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GUIDE FOR TREATMENT AND DISPOSAL OF STEEL PLANT EFFLUENTS

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BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

Indian Standard

GUIDE FOR TREATMENT AND DISPOSAL OF STEEL PLANT EFFLUENTS

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Indian Standard

GUIDE FOR TREATMENT AND DISPOSAL OF STEEL PLANT EFFLUENTS

0. FOREWORD

0.1 This Indian Standard was adopted by the Indian Standards Institution on 4 June 1976, after the draft finalized by the Water Sectional Committee had been approved by the Chemical Division Council.

0.2 The production of iron and steel involves the use of vast amounts of water. The actual amount required at any one works depends on the manufacturing processes and water usage practices employed. In an integrated steel plant comprising coke ovens, blast furnaces, SMS furnaces, rolling and finishing operations, the fresh water intake may be as high as 200 tonnes/tonne of steel produced for once-through process or as low as 4 tonnes/tonne of steel produced when intensive recirculation and cascade reuse practices are adopted. In India plants using normal recirculation of water use 30 to 60 tonnes of make-up water per tonne of steel. A part of the fresh water intake is lost by evaporation and the remainder, in a more or less degraded condition, is returned to inland water courses or to tidal waters. Waste water from a steel plant may cause water pollution on the following aspects :

- a) Suspended solids (scale, sand, burden fines, fly ash, coal, coke, etc);
- b) Heat (cooling water, boiler blowdown, etc);
- c) Oil (rolling mill oils, lubricants, hydraulic oils, quench oil, fuel oil, solvents, tar, pitch, etc);
- d) Chemicals (pickle liquor, acid sludge, caustic wash, lime, brine cleaners, spent ammoniacal liquor, toxic chemicals, boiler blow-down, etc); and
- e) Sanitary wastes (domestic sewage from change rooms, toilets, canteen, etc).

The steel plant waste, therefore, may cause sedimentation on the bed of the receiving water course or may be injurious to aquatic life, and render water sources unfit for human consumption as well as for industrial use. In view of this, adequate treatment is necessary before waste water can be disposed of.

0.3 The object of this standard is to give guidelines on methods of treatment and disposal of steel plant effluents in order to reuse as much as possible the treated effluent in the system, so that fresh make-up water requirement is reduced to minimum optimum level and to prevent water pollution. The

methods recommended have been selected taking into consideration the practicability of their adoption in this country. As better and more economical methods of treatment are worked out in future, revision of this guide will be taken up.

0.4 The extent of pollution of inland surface waters permitted by discharge of effluents is laid down in IS : 2296-1974*. The following standards lay down tolerance limits for industrial effluents:

IS : 2490 Tolerance limits for industrial effluents discharged into inland surface waters:

(Part I)-1974 General limits (*first revision*)

(Part VII)-1976 Coke ovens (*first revision*)

IS : 3306-1974 Tolerance limits for industrial effluents discharged into public sewers (*first revision*)

IS : 3307-1965 Tolerance limits for industrial effluents discharged on land for irrigation purposes

IS : 7968-1976 Tolerance limits for industrial effluents discharged into marine coastal areas

0.4.1 The extent of pollution of marine coastal areas is laid down in IS : 7967-1976†.

0.5 Methods of sampling and test for industrial effluents have been published in the form of various parts of IS : 2488‡.

0.6 A bibliography of references is given in Appendix A.

1. SCOPE

1.1 This standard covers methods of treatment and disposal of effluents of steel plants. It is a compilation of the available data and information on the sources, nature, volumes and pollutional effects of the effluents, ways of waste prevention and methods of their treatment and disposal.

2. PROCESSES INVOLVED IN INTEGRATED STEEL PLANT AND EFFLUENT CHARACTERISTICS

2.0 The broad outline of processes in different units of a steel plant indicating the generation of waste is briefly described below.

2.1 Raw Material Handling System — An integrated steel plant has to stockpile and handle large tonnages of solid materials to supply the burden

*Tolerance limits for inland surface waters subject to pollution (*first revision*).

†Criteria for controlling pollution of marine coastal areas:

‡Methods of sampling and test for industrial effluents.

to the blast furnace. Water is used for dust suppression by spraying on stockpiles and on wagons at the tippler house. Water is used for washing the conveyor belts, floors of galleries and junction houses as well as for scrubbing air, resulting in a waste water high in suspended solids.

2.1.1 Coal Washery — Some of the steel plants have coal washery wherein coal is washed with water to remove soil, dirt and other unwanted substances in order to beneficiate it and to remove the fines. Effluents from coal washing plant generally contain large quantities of suspended solids (13 400-42 600 mg/l). On an average 450 to 500 litres of water is used per tonne of coal charged.

2.2 Coke Oven and By-Products Plant

2.2.1 The production of coke by high temperature carbonization is an integral part of steel plants in India. The gas produced during the coking of coal contains valuable substances which are recovered in the by-product plant. These include ammonia, coal tar, benzene, xylene and toluene. In some plants, phenol and naphthalene are also recovered. Water is used in the different processes such as quenching of coke, cooling, washing and scrubbing of coke oven gas and for different by-product recovery processes. The bulk of water used in a coke plant is for cooling purposes, but the aqueous wastes from process operations contain tar, ammonia, benzole, phenols, hydrogen sulphide, cyanides, pyridine, oils, etc. The effluent from the quench tower, where the hot coke is deluged with water, contain coke dust called 'breeze' which is commonly recovered from the quench water. The waste waters from this plant contain toxic materials and hence require to be treated most carefully. Acid sludge of the benzole plant recovery should be separated out. The sludge can be utilized for recovery of indene-coumarone resins; if this cannot be done, the sludge should be dewatered and disposed of by dumping on land away from water courses.

2.2.2 The sources, toxic nature and characteristics of the waste waters from coke ovens and by-product plants are given in Fig. 1 and Tables 1 to 4.

2.3 Sinter Plant — To use the ore fines which cannot be charged directly to the blast furnace, they are mixed with coke breeze and limestone fines and fired on a travelling grate. This produces a sinter, or fused mass of material, which can then be charged directly into the blast furnace. This sinter plant area is quite dusty because of the nature of the materials handled and the air is cleaned either through washers or in a bag house. Water is used in the area for preparing the mix before it is fed to the furnace grate and for miscellaneous cooling purposes. Except for the heat in the cooling water, waste water from the sintering plant contains mostly suspended solids, that is, ore and coke dust in the effluent from air washers.

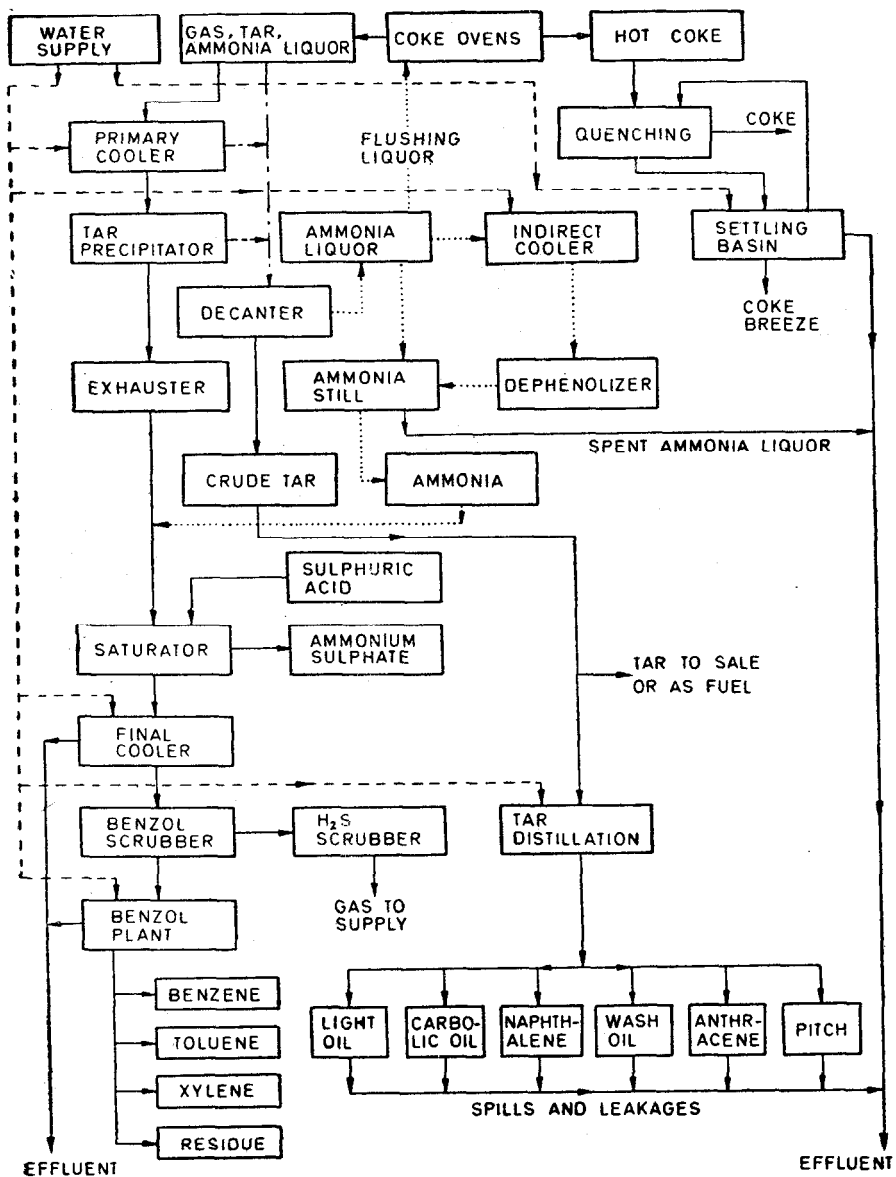


FIG. 1 FLOW SHEET OF COKE OVEN BY-PRODUCT PLANT

TABLE 1 SOURCES OF PROCESS WASTE WATER OF A BY-PRODUCT COKE PLANT

(Clause 2.2.2)

