MARPOL annex V Classification as “harmful to the marine environment”

Copper granules transported in bulk

IMSBC defines copper granules as:

DESCRIPTION: Sphere shaped pebbles. 75% copper with lead, tin, zinc, traces of others. Moisture content 1.5%approximately.

The assessment below is for particles containing 96-99.9% copper and does not address classification needs related to presence of trace elements such as lead, zinc.

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Abstract

It is proposed to consider the following classification of pure copper granules, transported in bulk, under MARPOL annex V

- granules with particle diameter >1 mm (specific surface area <0.67 mm2/mg) : NON-HME[1]
- granules with particles diameter <1 mm (specific surface area > 0.67 mm2/mg) : HME or NON-HME . The HME or NON-HME characterisation of such granules/powders depends on the surface area and can be accessed from application of the surface-specific release rates (data from Rodriguez et al., 2011 and 2012) or from novel transformation/dissolution tests on the bulk cargo material.

1. Introduction

This document provides an overview of the justification for the HME/non HME classification of copper in granulated/ powder forms.

The environmental and human health CLP (EU-GHS) hazards of copper and copper compounds have been assessed during the copper risk assessment. The Copper Voluntary Risk Assessment (VRAR), produced between 2000 and 2008 was peer reviewed by the Rapporteur Member State (Italy) and then underwent in-depth discussion and critical review by the EU Member States at the Technical Committee for New and Existing Substances (TCNES) of the European Commission. This dossier and the critical review and acceptance by Member States, the European Commission and the independent EC Scientific Committee for Health and Environmental Risk (SCHER) are available from *http://echa.europa.eu/chem_data/transit_measures/vrar en.asp)* .

The REACH Copper Consortium has integrated the data and conclusions from this copper VRAR into the copper Reach joint registration dossier. The copper REACH dossier differentiates three groups of materials with distinct properties.

- Copper massive forms: > 99.9 Cu°; sphere granules ≥1 mm diameter; specific surface area ≤ 0.67 mm^2/mg
- Copper powders: 99.7% Cu (depending on the particle size); particle size 10 µm to <1 mm; specific surface area of representative fine powder: 107 mm^2/mg
- Coated copper flakes: 96% Cu°, up to 3% Cu_2O; up to 3% stearic acid; particle sizes 5 to 100 µm; specific surface area of representative coated flakes > 2,000 mm^2/mg

Copper in massive forms, copper powders and coated copper flakes are produced by separate processes. Through the specific “coated copper flakes” process, fine flakes, characterized by a high specific surface area and organic coating, are produced. The normal handling and use of copper massives and powders do not produce such flakes.

COPPER POWDERS AND COPPER MASSIVE FORMS MAY BE TRANSPORTED IN BULK.

[1] HME = harmful to the marine environment, according to the criteria outlined in MARPOL annex V

Toxicity/ecotoxicity data are available on soluble copper compounds and coated copper flakes. (copper risk assessment report[2], copper reach registration [3]). The data clearly show that the "free copper ions" are responsible for the observed toxicity/ecotoxicity. Read across between copper-containing materials, is therefore based on information on particles size, surface area and copper-ion release data, and obtained from standard transformation/dissolution tests and bio-elution tests.

2. Environmental classification

The proposals for environmental classification of the copper forms, discussed below, follow the GHS guidance. They are based on defined acute and chronic toxicity thresholds. Special guidance is available for the environmental classification of metals and metal compounds.

- In accordance with the revised CLP and GHS guidance (CLP, 2012 and GHS 2013), ecotoxicity data of soluble inorganic compounds are combined to define the ecotoxicity reference value (ERV) of the metal ion under consideration.
- Classification of sparingly soluble metal and metal compound is based on comparing the soluble metal- concentration, measured after Transformation/Dissolution (T/D), with the ecotoxicity reference values of the corresponding soluble metal ion.

Accordingly, for the classification of the copper forms:

- To define the acute and chronic ERVs for the soluble copper compounds, all high quality data from tests performed with soluble copper compounds were combined and expressed as soluble copper concentration (mg dissolved Cu/L).

- To determine the acute and chronic environmental classification of copper metal in massive or powder forms, transformation/dissolution tests (OECD nr29, GHS Annex 10) were performed and used as appropriate.

