Guidance on Classification of Copper Concentrates for MHB

The aim of the International Maritime Solid Bulk Cargoes (IMSBC) Code is to ensure safe maritime transport of solid bulk materials. Specific criteria to identify Materials Hazardous only in Bulk (MHB) were adopted in the 2013 amendment to the International Maritime Solid Bulk Cargoes code (IMSBC 02-2013) through resolution MSC.354(92).

The assessed hazard classes, relevant to MHB are:
- Combustible solids
- Self-heating solids
- Solids that evolve into flammable gas when wet
- Solids that evolve toxic gas when wet
- Toxic solids
- Corrosive solids

To support the global copper industry in meeting its obligations, the International Copper Association has completed an initial assessment of the hazard characteristics of copper concentrates relevant to MHB. Information on chemical identity (mineral and elemental composition) and particle size distribution was combined with the results from solubility tests and UN tests, assessed for representative concentrates. The assessment, compliant with MSC.354(92), includes methodologies and data that have been used to assess copper concentrates under the UN's Global Harmonized System and IMO HME. This information can be used by companies as a guidance for future MHB classifications. The assessment of the specific concentrates is to be done on a case by case basis.

The baseline assessment, summarized below (Annex [1]), indicates that 30% of the copper concentrates may meet the requirements to be classified as toxic solids and therefore MHB, due to the presence of minor elements (especially lead but in some cases also cadmium, arsenic and/or nickel). For such concentrates, information on the solubility/bio-accessibility of these metals present may refine the classification outcome. Further work related to assessment of some of the MHB endpoints (corrosive solids, solids that evolve into flammable gases when wet and solids that evolve toxic gas when wet) is needed.

Dr. Katrien Delbeke, Director Health, Environment & Sustainable Development

In Co-operation with
Dr. P. Rodriguez, Universidad Adolfo Ibanez. Faculty of Engineering and Science, Santiago, Chile
Dr. C. Oates, Apllied Geochemistry Solutions,UK

8 December 2014

[1] The assessment made is focused on the metal/minerals and does not take into account chemicals used to produce the concentrates. The influence of these chemicals on the classification of the concentrate should be assessed by the companies.

Annex 1: Summary of the guidance relevant for the classification and assessment of substances as Materials Hazardous in Bulk (MHB).

The classification assessment procedure was carried out following the guidelines and criteria laid out in United Nations Recommendations on the Transport of Dangerous Goods, and the amendment to the International Maritime Solid Bulk Cargoes code (IMSBC 02-2013), adopted through resolution MSC.354(92). To account for the specificities related to the testing of ore and metal concentrates, the methodology is consistent with the 2014 ICMM guidelines "Hazard assessment of ores and concentrates for marine transport"[2]. The assessment made is focused on the metal/minerals and does not take into account chemicals used to produce the concentrates. The influence of these chemicals on the classification of the concentrate should be assessed by the companies.

1. Copper concentrates manufacturing process

Copper concentrates are mainly produced by flotation. The ore is crushed and milled to a particle size of less than 100 µm. This produces a mix of particles containing pure phases of primary or secondary copper sulfides. The ground ore is mixed with water and reagents, to form a slurry, where the copper sulfide mineral particles bind to the reagent, rendering a hydrophobic complex. Submitted to aeration, this complex binds preferentially to the air bubbles and floats to the surface producing a highly enriched, copper sulfide froth that can be skimmed off the top. This then passes through a cleaning process to remove unwanted impurities. In some cases, the concentrate is submitted to an additional processing step to extract a by-product (e.g. molybdenum sulfide). Finally, the copper concentrate is dried ready for transportation to the next step (smelting). The copper concentrate production process does not involve any chemical modification of the original ore body.

2. Chemical Identity –information on ingredients

The composition of copper concentrates was assessed for 122 samples, covering the world-wide copper concentrates production (table 1 and 2). Copper concentrates are dominated by copper, iron and sulphur. These elements are incorporated in sulphidic minerals such as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), diginite (Cu9S5), covellite (CuS), chalcocite (Cu_2S).