SL No.	UNIT OPERATION	CONTAMINANTS																	
(1)	(2)	(3)																	
i)	Coke quenching	Coke breeze, sulphurous acid (also tar, ammonia, phenol, cyanides and hydrogen sulphide when spent ammoniacal liquor is used for coke quenching)																	
ii)	Cooling, scrubbing and refining operations:																		
a)	Flushing liquor	Tar, free ammonia																	
b)	Condensate pits	Tar, crude ammoniacal liquor, some benzole																	
c)	Machine house	do																	
d)	Dephenolation plant	do																	
e)	Potash plant	Sodium carbonate and bicarbonate, sodium ferrocyanide, thiocyanate and hydrosulphide																	
f)	Final coolers	Ammonia solution, wash oil (230 to 315°C fraction of tar)																	
iii)	Ammonia stills	Ammoniacal liquor																	
iv)	Benzole plant	Wash oil and benzole																	
v)	Tar distillation plant	Tar, light oils, tar oils																	
vi)	Carbolic acid unit	Phenols, benzole, sodium sulphate-cum-sulphuric acid solution																	
vii)	Composite effluent*	<table border="0"> <tr> <td>pH value</td> <td>8.5 to 9.5</td> <td rowspan="8">} mg/l</td> </tr> <tr> <td>Thiocyanate</td> <td>50 ,, 100</td> </tr> <tr> <td>Thiosulphate</td> <td>110 ,, 220</td> </tr> <tr> <td>Total ammonia</td> <td>800 ,, 1 400</td> </tr> <tr> <td>Sulphide</td> <td>10 ,, 20</td> </tr> <tr> <td>Cyanide</td> <td>10 ,, 50</td> </tr> <tr> <td>Phenol</td> <td>500 ,, 1 000</td> </tr> <tr> <td>Chloride</td> <td>4 000 ,, 4 200</td> </tr> </table>	pH value	8.5 to 9.5	} mg/l	Thiocyanate	50 ,, 100	Thiosulphate	110 ,, 220	Total ammonia	800 ,, 1 400	Sulphide	10 ,, 20	Cyanide	10 ,, 50	Phenol	500 ,, 1 000	Chloride	4 000 ,, 4 200
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Chloride	4 000 ,, 4 200																		

* Volume of the composite effluent is usually 100 to 150 litres per tonne of coal carbonized but in some plants the volume is reported to be as high as 300 to 400 litres.

2.4 Blast Furnaces

2.4.1 Most of the iron produced in an integrated steel plant originates at the blast furnaces which are vertical water-cooled furnaces where iron ore, sinter, coke (fuel and also reducing agent), limestone and dolomite (fluxing material) are charged into the top and hot blast of air is blown from the bottom. Tremendous heat is generated inside the furnace, and some portion of its body is required to be cooled constantly and the hot gases coming out of the furnace are to be cooled and cleaned as they contain considerable amount of dust.

TABLE 2 RELATIVE TOXICITIES AND OXYGEN DEMAND OF SUBSTANCES FOUND IN AMMONIACAL LIQUOR* AND COKE OVEN EFFLUENTS

(Clauses 2.2.2, 3.2.1 and 3.2.2)

SL No.	CONSTITUENT	RELATIVE TOXICITY	OXYGEN ABSORPTION RATE	RATE OF BIOCHEMICAL OXIDATION
(1)	(2)	(3)	(4)	(5)
i)	Free ammonia	High (10 mg/l)	Nil	Very slow
ii)	Fixed ammonia	Nil	Nil	Very slow
iii)	Sulphide	High	High	Fast
iv)	Cyanide (as CN)	High (10 mg/l)	Slow	Very slow
v)	Thiocyanate (as CNS)	Low (200 mg/l)	Slow	Slow
vi)	Thiosulphate	Low	High	Fast
vii)	Phenol (as C ₆ H ₅ OH)	Medium (10 mg/l)	High	Fast
viii)	Higher tar acids	Low (10 mg/l)	High	Very slow

*Ref. Rudolfs (W). Industrial wastes, their disposal and treatment. 1953. Reinhold Publishing Corporation, New York.

TABLE 3 AVERAGE CHEMICAL CHARACTERISTICS OF BY-PRODUCT COKE OVEN EFFLUENTS

(Clause 2.2.2)

(All values except pH are expressed in terms of mg/l)

SL No.	CHARACTERISTIC*	COOLING, SCRUBBING AND REFINING PROCESS WASTES	AMMONIA STILL AND DEPHENOLATION WASTES	BENZOLE AND TAR DISTILLATION WASTES
(1)	(2)	(3)	(4)	(5)
i)	pH value	9.1	9.0	9.0
ii)	Dissolved solids	652	572	652
iii)	Suspended solids	48	26	48
iv)	Total alkalinity (as CaCO ₃)	1 500	1 140	980
v)	Phenol (as C ₆ H ₅ OH)	141	132†	154
vi)	Ammoniacal nitrogen (as N)	1 962	325†	106
vii)	Cyanide (as CN)	50	12	6.0
viii)	Sulphide (as S)	35	—	40
ix)	Chemical oxygen demand	1 494	2 000 to 2 500	561
x)	Biochemical oxygen demand (for 5 days at 20°C)	600	1 000	480
xi)	Hexane extractable material	—	50	Highly variable (up to 1 000)

*Characteristics of 24 hours composite samples.

†These concentrations indicate reasonably efficient operation of ammonia recovery and dephenolation wastes at the time of this study.

TABLE 4 VOLUME AND CHARACTERISTICS OF AMMONIACAL LIQUOR AND COKE OVEN WASTES FROM STEEL PLANTS

(Clause 2.2.2)

(All values except pH and flow are expressed in terms of mg/l)

SL No.	CHARACTERISTIC	CRUDE AMMONIACAL LIQUOR (AVERAGE)	COMBINED WASTE		
			Minimum	Maximum	Average
(1)	(2)	(3)	(4)	(5)	(6)
i)	Flow, litres/tonne of steel made	—	190	600	340
ii)	pH value	—	8.6	9.0	—
iii)	Phenol (as C_6H_5OH)	50 to 200	40	1 000	410
iv)	Cyanide (as CN)	290	12	60	26
v)	Thiocyanate (as CNS)	0 to 63	18	130	82
vi)	Sulphide (as S)	235	10	20	15
vii)	Free ammonia (as NH_3)	4 500	154	900	400
viii)	Fixed ammonia (as NH_3)	500	610	970	810
ix)	Total ammonia (as NH_3)	5 000	830	1 350	1 240
x)	Chemical oxygen demand	—	790	2 450	1 770
xi)	Biochemical oxygen demand (for 5 days at 20°C)	—	160	1 300	850

2.4.2 The individual water streams leaving the blast furnace area comprise the furnace cooling water, gas wash water (which includes water used on the electrostatic precipitators), wash water from scrubbers, and cooling water used to cool the valves for hot blast of air.

2.4.3 The cooling water on the blast furnace itself is collected from the various furnace zones and discharged through an air gap so that operators can verify the flow of water through all the circuits into a collection trough. This water leaves the furnace essentially as received except for the heat added.

2.4.4 Blast furnace gas is usually cleaned by passing the dirty gas through dry dust catchers or scrubbers or both, followed by electrostatic precipitators. The effluent comes primarily from the conditioning towers associated with the precipitators where gas is cooled and washed with water. Additionally, heavily polluted water, but in a smaller volume, comes from the precipitators when the collection plates or tubes are washed down to remove the collected dust.

2.4.5 The pollutants normally encountered in this wash water are suspended solids, oxygen demanding substances, cyanide, oil and to lesser extent other toxic constituents. Suspended solids generally consist of insoluble particles of burden material, mostly coke, iron ore or sinter. On some occasions an appreciable quantity of dissolved iron may be present

as bicarbonate, which precipitates on oxidation in the treatment plant or the stream, producing a characteristic rusty brown colour. This is caused by extremely fine particles of ferric hydroxide which are difficult to settle.

