Draft

Guidelines on Management of Pyro-metallurgical Slags

(Copper Smelters)

Central Pollution Control Board

(Ministry of Environment, Forest and Climate Change)

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CONTENTS

1.0 INTRODUCTION

The Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016 notified by Ministry of Environment, Forest and Climate Change, Government of India for the management of hazardous and other wastes define the hazardous waste as below:

"hazardous waste" means any waste which by reason of characteristics such as physical, chemical, biological, reactive, toxic, flammable, explosive or corrosive, causes danger or is likely to cause danger to health or environment, whether alone or in contact with other wastes or substances, and shall include –

i. *waste specified under column (3) of Schedule I;*

ii. *waste having equal to or more than the concentration limits specified for the constituents in class A and class B of Schedule II or any of the characteristics as specified in class C of Schedule II; and*

iii. *wastes specified in Part A of Schedule III in respect of import or export of such wastes or the wastes not specified in Part A but exhibit hazardous characteristics specified in Part C of Schedule III;*

Pyro-metallurgical slags are defined as "High Volume Low Effect Waste" (herein referred as HVLE wastes) under the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016 (HOWM Rules 2016). The relevant provision given as note at the end of Schedule-I of the HOWM Rules 2016 is as follow:

"The high volume low effect wastes such as fly ash, Phosphogypsum, Red Mud, Jarosite, ***Slags from pyro-metallurgical operations****, mine tailings and ore beneficiation rejects are excluded from the category of hazardous wastes. Separate guidelines on the management of these wastes shall be issued by Central Pollution Control Board."*

NITI Aayog constituted a Committee on Circular Economy: Scrap Metal (ferrous and non-ferrous) to promote initiatives for Circular Economy in the metal sector (ferrous and non-ferrous) through Action plan which also include and action point about - *Issue of SOP for use of Iron and steel slag under Hazardous and Waste Management Rules 2016.*

The guidelines are prepared to deal with the handling and management of slags generated from pyro-metallurgical operations in Copper Smelters.

2.0 MANUFACTURING PROCESS – COPPER SMELTERS

The process of extracting copper from copper ore varies according to the type of ore and the desired purity of the final product. Each process consists of several steps in which unwanted materials are physically or chemically removed, and the concentration of copper is progressively increased. Some of these steps are conducted at the mine site itself, while others may be conducted at separate facilities. The steps used to process the sulfide ores are mining, grinding and concentration of ore.

As per Indian Minerals Year Book 2020, the production of copper ore was 3.95 million tonnes in 2019-2020 and production of copper concentrates was 124692 tonnes in 2019-2020. The production of copper concentrates was carried in Madhya Pradesh, Rajasthan and Jharkhand. The percentage of average metal content in copper concentrate was 21.58 % Cu in 2019-2020 and the state-wise statistics is as below:

1.	Madhya Pradesh	0.70 % Cu
2.	Rajasthan	0.87 % Cu
3.	Jharkhand	0.78 % Cu

Source: Indian Minerals Year Book 2020

2.1 PROCESS OVERVIEW:

The copper concentrates after beneficiation at mine site are transferred to copper smelters for processing. The first stage is drying of copper concentrate through dryer and taken to furnace for smelting. The second stage is smelting of copper concentrate in furnace in presence of oxygen to produce copper matte along with production of sulphur dioxide gas and pyrometallurgical slag (termed as furnace slag at this stage). The sulphur dioxide gas along with off gases after cleaning are being taken to sulphuric acid plant for production of sulphuric acidthrough double absorption double contact. The slag is tapped out from furnace and transferred to slag handling plant. The third stage in smelting after production of copper matte is smelting in converter furnace to produce blister copper having copper percentage approx. 98.5 %, where air is blown to liquid matter and flux (if required) are added. The fourth stage is production of copper anode from blister copper to reach copper percentage from approx. 98.5 % to approx. 99.5 %. The fifth stage is transfer of copper anode to production of copper cathode through electrolytic refining with copper percentage from approx. 99.5 % to approx. 99.9% purity.

2.2 COPPER SMELTERS:

The total installed capacity of copper smelting in the country is 01 Million Tonne per annum, which includes primary smelters, secondary smelters and continuous casting plant.

