Integrated pollution control and waste management in copper base processing industries

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ABSTRACT
In the present day context pollution problems have become important as a result of spurt in industrial activities during the past couple of decades and more importantly with the promise of unprecedented growth in economic and industrial activities in the future. An integrated approach to pollution control and waste management through waste reduction, treatment and recovery, with particular reference to copper base processing and fabricating industries are discussed in this paper.

Keywords: Pollution control, Waste management, Copper based industries, Waste reduction.

INTRODUCTION
The human population and its economic and industrial activity continue to increase and so does the consumption of metals and materials. Generation of waste is an integral part of production, processing, fabrication and use of metals and materials. The environmental pollution by industrial wastes is increasing at an alarming rate. A significant share of this gigantic problem is due to the contribution from industrial wastes, which are freely jettisoned to the environment with little concern for the consequences. This acquires special significance as there is a distinct trend for locating the new industries around major metropolitan urban centres. In this respect the pollution problem of processing and fabricating industries deserve special attention.

Indian non-ferrous metal industry in general and copper base industry in particular is essentially a feature of the post independence era and these industries have shown significant growth during the past couple of decades. It is therefore not surprising that the pollution issues and waste management have received some attention only during the past few years.
Recent changes in the policies of the Government towards liberalisation and globalisation have exposed the Indian industry to international competition. Quality, productivity and performance efficiency have become the catchwords to achieve international standard. These are difficult to achieve without due consideration to pollution issues and waste management, which have a profound bearing on production economics. An integrated approach to pollution control and waste management with particular reference to copper base fabricating industry are discussed in this paper.

**COPPER AND POLLUTION**

At the outset let us consider the implications of copper vis-a-vis pollution. Copper is the only metal to be classified as electrochemically noble and is the most corrosion resistant among the structural metals. Copper resists corrosion and oxidation in most natural environments and hence offers least scope for environmental pollution.

The word pollution means contamination by harmful, toxic and poisonous substances. But copper is the least toxic among most heavy metals. On the other hand, it has favourable influences. Copper compounds have found a place among medicines over the past 4500 years. The fungicidal, bactericidal and pesticidal properties of copper are ever now recognised and widely used. Moreover, copper is an essential micronutrient for not only human beings and animals but also for plants and vegetation. It is for this reason that copper is widely used as material for containers of water and for water boilers. It is, therefore, not surprising that the permissible limits of copper in environment is much higher than most other heavy metals.

**Copper Based Processing Industries**

Copper based industrial activity in India dates back to antiquity. However, large scale industrial activity began mostly after independence and started gaining momentum during the past couple of decades only as is evident from the

<table>
<thead>
<tr>
<th>Year</th>
<th>Consumption (tonnes)</th>
<th>Year</th>
<th>Consumption (tonnes)</th>
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</thead>
<tbody>
<tr>
<td>1948-49</td>
<td>... 25,000</td>
<td>1980-81</td>
<td>... 117,363</td>
</tr>
<tr>
<td>1950-51</td>
<td>... 32,000</td>
<td>1985-86</td>
<td>... 179,331</td>
</tr>
<tr>
<td>1960-61</td>
<td>... 62,400</td>
<td>1990-91</td>
<td>... 207,170</td>
</tr>
<tr>
<td>1970-71</td>
<td>... 31,715</td>
<td>1995-96</td>
<td>... 321,080</td>
</tr>
<tr>
<td>1975-76</td>
<td>... 48,044</td>
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</tbody>
</table>
increase in copper consumption, which is also a measure of the activities of the processing and fabricating industries. The approximate break-up of the processing activity is given by the following break-up for copper usage in various forms.