2.4.6 The characteristics of scrubber effluents are given in Table 5.

TABLE 5 CHARACTERISTICS OF SCRUBBER EFFLUENTS

Sl. No.	CHARACTERISTIC	CONCENTRATION
(1)	(2)	(3)
i)	Suspended solids content range, mg/l*	1 000 to 20 000
ii)	Suspended solids passing 150-micron sieve, percent by mass	86 ,, 99
iii)	Suspended solids passing 75-micron sieve, percent by mass	74 ,, 97
iv)	Temperature, °C	38 ,, 45
v)	pH value	7.0 ,, 9.5
vi)	Relative density, 40°C	3.0 ,, 3.8

* The concentration of suspended solids varies considerably not only from plant to plant but even from hour to hour on the same furnace.

2.4.7 The gas wash water also dissolves contaminants in the vapour phase, which include cyanide and carbon dioxide. The wash water dissolves alkali from the dust as well; so there is a net increase in sodium and potassium bicarbonates along with the solution of other contaminants.

2.5 Pig Casting

2.5.1 When the blast furnace is tapped, molten iron is directed through sand-lined sluices, controlled by gates in the casting floors, to the ladles, and slag is directed to the slag pots.

2.5.2 In the pouring of cast iron into the pigs, water is used for the spraying of heavy lime solution on to the moulds of the pig casting machines to prevent sticking of pig iron in the moulds and to ensure release from the moulds after the metal has solidified and the moulds are inverted. Water is also sprayed on to the moulds and pigs for cooling. This cooling water particularly contains solid particles (scales and sand) with high settling velocity.

2.6 Steel Making

2.6.1 Open Hearth Furnaces

2.6.1.1 The open hearth furnace produces steel (below 1 percent carbon) from a charge of steel scrap, iron and fluxing materials. As in the blast furnace area, open hearth furnaces use large quantities of cooling water, which leaves the furnace essentially as received except for the heat added.

2.6.1.2 The gases from the open hearth furnaces contain high concentration of dust, which is removed by washing, precipitation equipment or both. The dust loading varies appreciably during the heat from a range of 0.45 to 1.4 g/m³/sec during charging to about 4.5 to 7 g/m³/sec several hours after start of oxygen lancing. The dust particles from open hearth furnace are much finer than from the blast furnace, and oxygen lanced furnaces discharge a higher dust load than older conventionally fired furnaces.

2.6.1.3 Whereas the wash water from the blast furnace is alkaline, that from open hearth furnace may be quite acidic. A third source of waste water from the open hearth furnace is the blowdown from the waste heat boilers, which recover heat from the exit gases and produce by-product steam. If there is a separate water treatment plant to supply make-up for the waste heat boilers, wastes from regeneration of the water treatment system may also constitute one of the pollutional loads from the open hearth furnace area.

2.6.2 Basic Oxygen Furnaces (BOF)

2.6.2.1 The BOF shop is a facility for conversion of iron to steel at much higher rates than attainable in the open hearth. The molten metal charge is reacted with oxygen, introduced through a water cooled lance, which burns off the impurities in a period of about 20 to 25 minutes. Total heat requires about one hour compared to 8 to 12 hours required for steel making in the open hearth furnaces. Because of the high heat release, gases leaving the furnace hood during lancing are very hot. The hood may be cooled with circulating water or heat may be recovered from the gas through a boiler mounted directly above the hood.

2.6.2.2 Because of the high temperatures encountered, the cooling water is especially treated to prevent corrosion or scale formation at high temperatures; this circuit may be completely closed and heat extracted from cooling water through a secondary cooling water circuit using a surface type heat exchanger.

2.6.2.3 The gas is cleaned in equipment similar to that used on the open hearth, although there are differences in methods of washing and removing accumulated dust from the washers and precipitators.

2.6.2.4 The dust loading is usually appreciably higher in the BOF discharge (20 to 30 kg/tonne of steel) than in either the blast furnace gas (14 to 20 kg/tonne) or open hearth (about 9 kg/tonne). There is appreciable variation in temperature and pH value of the wash water during the heat as different ingredients are added to the charge during the oxygen blow.

2.6.3 Electric Furnaces

2.6.3.1 A third process for manufacturing steel, the electric arc furnace process, can either produce the common grades of low-carbon steel from scrap or can be charged with alloying materials to produce special steels

such as stainless steel or tool steel. Electric furnaces are also used for production of ferro-alloys which are the alloying elements for special steels such as ferro-manganese, ferro-vanadium and ferro-chrome.

2.6.3.2 In the operation of electric furnace, fluxing materials are added to the charge along with metallic components so that a slag is produced as in other furnace operations. The charge is oxidized by an electric arc and the violent activity in the area of the electrodes causes a rather high discharge of dust to the atmosphere amounting to approximately 11 to 14 kg/tonne of production. The duration of each heating period is 2 to 4 hours.

2.6.3.3 Water is used to cool the furnaces and certain components of the electrical gear. This water leaves the furnace and transformer essentially as received except for the heat added. The dust load in the shop is generally controlled by wet scrubbers. The suspended solids content of this water is usually around 1 000 mg/l but may be as high as 5 000 mg/l.

2.6.4 Vacuum Degassing — Molten steel is often degassed under vacuum to improve the physical properties. In many plants the vacuum is obtained through barometric condensers. Since the vapour will contain volatile components from the metal and the flux, the discharge from the vacuum degassing operation usually contains iron, manganese and fluorides.

2.7 Finishing

2.7.1 Rolling Mills

2.7.1.1 Although there is a variety of rolling operations in the steel industry, each having its own characteristic waste problem, the types of wastes can be classified into categories as to the size of the particles of the scale removed from the steel surface during rolling and by the type of oil used for lubrication of the sheets passing through the rolls.

2.7.1.2 The largest pieces of scale and debris are produced on the slower speed scale breakers and primary rolling mills which reduce ingots to blooms, billets and slabs. The scale or metal chips dropping into the plume below the stands of these mills may be chunks of heavy metal or fine flakes of 1 to 2 mm particle size. Although there will be some particles finer than this, the percentage will usually be small. Oil in the water from these mills is generally lubricating oil from bearings and usually non-emulsified, readily breaking from the water surface in a short period of time. Some oil, however, adheres to the scale and metal chips. Because the particles of scale from primary rolls are large, the scale pit overflow is quite low in suspended solids — about 100 to 400 mg/l with 100 to 200 mg/l oil before skimming and 10 to 25 mg/l after skimming.

2.7.1.3 As the metal is further reduced in thickness through roughing stands and finishing stands, the scale is reduced in particle size to micron range, producing a particle which settles very slowly in water.

2.7.1.4 On hot strip mills and structural rolling mills there is generally less oil found in the waste water than in the blooming mills and it is also a non-emulsified oil which separates quite readily from water.

2.7.1.5 When steel is rolled cold, the scale is quite similar to what is found with hot rolling, but oil problem is considerably more difficult to handle, since emulsified rolling oils are added directly to the water sprayed on the metal as it is being rolled. Because this is a very difficult problem, the trend in modern mills is to recirculate this water to separate the free oil from the emulsified oil in the recirculation stream by centrifuging a part of the stream, and fine scale particles by sedimentation. Even then the sludge formed after sedimentation poses a problem. In the older mills, however, the rolling oil was being added directly to a once-through flow of water in the form of a spray on the metal. Hence such emulsified oil remained in the water collected from the mills and created a difficult problem.

2.7.1.6 Accessory equipment related to the rolling mills includes motors, oil celler, reheating furnace, shears, hot scarfing machines, cold saws and hot saws. All these require water, the one used for cooling of the reheating furnaces being the largest in volume. This cooling water generally leaves without picking up contamination, except that the water may contain some oil which leaks into the water pumps from hydraulic oil lines and from lubricated bearings.

2.7.2 Acid Pickling

2.7.2.1 The treatment of steel in an acid bath, known as pickling, removes oxides, dirt, grease, etc, from the metal surface and produces a bright sheet stripped down to bare metal and suitable for finishing operations such as plating, galvanizing or other surface coating. Both sulphuric acid and hydrochloric acid are used for pickling. The latter reduces the water pollution problem and is also preferable on other considerations. Spent pickle liquor is a problem that is yet to be solved for the steel industry within reasonable costs.

2.7.2.2 Pickling may be done either batchwise or as a continuous operation. The acid is prepared at about 10 to 20 percent strength depending on the 'work' to be processed in the pickle tank and the type of acid used for pickling. As the acid works on the scales there is a gradual build up of iron compounds in the pickle bath and a reduction in acid content. When the iron content reaches a level which begins to slow the pickling operation, the bath is either discarded or reprocessed. In modern pickling operation, the acid is continuously withdrawn for disposal or reprocessing, in order to maintain a fairly constant ratio of iron to free acid in the pickle vat, thereby maintaining uniform pickling conditions for all the steel passing through the operation.

2.7.2.3 The metal leaving the pickle vat will drag out some of the liquor with it and carry this liquor into the subsequent rinsing and neutralizing operations. The loss of acid by dragout varies depending on the type

of work being done, the shape of the product being pickled, and the speed of operation, and sometimes can be as high as 12 percent of the acid used.