2.3 PYROMETALLURGICAL SLAG:

Copper slag is an industrial by-product material produced from the process of manufacturing copper. It is produced by:

- **Roasting,** in which Sulphur in the ore is eliminated as Sulphur Dioxide (SO2);
- **Smelting,** in which the roasted product is melted in a siliceous flux and themetal is reduced; and
- **Converting,** where the melt is de-sulphurized with lime flux, iron ore, or a basic slag and then oxygen lanced to remove other impurities.

Once the waste materials have been physically removed from the ore, the remaining copper concentrate must undergo several chemical reactions to remove the iron and sulfur. This process is called smelting.

The copper concentrate is fed into a furnace along with a silica flux. Most copper smelters utilize oxygen-enriched flash furnaces in which preheated, oxygen-enriched air is forced into the furnace to combust with fuel oil. The copper concentrate and flux melt, and collect in the bottom of the furnace. Much of the iron in the concentrate chemically combines with the flux to form a **slag**, which is skimmed off the surface of the molten material. Much of the sulfur in the concentrate combines with the oxygen to form sulfur dioxide, which is exhausted from the furnace as a gas and is further treated in an acid plant to produce sulfuric acid. The molten material in the bottom of the furnace is called the matte. It is a mixture of copper sulfides and iron sulfides and contains 60% copper by weight. The molten matte is drawn from the furnace and poured into a second furnace called a converter. Additional silica flux is added and oxygen is blown through the molten material. The chemical reactions in the converter are similar to those in the flash furnace. The silica flux reacts with the remaining iron to form a **slag**, and the oxygen reacts with the remaining sulfur to form sulfur dioxide. The slag may be fed back into the flash furnace to act as a flux, and the sulfur dioxide is processed through the acid plant. After the slag is removed, a final injection of oxygen removes all but a trace of sulfur. The resulting molten material is called the blister and contains about 99% copper by weight.

2.4 REFINING/ PURIFICATION OF COPPER

Even though copper blister is 99% pure copper, it still contains high enough levels of sulfur, oxygen, and other impurities to hamper further refining. To remove or adjust the levels of these materials, the blister copper is first fire refined before it is sent to the final electro-refining process.

The blister copper is heated in a refining furnace. Air is blown into the molten blister to oxidize some impurities. A sodium carbonate flux may be added to remove traces of arsenic and antimony. A sample of the molten material is drawn and an experienced operator determines when the impurities have reached an acceptable level. The molten copper, which is about 99.5% pure, is then poured into molds to form large electrical anodes, which act as the positive terminals for the electro-refining process.

Slabs of impure copper (blister copper), together with thin sheets of pure copper metal or stainless steel or titanium are immersed in a solution of copper(ll) sulfate (0.3 mol dm-3) and sulfuric acid (2 mol dm-3). The pure copper or steel sheets make the cathode (Figure 6) of an electrolysis cell, and the impure slabs are the anode.

Each copper anode is placed in an individual tank, or cell, made of polymer-concrete. There may be as many as 1,250 tanks in operation at one time. A sheet of copper is placed on the opposite end of the tank to act as the cathode, or negative terminal. The tanks are filled with an acidic copper sulfate solution, which acts as an electrical conductor between the anode and cathode. When an electrical current is passed through each tank, the copper is stripped off the anode and is deposited on the cathode. Most of the remaining impurities fall out of the copper sulfate solution and form a slime at the bottom of the tank. After about 9-15 days, the current is turned off and the cathodes are removed. The cathodes now weigh about 300 lb (136 kg) and are 99.95-99.99% pure copper.

The slime that collects at the bottom of the tank contains gold, silver, selenium, and tellurium. It is collected and processed to recover these precious metals.

2.5 CASTING

After refining, the copper cathodes are melted and cast into ingots, cakes, billets, or rods depending on the final application. Ingots are rectangular or trapezoidal bricks, which are remelted along with other metals to make brass and bronze products. Cakes are rectangular slabs about 8 in (20 cm) thick and up to 28 ft (8.5 m) long. They are rolled to make copper plate, strip, sheet, and foil products. Billets are cylindrical logs about 8 in (20 cm) in diameter and several feet (meters) long. They are extruded or drawn to make copper tubing and pipe. Rods have a round cross-section about 0.5 in (1.3 cm) in diameter. They are usually cast into very long lengths, which are coiled. This coiled material is then drawn down further to make copper wire.