2.1. Derivation of ecotoxicity reference values (ERV) of Copper-ions[4]

Relevant ecotoxicity data for acute and chronic effects for soluble copper compounds were compiled and the results (L(E)C_{50}, EC_{50}, NOEC/EC_{10} values) were expressed as soluble Cu^{2+}. After a data quality assessment (e.g. dose-response relationship, measured test concentrations) and applying relevance criteria (e.g. standard OECD species, endpoints, test durations and test media (pH between 5.5 and 8.5), the high quality acute L(E)C_{50} values and chronic NOEC/EC_{10} values were retained.

Acute reference values for classification

451 high quality acute data points were retained.

- For the algae, 66 individual data points for 3 standard species (*Pseudokirchnerella subcapitata, Chamydomonas reinhardtii* and *Chlorella vulgaris*).

[2] http://echa.europa.eu/chem_data/transit_measures/vrar_en.asp)
[3] Copper Reach registration available from the ECHA website
[4] More details in Van Sprang and Delbeke, 2010 (attached to the IUCLID "endpoint summary – ecotoxicological information"

- For the invertebrates, 123 individual data points for 2 standard species (*Ceriodaphnia dubia* and *Daphnia magna*)
- For the fish, 262 individual data points for 5 standard species (*Oncorhynchus mykiss*, *Pimephales promelas, Lepomis macrochirus, Brachydanio rerio* and *Cyprinus carpio*).

Chronic reference values for classification

90 high quality chronic data points were retained:

- For the algae/aquatic plants, 33 individual data points for 4 standard species (*Raphidocelis subcapitata, Chlorella vulgaris, Chlamydomonas reinhardti* and *Lemna minor*).
- For the invertebrates, 23 individual data points for 2 standard species (*Ceriodaphnia dubia, Daphnia magna*).
- For the fish, 34 individual data points for 3 standard species (*Oncorhynchus mykiss, Pimephales promelas* and *Salvelinus fontanilis*).

The lowest species-specific acute $L(E)C_{50}$ and chronic NOEC/EC10 values, at the three pH levels and across pHs, were selected as final environmental classification reference values. Geometric mean values were calculated if more than 4 data-points were available for the same species/endpoint. The derived acute and chronic reference values for soluble Cu^{2+} are provided in Table 1.

Table 1: Acute and chronic reference values for soluble copper ions

pH range	**Acute ERV $L(E)C_{50}$ (mg Cu/L)**	**Chronic ERV NOEC (mg Cu/L)**
pH 5.5-6.5	0.025	0.020
pH >6.5-7.5	0.035	0.0074
pH >7.5-8.5	0.0298	0.0114
Across pHs	0.0344	0.0149

The classification of copper metal will depend on its maximum solubility (at the relevant pH), which will in turn depend on its physico-chemical form (massive, powder, coated flakes or compounds) and evidence for rapid degradability.

2.2. Transformation dissolution data and resulting environmental classification

Copper metal (Cu°) is insoluble and needs to be transformed to solubilised species in order to produce an effect to the aquatic environment.

In accordance with the GHS and EU CLP classification system, evaluation of the short term and long term aquatic toxicity for copper powder and copper massive forms is accomplished by comparison of:

(a) The concentrations of the metal ions in solution, produced during transformation and/or dissolution in a standard aqueous medium at different pHs and times, with

(b) Appropriate standard ecotoxicity reference values as determined from tests carried out with the corresponding soluble metal species (acute and chronic values).

2.2.1. Copper in massive form (Particle size >1 mm)

Rodriguez *et al*., 2007 assessed the need for classification of pure massive copper materials and tested, during 7 and 28 days Transformation/Dissolution (T/D) tests, copper releases from copper wire pieces (99.9% purity) with varying diameters. The tests were carried out with various mass loadings (1-100 mg/L), surface area loadings (1-281 mm^2/L) and covering pH 6, 7 and 8. The data demonstrate that copper ion releases during transformation/dissolution tests are dependent on the pH and the exposed surface loading (Figure 1)[5]

