



Addressing aquatic hazard classification for metals, metal compounds and alloys in marine systems



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ABSTRACT

New International Maritime Organization regulations require shippers to classify all solid bulk cargo to indicate whether they are Harmful to the Marine Environment (HME). The objective of this work was to adapt the freshwater Transformation/Dissolution Protocol (T/DP) to marine water to provide a method to determine, when compared with marine Ecotoxicity Reference Values (ERVs), whether a metal-bearing substance is HME. The substances examined were: Cu₂O powder; Ni metal powder; Co₃O₄ powder; and a Ni–Co–Fe alloy, as wire cuttings, which were the same substances examined in the freshwater T/D validation study and afforded comparisons of the reactivity, or measure of the rate and extent of metal release from the metal-bearing substances in freshwater versus marine conditions. The marine T/D method is suitable for conducting examinations of metal-bearing substances with a wide range of reactivities, from the relatively reactive Cu₂O powder and the alloy to the Co₃O₄ powder, which was the least reactive.

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1. Introduction

The International Maritime Organization (IMO) is the United Nations (UN) technical agency with responsibility for the safety and security of shipping and the prevention of marine pollution by ships. Covering all aspects of international shipping, including ship design, construction, equipment, manning, operation and disposal, its main role is to create a regulatory framework for the shipping industry that is universally adopted and implemented. Recent amendments to Annex V of its International Convention for the Prevention of Pollution from Ships (MARPOL) are currently being phased in (IMO, 2012). The revised Annex V provides that the discharge of garbage into the sea is prohibited, with limited exceptions. These exceptions include discharge into the sea of food wastes, animal carcasses, cleaning agents and additives contained in hold washwater, deck and external surface washwater and cargo residues which are not considered to be Harmful to the Marine Environment (HME).

Cargo residues are included in the definition of garbage and are considered HME if they are residues of solid bulk substances which are classified according to both environmental and human health criteria of the UN Globally Harmonized System for Classification and Labelling of Chemicals (GHS). The environmental endpoints for HME classification are Acute Aquatic Toxicity Category 1; and/or Chronic

Aquatic Toxicity Category 1 or 2. Under the new rules, cargoes classified as HME need adequate port reception facilities to collect and properly treat the wash water (IMO, 2012) prior to discharge.

Developed within the framework of the Organization for Economic Cooperation and Development (OECD, 2001), and adopted by the UN in 2002, the GHS is intended to provide a foundation for the safe management of chemicals in commerce (UN, 2015). The hazard classification scheme was developed with the purpose of identifying those chemical substances that present a hazard to the aquatic environment, both freshwater and marine. The hazard classification scheme for metals and metal compounds considers hazards posed by metals when they are available (i.e. exist as dissolved metal ions). The concentration of the metal ion which may be present in solution is largely determined by two processes: the extent to which the metal can be dissolved and the extent to which it can react with the media to transform to water soluble forms (UN, 2015).

The GHS criteria for establishing potential hazard to the aquatic environment are based on the substance's acute and chronic aquatic toxicity (UN, 2015). Annex 9 (A9.3.2.1) of the UN GHS states that "for classifying substances in the harmonized system, freshwater and marine species toxicity data can be considered as equivalent data... Since the purpose of classification is to characterize hazard in the aquatic environment, the result showing the highest toxicity should be chosen."

Annex 10 (A10.5.1.5) gives guidance on the Transformation/Dissolution (T/D) of metals and metal compounds in aqueous media. It states that "in addition to the fresh water medium, the use of a standardized marine medium may also be considered when the solubility or

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transformation of the metal compound is expected to be significantly affected by the high chloride content or other unique chemical characteristics of the marine waters and when toxicity test data are available on marine species." Annex 10 then provides the composition of a standard marine medium to be used in T/D examinations.

1.1. The Transformation/Dissolution Protocol and aquatic hazard classification

The T/D Protocol (T/DP) generates data to be applied within the UN GHS framework to derive hazard classification proposals for metals and inorganic metal compounds. It is designed to determine the rate and extent to which metals and sparingly soluble metal compounds can produce soluble, bioavailable metal species under conditions representative of those generally occurring in the environment (UN, 2015). The T/DP (described in detail in Skeaff and Beaudoin, 2014; Skeaff et al., 2006, 2008, 2012) is aimed at standardizing the principal laboratory variables such that the concentration of dissolved ion can be directly related to the loading of the substance added to the aqueous medium.

The OECD subjected the T/DP to a three-laboratory ring test freshwater validation exercise and accordingly declassified it in June, 2008. Subsequently, Skeaff et al. (2011) reported on the validation study, which revealed that properly equipped and operated laboratories can apply the UN T/DP to metal-bearing substances to yield acute and chronic classification outcomes that are reliable, consistent and in agreement.