<table>
<thead>
<tr>
<th>Description</th>
<th>Percentage</th>
</tr>
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<tbody>
<tr>
<td>Rod, wire, etc.</td>
<td>45%</td>
</tr>
<tr>
<td>Flat rolled products</td>
<td>15%</td>
</tr>
<tr>
<td>Extruded products</td>
<td>10%</td>
</tr>
<tr>
<td>Castings &amp; forgings</td>
<td>25%</td>
</tr>
<tr>
<td>Others (powder, chemicals, etc.)</td>
<td>5%</td>
</tr>
</tbody>
</table>

**Sources of Pollution**

Notwithstanding the least harmful effects of copper, copper base industries do generate a host of industrial wastes which can contaminate the environment. Copper mining, smelting and refining activities are associated with generation of large quantities of overburden and mine tailings, sediments from concentrator effluents, acidic fumes and smoke from smelters, effluent from refinery tank house etc., all from a single industrial complex. Major smelter refinery complexes are usually set up close to mine sites, which are generally away from urban centres. However, some of the new copper smelter refinery units based on imported concentrates are, however, located closer to the end use markets and hence thickly populated centres. The increased awareness of pollution problem has forced some of the units to change the location of the new plants. Moreover, the new plants do have adequate provisions for pollution control integrated into the plant and machinery.

The downstream processing and fabrication industries on the other hand are mostly located in and around major industrial or metropolitan centres and hence deserve greater attention. Capacity of each processing or fabricating unit is much smaller compared to a smelter and the quantum of pollutants generated is also much lower. But considering the fact that the entire metal produced in the country, together with additional quantities imported, undergo several stages of processing, fabrication and finishing in multitudes of small, medium and large units, the aggregate of the contribution becomes significant. Moreover, majority of the units in unorganised sector are not fully aware of the adverse effects of environmental pollution and the means for their control. This coupled with the apathy of the larger units add to the magnitude of the problem.

Some of the important sources of pollution from metal processing and fabrication units include:
- Flue gases from fuel fired melting or preheating furnaces
- Furnace fumes with volatile metallic and other contaminants
- Liquid effluents from pickling, electroplating, etching, chemical and electropolishing, anti-tarnishing treatments, etc.
- Solid wastes such as slags, scales, ashes, dross, slimes, floor dust, effluent sludges, etc.

It may be noted that most of these wastes not only contribute to environmental pollution but also affect the yield, productivity and sometimes even quality. It may be of interest to note that nearly 50% of the surface tarnishing problem of processed semis and fabricated components are caused by many of these atmospheric pollutants. Moreover, generation of copper bearing wastes mean loss of metal or value and generation of waste affects yield and productivity,

**PROCESS**

- Melting & Casting
- Hot Rolling/ Extrusion
- Cold Rolling/ Drawing
- Pickling/ Finishing
- Finish Fabrication

**POLLUTANTS**

- Flue Gases
- Furnace Fumes
- Slag
- Dross
- Spillages
- Ash
- Scrap
- Mill Scale
- Spent Pickling Bath
- Spent Electro Plating Bath
- Etchants
- Spent Finishing Compositions
- Wash Liquid
- Scrap
- Pickling, Etching, Finishing Effluents
- Fumes from Enamelling/backing
- Etchants

*Fig. 1: Sources of pollution from copper processing/fabricating industries*
INTEGRATED POLLUTION CONTROL AND WASTE MANAGEMENT.....

besides its adverse influence on production economics. Today pollution control measures to plug the source of pollution are no more looked down upon as wasteful expenditure.

Fig. 1 list the different types of wastes generated during different processing and fabricating processes.

WASTE MANAGEMENT AND POLLUTION CONTROL

Waste by dictionary definition is “something rejected as useless or a product thrown away as unwanted”. The most common approach to the disposal of industrial wastes generated is to discharge them into the environment. In many cases the wastes get dissipated and their adverse effects become less conspicuous. As the statutory regulations in respect of pollution are now being invoked and implemented more strictly, thanks to the increasing awareness of the public and the activities of the consumer forums, the industries can not afford to continue their past apathy.