2.7.2.4 Appreciable rinse water has to be put into the rinse tank and withdrawn continuously for discharge.

2.7.2.5 The discharge from the pickling area generally includes spent strong liquor and acidic rinse water. In addition, there may be effluents from degreasing, fume scrubbers, passivating plants, and other ancillary processes together with floor washings and spillages. The liquors may also be contaminated with oil and grease from rolling mills and by leakages from hydraulic equipment. The spent pickle liquor may contain anything from 5 to 15 percent free acid and 2 to 10 percent ferrous iron. The volume of water used for rinsing is in the range of about 250 to 450 litres/tonne of steel pickled.

2.7.3 Heat Treatment

2.7.3.1 To produce special physical properties in certain grades of steel, the metal may be put through a series of heat treatment operations. These would include heating in a furnace, annealing at a carefully controlled temperature for a specified period of time, quenching in water or oil, and final cooling in air on hot beds.

2.7.3.2 The temperatures in the annealing furnaces are generally not so high as to require water cooling of the furnace elements, but such cooling may be needed in high temperature furnaces. The temperature of the quench oil or quenching water is carefully controlled. Hence the contents of the quench are usually recirculated through a heat exchanger to remove the heat brought into the system from the hot metal and to pass on to cooling water flowing across the other side of the heat-exchange surface. Except for the heat in the cooling water oil is generally the only likely contaminant to enter by overflowing the quench oil system or by rupture of a heat exchanger tube in the oil-water heat exchanger.

2.7.4 Continuous Casting

2.7.4.1 An alternative route to production of slabs, blooms and billets from molten steel is continuous casting. It eliminates the conventional ingot casting, stripping and roughing mill operations. Molten steel is poured continuously into moulds and the cast slabs, blooms and billets come out through a number of rollers and then on a 'runout' table.

2.7.4.2 Water is used to cool the moulds and machineries and for spraying into the apron of the continuous casting machine. The water from the moulds leaves essentially as received except for the addition of heat. However, the water required for machinery cooling and for apron spray gets contaminated and carries fine scale particles as well as heat. In addition, it may get contaminated with oil used for lubrication purposes.

2.8 Services

2.8.1 Thermal Power Plant

2.8.1.1 The operation of steam power plants and turbo-blower station involves the generation of heat from coal, oil or other fuel to produce steam from demineralized water. The steam is used to drive turbines which, in turn, are coupled with generators or blowers. After driving the turbine or blowers, the steam is condensed and re-used as boiler-water feed. Some steam is also used for various processes in the steel plant and therefore some make up water is required to balance the water cycle. Enormous quantity of cooling water is required for condensing steam but this water leaves the condensers essentially as received except for the heat added. Apart from the heated cooling water, the following classes of waste water may emanate from the power plant :

- a) Hot, concentrated water salines from the boiler and evaporator blow down contain impurities in considerable concentration which are removed from the boiler circulating system. This waste water, depending on the type of boiler, operating pressure and the type of boiler feed may have a pH value of around 11 and total solids content of about 1 000 mg/l, anti-foam materials or high phosphate organic agents.
- b) Acid and alkaline chemical solutions (brine, hydrochloric acid, sulphuric acid, hydrazine, phosphates, sodium hydroxide) used for regeneration of exchange resins, flushing and cleaning of boilers.

2.8.1.2 Another water pollution problem is presented by waste water containing fly ash and solid waste, which results from the use of pulverized coal in the boiler house. Fly ash weighs about 490 kg/m³ and constitutes about 10 percent of the coal burnt. Fly ash contains carbon (1 to 10 percent by mass), iron, aluminium, calcium, magnesium, silicon, sulphur, titanium and phosphorus. The particle size distribution depends on the manner in which the fuel is burnt. Normally, with ordinary stokers, 20 to 40 percent of ash has a diameter less than 10 microns whereas 80 to 90 percent of the ash has a diameter of less than 200 microns.

2.8.2 Foundry

2.8.2.1 Most integrated steel plants operate foundries, which may cast ingot moulds for use within the plant or may supply castings for machinery to be built by outside equipment manufacturers. As dust is a common problem, it is necessary to provide adequate ventilation to hold the dust concentration at acceptable levels. Before discharge to the outside, the air may be scrubbed in water spray type units or filtered through bag filters. In the latter case, the collected dust has to be wetted before it can be removed and hauled to a disposal area. The waste water from air scrubbers is very high in suspended solids and shall be processed for removal of these solids for final disposal.

2.8.2.2 Where the foundry pours castings in addition to ingots and pigs, it is usually necessary to clean the metal surfaces after shake-out.

This is done with a high pressure water jet. The water is collected, the large particles separated by settling and the clear water reused or disposed of. However, it is necessary to remove a small volume of bleed off usually very high in suspended solids (1 500 to 2 500 mg/l).

2.8.3 Slag Plant

2.8.3.1 Various useful products can be recovered from slag, some being produced from the slag in a molten form and others after the slag has solidified.

2.8.3.2 The blast furnace slag can be quenched in a mill to produce light weight expanded aggregate for the manufacture of cinder block or can also be spun into mineral wool insulation. In plants handling slag, there is a high dust loading in the surrounding atmosphere which tends to cake on the conveyor belts or interfere with proper operation of mechanical equipment. Water is used either to wash the air or for washing the conveyor belting, generating a waste water high in suspended solids.

2.8.4 Calcining and Refractory Materials Plant

2.8.4.1 The refractory material plant usually consists of lime and dolomite shop, tar-bonded dolomite refractories shop and refractory compounds and powder shop.

2.8.4.2 In lime and dolomite shop consisting of rotary kilns, waste heat boilers, gas cleaning plant, etc, limestone and dolomite are burnt in rotary kilns at 1 150-1 200°C and 1 700-1 750°C respectively. The burnt dolomite is delivered to tar dolomite refractories shop and graded lime (20-50 mm size) is sent to converter shop. Lime of lower size is sent to sintering plant and other consumers. The heat of the flue gases emanating from the rotary kiln is used for raising steam in waste heat boilers. The flue gases then pass through a dust catcher. The recovered dust is recycled back to sinter plant and other units.

2.8.4.3 Tar-bonded dolomite refractories shop produces a range of tar dolomite products for the lining of oxygen blower converters. Raw materials required include burnt dolomite, broken tar-bonded dolomite refractory products and dehydrated coal tar from coke oven.

2.8.4.4 Refractory compounds and powders shop produces a wide range of refractory mortar compounds and powders. The process involves crushing, drying and grinding of clay, successive drying of coke fines, diatomaceous earth, crushing and grinding of grog and broken fire clay products, crushing of quartzite and broken silica, etc, and mixing all these products.

2.8.5 Fuel Handling — All integrated steel plants have facilities for storing solid and liquid fuels. Some of these may escape into waste streams due to spillage and loss.

3. POLLUTIONAL EFFECTS AND EFFLUENT QUALITY CRITERIA

3.0 General — Pollutional effects are described in 3.1, 3.2 and 3.3 and the effluent quality criteria in 3.4 and 3.5. Water in an integrated steel plant gets polluted due to the following operations :

- a) Coal beneficiation operations;
- b) Coal carbonization;
- c) Pig iron manufacture;
- d) Ingot steel manufacture;
- e) Steel products manufacture; and
- f) Auxiliary units generating power, steam and others.

3.1 The water pollutants from the steel industry vary from mere rise in temperature of water (waste heat) to toxic chemicals. Suspended and colloidal solids (mostly inorganic) emanate in this industry by either washing the raw materials and products or scrubbing the dust and gases with water. Oils and grease, mineral as well as vegetable, are used for lubrication and in cold rolling mills and ultimately find their way into the waste waters. Toxic and oxygen demanding organic chemicals and tar are released in the coal carbonization and by-product recovery units and may be considered as the most serious water pollutants.

3.1.1 Acids and alkalis are utilized for regenerating the ion exchange resins used in demineralization of boiler waters. Acid is also utilized for cleaning the metal (pickling).

3.2 The major pollutional effects due to the waste waters from an integrated steel plant are the following:

- a) Toxicity to aquatic life,
- b) Lowering of dissolved oxygen in the receiving water course,
- c) Deposition of suspended matter on the bed of the receiving water course,
- d) Causing taste and odour problems in the receiving water,
- e) Coal tar choking pipes and waste treatment appurtenances,
- f) Raising the temperature of the receiving water, and
- g) Floating of oils and grease on water leading to ugly oil slicks.

3.2.1 Ammonia, phenols (monohydric, polyhydric and derivatives of phenol), cyanides and sulphides are well known for their toxicity to aquatic life. Among the toxicants mentioned above, free ammonia and cyanide are the most toxic substances. The concentration of free ammonia increases with increase in the pH value of the medium. Hence ammonia toxicity is particularly severe at high pH values. The relative toxicities of the compounds found in ammoniacal liquor are given in Table 2.

3.2.2 When bio-degradable organic substances are discharged into water courses, the soil and water bacteria utilize the organic matter as their source

of carbon and the dissolved oxygen in the water body for their respiratory requirement. Coke oven wastes have enough types and quantities of biodegradable organic matter that can lead to depletion of dissolved oxygen in the stream. When the dissolved oxygen is depleted to zero anaerobic conditions set in leading to foul odours and ugly conditions. At low dissolved oxygen levels sensitive fish do not survive. The toxicity of other substances is compounded at low dissolved oxygen levels. The relative toxicity of different organic matter occurring in coke oven wastes is also depicted in Table 2.