The scheme works by comparing the dissolved (<0.2 µm) metal concentrations released from the substance at specified intervals under standard T/D conditions against the metal's acute Ecotoxicity Reference Value (ERV), which is the dissolved metal concentration required to induce mortality to 50% of the most sensitive environmental test species among fish, crustacea, and algae. Mass loadings of 1, 10 and 100 mg/L are weighed into freshwater media based on the OECD 203 medium for ecotoxicity testing (OECD, 1992) in the temperature range 20 °C to 23 °C with agitation, followed by sampling and analysing the solutions for the metals of interest. If the 1 mg/L loading delivers the dissolved metal ion concentration that meets or exceeds the ERV within 7 days, then the substance classifies as Acute 1, the most severe. The 10 mg/L loading applies to the Acute 2 classification and the 100 mg/L loading applies to Acute 3, the least severe. Corresponding Chronic 1, 2, and 3 classification levels are also established unless there is evidence of both rapid removal or partitioning from the water column and no bioaccumulation (UN, 2015). If a metal or metal compound classifies as Acute 1-Chronic 1, no further information can change the classification. If, however, a loading of 1 mg/L of a metal or metal compound classified at another level does not exceed the long-term no observable effects concentration (NOEC; or chronic ERV) over 28-d, then the Chronic classification is removed (UN, 2015).

1.2. Study objectives

The objective of this work was to adapt the freshwater T/DP to a synthetic marine medium to provide reliable and reproducible metal concentrations to determine, when compared with marine ERVs, whether a metal-bearing substance is potentially HME or not. Using the same substances examined in the freshwater T/D validation study (Skeaff et al., 2011) afforded the opportunity to compare the reactivity, or rate and extent of metal release from three metal-bearing substances (one metal, two metal oxides and an alloy) in freshwater versus marine conditions.

As other substances such as ores and concentrates that contain several elements of environmental significance may be examined in the future; the concentrations of a suite of analytes in all T/D solutions were determined to gauge the capability of the chelation method to remove trace metals from the marine medium to µg/L background concentrations. Low background concentrations are important when

deriving a chronic classification as chronic ERVs can be in the low µg/L range. Therefore a secondary objective of this study was to examine the extent µg/L background analyte concentrations in the reconstituted marine medium can be achieved.

2. Materials and methods

2.1. Substances

The substances examined in this study were the same as those examined in the OECD freshwater validation study (Skeaff et al., 2011): cuprous oxide (Cu₂O) containing 83.5% Cu; nickel metal (Ni) with typically 99.9% Ni; tricobalt tetraoxide (Co₃O₄) with a minimum of 71.0% Co (Co₃O₄ is 73.4% Co, so Co₃O₄ is minimum 97.6% purity); and a Ni–Co–Fe alloy with a composition of 29.5% Ni, 17.0% Co and 53.0% Fe. The first three substances were received as a powder and the alloy was in the form of cuttings from a 1-mm diameter wire in lengths ranging from 1 to 3.5 mm.

2.2. Aqueous medium

The composition of the synthetic marine T/D medium is given in Annex 10 of the GHS (UN, 2015) and contains the reagents NaF, Na₂SiO₃·9H₂O, SrCl₂·6H₂O, H₃BO₃, KBr, NaHCO₃, KCl, CaCl₂·2H₂O, Na₂SO₄, MgCl₂·6H₂O and NaCl in the concentrations listed in Table A1 in Appendix A (Supplementary Data). All reagents were carefully selected for their low trace metal contents and the marine T/D media was stripped of trace metals prior to use as required by the GHS. The marine T/D matrix has a salinity of 34 ± 0.5 g/kg and a pH of 8.0 ± 0.2. A synthetic marine medium is preferable over natural seawater, as the use of a standardized aqueous medium allows for comparable results among laboratories and also for logistical purposes as one T/D test requires approximately 20 L of marine medium.

The procedure to prepare the 20 L of the marine medium is described in Appendix B (Supplementary Data). Following preparation, the medium was filtered through a 90-mm Pall Life Science Supor-200 0.2 µm filter (VWR International) and, using a Toyo Pearl AF-Chelate-650M resin (Sigma-Aldrich), trace metals were removed. Details of this procedure are described in Appendix B.

2.3. Procedure and research scheme

A detailed description of the T/D procedure used in this work is given in Appendix B but in brief, approximately 48 h before the start of a set of tests, 1 L of the marine medium was transferred to each of acid-washed Schott Duran jars (VWR International) and the jars were placed in a refrigerated New Brunswick Anova 43 orbital shaker set at 100 rpm with the temperature controlled in the range of 20–23 °C. Air was bubbled through the solutions whilst the tests were running at a flowrate of 2 L/h.

At 0 h, the pH, temperature and dissolved oxygen (D.O.) concentration of the marine medium were measured (details of meters in Appendix B), and triplicate 12 mL solution samples were drawn from each jar with a syringe. These T/D solution samples were passed through a 0.8/0.2 µm Acrodisc filter (Canadawide Scientific), and acidified for preservation with two drops of Optima Ultrapure grade HNO₃ (68–71%) (Fisher Scientific), which lowers the pH to ~1.5. The respective substance loadings were then added to the jars.

As in the freshwater T/DP, each substance was examined at the 1, 10 and 100 mg/L loadings in triplicate (n = 3) and triplicate solution samples were taken at each sampling interval of 24, 48, 96, 168, 336, 504 and 672-h. At 2 and 6-h, a single sample was taken. The T/DP does not require the 10 and 100 mg/L loadings to continue until 672-h, but for this study, to observe the reactivities for the full test, all three loadings ran for 672-h. One procedural blank was run with each loading.

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