Other major elemental constituents (Al, Ca, Mg, K, Si, Mn) are incorporated in minerals, usually defined as 'gange", such as calcite, dolomite, hornblende, quartz, chlinochlore, feldspar, kaolinite, biotite...

Copper concentrates may also contain small amounts of zinc, lead, arsenic, nickel, cobalt, silver. These metals are incorporated in distinct minerals such as sphalerite (ZnS), galena (PbS), enargite (Cu_3AsS_4), arsenopyrite (FeAsS).

The reported water content of the final concentrate, transported, typically varies between 7 and 10% water.

Mineral	Min	50^{th}P	60^{th}P	70^{th}P	80^{th}P	90^{th}P	Max
Tennantite	0.00	0.00	0.00	0.00	0.08	0.71	5.80
Tetrahedrite	0.00	0.00	0.00	0.00	0.00	0.27	5.50
Copper (II) oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.15
Enargite	0.00	0.00	0.00	0.00	0.00	0.08	25.00
Arsenopyrite	0.00	0.00	0.00	0.00	0.00	0.02	2.50
Galena	0.00	0.10	0.30	0.70	1.50	3.90	15.00
Quartz	0.00	2.10	3.00	4.27	7.00	9.95	30.00
Chalcocite	0.00	0.00	0.43	1.13	3.05	7.97	44.32
Sphalerite	0.00	0.80	1.20	4.40	5.96	8.00	18.84
Bornite	0.00	0.13	1.08	3.73	6.10	15.06	42.10

[2] http://www.icmm.com/publication/hazard-assessment-ores-and-concentrates

Digenite	0.00	0.00	0.00	0.00	0.00	0.00	4.70
Chalcopyrite	0.00	63.00	67.50	73.00	77.50	81.20	85.00
Covellite	0.00	0.00	0.42	0.84	1.72	3.77	25.00
Anglesite	0.00	0.00	0.00	0.00	0.00	0.00	6.00
Pyrite	0.09	12.73	16.14	18.82	20.37	30.05	55.30

Table 1: Mineralogical composition of 110 copper concentrates. Only minerals present in more than 5 samples are reported.

	Cu	Sb	As	Zn	Pb	Ni	Ag	Cd	Co
Min	14	0	0	0	0	0	0	0	0
50thP	26.7	0.01	0.12	0.65	0.14	0.003	0.007	0.005	0.01
60thP	27.6	0.02	0.15	1.4	0.27	0.005	0.01	0.007	0.013
70thP	28.5	0.024	0.19	2.9	0.57	0.01	0.013	0.01	0.02
80thP	30	0.05	0.3	3.67	1.49	0.011	0.021	0.015	0.03
90thP	34	0.12	0.52	5.63	3.01	0.032	0.072	0.026	0.04
Max	51	7.25	7.5	9.28	12.71	0.83	1.91	0.07	0.25

Table 2: Elemental composition of world-wide copper concentrates (n= 120)

3. Physical and chemical properties

The physico-chemical properties are summarized below

Appearance	Solid, grey powder (particle sizes : see below)
Odour	Odourless
Odour threshold	Not applicable because odourless
pH	Some concentrates are slightly acidic with recorded pHs between 4 and 8
melting point	900-1170°C
Initial boiling point and boiling range	Not applicable because solid melting above 1000°C
Flash point	Not applicable to inorganic solid
Evaporation rate	Not applicable (solid)
Vapour pressure	Not applicable (inorganic solid melting above 300°C)
Vapour density	Not applicable (inorganic solid melting above 300°C)
Relative density	Range from 3.5-4.7 g/cm3 at 20°C (from 18 copper concentrates)
Solubility(ies)	Sparingly soluble in water
Partition coefficient n-octanol/water	Not applicable to inorganic substances. Decomposition and/or melting starts above 900°C.
Oxidising properties	Not classified under UN O.1, based on chemistry (inorganic solid) and some company data in accordance to the UN test

4. Particle size

Copper concentrates have particles sizes <100 µm. Table 3 summarizes the particle size distributions of 23 copper concentrates and concludes on a typical median particle diameter of 27 µm. The respirable fraction (<10µm) is typically less than 33%.

