Guidelines on Management of Pyro-metallurgical Slags

(Copper Smelters)

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Central Pollution Control Board

(Ministry of Environment, Forest and Climate Change)

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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) and were similarly defined earlier under Hazardous Waste (Management, Handling & Transboundary Movement) Rules, 2008. 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, which recommended to promote initiatives for circular economy in the metal sector (ferrous and non-ferrous) through an Action Plan. The said action plan includes issuance of SOPs for utilization of resource material from pyro-metallurgical slags generated from Iron and Copper smelters of Iron and steel slags, which is already stipulated under Hazardous and Waste Management Rules *2016.*

These guidelines will facilitate Copper Smelters units in handling and management of large volumes of slags generated from pyro-metallurgical operations due to increased processing of copper concentrates.

2.0 Copper Smelters - Manufacturing Process

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 % while the average concentration of copper metal was about 0.8%. The state-wise concentration of copper metal in ores 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 copper concentrate is fed into a furnace along with silica flux. Most copper smelters utilize oxygen-enriched flash furnace smelter in which preheated, oxygen-enriched air is forced into the furnace to combust with fuel oil to produce copper metal (in the form of matte) along with production of sulphur dioxide gas and pyro-metallurgical slag (flash furnace slag). 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 through double conversion and double absorption. The slag is tapped out from furnace and transferred to slag handling plant. The molten material in the bottom of the smelting furnace is called the matte. It is a mixture of copper sulfides and iron sulfides and contains 60% copper by weight. The matte is drawn from the furnace and transferred to a second furnace called a converter.

In converter furnace, additional silica flux is added and oxygen is blown through the molten material. 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 sulphur. The resulting molten material is called the blister (ingot) and contains about 99% copper by weight. Slag contains materials like iron, alumina, calcium oxide, silica, etc.

The third stage is production of copper anode from blister copper to reach copper percentage from approx. 98.5 % to approx. 99.5 %. The fourth 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 Refining / Purification of Copper

Copper blister still contains trace 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. After this stage, the molten copper, with more than 99.5% purity is moulded to form large electrical anodes, which act as the positive terminals for the electro-refining process.

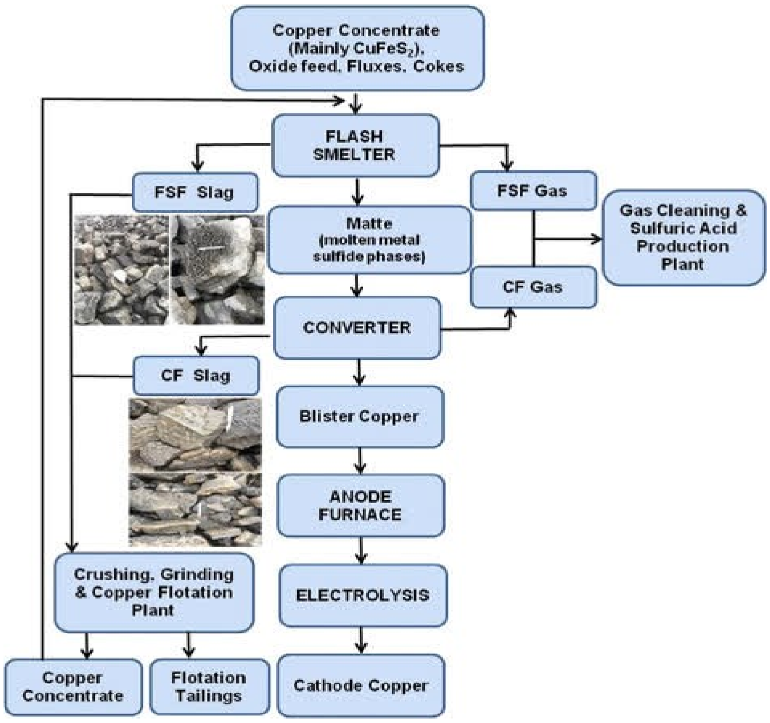

Fig-1: Flowchart for copper smelting process (Seyrankaya,A.2022)

Slabs of impure copper (blister copper) sheets are refined by electrolysis process, where thin sheets of pure copper metal or stainless steel or titanium are immersed in a solution of copper(ll) sulfate and sulfuric acid, where thin sheets acts as cathode, and the impure slabs are the anode. When an electrical current is passed, 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 cell is turned off and pure copper in the form of the cathodes 99.95-99.99% purity is produced.