The integrated approach to pollution control and waste management consists of three basic approaches -

i) Waste Reduction - to reduce the rate or quantum of generation of wastes and pollutants.

ii) Waste Treatment - Treatment to reduce the level of contaminants within permissible limits, before being jettisoned into the environment.

iii) Waste Recovery - Recovery of material and energy values from the waste streams.

In many cases an integrated approach combining all the three is very much possible with attractive benefits. Possibilities of controlling pollution from the sources mentioned earlier by the three approaches are briefly discuss below.

Waste Reduction

This approach offers the greatest attraction in that any reduction in the quantum of wastes generated would directly reduce the problems of pollution associated with their disposal proportionately, in addition to material and energy savings. In fact all the machinery and plant manufacturers in recent times keep this in mind while designing the new machines, so as to achieve benefits of energy savings, material savings and improved product quality. Besides the choice of suitable plant and machinery, adoption of some of the more recent practices and manufacturing processes can also contribute to waste reduction.
Gaseous effluents emanating from melting and heating furnaces can be greatly reduced through choice of furnace and better melting practices. Use of electric furnaces in the place of the fuel fired furnaces, where possible, will practically eliminate the major portion of smoke associated with the burning of fuel. Electric furnaces are also much more efficient in terms of energy consumption. Energy consumption for melting 1 kg of metal in electric induction furnace is about 15% of that in coke fired crucible furnace and 30% of that in oil fired crucible furnace. Even when fuel fired furnaces are employed, effective control through optimum preheating of fuel oil, correct fuel/air ratio, proper burner design etc., can not only minimise pollution but also improve process efficiency.

Preparation of melting charge can also contribute to significant reduction in emission of fumes from the furnace. Pretreatment to remove lubricant oil, moisture and other organic contaminants can greatly reduce the fume liberation from the furnace. It is also known that removal of such contaminants can also help in achieving better melt quality. Use of enriched oxygen in copper flash smelter is another example of reducing total flue gas generation.

Technological developments in metal fabrication has also contributed significantly in this direction. A typical example is the advent of semi continuous casting and continuous casting of billets, strips, rods, tubes, and sections. This route directly contributes to an yield improvement ranging from 15 to 25%. Continuous casting of rods, strip and other semis has eliminated the intermediate stages of preheating, hot working, pickling, etc., which not only consume energy but also generate wastes in the form of scales and pickling waste.

Other examples in this direction include substitution of fume generating brazing by welding; hot dip tinning and soldering by electroplating; spray painting by powder coating; use of acid free descaling and cleaning composition, etc.

It will be of interest to note that this approach also offers the best solution to the recently recognised phenomenon of noise pollution. Better grounding and damping of machines, improved design, proper maintenance etc., are the main means of reducing the levels of noise pollution.

**Waste Treatment**

Generation of polluting wastes, even with the best of intentions and efforts, can not be totally eliminated. In such cases the least that can be done is to treat the wastes so that when discharged into the environment, they do not cause undue damage. This constitutes the most traditional approach of the industries, compliant with the statutory regulations. Essentially the gaseous and liquid
effluents are treated to reduce the contamination levels with reference to recognised toxic materials, while solid wastes are either dumped in approved land fills or passed onto agents for disposal.

Treatment of gaseous effluents are employed in practically all major primary metal producing units to treat flue gases from furnaces, fumes and gases from smelters and converters, exhaust gases from pulverisers, etc. Gas treatment plants and devices include cyclones, settling chambers, shutter collectors, electrostatic precipitators and different types of filters for removing suspended solid contaminants in the flue gases. Spray towers, jet impingements and fluidised bed scrubbers, disintegrators etc., are effective for removing water soluble gases as well. A wide variety of plants, over a range of sizes and capacities are available for this purpose, depending on the plant size and quantity of gas generated. However, use of such gas treatment plants are limited to major smelters only, while these are practically nonexistent in processing and fabricating industries in India, although they are widely employed by their counterparts in industrially developed countries. The relatively small sizes of the units in India and the low intensity of pollution from these industries, and the resilience of the atmosphere to withstand the present rate of induction of gaseous effluents, together with the general apathy of the society are responsible for the present situation. However, things are bound to change in the future, with the mushrooming of industrial estates around major cities.

