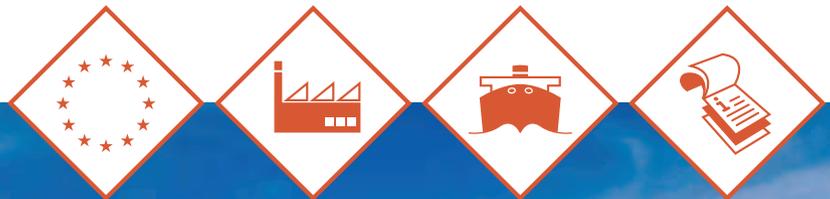


# Ores and Concentrates

An industry approach to EU Hazard Classification

M 2020



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The extraction and processing of mineral ores to create concentrates is the primary step in the life cycle of minerals and metals, and management of the chemical hazards and risks posed is an important part of an integrated approach to chemicals management in our sector. It is part of the industry's commitment to sustainable development and influences our social licence to operate and market the materials we produce.

Hazard classification and labelling is one of the first stages in ensuring that risks associated with production, transport and storage of ores and ore concentrates containing hazardous metal compounds are properly controlled. Companies are already beginning to deal with the new UN Globally Harmonised System (GHS) as it emerges in various regulations around the globe. Since there are many producers of ores and concentrates as well as huge variations in types of ores and concentrates, a number of challenges exist in identifying a workable way for our industry to agree scientifically robust and consistent classifications across commodities and business units.

The introduction of the new CLP Regulation ((EC) No 1272/2008), which applies the general principles of the GHS in the EU, means that producers of ores and concentrates will, for the first time, be required to officially notify hazard classification for these materials to a regulatory database. This will be the first major challenge faced by many companies and this document has accordingly been written specifically to address the requirements for classifying ores and concentrates which occur in nature (i.e. ores and concentrates prior to any chemical modification) for notification under CLP. However, the general framework can be applied to other systems of GHS providing the rules of particular national systems are taken into account as globally there are some significant differences.

Euromines and ICMM have prepared this general guidance for the industry based on consultation with member companies and commodity associations. While we recognize that classifying ores and concentrates is ultimately an individual company's responsibility, this guidance presents a framework that can be applied towards the goal of achieving a harmonized approach to classification.

**Corina Hebestreit**  
Director, Euromines

**R Anthony Hodge**  
President, ICMM

# 1. Introduction

Please note that throughout this document 'O&C' is used to denote 'ore and/or concentrate'



## 1.1 Background

Various emerging international chemical classification and labelling requirements for the protection of health and environment (e.g. GHS<sup>2</sup>, EU-CLP<sup>1</sup>) require a renewed understanding of the potential hazard associated with ores and concentrates (O&Cs). Determining human health and environmental classifications for O&Cs using GHS criteria raises unique issues that require special measures for accurate, realistic and consistent classifications.

### Ores and Concentrates under REACH

O&Cs are considered to be substances in the regulatory context of the European Union's REACH initiative, although as naturally occurring substances they are exempt from registration. However, O&Cs are more complex and less well-defined than most substances, making hazard identification and subsequent classification difficult.

O&Cs are unique in their nature and composition, given their inherent heterogeneity and variability and are identified under REACH as UVCB Sub-type 4 Substances<sup>3</sup> (Substance of Unknown or Variable composition, Complex reaction products or Biological materials). For further information on definitions and interpretation see the Eurometaux Fact Sheet on Identification of Materials for REACH.