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. The overall process flow diagram is shown in fig-1.

2.3 Casting

After refining, the copper cathodes are melted and cast into ingots, cakes, billets, or rods depending on the final application. Ingots are also re-melted along with other metals to make brass and bronze products. They are rolled to make copper plate, strip, sheet, and foil products. Billets are cylindrical logs that are extruded or drawn to make copper tubing and pipe. Rods are usually cast into very long lengths, which are coiled. This coiled material is then drawn down further to make copper wire.

2.4 Copper Manufacturing units 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 M/s Birla Copper of M/s Hindalco Industries Limited and M/s Sterlite Copper of M/s Vedanta Limited that produces copper metal in smelters located in the States of Gujarat and Tamil Nadu, respectively. The total installed capacity of copper smelting in the country is about 01 Million Tonnes per annum, which includes primary smelters, secondary smelters and continuous casting plant.

Major copper mines are the Khetri copper belt in Rajasthan, Singhbhum copper belt in Jharkhand and Malanjkhand copper belt in Madhya Pradesh. Major mining operators are M/s HCL, Khetri, M/s Indian Copper Complex, Singhbhum , M/s Hutti Gold Mines Ltd, Ingeldhal and M/s Sikkim Mining Corporation (SMC), Dikchu.

3.0 Generation and Characteristics of Slag

As discussed above, copper slag is generated during copper extraction through smelting furnaces. In smelting, impurities become part of slag which floats on the molten metal. Light density floating slag is separated and channelized for recovery, utilization or disposal. Hot liquid slag is granulated by quenching with water to facilitate cooling and crystallization. The slag generated from primary smelters – flash smelters and converters generally have recoverable copper content.

Copper from slag is recovered by pulverising and gravity separation.

Granulated Copper Slag

After recovery of copper, the slag is required to be handled further for possible utilization and storage prior to disposal. Due to presence of Iron and silica, granulated copper slag is also called ferro-sand. It is estimated that for every tonne of copper produced, about 1.6-1.9 tonnes of copper slag is generated as a waste. Since large quantities of slag is getting accumulated with the increase in the production capacities, smelter units are required to explore various options for recovery of resource material, storage and disposal. Improper storage of slag in huge quantities over a long period may consume land resource and also there is risk of seepage of heavy metals from unlined open disposal sites. Globally, various options for utilization of copper slag are being explored. Status of slag generation, utilization and storage of 3 smelter units in the country is given below.

Slag generation, utilisation and storage data*

Plant	Slag Type	Slag stored on 31.03.2021 (in MT)	Generated (2021-22) (in MT)	Utilised (2021-22) (in MT)	Slag stored on 31.03.2022 (in MT)
A	Granulated Slag	325837	693128	695141	323824

<table>
<tr><th>Plant</th><th>Slag Type</th><th>Slag stored on 31.03.2021 (in MT)</th><th>Generated (2021-22) (in MT)</th><th>Utilised (2021-22) (in MT)</th><th>Slag stored on 31.03.2022 (in MT)</th></tr>
<tr><td></td><td>Converter Slag</td><td>22625</td><td>3726</td><td>806</td><td>25544</td></tr>
<tr><td>B</td><td>Granulated Slag</td><td>344189</td><td>0</td><td>23661</td><td>320528</td></tr>
<tr><td rowspan="3">C</td><td rowspan="3">Granulated Slag</td><td>30000</td><td>0</td><td>0</td><td>30000</td></tr>
<tr><td colspan="4">For 2017-18</td></tr>
<tr><td></td><td>666007</td><td>684152</td><td></td></tr>
</table>

*as per industry response

3.1 Properties of Copper Slag

Copper smelter slag is a black coloured glassy, shiny and granular material. Main constituents of copper slag are iron, copper, sulphur, lime and silica. The elements in copper slag are present in the form of FeO, Fe_3O_4, CaO, $Al2O_3$, SiO_2, Cu, MgO, S, Zn and others. The particle size of granulated slag is similar to the range of size of sand particles used in construction. The chemical composition, physical and geo-technical properties of slag is presented in Tables below.

