiratory irritation[5].

Smoke : These are formed due to incomplete combustion of carbonaceous fuels. The flue gases contain mainly CO_2 and CO which go into the human blood, paralyse the physiological system.

SO_2 gas : This is the second major pollutant. It is readily adsorbed by vegitation soil and accelerates the corrosion and deterioration of metals, textiles and building materials.

HF and chloride : These gases accumulates in the leaves, and when the animals consume these, can cause fluorosis in them.

NO_2 gas : Nitrogen dioxide when inhaled by man gives rise to nose and eye irritation at concentration of about 13 to 25 ppm. Inhaling concentration of more than 200 ppm causes pneumonities and still higher concentration may be fatal. Small concentration of 0.02 to 0.25 ppm. of NO_2 are considered to be harmless.

NO gas : Inhaling nitrogen monoxide fumes of dilute concentration gives rise to smog through photochemical chain reaction which are harmful to respiratory system.

Treatment of air pollution effluents

The effluents can be kept within the controlable limits before letting off to the air by proper treatment.

The treatment depends mainly on the nature of the pollutant. Mist collectors and air washers with power or self-induced water spray principle should be used for washing air pollutants from the air stream. They are further heated before let off[6,7].

For the treatment of waste gases coming out of the stack, the following can be used. 1. activated carbon adsorption, 2. condensation, 3. catalytic combustion 4. washing and scrubbing, 5. chemical oxidation. 6. direct incineration. The equipments used for this are mainly gravity settling chamber, industrial separators and scrubbers.

Waste water effluents

Most of the metal finishing effluents are of toxic and before letting off into a sewage or river, they have to be given proper treatment to reduce the effect of the chemicals. The process by which these effluents coming from the finishing industry include[8,9]. 1. alkaline cleaners-etches, dips etc., 2. brightening solutions 3. anodising solution. 4. pickling and cleaning 5. electroless plating bath, 6. dye baths, descaling baths etc.

In addition to the metal concerned during the process, the effluents also contain surfactants, complexing agents and rust inhibitors in various degrees of degradation. Electroplating solutions are usually acid or alkaline in nature. Acid pickling solutions could contain free acid and heavy metals such as Cr, Ni, Cu and Zn. Alkaline plating baths consist of metal cyanides, ammonia complexes of Cu, Zn and Cd. Some of the solutions contain toxic materials as cyanides and chromates.

Waste arising in the metal finishing industry comes from : 1. concentrated plating and finishing baths 2. spills and, 3. drag out.

Spills and drag out are the major sources of waste. The effluent treatment often gives sludges which do not generally present environmental hazard. Most of the metals dissolved in the waste solution are often treated not because they contain some toxic materials but to recover some valuable materials.[10] Metals like Cu, Ni, Pb, Sn and Zn will become increasingly short of supply over the next 20 years ; so it is economical to recover the metal wastes in the plating industry. These will also help in sludge handling [10, 11, 12]

Treatment of wastes

A good waste treatment plant should have the following operations : 1. neutralisation, 2. cyanide oxidation, 3. chromate reduction, 4. metals precipitation 5. solid removal and 6. sludge removal

Waste water containing chromates and cyanides are treated in the following way. Waste water containing cyanide is seggregated from wastes containing hexavalent chromium and treated separately prior to final treatment to remove heavy metals. Cyanide is oxidised while Cr^{+6} is reduced to Cr^{+3}. The treated chrome, cyanide and neutralised acid or alkali stream are run into a common tank where the precipitation of heavy metals occurs with the control of pH. Treatment may be batch, continuous or integrated. For precipitation of heavy metals complexing agents or chelating ions such as tartrate or ethylene diamine tetracetate are added to the tank.

Treatment of cyanide wastes [13]

Electroplating and photographic processing are the two major sources of cyanide wastes. Several processes are available [7,14]. The majority of methods use chemical oxidation, In the Pont Kestone Process [15] cyanide can be oxidized to cyanate through addition of peroxygen compound (eg. Hydrogen peroxide) and formaldehyde. Heavy metals are participated at the same time and it gives reusable Zinc and Cadmium.