3.2.3 Iron and steel industry leads to the discharge of a considerable quantity of suspended and colloidal matter. Unless trapped, these solids can reduce the penetration of sunlight and reduce the photosynthetic activity of micro-organisms, an essential feature of the self-purification of polluted water bodies. Suspended and colloidal solids can also smother bottom dwelling aquatic organisms thus affecting the life of a stream or lake. Dense suspended matter normally encountered in steel industry can lead to heavy siltation of streams and lakes and affect the flow and life in the water body.

3.2.4 Oils and grease unless trapped from the wastes will lead to the formation of ugly oil slicks and iridescent colours, all leading to poor aesthetics. Oil slicks reduce the diffusion of oxygen from the air into water and affect self-purification of water bodies. Where steel plants are located on the coast, wave action invariably brings the oils and grease to the coast and spoil the beaches.

3.2.5 Coal tar is a component of the coke oven wastes that creates maximum physical problems. Light tar floats on water and attaches itself to anything on its way giving ugly appearance. Heavy tar settles down and has a tendency to choke pipes and cavities (of all sorts) in wastes treatment units and seriously interferes with the treatment processes.

3.2.6 The phenolic substances in the coke oven wastes are known to create taste and odour problems. Fish living in waters containing non-toxic levels of phenol are found to be tainted (that is, acquire an unpleasant phenolic taste in its flesh). Waters containing 0.002 mg/l of phenol are known to give rise to unpleasant taste to water when chlorinated. Soluble iron and manganese are known to give rise to bad taste in drinking water at 0.1 mg/l level.

3.2.7 Steel plants have to discharge considerable waste heat in the form of heated cooling water otherwise uncontaminated. The mere rise in temperature of water due to such discharges can reduce the dissolved oxygen levels by increased biological activity and decreased solubility of oxygen.

3.3 Nearly two-thirds of the water used in a steel plant is utilized for heat exchange. It is not directly brought into contact with either the raw materials or the finished products and hence remains clean. Such flows,

if segregated from the dirty streams, do not require any treatment other than cooling. The rest of the discharges require primary, secondary and tertiary treatment depending upon the type and degree of contamination they are subjected to.

3.4 No water body receiving effluents can be kept as clean as virgin streams. However, it is essential to keep them clean enough so that the downstream users do not have to resort to special treatment processes which would raise the cost of water treatment from its normal values.

For meeting the effluent quality criteria two parameters may be suggested:

- a) The plant should be able to discharge effluent of such a character that the treated water can be used within the plant; the best test to verify this is the ability of the plant to recycle the effluent into its own service water system; and
- b) The effluent character is such that the desired quality of the receiving water is attainable with a minimal dilution and at a minimum distance from the discharge of the treated plant effluent.

3.5 As described in 3.1 to 3.3, steel plant effluents need correction in quality in the following parameters:

- a) Temperature,
- b) Colloidal and suspended matter,
- c) Soluble inorganics (acid and iron salts in pickling wastes) and salts in cooling water,
- d) Soluble organics including toxic ones (from coke oven wastes), and
- e) Floating and suspended organics (oil and tar).

As correction of quality to the extent desired for in-plant recirculation is not economical for all the streams it is highly desirable to segregate the streams of cooling water and less contaminated wastes from the more severely contaminated wastes. The procedures for correction of effluent quality (that is, treatment methods) are described in 4.

4. TREATMENT METHODS

4.0 Possible methods of treatment of various types of waste waters are described in Tables 6, 7 and 8.

4.1 Coke Oven and By-Product Recovery Wastes

4.1.1 In a majority of plants, ammonia is recovered from the coke oven liquor as it is in substantial concentration. The water pollution problems would be worse if ammonia is not recovered. Among the wastes from all the operational units, the spent liquor from the ammonia stills is the most polluting one.

TABLE 6 TYPICAL QUALITY TOLERANCES FOR RECIRCULATED COOLING WATER WHERE HEAT TRANSFER THROUGH A WALL IS EMPLOYED, AND METHODS OF CONDITIONING REQUIRED

(Clause 4.0)

Sl. No.	APPLICATION OF WATER	FACTORS TO BE STANDARDIZED*	NORMAL VALUE	METHODS OF ENSURING NORMAL VALUES
(1)	(2)	(3)	(4)	(5)
i)	For steam turbine condensers, oil and air coolers of works, power plants and boiler houses and steam blower stations (non-combustion fired coolers)	a) SS† mg/l (<0.1)	200	Cooling in pond, spray basin or cooling tower, settling of suspended matter in make-up water in sedimentation tanks with or without coagulation Chlorination
		b) Tendency to promote growths	Not allowed	
		c) Tendency to deposit salts (carbonates, etc)	HS‡	Renewal (purging); treatment of make-up water with sulphuric acid, and of recirculation water with super-phosphate or flue gases (preferably blast furnace gas after combustion)
ii)	For blast furnaces, steel-making and reheating furnaces (combustion fired coolers)	a) SS† mg/l (<0.05)	100	Cooling in pond, spray basin or cooling tower, settling of suspended matter in make-up water in sedimentation tanks without coagulation
		b) Tendency to deposit salts	HS‡	Renewal (purging); treatment of make-up water with sulphuric acid and of recirculation water with blast furnace gas after it has been used for firing boilers or hot blast (copper) stoves, or with super-phosphate

iii) For non-combustion fired heat exchange equipment (coolers for oil, air, gas, benzole, etc)	a) SS† (< 0.05)	40	i) Cooling in cooling tower, preferably in induced-draught type ii) Settling of suspended matter in make-up water in sedimentation tanks, or filtration through rapid sand filters
	b) Tendency to promote growths	Not allowed	Chlorination or treatment with copper sulphate
	c) Tendency to deposit salts	HS‡	Renewal (purging); treatment of make-up water with sulphuric acid, and of recirculation water with super-phosphate or flue gas (preferably coke oven gas)

*In all cases the tendency to cause corrosion of metal and concrete shall be eliminated by treatment with super-phosphate (phosphatization), lime (alkalization), etc.

†SS=suspended solids (figures in parenthesis indicate particle size in mm).

‡HS=heat-stable water (which does not produce deposits).

TABLE 7 TYPICAL QUALITY TOLERANCES FOR RECIRCULATION WATER SUPPLIED FOR COOLING, CLEANING AND TREATMENT OF RAW MATERIALS OR PRODUCTS BY DIRECT CONTACT, AND METHODS OF CONDITIONING REQUIRED

(Clause 4.0)

(All values except temperature are in g/l)

SL No.	APPLICATION OF WATER	FACTORS TO BE STANDARDIZED*				METHODS OF ENSURING NORMAL VALUES
		Item	Ingoing Water, Normal Value	Outgoing Water		
				Before purification (cooling)	After purification	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
22 i)	Ore dressing:					
	a) Washing and comminution	SS†	0.2 (≤0.05)	30-120	0.02-0.2	Settling in clarification pond (sludge accumulator) without coagulation of suspended matter
	b) Floatation	SS†	0.1 (≤0.05)	30-120	0.08-0.2 (≤0.05)	Settling in clarification pond (sludge accumulator) without coagulation of suspended matter When outgoing water is coagulated with 0.2-0.3 g/l iron sulphate and alkalized with lime, SS content is reduced to 0.02-0.06 g/l
ii)	Coal dressing by washing and floatation	SS†	10	60-100	10	Settling in horizontal-flow sedimentation tank without coagulation of suspended matter
iii)	Cleaning and cooling of blast furnace gas	SS†	0.5 (≤0.05)	0.8-2.0 (≤0.05)	0.08-0.15	Settling in radial-flow sedimentation tank without coagulation of suspended matter

a)	When smelting conversion and foundry iron	Temperature °C	30	45-55	30-33	Cooling of purified recirculation water in spray basin or cooling tower, preferably in induced-draught cooling tower with spray irrigator
b)	When smelting ferro-manganese	SS†	0.25 (<0.05)	1.5-3.5	0.25-0.6	Settling in radial-flow sedimentation tank without coagulation of suspended matter. When coagulated with 150 mg/l iron chloride and further clarified by filtering through suspended granular material, SS content is reduced to 0.15 g/l
		Temperature °C	30	45-55	30-33	Cooling of purified recirculation water in spray basin or cooling tower, preferably in induced-draught cooling tower with spray irrigator
		Cyanides	Not standardized	0.005-0.035	—	—
iv)	Rolling mills:					
a)	Flushing of scale from beneath mills	SS†	0.4	1.6-2.1	0.4	} Settling in primary sedimentation tank (mill scale collection sump)
b)	Heavy and medium section strip mills	SS†	0.4	0.6-1.5	0.2	
c)	Light section	SS†	0.4	0.5-0.6	0.06	
d)	Cooling of rolls	SS†	0.08	0.06-0.3	0.03-0.08	Settling in secondary sedimentation tanks
		Oil	0.02	0.01-0.15	0.005-0.05	Separation in secondary sedimentation tanks with oil-retaining screen
		Temperature °C	30	35-38	28-33	Cooling of purified recirculation water in spray basin or cooling tower with spray irrigator