Particle size distribution	Range	10th P	50th P	90th P
D50 - µm	6-80	16	27	55
<10 µm – volume based %	5-71	18	24	33

Table 3: Summary of the particle size distribution measured (usually by laser diffraction) in 23 copper concentrates (D50 = median diameter; P = percentile).

5. MHB physico-chemical hazards assessment

Combustible solid:

5 copper concentrates, with varying physico-chemical characteristics (chalcopyrite as well as Bornite/chalcocite dominated concentrates), were subjected to a test in accordance to the United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria – United Nations Manual of Tests and Criteria, part III, 33.2.1.4.3.1 (Test N.1).

From the tests it was concluded that these copper concentrates are not readily combustible substances of Division 4.1. and are not a Material Hazardous only in Bulk (MHB) of the IMSBC Code

Solid – self-heating:

5 copper concentrates were subjected to a test in accordance to the United Nations Recommendations on the Transport of Dangerous Goods According to United Nations Manual of Tests and Criteria, part III, 33.4.1.4.3.5 (Test N.4)

From the tests, it was concluded that none of the tested copper concentrate show signs of exothermic activity during the first trial, and therefore they are not subject to transportation restrictions of UN Class 4 Division 4.2 nor does it meet the criteria to be classed as a Material Hazardous only in Bulk (MHB) of the IMSBC Code.

Solids that evolve into flammable gases when wet:

No test was carried out. The substance is manufactured with water and the final product contains 7-10% water whereby long term experience may or may not indicate the production of flammable gases. The outcome is therefore not considered as conclusive.

Solids that evolve toxic gas when wet:

No test was carried out. Copper concentrates contains up to 43% sulphides. These may slowly react with water and generate H_2S, being toxic by inhalation – acute 2. The outcome is therefore not considered as conclusive.

6. MHB Human Health hazards assessment:

The amendment to the International Maritime Solid Bulk Cargoes code (IMSBC 02-2013) adopted through resolution MSC.354(92) identifies that materials that have toxic hazards to humans if inhaled or when in contact with skin when loaded, unloaded, or transported in bulk shall be classified as MHB.

A material shall be classified as MHB – toxic solid, in accordance with the criteria laid down in GHS

- GHS Acute Toxicity Dusts Category 4 [3]

[3] Concentrates classified as categories 1 to 3 are considered as dangerous goods (IMDG)

- GHS Specific Target Organ Toxicity Single Exposure Inhalation Dust Category 1
- GHS Specific Target Organ Toxicity Repeated Dose Inhalation Dust Category 1
- GHS Acute Toxicity Dermal Category 4 [3]
- GHS Specific Target Organ Toxicity Single Exposure Dermal Category 1
- GHS Specific Target Organ Toxicity Repeated Dose Dermal Category 1
- GHS CMR Category 1A and 1B

A hazard evaluation was carried out considering the hazardous properties of the constituents.

The dominant minerals (median values above >1%) in copper concentrates are copper sulphides (chalcopyrite (63%), pyrite (11%), quartz (2%) and "gange". Their hazard profiles are summarized as:

- The hazard profile of copper and copper compounds, available from the OECD SIDs Initial assessment Report summary (SIAP on copper and copper compounds, 2014) and the REACH dossiers, concludes
  - No acute oral, dermal nor acute inhalation toxicity of copper sulphides.
  - No concern for repeated dose toxicity (STOT), genotoxicity, reprotoxicity and carcinogenicity for copper containing materials.
- Pyrite is a benign iron containing mineral with no known hazards.
- Quartz, a crystalline silica, is present at a median concentration of 2% with a 90th percentile of 10% (table 1). Respirable quartz is classified as STOT-RE – cat 1 at 10%. The small probability of copper concentrates particles being respirable (3-11%), calculated based on detailed laser diffraction particle size analysis for 10 concentrates and SWERF[4], indicates that the presence of "respirable quartz" is usually expected to be below 1%. STOT-RE-cat 1 is therefore unlikely.
- Other major elemental constituents (Al, Ca, Mg, K, Si, Mn) are major elements of terrestrial environments and incorporated in other minerals called "gange": calcite, dolomite, hornblende, chlinochlore, feldspar, kaolinite, biotite. No hazards are attributed to these elements.