Two stage chlorination

In the first stage cyanide is converted to cyanogen chloride and then cyanate at a pH of approximately 11. In the second, at a pH of approximately 8.5 cyanide is oxidised to N_2 and bicarbonate.

Electrolytic treatment [7,16]

The application of electrolytic treatment is well known. The electrochemical oxidation of the cyanide ion to the cyanate may proceed via cyanogen as an intermediate :

$$CN^- = CN + C^-$$

$$2CN = (CN)_2$$

$$(CN)_2 + 2(OH^-) = CN^- + CNO^- + H_2O$$

Alternatively direct production of cyanate may take place

$$CN^- + 2(OH)^- = CNO^- + 2e^- + H_2O$$

once formed cyanate is further broken down by hydrolysis.

$$CNO^- + 2H_2O = NH^+_4 + CO_3$$

$$CNO^- + NH_4^+ = NH_2 . CO.NH_2$$

The electrolytic treatment is usually carried out at high temperature and ventilation above the cell should be provided. In the case of cyanide solution containing metals such as Cu or Zn, the metals are either precipitated or plated out on cathode. The rinse water which contains very low concentration of cyanide (less than 1000 mg/l)

can be treated by the addition of NaCl and then electrolytically treated[16].

Ion exchange

This is one of the methods of separation of effluents. This method is based on the distribution of the element /elements between the solution and solid ion exchange. It is an insoluble but permeable organic or inorganic high polymer with fixed positive or negative charges. The technique used in column operation consists of 3 steps : absorption, washing, and elution. High concentration tends to deteriorate the resin. So processing of cyanide effluents does not appear practical.

Treatment of fluoride and ammonia waste water[17]

In the production of semiconductor and thin film components, fluoride wastes are generated from etching and cleaning operations. Different methods have been given. Chemical precipitation with lime, magnesia or alum, adsorption onto calcium hydroxyl apatite or activated alumina and ion exchange. Lime precipitation gives better result.

Ammonia wastes are coming from fluoride wastes when they are added as a buffering agent to the fluoride etches. Several methods of treatment are available like nitrification, denitrification, air stripping and chlorination.

Treatment of chromate wastes[18]

These arise from the rinse during plating, anodising conversion of coatings, corrosion, inhibition, pickling and brightening. These chromium bearing wastes should not enter the stream untreated, because of its toxicity in hexavalent and trivalent condition. Treatment of chromium wastes can be done by any of the following :

Chemical reduction and precipitation

The common method of treating chromate wastes is first to reduce the Cr^{+6} to Cr^{+3} and then, by proper pH adjustment, precipitate chromium as hydroxide. Various reducing agents like SO_2, ferrous sulphate etc., are used.

Electrolytic reduction

It is working on the same principles of treating waste effluents by electrolytic treatment. Cell employs a semiconductive bed of carbonaceous particles between the electrodes under an applied D. C. potential. The effluent after treating contains less than 1ppm of Cr^{+6}. The trivalent chromium is disposed off by adjusting the pH with alkalies to precipitate metallic hydroxides.

Direct precipitation with Barium salts

Chromium is removed from the effluent as barium chromate by concurrent addition of barium carbonate and an acidic constituent. The addition of acid (HCl or HNO_3) is due to the following :

1. to convert all the heavy metal chromates to chloride and nitrate salts.
2. to keep the pH of the solution within limits to dissolve the $BaCO_3$.

Activated carbon

Rinse water containing Cr^{+6} are passed through a carbon bed. The carbon bed can be regenerated either with H_2SO_4 or with NaOH. The following treatments will give the useful recovery of chromium.