(Continued)

TABLE 7 TYPICAL QUALITY TOLERANCES FOR RECIRCULATION WATER SUPPLIED FOR COOLING, CLEANING AND TREATMENT OF RAW MATERIALS OR PRODUCTS BY DIRECT CONTACT, AND METHODS OF CONDITIONING REQUIRED — Contd

(All values except temperature are in g/l)

Sl No.	APPLICATION OF WATER	FACTORS TO BE STANDARDIZED*				METHODS OF ENSURING NORMAL VALUES
		Item	Ingoing Water, Normal Value	Outgoing Water		
				Before purification (cooling)	After purification	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
v)	Treatment of metal with acids:					
	a) For preparation of working solutions	FeSO ₄	0.05	0.15 - 1.5	0.05-0.07	Regeneration of sulphuric acid in vitriol plant to ferrous sulphate
		H ₂ SO ₄	Unlimited	30-70	‡	
		Fe ₂ (SO ₄) ₂	0.005	0.15 - 0.30	0.0-0.08 (Total Iron)	Neutralization with lime and settling of suspended matter in clarifier with suspended granular material or in clarification pond
	b) For rinsing of metal treated in acid	H ₂ SO ₄	0	1.5	0	
		FeSO ₄	0.5	0.01-0.02	0.02-0.08 (Total Iron)	Settling of suspended matter in clarification pond (ash-sludge accumulator)
	c) Removal of hydrosols from boilers	SS†	1	—	0.2-1.0	

*In all cases the tendency to cause corrosion of metal and concrete shall be eliminated by treatment of the water with lime (alkalization).

†SS=suspended solids (figures in parenthesis indicate particle size in mm).

‡Serviceable acid is reused.

TABLE 8 WATER POLLUTANTS IN AN INTEGRATED STEEL PLANT

(Clause 4.0)

Sl. No.	DESCRIPTION	SOURCE	DISPOSITION
(1)	(2)	(3)	(4)
i) Oil:			
a)	Rolling oils	Rolling mills, cold and hot rolling	Part adheres to scale; free oil collected for incineration
b)	Lubricants	Motor power, steam engines, forge and hammer pistons, gear drives, electric motors, fabrication machinery, machining, forging, drawing, etc	Floor spills soaked up on adsorption compounds; cutting oils and other emulsions segregated for incineration; oily water skimmed at source, and free oil collected for incineration
c)	Hydraulic oils	Motive power pumps for positioning devices or for press operation	Spills segregated for pick up and incineration
d)	Quench oil	Heat treatment	Seldom replaced; can be incinerated
e)	Fuel oil	Boiler plant, furnaces, soaking pits	Spills segregated by dikes around storage tanks; incinerated
f)	Solvents	Paint shops, degreasing operation	Collected for incineration
g)	Tar and pitch	Coke plant by-products recovery	Collected for incineration
ii) Suspended solids:			
a)	Scale	Rolling mills	Sinter plant for recovery as sinter
b)	Sand	Foundry	Slag pile, landfill
c)	Burden fines	Air washers at sinter plant and skip hoist charging area, blast furnace gas washers Open hearth and basic oxygen furnace fines	Sinter plant for recovery as sinter Sinter plant if zinc is low; otherwise buried in slag pile
d)	Fly ash	Coal fired furnaces and power plant	Cement or cement block additive
e)	Coal and coke	Coke plant	Collected and burnt
iii) Chemicals:			
a)	Pickle liquor	Acid pickling	Regenerated or neutralized
b)	Acid sludge	By-product plant	Regenerated or burnt
c)	Caustic wash	By-product plant	Incinerated
d)	Lime	Mould or steel coating; water softener sludge	Recovered for pickle liquor treatment; controlled release to waste water
e)	Brinc	Ion exchange resin regeneration	Reclaimed or controlled release to waste water

(Continued)

TABLE 8 WATER POLLUTANTS IN AN INTEGRATED STEEL PLANT — Contd

Sl. No.	DESCRIPTION	SOURCE	DISPOSITION
(1)	(2)	(3)	(4)
	f) Cleaners	Surface treatment, degreasing	Segregated for oil breakout or incineration
	g) Toxic chemicals	Coke plant, gas line drip legs, metal treatment	Chemical or biological destruction; incineration
iv) Heat:			
	a) Cooling water	Furnaces, heat treatment, roll cooling, air conditioning, heat exchangers	Cooling towers
	b) Boiler blow down	Steam plant	Recover to heat feed water
v)	Domestic sanitary wastes	Change rooms, toilets, cafeterias, etc	Segregate and treat by standard methods

4.1.2 As most of the contaminants are soluble, biological treatment is the most common form of treatment used. As phenols (both crude and refined) have a market value, they are most often recovered. Other pollutants are subjected to a biological treatment along with the residues of ammonia and phenols.

4.1.3 Trickling filters and activated sludge process are the two most common processes used for the treatment of coke oven wastes. It is possible to treat these wastes in admixture with raw sewage preferably diluted by a factor of 50 or more. However, it is not possible to obtain such a quantity of sewage in many steel plants in India. The coke oven wastes are biologically treatable even without sewage. But it is advisable to dilute the waste with water or some non-toxic wastes so as to keep the phenol concentration below 200 mg/l and preferably below 100 mg/l. It is also possible to treat the coke oven wastes undiluted in a complete mixing activated sludge system based on extended aeration at low organic loadings.

4.1.3.1 Standard rate trickling filters are not commonly used for treating phenolic wastes as the biological growths are likely to clog the pores of the filter. High rate trickling filters with reasonably high recirculation can be used. In England plastic media trickling filters have been found to give good phenol removals from gas liquor effluents which are considerably stronger than coke oven wastes. Deeper filters (2 to 3 m) were found to be better than conventional filters for phenol removal.

4.1.3.2 Activated sludge process is the more common process used for the destruction of phenols. Although earlier investigations showed that

trickling filters of high rate type resist shock loadings (hydraulic as well as organic) recent investigations have proved that in the case of toxic organic materials it is the complete mixing activated sludge system (CMASS) that can best resist shock loadings as it has a tendency to equalize flows as well as concentrations. The CMASS operates at low substrate concentrations and hence can tolerate the toxic wastes better. The conventional activated sludge system working on plug flow basis is likely to be more vulnerable than the high rate trickling filters.

4.1.3.3 It has been found that the extended aeration activated sludge system which normally works on a complete mixing system would operate best as the organic loading is usually low and there is a much higher microbial mass per unit of toxic matter fed to the unit.

4.1.4 If the waste is let out at higher temperature than normal, the waste has to be cooled before being treated in a biological system.

4.1.5 In the biological treatment of any waste, it is essential to ensure that the micro-organisms have all the nutrients they require. The coke oven wastes are rich in nitrogen but not so in phosphorus. As phosphorus is required to the extent of about 1 percent of the BOD it needs to be supplemented in coke oven waste treatment.

4.1.6 The phenols contained in the coke oven wastes are high in their oxygen demand (2 to 25 mg oxygen per mg phenol). Hence adequate oxygen has to be supplied. The coke oven wastes also produce considerable quantities of excess sludge for which sludge handling facilities are to be provided.

4.2 Waste Water from Gas Cleaning Plants of Blast Furnace

4.2.1 The treatment and disposal of effluents from gas cleaning plants of blast furnaces consist of removal of flue dust by plain sedimentation or sedimentation after chemical coagulation and recirculation of the clarified effluent.

4.2.2 Since recycle will build up the temperature of the system, such systems require the inclusion of a cooling tower in the circuit. To avoid deposits in the system brought about by the build-up of alkalinity, acid may be fed to these closed systems to maintain an acceptable stability index; these may result in pH in the range of 6.5 to 7.5, at which level the pick-up of cyanides is minimized and the stripping of cyanides at the cooling tower is promoted. If the pick-up of alkaline salts is relatively moderate, stabilization of the recirculated water with polyphosphates to control deposits is quite practical and eliminates the needs for acid feeding. The latter has been found to be preferable.

4.2.3 A well designed clarifier (generally requiring overflow rates less than 112 litres per minute/m² and weir overflow rates below 225 litres per minute/m) can reduce the concentration of suspended solids (range 1 000 to

10 000 mg/l) to less than 100 mg/l. Various chemical coagulants, such as aluminium sulphate, ferric chloride or ferric sulphate (pickle liquor along with slaked lime may sometimes be used) and poly-electrolytes are helpful not only in reducing effluent turbidity but also in compacting the sludge (12 to 20 percent solid content) the latter assisting in the production of drier filter cake. The underflow is further thickened to 30 to 60 percent and dewatered in a vacuum filter to produce a relatively dry cake (usually 80 percent solids) which can easily be handled in rail cars for ultimate disposal. These dry cakes can either be blended with other fines to produce sinter which can be charged to the blast furnace or disposed of as a landfill.