2.5 COPPER MANUFACTURING UNITS SCENARIO IN INDIA

In India, Rajasthan, Madhya Pradesh and Jharkhand are the only states involved in production of copper ore in the country. However, copper concentrates are imported by the Birla Copper of Hindalco Industries Limited and Sterlite Copper

. a unit of Vedanta Limited to produce copper metal located in the States of Gujarat and Tamil Nadu, respectively.

The major copper mines are the Khetri copper belt in Rajasthan, Singhbhum copper belt in Jharkhand and Malanjkhand copper belt in Madhya Pradesh which are mined by HCL; Singhbhum belt is mined by M/s Indian Copper Complex. While the Ingeldhal mine is operated by M/s Hutti Gold Mines Ltd, the Dikchu mine is in Sikkim under the Sikkim Mining Corporation (SMC).

3.0 PYRO-METALLURGICAL SLAGS GENERATION AND ITS PROPERTIES – COPPER SMELTERS

Copper slag is a by-product of copper extraction by smelting. During smelting, impurities become slag which floats on the molten metal. Slag that is quenched in water produces angular granules which are disposed of as waste or utilized.

Dumping or disposal of such huge quantities of slag cause environmental and space problems. During the past two decades attempts have been made by several investigators and copper producing units all over the world to explore the possible utilisation of copper slag. Large quantities of Ferro sand (copper slag, CS) are generated as waste during the copper smelting process and it has been estimated that for every tone of copper produced, about 1.6-1.9 tonnes of Ferro sand is generated as a waste. Since the quantity of Ferro sand getting accumulated with the increase in the production capacities requiring additional dumping space, the recovery of some of the value added product has been attempted. The current stock piling of Ferro sand at Sterlite Copper, Tuticorin is around of 30 thousand tonnes.

The slag generated from primary smelters – flash smelters and converters are considered to have recoverable copper content before transfer to slag granulation/handling plant.

3.1 PROPERTIES OF COPPER SLAG

Copper slag is black in colour, a glassy, granular material, having a shiny appearance. Molten slag is partially crushed through water jet to smaller particles and stockpiled after the refining process. Copper slag, ores contains materials like iron, alumina, calcium oxide, silica etc. For every tonne of metal production about 1.6 to 1.9 ton of slag is generated. The properties of the copper slag are as follows:

Chemical composition of Ferro sand (copper slag)

Elements	**Ferro Sand or Copper slag**	**Industry A (Dry Basis)**	**Industry B**
Copper (%)	0.4 - 0.5	0.7 – 1.3	0.31
Iron (%)	55 – 65	40 – 46	52.55
Sulphur (%)	0.5 - 1.5	0.20 – 0.46	--
Silica (%)	28 – 35	26 - 30	26.60
Lime-CaO (%)	3 – 5	0.015 – 0.032	3.00
Arsenic (ppm)	10 – 250	--	--
Cadmium	5 – 8 ppm	0.0002 – 0.0006 %	--
Chromium	0.5 - 1.0 ppm	0.018 – 0.04 %	--
Cobalt	100 – 200 ppm	0.020 – 0.069 %	--
Nickel	25 – 50 ppm	0.020 – 0.028 %	--
Lead	200 – 250 ppm	0.01 – 0.032 %	613 ppm
Zinc	500 – 1500 ppm	0.05 – 0.14 %	--

Source: Industry

Physical properties of Ferro sand (copper slag)

Specific gravity	3.58
Bulk density	1.7-1.8
Loss on ignition	NIL
Proportion of coarse sand size particles,2mm–4.75mm	28%

Source: Industry

Geotechnical characteristics of Copper slag

Property	Ferro Sand or Copper Slag
Grain size analysis	
Gravel (%)	2
Sand (%)	98
Silt (%)	0
Clay (%)	0
Atterberg limit test	
Liquid limit (%)	-
Plastic limit (%)	NP
Plasticity index (%)	-
Modified Proctor test	
MDD (kN/m2)	23.2
OMC (%)	7
Direct shear test (saturated)	
c (kN/m2)	0
(degree)	35
Permeability (m/sec)	1.7x10-4
CBR (%)	35

Source: Industry

4.0 CURRENT PRACTICES FOR HANDLING AND MANAGEMENT OF PYRO-METALLURGICAL SLAGS

Copper slag is used for several purposes, mainly for the manufacture of abrasive tools and grid blasting. This process consumes about 15% to 20% of the slag generated. The copper slag can be used as constituent for blended cement. International Practices for utilization of Copper Slag are summarized in Annexure-I.