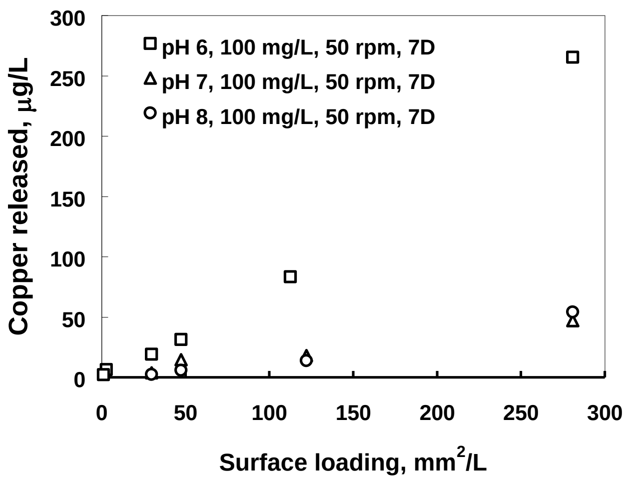

Figure 1: Copper release from 7days transformation/dissolution of various copper wire pieces, at different surface loadings and pHs (Rodriguez et al, 2007).

Since the GHS and CLP agreed on a default value of 1 mm particles for the massive classification, the specific surface loading applicable to a 1 mm copper particle (density of 8.9 $g.cm^3$) at 1mg/L was calculated as 0.67mm^2/L. The surface loading approach avoids issues associated with the selection of a given particle type, or preparation of particles specifically for classification purposes (non-commercial particles), and allows easy and precise measurements of the surface area.

To ensure consistency with the GHS guidance (stirring at 100 rpm, without causing abrasion of particles), Rodriguez *et al*., 2011 and 2012 applied specific non-abrasion devices: copper wires mounted in polypropylene disks and copper massive samples mounted in epoxy. The lowest coefficient of variation (and somewhat higher releases) were obtained for copper massive samples mounted in epoxy (Figure 2).

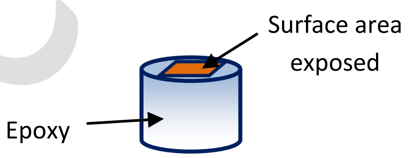

Figure 2: Massive samples mounted in epoxy

The resulting copper releases (Rodriguez *et al*., 2012) from particles of 1 mm at pH 6 and loading of 1 mg/L, (surface loading of 0.67 mm^2/L) are:

[5] Some particle abrasion was observed at high stirring rates (>50 rpm)

- 1 µg dissolved Cu/L released after 7 days T/D tests (copper release rate of 1.5 µg Cu/7 days.mm^2)
- 3.4 µg dissolved Cu/L released after 28 days T/D test at 1mg/L (copper release rate of 5.0 µg Cu/28 days. mm^2)

These releases (Rodriguez *et al*., 2012) are retained for the classification of copper massive and the following conclusions can be drawn:

Aquatic Acute classification for copper massive:

- Worst case release rates are observed at pH 6.
- The ratio between the 0.001 mg/L copper release after 7 days T/D, at a loading of 1 mg/L at pH 6, and the acute ERVs (0.025-0.035 mg dissolved Cu/L) is <1.
- This does not trigger acute classification.

Aquatic Chronic classification for copper massive:

- The ratio between the 0.0034mg/L copper release, after 28days T/D, at a loading of 1 mg/L and pH 6, and the acute ERVs (0.007 - 0.020 mg dissolved Cu/L) is <1.
- This does not trigger chronic classification.

Copper massive (particle diameter $\geq$ 1mm, SA $\leq$ 0.67 mm2/mg) do therefore NOT merit to be classified for aquatic hazards nor HME classification under MARPOL annex V.

2.2.2. Fine Copper powders

As described above, metallic copper (Cu°) is insoluble and needs to be transformed to solubilised species in order to produce an effect to the aquatic environment. The transformation/dissolution rate of metallic copper is pH dependent with higher release rates at lower pH (Rodriguez et al., 2007).

Following the surface loading approach, copper release rates for reasonable worst case powder surface loadings were assessed for the classification of copper powders at 1 mg/L mass loading. Different data-sets are available:

- Skeaff and Hardy, 2005 performed T/D tests (7 days at pH6) on a fine representative copper powder sample (107 mm^2/mg, measured by BET)) at loadings of 1 and 100 mg/L.
- Surface area-specific release rates, measured by Rodriguez et al., 2007 , 2011, 2012, applied to the measure surface area of copper powders.