4.3 Waste Water from Steel Making Furnaces

4.3.1 Treatment of these waste waters presents certain difficulties due to the nature of the wastes. Characteristics causing problems include:

- a) wide distribution in the sizes of the particles,
- b) high density of the particles (relative density about 5),
- c) abrasiveness of the particles, and
- d) temperature variations and intermittency of flow due to cyclic character of the operation (in the case of BOF).

4.3.2 Because of factors mentioned in **4.3.1**, treating these waste waters by plain sedimentation in standard type clarifiers had at times resulted in clogging the sludge lines, break down of the sludge cleaning mechanism and wearing out of the slurry pumps. The fluctuation in the flow and temperature causes considerable upsets in this type of units, resulting in an effluent with considerable concentration of suspended solids.

4.3.3 The recommended procedure for the effluent, after passage through primary tanks is to treat it in thickeners and subsequently treat in clarifloculators and reuse. The sludge disposal is same as in blast furnace and gas cleaning plants but not as a feed to sinter plant. Where dry cyclones are used and suspended solids are low, the effluents can be utilized for secondary purposes such as slag quenching, coke quenching, etc.

4.4 Waste Waters from Rolling Mills

4.4.1 The cooling water from reheating furnaces and motor room is clean and does not require any treatment other than cooling.

4.4.2 Water coming from roughing stand contains predominantly coarse scale which settles out quickly. The concentration of oils and grease in these effluents is low but occasionally lubrication line bursting, leakage of lubricating oils, wash-down of equipment result in high concentration. The treatment facilities now being designed for such effluents usually consist of two stage tanks. The first stage providing a retention time of only a few minutes removes the coarse scales while the second stage consisting of two to three compartments with a retention time of about 30 minutes

is specially suited for the removal of smaller scale particles and floating oils. Adequate oil skimming should be provided and the level of the water in the basins be closely controlled by effluent weirs. Inlet and outlet devices should be designed for minimum short circuiting and scouring to achieve maximum tank efficiencies. The settled scales may be dredged out by buckets or by drag out conveyors. In either case it is usually loaded into rail/road cars or trucks for delivery to the furnaces. During the removal of the scale from the pit, turbulent conditions should be minimized to prevent excessive amounts of scales passing over the weir. This can be accomplished by shutting down the compartment of the scale pit being cleaned. The intercepted oils may be pumped into decanting and storage tanks, which can be reused after necessary treatment or may be burnt. The resulting effluent is normally quite clear and of adequate quality to permit it to be recirculated in the mill.

4.4.3 Discharges from the finishing stand and scarfer machines contain scale which is too fine to be intercepted by simple settling. These waste flows should be segregated from the coarse mill scale water as they require secondary treatment. Primary treatment for these waste waters is the same as for those from coarse mill scales. Secondary treatment may simply consist of large holding lagoons where space permits. Where space does not permit such lagoons, the waste water may be treated with chemicals that coagulate and settle the fine particles in flocculator-clarifier units. The coagulated and settled effluent may be further purified by passing through sand filters.

4.4.4 Waste water emanating from cold reduction of coils in tandem mills, from cleaning lines and from secondary cold reduction mills carry a variety of floating and emulsified oils, detergents, mill scales, cleaning chemicals and dirt as mentioned earlier (see 2.7.1). Discharge of such waste waters into a water course without treatment will deplete dissolved oxygen and cause sludge banks resulting in odour and unsightly appearance due to biological decomposition and foaming.

4.4.5 The circulated rolling solution is usually reconditioned by skimming tramp oils and filtering out the mill scale and dirt. The waste treatment facilities for waste waters from cleaning lines and from secondary cold reduction usually comprise primary gravity separation, in which floatable oils and settleable sludges are removed and chemical treatment with salts of heavy metals usually ferric sulphate or ferric chloride. They react with the alkalinity naturally present or added as lime to produce an easily settleable floc which is usually removed from the water by gravity separation and occasionally by air floatation.

4.4.6 In most plants, it is advantageous to combine the waste rinse waters from the pickling lines to provide the iron salt for floc formation and to take advantage of the alkalinity in the cold reduction waste water for partial neutralization. In all cases oil skimmed in these facilities is collected in

concentration tanks from which the oils may be reclaimed or disposed of by incineration. Sludges produced in the treatment in these facilities are disposed of into low lying areas.

4.5 Waste Water from Pickling Lines

4.5.1 One of the most troublesome wastes from the steel plant is the pickle liquor. The most common method of treating pickle liquor is to add lime to neutralize the acid. Extensive lagoons are required to dispose of the voluminous watery sludge. It is usually impractical to dewater this sludge in a vacuum filter.

4.5.2 Special neutralization processes carried out under carefully controlled conditions of pH, temperature and aeration will result in the oxidation of the ferrous hydroxide to a rapidly settling and insoluble ferric hydroxide. The volume of sludge from this process can be greatly reduced by vacuum filtration, centrifuging or gravity sedimentation. The volume of the sludge to be disposed of can be reduced by keeping the gypsum in solution in the reactor by suitable dilution or washing. The residual solids would consist mainly of iron oxides which can be removed from the waste stream by sedimentation and recovered.

4.5.3 In the case of pickle liquor rinse water, the acid concentration being very low can be treated with other cold mill wastes particularly the oily waste from the cold rolling mills. After the addition of lime and air, the iron in the rinse water produces ferric hydroxide which is an excellent floc and aids in the removal of oil from the waste water discharge.

4.5.4 Recovery of copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) from pickle liquor is fairly simple. Where recovery of free acid is not desired, the waste liquor is heated with scrap iron to neutralize the acid and the resulting solution is settled to remove suspended matter and the copperas is recovered as crystals following either evaporation or refrigeration. It is possible to produce lower hydrates by careful drying. However, drying is not carried beyond trihydrate. Copperas and lime and chlorinated copperas are valuable coagulants for the treatment of water and certain industrial wastes.

4.6 Waste Water from Power Plant

4.6.1 Brine or acid and caustic solutions resulting from regeneration of ion exchange beds of water treatment plant are usually collected in an equalization tank having two to three hours holding capacity. For proper mixing either aeration or mechanical mixing may be adopted. The effluent from the equalization tank is usually slightly acidic and may be neutralized with lime or caustic. These neutralized effluents are disposed of with other treated or less contaminated effluents.

4.6.2 The slurry containing fly ash is pumped to a settling basin or into low lying areas with dykes. The supernatant water may be

discharged into water courses or taken back into the plant water system. The slurry should not be discharged into streams or fresh water lakes.

4.7 Waste Water from Other Sections of the Steel Plants, Namely Raw Material Handling System, Pig Casting Machines, Foundry, Slag Plant, etc — Wastes from the above plants contain mainly suspended solids in varying concentrations. Plain sedimentation adjacent to the respective source of origin will render them fit for disposal into water courses or may be taken back into the recirculation system. Sludges from the settling tank shall preferably be taken to a central sludge collector along with sludges containing metal and fly ashes from other sections of the steel plant and supernatant water may be either discharged into a water course or taken back into the plant recirculating system.

4.8 Waste Water from Continuous Casting Plant

4.8.1 The water from the mould is clean and needs only cooling.

4.8.2 The water coming from the machinery and the apron is contaminated with scale and oil leaking from the lubrication system. The treatment facilities for this consist of a settling tank where heavier particles settle and the oil is skimmed off. The effluent is then passed through a line filter where finer scales are removed. The effluent is then cooled for further reuse.

4.9 Coal Washery Wastes — A well designed clari-flocculator can reduce the concentration of suspended solids (13 400 to 42 600 mg/l) to less than 50 mg/l. Chemical coagulants such as alum, ferric chloride or sulphate and coagulant aids such as starch and polyelectrolytes may be necessary to reduce the suspended solids concentration.

5. METHODS RECOMMENDED FOR ADOPTION IN INDIA

5.1 Treatment of steel plant effluents consists of cooling some streams, separation and disposal of oil and suspended solids, biological oxidation of soluble organics, neutralization of acids and crystallization and removal of inorganic soluble salts.

5.2 Waste waters from coke ovens, pickling and rest of the operations may be segregated and treated separately.

5.3 The waste waters which contain high suspended solids, such as from gas cleaning plant of blast furnace, steel making furnace, rolling mills and other sections of the steel plant, namely, raw material handling system, pig casting machine, foundry and slag plant may be collected individually or jointly and treated by settling or chemical coagulation. Clarifiers and clari-flocculators may be used for the wastes from gas cleaning plant and steel making furnaces. Use of coagulants such as alum, ferric chloride and ferric sulphate (pickle liquor along with slaked lime may sometimes be used)

and polyelectrolytes may be helpful not only in reducing effluent turbidity but also in compacting the sludge. Wastes from other plants such as raw material handling system, pig casting machine, foundry, etc, containing mainly varying concentrations of suspended solids may be settled in primary settling tanks to render them fit for disposal into water courses or for reuse. Sludges from settling tanks may preferably be taken to a central sludge collector along with sludge containing metal and fly ash. Slurry containing fly ash may be pumped to a settling tank or into low lying areas with dykes. Effluents from the various operations in steel making are not of a polluting type and their treatment and disposal do not present serious difficulty. Recirculation of process waters in closed systems is universally practised.