Treatment of liquid effluents has, however, received relatively greater attention from the processing and fabricating industries as well. Although there is greater public awareness of the adverse effects of chemical effluents from industries on natural clean water courses such as rivers and lakes, which are widely used for drinking and cooking, the practice of discharging of untreated polluting effluents by industry still continues.

Treatment and disposal of more concentrated liquid wastes like spent pickling liquor, etching and stripping solutions, used plating solutions, etc., have ceased long back, with the recognition of metal values in these wastes. Thus the liquid wastes required to be treated are restricted to wash and rinse waters from pickling, electroplating and other metal finishing and chemical treatment. The low concentration of most of the contaminants and absence of simple and economic means of metal recovery concerned permit them to be treated as total waste deserving disposal. However, concentration of many heavy metals in these effluents are too high for direct discharge into sewers or natural water courses. Hence treatment of these wastes has received considerable attention. Some of the commonly employed treatments include neutralisation, chlorination,
electrolyses, sedimentation, precipitation, filtration and absorption.

Neutralisation is the most commonly employed effluent treatment process. Lime is the preferred alkali for neutralising the acid and for the precipitation of most of the heavy metal contaminants in the form of insoluble hydroxide. Neutralisation usually followed by flocculation, sedimentation and filtration, sufficiently reduces the residual dissolved and suspended impurities to conform to most of the statutory regulations for discharge into rivers and waterways. Effluents containing poisonous and toxic materials like cyanides, chromates, etc. call for special treatments to destroy the toxic chemicals.

An integrated effluent treatment employing one or more of the recently developed techniques including reverse osmosis, ion exchange, electrodialysis, solvent extraction, etc., is considered if greater levels of cleanliness is required. The integrated close circuit process besides eliminating the effluent discharge problem enables both recovery of valuable metal values and reuse of water.

Waste Recovery

This approach to pollution control through recovery of metal values by waste recycling and treatment has been prompted by the increased interest in conservation of metals and materials in the context of fast depleting mineral resources and the consequent price escalation. This approach is of particular interest to non-ferrous metals in general and copper in particular in view of the high cost of metal. Recycle value of copper is the highest and is well above 90% of the primary metal produced. Nearly 40% of the total copper usage in the world is from secondary sources. Energy consumption and cost of production of a secondary metal is only a fraction of that of primary metal and hence is of considerable interest.

Recovery of metal values from waste also helps in recovering a part or in some cases the entire cost of water treatment. Recovery of metal values from wastes is not new to India and is often carried out with astonishing efficiency. Practices of mobile utensil tinning units, jewellers etc. to recover traces of metal value from the waste are typical examples. Bulk of copper sulphate and copper chemicals are produced by small scale units mainly from foundry dross, ash, scales, floor sweepings, etc. In the context of large scale operation and need for greater efficiency in recovery, there is scope for selection and development of proper process routes and techniques, so as to treat the wastes in an effective and efficient manner and achieve maximum recovery.

The practice of dumping solid wastes like mill scale, furnace revert, fine
scrap, etc., have been discontinued. However, certain less conspicuous wastes such as used catalysts, sludges, slags, foundry ash, dross, etc., are still being disposed of for practically nothing even though they are not dumped in landfill as is done in industrially advanced countries.

Many copper bearing wastes including low grade scrap, slag, dross and reverts are pyrometallurgically smelted to produce black copper, which is then fire refined and electro-refined. However, this process consumes 0.6 to 0.9 M.T. of coke and 3.6 m³/sec of air per tonne of copper, which produces a large quantity of smoke contributing to atmospheric pollution. Hydrometallurgical route of recovery, on the other hand ensures better efficiency, lower pollution and flexibility to produce a variety of value added products at low capital cost.