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

Elements	Ferro Sand or Copper slag	Industry A (Dry Basis)	Industry B
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

Property	Ferro Sand or Copper Slag
Permeability (m/sec)	1.7x10-4
CBR (%)	35

Source: Industry

4.0 Current Practices for Handling and Management of Pyro-Metallurgical Slags

Copper slag can be used for several purposes, most value added product from the slag is the production of abrasive tools and blasting material. This utilization option can consume up to about 15% to 20% of the slag generated. Rest of the copper slag can be utilised as construction material and aggregate of cement. Some of the international practices for utilization of Copper Slag are given at Annexure-I.

4.1 Utilization of 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 along with the possible utilization options.

The Indian Standards IS-383: 2016 of the Bureau of Indian Standards on "Specifications of Coarse and Fine Aggregates for Concretes" permits use of aggregates other than natural sources including slags as given at Annexure-A of said standards. Engineering quality requirements of aggregates are specified in main document.

5.0 Guidelines for management of pyro-metallurgical copper slags:

i.) Smelter units shall use best available options for maximising internal use and recovery of resource material from slags.

ii.) Smelter units shall adopt appropriate cooling/quenching/treatment techniques to maximise recovery of resource material from slag. Further, the unit shall install facilities for recovery of copper and other metals from slags such as grinding, gravity separation, flotation based separation, hydro-metallurgical process etc.

iii.) The residual copper in slags prior to disposal or further utilization shall preferably be less than 0.8% by dry-weight and shall not exceed 1.2%.

If the slag is processed for recovery of remaining metals by adopting hydrometallurgical/chemical processes, the residual material shall undergo TCLP test as per Schedule-II of Hazardous and Other Wastes (Management and Transboundary Movement) Rules 2016 to determine disposal pathways.

iv.) Smelter units shall adopt environmental friendly practices in collection, handling, storage and transportation of copper slag.

v.) Smelter units shall have environmental policy for continuous improvement by adopting cleaner / new techniques. Environment management should be supervised by senior management.

vi.) Un-utilizable waste slag shall be stored in captive landfill having impermeable base and garland drain, to prevent the soil and water/groundwater contamination. Units shall not store un-utilised or waste slag in unlined landfills beyond one year from date of issuance of these guidelines.

vii.) A new landfill for waste slag storage having a single layer of geo-membrane of thickness 1.5 mm over a compacted clay along with drainage and leachate collection system is recommended.

viii.) All units shall monitor the ground water quality around storage area during pre and post monsoon seasons through a recognised laboratory (under the Environment (Protection) Act, 1986 or any NABL Accredited) for assessment of the contamination (if any) and such assessment reports shall be submitted to respective SPCB/PCC annually.

ix.) After recovery of copper, slag from pyro-metallurgical route may be used in following areas subject to meeting the quality requirement/standards.

   i. Abrasive materials
   ii. Aggregate in cement-concrete
   iii. Cement-concrete blocks/bricks/tiles
   iv. Cement Production
   v. Construction of subsurface for Construction of roads / railways

x.) Industry intending to utilise copper slag for any other purpose, not mentioned above may submit the proposal along with relevant details to CPCB through the respective SPCB/PCC with their assessment and recommendations for permitting the same by SPCB/PCC.

xi.) Industry shall maximize external use or recycling of slag which cannot be used or recycled internally. Industry shall take steps to achieve 100% slag utilization for current generation, with effective from the F/Y 2024-25. Thereafter, the maximum allowable storage of fresh slag at any point of time shall not be more than 03 months' generation.

xii.) Smelter units shall take steps to utilise the legacy slag stored in industry premises within two years.

xiii.) Industry should submit the annual report on generation, quantity stored, quantity utilized and the concerned usage, and disposal as per format given in Annexure–II, or on online waste reporting portal as and when developed by CPCB, by 30th June of the following year to SPCB/PCC and CPCB.

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Annexure – I

Some of the international practices for utilization of Copper Slag

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.

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

Annexure – II

Format for Reporting Annual Generation, Storage, Utilization and Disposal

1. Name and Address of the Plant
2. Contact Person Responsible for Management of Copper Slag
   a) Name and Designation:
   b) Mobile Number:
   c) Email ID:

Financial year	Slag Type*	Opening Stock(in MT)	Quantity Generated after Cu recovery during the F/Y (in MT)	Utilised during the financial year (in MT)		Slag stored at the end of the financial year (in MT)
				Quantity	Usage Type	
	(a) Primary smelter Slag					
	(b) Flash Smelter slag					
	(c) Converter Slag / Dore Furnace slag					
	d) Other slag (pl specify)					

*****As applicable*