April 2008, [www.reach-metals.eu/extranet/index.php?option=com\\_content&task=view&id=69&Itemid=98](http://www.reach-metals.eu/extranet/index.php?option=com_content&task=view&id=69&Itemid=98)

In general, the major challenges in determining GHS classification for O&Cs include:

### 1. Heterogeneity and spatial/temporal variability

Heterogeneity in mineral composition and physical form, and the variability imposed by an ore body, complicates precise product characterization. There are robust conventions emerging for defining O&C composition more accurately, such as listing constituents in mineralogical terms, rather than chemical (i.e. molecular) terms. Also, in defining product compositions for O&C, use of average/typical constituent compositions and ranges sufficient to address normal variability is important. In most cases, chronic, endpoint-specific data are lacking for O&Cs themselves as substances. Furthermore the variability in composition can sometimes limit broad extrapolation to other O&C due to cost, timing or feasibility of testing.

### 2. Presence of constituents in O&Cs currently classified as: dangerous for the environment; reproductive toxicant; mutagenic; and/or carcinogenic.

Often, the minor constituents ( $\geq 0.1\%$ ) of an O&C drive the most stringent classifications for these endpoints. It may not however be clear whether an O&C with these constituents embedded in a mineral matrix should in-fact be classified similarly for that hazard.

### 3. Mitigating factors

The bioavailability and toxicity of O&Cs are mitigated by the physical form of the particle, the mineral composition and structure (crystalline versus amorphous) as well as environmental and physiological variables. Dusts and powders for example pose different hazards than massive forms. Prevailing conditions (pH, electrolytes, ligands, redox in the environment; route of exposure, ADME<sup>4</sup> process in humans) can also influence hazard potential of O&Cs.

## 1.2 Objective and goals

The primary objective of this document is to provide broad guidance on the classification of O&Cs under EU-CLP. At this stage the guidance is intended to promote and trigger the continued development of sound and consistent approaches for the classification of O&Cs under GHS criteria generally.

<sup>1</sup> GHS Globally Harmonized System GHS, 2007. Globally Harmonized System of Classification and Labeling of Chemicals. United Nations, New York and Geneva.

<sup>2</sup> EU-CLP – CLP-Regulation (EC) No 1272/2008 – (European interpretation of GHS).

<sup>3</sup> The material is the result of a process-step, which is not considered to be a 'chemical modification'.

<sup>4</sup> ADME: absorption, distribution, metabolism and excretion.

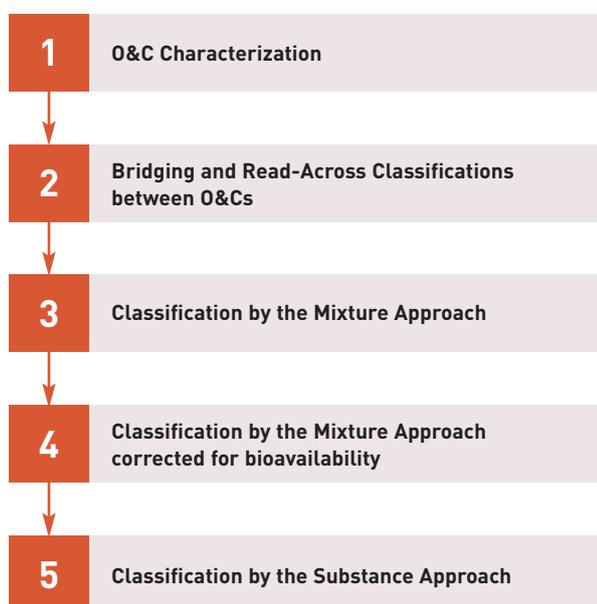
## 2. Hazard identification and classification of ores and concentrates



### 2.1 Conceptual outline

Accurate and realistic GHS classifications of ores and concentrates for both human health and environmental hazard classification of metals can be determined by following similar conceptual frameworks. These are illustrated in further detail later in this document. Both approaches follow the general conceptual scheme shown in Figure 1 and described in the following paragraphs:

**Figure 1: Conceptual overview for the hazard evaluation for O&Cs**



#### 1. O&C Characterization

Accurate characterization of the O&C composition, and existing data relevant to each GHS endpoint is required to initiate the classification process.