The results on copper releases from the T/D of *the finest powders put on the market*, using measured data and calculated from surface-specific release equations obtained by respectively Skeaff and Hardy (2005) and Rodriguez *et al*. (2007 and 2011), are summarised below. The table also provides the ERVs of the soluble copper ions.

Transformation/dissolution of fine copper powders						
loading (mg/L)	**loading (mm^2/L)**	**Time (Days)**	**mg dissolved Cu/L**			**comment**
			At pH 6	**At pH 7**	**At pH 8**	
1	47 - 107	**7**	0.082	**-**	**-**	Direct results of T/D of fine copper powder[6] from Skeaff and Hardy, 2005.
1	67.5	7	0.098	-	-	Calculated T/D of 10 µm powder[4] from $C^{168}_{Cu(aq)} = 8.9246\ A^{0.5694}_{calc}$ (Skeaff and Hardy, 2005) See discussion below.*
1	67.5 – 107	7	0.078-0.123	0.013-0.021	0.009-0.014	Calculated T/D of 10 µm powder [4] from surface area-specific releases (Rodriguez *et al*., 2007).
1	67.5 - 107	7	0.028-0.044	-	-	Calculated T/D of 10 µm powder from non-abrasive T/D tests at 47 mm^2/L, pH 6 , 0.41 µg Cu/mm^2 (Rodriguez *et al*., 2011)
Additional data:						
LC_{50}			0.025	0.035	0.0298	

[4] Includes abrasion of the particles observed

The ratio between the soluble copper ion releases from T/D tests (at 7 days) and the acute ERV of the dissolved copper ions results in the following classification outcome:

Aquatic Acute classification for fine copper powders:

- The ratio between the copper release, after 7 days T/D at a loading of 1 mg/L at pH 6 (0.028 - 0.098 mg dissolved Cu/L), and the acute ERV (0.025 mg dissolved Cu/L) triggers environmental classification as Acute 1, M factor 1.
- The ratios between the copper releases after 7 days T/D (Rodriguez et al., 2007), at a loading of 1 mg/L at pH 7 & 8 (0.013 - 0.021 and 0.009 - 0.0014 mg dissolved Cu/L), and the pH specific acute ERVs (0.035 and 0.030 mg dissolved Cu/L) are <1. The release data at pH 7 and 8 include particle abrasion.
  The pH 6 data leads to the highest classification outcome and are retained for the final proposal.

Conclusion copper powder:

Fine copper powders (10 µm particles, specific surface area >67 mm2/mg). require classification as Aquatic Acute 1 with M-factor 1 and therefore triggers HME classification[7].

[7] Information of chronic classification is therefore not relevant

The acute and chronic classification of coarser granules (between 10 µm and 1mm) can be assessed on a case by case basis, using the surface-specific release rates determined by Rodriguez et al., 2011 and 2012 or performing transformation/dissolution tests on the cargo material transported[8].

3. Human health Classification Proposals

The RA report[9] and REACH joint registration dossiers concluded that copper in the form of soluble copper compounds (eg $CuSO_4$) do not merit to be classified as CMR nor STOT.

Therefore, human health classification is not a trigger for HME for copper nor copper compounds

4. Overall conclusions classification

Copper is not a CMR nor STOT-RE and therefore, these endpoints do not trigger classification as "Harmful to the marine environment" under MARPOL annex V

With regard to the environmental endpoints, the data show that

- Copper granules with particle size >1 mm (and specific surface < 0.67 mm2/mg) do not merit environmental classification and can thus be characterised as NON-HME
- fine powders where specific surface is > 67 mm2/mg do merit classification as aquatic –acute 1 and can thus be characterised as HME
- the classification of coarse granules can be assessed on a case by case basis, using the release rates determined by Skeaff and heady, 2005 or Rodriguez et al., 2007- 2012 or by performing transformation/dissolution tests on the cargo material transported.

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[8] For assessing chronic classification, information on "rapid degradability" may also be needed

[9] *http://echa.europa.eu/chem_data/transit_measures/vrar en.asp)*

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