5.4 It was observed in one of the Indian steel plants that the mixing of the oxygen plant waste and scrubbing waste permitted the reuse of more than 95 percent water. The sedimented slurry treated with oxygen plant waste permitted the recovery of considerable quantities of self-fluxing ore fines daily.

5.5 It is advisable to recover ammonia and phenols from coke oven wastes to the extent possible. The waste water left over after recovery of phenols and ammonia may be treated in an extended aeration activated sludge process which normally works on a complete mixing system. This system would operate best as the organic loading is usually low and there is much higher microbial mass per unit of toxic organic matter fed to the unit. Coke oven waste needs supplementation of phosphorus to make it balanced for nutrients required for microbial decomposition. If raw sewage is available, it is advisable to treat these wastes in admixture with sewage. If dilution water is available, the coke oven wastes can be diluted to a phenol concentration below 200 mg/l and treated in a trickling filter.

5.6 Acid and copperas should be recovered from pickle liquor to the extent possible economically. Where recovery of free acid is not desired, the waste liquor may be treated with scrap iron to neutralize the acid and the resulting solution settled to remove suspended matter and copperas recovered as crystals following either evaporation or refrigeration. After recovery of acid and/or copperas the pickle liquor may be neutralized using lime and the sludge obtained may be disposed of in lagoons.

5.7 In the case of pickle liquor rinse water, it may be treated along with other cold mill wastes, particularly oil bearing wastes, after neutralization with lime.

5.8 It is advantageous to mix water from rolling mills and waste rinse water from pickling lines to provide the iron salt for floc formation and to take advantage of the alkalinity in the cold reduction waste water for partial neutralization.

5.9 Brine or acid and caustic solutions resulting from regeneration of ion exchange beds of water treatment plant may be collected in an equalization

tank, mixed either by aeration or mechanical mixing and settled for two to three hours. The effluent from the equalization tank is usually slightly acidic and may be neutralized with lime.

5.10 Recommended flow sheets for the treatment and disposal of phenolic wastes through coke quenching use, and for the complete treatment and disposal of effluents of an integrated steel plant are given in Fig. 2 and 3.

APPENDIX A

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(Clause 0.6)

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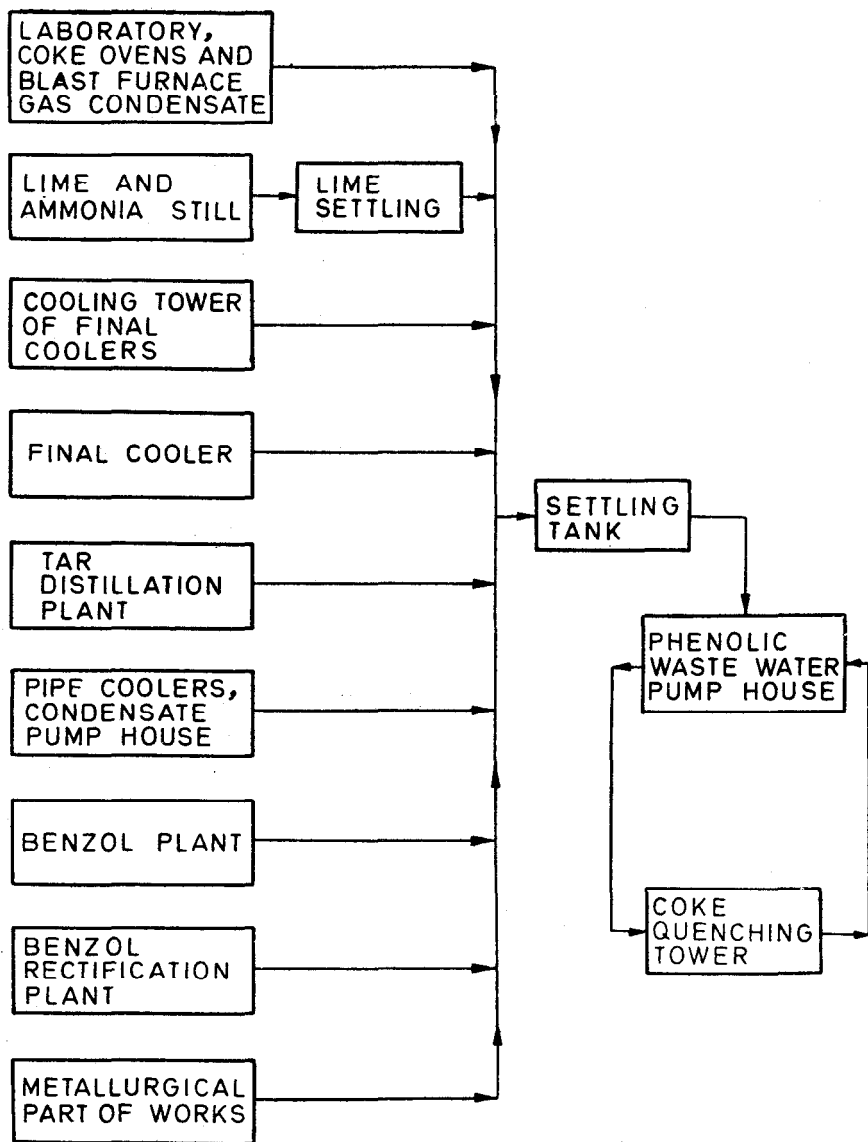


FIG. 2 FLOW SHEET FOR DISPOSAL OF PHENOLIC EFFLUENTS THROUGH COKE QUENCHING USE

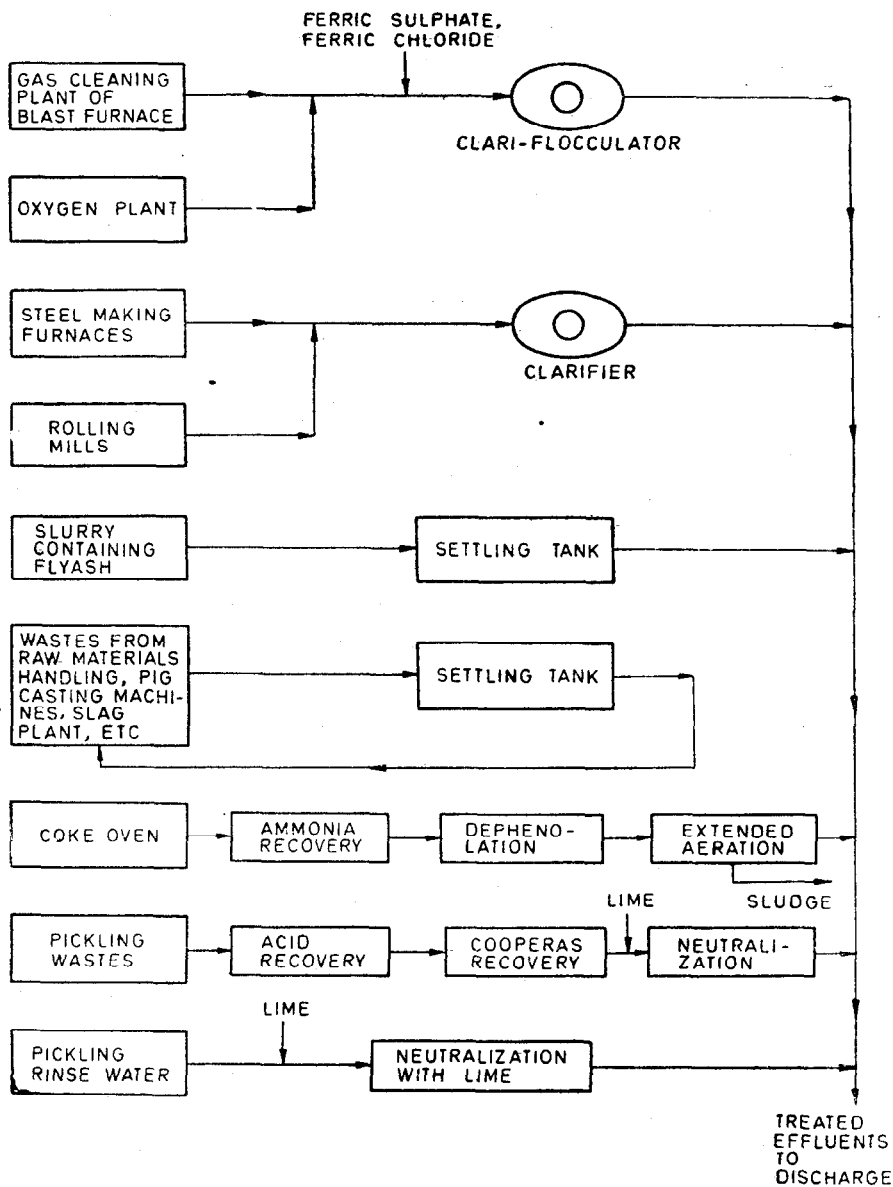


FIG. 3 FLOW SHEET FOR THE TREATMENT OF STEEL PLANT EFFLUENTS

(Continued from page 2)

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