The slag generated from copper smelter are transferred to slag handling plant for processing of slag including granulation, and further storage in open areas.

5.0 UTILIZATION OF COPPER SLAGS IN ROAD CONSTRUCTION AND AS AGGREGATES IN CONCRETE

Indian Road Congress has published "Guidelines for Use of Iron, Steel and Copper Slag in Construction of Rural Roads – 2018". These guidelines provide detailed information on engineering properties of these slags. Properties of slags in respect of toxic inorganic constituents is not covered in the guidelines.

The Indian Standards IS-383: 2016 of the Bureau of Indian Standards on "Specifications of Coarse and Fine Aggregates for Concretes" permits use of manufactured aggregates, including slags, in concretes to the specified extent. Engineering quality requirements of aggregates are specified in main document. Brief information on other than natural is given in Annexure-A, which include BIS quality standards for slags. However, the quality parameter / permissible concentration are not as per criteria in Schedule II of HoWM Rules 2016. The above mentioned guidelines of IRC also referred to in IS-383: 2016

6.0 GUIDELINES FOR MANAGEMENT OF PYRO-METALLURGICAL SLAGS:

6.1 Use best available options for maximising internal use and recycling of slags. Process the slag generated from primary copper smelting for copper recovery.

6.2 Adopt appropriate cooling/treatment techniques to maximise reuse of slag as a resource.

6.3 Use best practices in collection, handling, storage and transport of slag to avoid water and air pollution.

6.4 Implement appropriate measures, such as impermeable base and garland drain, in slag storage area to avoid fluid leakage and prevent soil and water / groundwater contamination.

6.5 Maximize external use or recycling of slag which cannot be used or recycled internally.

6.6 SPCB's/PCCs may permit utilization of copper slag from pyro-metallurgical route for use in following areas as per quality requirement/standard of the materials and subject to meeting the concentration levels specified in Schedule II of HoWM Rules 2016;

i. Production of Cement
ii. Coarse and Fine Aggregates for Concretes
iii. Cement-concrete blocks / bricks / tiles
iv. Subsurface material for roads / railways
v. Abrasive materials

Industry intending to utilise copper slag for any other purpose, not mentioned above may approach CPCB for inclusion of the same.

6.7 Adopt environmental policy for continuous improvement by adopting cleaner / new techniques.

6.8 Environment management should be supervised by senior management.

7.0 RECOMMENDED UTILIZATION TARGETS

i. 100% copper slag utilization for current generation shall be achieved within one year.

ii. 100 % utilization of legacy copper slag shall be achieved within two years.

iii. Maximum allowable storage at any point of time will not be more than 06 months’ generation.

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Annexure – I

Options for Utilization of Copper Slag – Some Global Initiatives

1. Transportation Research Board, Washington (Collins and Cielieski, 1994) used fine copper slag in hot mix asphalt pavements built in California. The use of granulated copper slag into asphalt mixes in Georgia to improve stability.
2. Michigan Department of Transportation Specifications indicate about the use of reverberatory copper slag for hot mix asphalt pavement as coarse and fine aggregate.
3. American Concrete Institute studied about use of copper slag as construction materials and characteristics observed to be equivalent to traditional ones.
4. Building and Construction Authority, Singapore mentions about use of washed copper slag as recycled materials for construction.
5. US Department of Transportation: (User Guidelines for Waste and By-product Materials in Pavement Construction) – mentions about use of air-cooled and granulated copper slag for granular road base and reverberatory copper slag for granular aggregate in Michigan.

6. Minerals Research and Recovery, Arizona, USA prepared a grained abrasive through use of copper slag and product found to be consistent in composition and physical properties and environmentally safe.

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Source:

[1, 2, 3, 6] - B. Gorai et al. | Resources, Conservation and Recycling 39 (2003) 299-313.

[4] - Guidelines for management, handling, utilisation and disposal of slag generated from copper manufacturing plants.

[5] - User Guidelines for Waste and By-product Materials in Pavement Construction