Copper bearing industrial wastes suitable for recovery of copper can be conveniently classified on the basis of physical form, copper content, chemical nature and the possible recovery processes. Some of the more important copper bearing wastes amenable to copper recovery include the following:

- Metallic wastes - heavy, medium and fine scrap
- Compound wastes - oxide scale
- Oxidised bulk wastes - slag, dross, etc.
- Oxidised powdered wastes - anode slime, pickling sludge, floor dust, flue dust, ash, spent catalysts, effluent sludge, mine tailings, etc.
- Liquid wastes - spent pickling liquors, electroplating baths, industrial effluents, mine water, etc.
- Miscellaneous wastes.

The selection of the recovery process and the type of value added product to be produced depend largely on the copper content, chemical form in which copper is present, nature and relative proportion of other interfering elements or compounds present, physical form, quantity of waste generated and its regular availability etc. Metallic wastes including heavy medium and fine scrap and certain other wastes containing large proportion of metal in chunk form such as dross, reverts, etc., are best recycled by pyrometallurgical process including smelting, fire refining and electrorefining. This process is employed widely world over to produce secondary refined copper from the above wastes. Fig.2 shows the recycling chain for copper. Among the other wastes except for high grade mill scale which is well suited to produce copper powder by gaseous reduction, other oxidised wastes are most amenable to recovery by hydrometallurgical processing.
Fig. 2: Recycling chain of copper.

Important processes involved in the hydrometallurgical recovery process include the following:

- Crushing and pulverising to about 100 μm size.
- Drying and roasting to remove volatile impurities and to convert copper into a form amenable to acid leaching.
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- Leaching in dilute sulphuric acid under optimum conditions of acid concentration, temperature, agitation, aeration, etc. so as to achieve maximum possible recovery.
- Leaching may be done in two or more stages also.
- Coagulation, settling and filtration to separate the clear copper sulphate solution from undissolved impurities.
- Purification by either chemical methods or solvent extraction.

Considering the large number of impurities which may get leached and possible changes in their relative proportions, solvent extraction provides the most effective and efficient method of purification.

- Composition adjustment so as to make it ideal for the subsequent metal winning.
- Copper can be recovered in the form of copper sulphate, copper powder or copper cathodes.

Copper sulphate is the simplest product to produce from leached copper sulphate solution. The slightly acidic solution is concentrated by heating and crystallised in crystallisation tanks. If the solution is not purified by solvent extraction, the impure copper sulphate is dissolved in acidified water and recrystallised to produce large crystals of pure copper sulphate. The market price of copper sulphate varies depending on purity and crystal size. Copper powder can be produced from leached solution by cementation with iron or precipitation as hydroxide followed by filtration drying and reduction in hydrogen, cracked ammonia or endogas (cracked and partially burnt hydrocarbon). Purification by solvent extraction is not essential for the above two processes. If the solution is purified by solvent extraction, copper powder can be produced by direct electrodeposition employing insoluble anodes. Copper powders fetch much higher price compared to cathode copper.

Copper can also be produced in the form of pure copper cathodes by electrowinning using insoluble anodes. It may be noted that while electrowon cathodes were considered inferior to electrorefined copper in the past, since the adoption of purification by solvent extraction, electrowon cathodes of purity comparable to Grade 'A' electrorefined copper cathodes have been produced.

It may be of interest to note that the technology for production of high grade cathode, copper powders and copper sulphate have been perfected in the country and some units are under commercial production and many more are being planned.
CONCLUSION

The need for effective control of environmental pollution in the copper production, processing and fabricating industry is becoming more important in the context of the anticipated accelerated growth in industrial activity and to become competitive in the international market in this era of globalisation. A more integrated approach to pollution control through waste reduction, treatment and recovery would go a long way in not only making the environmental cleaner and safer, but also help in conserving the much needed metal resources and energy and also contribute to improved quality, enhanced productivity and better economics of production.