Ion exchange

Chromic acid wastes from anodizing solution contain about 100 g/l of chromic acid. It is rejuvenated by passing it through oxidation resistance cation exchange resin. Aluminium and Cr^{+3} ions, the principal contaminants of chromic acid, are retained in the resin. For higher concentrations, rejuvenation is possible by diluting the solution. Higher chromic acid concentration are likely to cause oxidative attack and affect the life of the resin. Rinse water containing chromic acid can also be treated by this method.

Evaporation

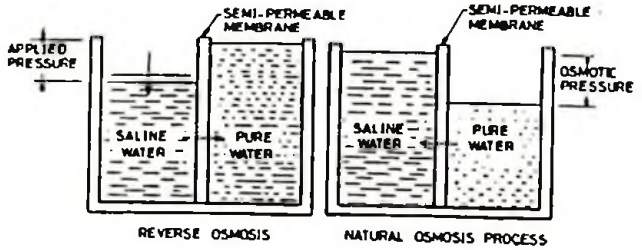
It can be used to reclaim chromic acid rinses for return to the plating bath. Since rinse water contains some other contaminants, it is better to treat with cation exchanger to remove all the contaminants and then evaporate it.

Electrodialysis

It is a membrane separation process in which ions are transferred through an ion selective membrane as a result of the application of a direct current. Chromic acid rinses and those containing some impurities can be treated by this method.

Treatment of wastes by reverse osmosis[19-21]

Reverse osmosis is a method of separating contaminated dilute bath such as rinse into a more dilute phase and a concentrated one containing most of the chemicals. The principle is the spontaneous diffusion of dilute solution or solvent into a stronger through a semipermeable membrane as shown in Fig. 1. The natural osmosis pressure is reversed by the application of an



opposing pressure, so that the net result is a transfer of solvent from the stronger solution to the weaker solution (or solvent) through the membrane. The membranes are based on cellulose materials or synthetic polymers (such as polyamide).

The reverse osmosis is like evaporation, a concentration device that is applicable in a recycle procedure. The advantage is that it is carried out at room temperature ; it does not present the risk of possible breakdown ; and cleaning is also possible. It involves the application of very high pressure (300–1000 psi) and it increases substantially as the concentration of the concentrate obtained increases. Suppose one wants to get a plating solution from rinse then very high pressures should be applied In practice one can get at the maximum 1/3 or 1/2 of the normal bath solution concentration (even if we use sequential concentration arrangement).

The membranes are not entirely adequate so far as chemical resistance to most plating solutions is concerned, since they will not stand extreme pH or strongly oxidising condition. This means that in practice, its applications have been mainly limited to rinses although there is some evidence to indicate that its application could be extended to $ZnCl_2$ $CuSO_4$, nickle sulphamate nickle fluoborate, cyanide copper and cyanide cadmium Its application has now been extended to process solution recycling.

Economy

Since pollution is mainly a by-product of industrialisation, the treatments of these plays a very important role in the economy. By recovering all the considerable quantities of metals and most of the water, effluent treatments can make a good contribution to economy. In addition, the recovery of materials is also gaining importance because the cost of materials is increasing and waste disposal is becoming more difficult and expensive.

The economy of any treatment will be improved significantly by minimising drag out losses and by good house keeping. Dragout losses can be minimised by recycling procedure using reverse osmosis, evaporation, ion exchange etc.[19,22]. The cost of chemicals used in treating toxic wastes as well as the cost of the equipment can be minimised by decreasing solution losses. The cost of disposal of sludge can be minimised by dewatering of sludge. Gravity, pressure and vacuum filtration can be used for dewatering of sludge. Electrolytic extraction[16] the only method capable of recovering metal as such should be used compared with other methods which recover the metal as concentrated solution or sludge. But before selecting the effluent treatment, we have to consider the following :

1. the type of effluent
2. capital cost of equipment and chemicals
3. operating cost
4. return from the treatment

No one process can eliminate all the wastes from effluents to meet the effluent standards. A combination probably have to be used to optimize the operating of processes will equipment and cost. Here lies the success of the industry.

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