As indicated in tables 1 and 2, copper concentrate contain minor amounts of As, Cd, Co, Ni, Pb. The occurrence/concentration of these elements depends on the particular geochemistry of the originator ore body. Therefore the toxicity profiles of the copper concentrates were further assessed, considering the hazard profiles of the relevant metals/metal compounds (obtained from REACH dossiers), the potential release of the relevant metal ions in body fluids[5] and the GHS mixtures rules. This assessment was done using the MECLAS tool (http://www.meclas.eu) for 122 concentrates with known elemental/mineral composition.

From the assessment, the following conclusions are drawn for dry concentrates":

- GHS Acute Toxicity Category 1-4: only 1/122 classified as Cat 4 inhalation toxicity
- GHS Specific Target Organ Toxicity Single Exposure Inhalation Dust Category 1: none classified
- GHS Specific Target Organ Toxicity Repeated Dose Inhalation Dust Category 1: based on the worst case bio-accessibility (in gastric fluid), reported above, concentrates with lead content > 1.8 % Pb have the potential to be classified as Cat 1 [5].
- GHS Acute Toxicity Dermal Category 1-4: none classified
- GHS Specific Target Organ Toxicity Single Exposure Dermal Category 1: since metals are poorly absorbed through the skin (REACH dossiers), the potential for dermal toxicity is expected to be limited.

[4] http://www.ima-europe.eu/content/swerf-method-quantify-fine-fraction-of-cs-bulk-material

[5] The worst case bio- accessibility factors measured from 10 concentrates, in the worst case body fluid (gastric fluids, pH 1.5) were used for the initial assessment : As (2%), Cd (14%), Co (4%), Ni (11%), Pb (57%).

- GHS Specific Target Organ Toxicity Repeated Dose Dermal Category 1: since metals are poorly absorbed through the skin (REACH dossiers), the potential for dermal toxicity is expected to be limited.
- GHS CMR Category 1A and 1B:
    - Mutagenicity Cat 1 are not expected (none of the concentrates assessed demonstrated a potential for mutagenicity cat 1).
    - Carcinogenicity Cat 1: the assessment showed that even when considering the worst case bio-accessibility factors, the potential for a carcinogenicity cat 1 classification is very limited (4% of the samples had a marginal exceedance due to Cd, Ni or As).
    - Reproductive toxicity Cat 1: based on the worst case bio-accessibility (in gastric fluid), reported above, concentrates with lead content > 0.53 % Pb have the potential to be classified for reproductive toxicity Cat 1.
- Based on the information of the mineral constituents, additional hazard classes, relevant to the MHB category (corrosive solids-see below) were assessed:
    - Based on the information of the mineral constituents, and using the MECLAS tool (http://www.meclas.eu) in accordance to the GHS guidance (2011), respiratory sensitization cat1, skin corrosion/irritation cat 1 or cat 2 or eye damage/irritation cat 1 or 2 is not expected.

Lead is therefore a main driver for the CMR property of copper concentrates and thus a potential main driver for its MHB property. For lead, reproductive toxicity is a consequence of systemic toxicity induced by oral or inhalation exposures.

7. Corrosive solids – corrosive to metals:

5 copper concentrates, with varying physico-chemical characteristics (chalcopyrite as well as Bornite/chalcocite dominated concentrates), were subjected to a test in accordance to the United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria (Test C.1).

This test is described as a "Test for determining the corrosive properties of liquids and solids that may become liquid during transport as dangerous goods of Class 8, packing group III". Some evidence of corrosivity has been found and it is under research.

From the currently available information it can been concluded that some copper concentrates may be classified as MHB due to the presence of minor constituents classified as toxic solids (STOT-RE, carcinogenicity or reproductive toxicity). The potential of copper concentrates to be corrosive or to be classified as solids that evolve into flammable gases when wet and solids that evolve toxic gas needs further investigation.

More information from: Dr. Katrien Delbeke, Director Health, Environment & Sustainable Development
European Copper Institute, Avenue de Tervueren 168 b-10, B-1150 Brussels.
Tel: +32 2 777 7083
katrien.delbeke@copperalliance.eu