#### 2. Bridging and Read-Across classifications between ores and concentrates

When toxicological data are not available for the specific O&C being evaluated, classification can be based on read across to toxicological data for one or more chemical surrogates with similar physical/chemical properties to the O&C. In this way, for each endpoint, a classification is based upon data available for the surrogate substances (e.g., another O&C that is used to produce the same commodity). The GHS offers guidance on the criteria for selecting or deselecting surrogates for particular endpoints. Each toxicological endpoint has its own specific rules on bridging, as to the concentration limits that impact the final hazard classification.

#### 3. Classification by the Mixture Approach

In this approach, the O&C is treated as a mixture with a number of discrete constituents. The hazard classifications of each constituent are then factored into classification of the O&C as a whole. For health endpoints, O&C classifications are based on the properties of the constituents. Additivity or key cutoff levels specified in lookup tables can be used, depending on the endpoint and amount of information available for the constituents. For environmental endpoints, additivity and/or summation algorithms are applied to quantitatively estimate the mixture's toxicity to aquatic organisms. Currently these concepts and rules are incorporated in easy to use IT tools, which can be used to classify O&Cs.

#### 4. Classification by the Mixture Approach corrected for (bio)availability

If specific information is available on the (bio)availability of a constituent (e.g. PbS), then this should be taken into account. For example the availability of PbS tested in salt form is completely different from PbS that is integrated in the mineral structure of an O&C. While lead compounds (soluble forms) are indeed classified in the EU under the Dangerous Substances Directive<sup>5</sup> and now EU-CLP only the (bio)available fraction in the mineral structure should be taken into account for a relevant classification of O&Cs.

<sup>5</sup> Dangerous Substances Directive (67/548/EEC)



## 5. Classification by the Substance Approach

The O&C is regarded as a single substance with properties that can be determined by empirical testing. Some endpoints are suited to testing the specific O&C (e.g. transformation/dissolution testing, eye and skin irritation), allowing the use of the Substance Approach. Other endpoints however are limited to the Mixture Approach where testing only the key constituents and applying bridging, read-across or additivity conventions is possible.

It is important to note that if empirical testing data is generated under this Step 5, it may subsequently become available for classification of similar O&Cs under Step 2 above.

Each of these elements is discussed below, with distinctions identified between human health and environmental endpoints where relevant.

## 2.2 Guidance on O&C Characterization

**In this chapter, only limited guidance is given on O&C characterization (although it is recognized that the subject itself may warrant dedicated guidance). It is hoped that this section will provide the reader with at least an overview of the key issues.**

Accurate and precise analytical characterization of O&Cs is critical to ensure accurate GHS classification for health and environmental endpoints. This characterization often requires collection of the best available analytical information on the O&C and its original ore body, as well as best professional judgment on the part of experienced geologists, geochemists and mineralogists familiar with both the ore body and concentration process. In cases where uncertainty exists about the form of a particular O&C constituent and the appropriate GHS classification, additional analytical work using more advanced technologies may resolve this uncertainty and ensure classifications are accurate and realistic.

The characterization of O&Cs has the following elements:

1. sampling of the O&C;
2. analyzing the O&C composition (elemental, chemical, mineralogical);
3. geological interpretation of the results and defining the O&C composition;
4. documenting current classifications; and
5. assembling the best available (eco)toxicological hazard data that exists for the O&C and its constituents.

### Defining O&C product compositions

Specific mineralogical data can help to ensure that O&Cs are classified accurately and realistically. Key properties that may drive GHS classifications are the concentration, form (e.g., valence and particle size), and solubility of minerals in an O&C, e.g., as a carbonate mineral, an oxide mineral, a sulfide mineral, etc. In the absence of information on the specific form of constituents in an O&C, some may assume a worst-case approach in which constituents are treated as highly soluble and highly bioavailable.

Often, current or historical Safety Data Sheets (SDSs) for O&Cs do not provide the necessary level of specificity needed for GHS classification.



### Example 2.1: Comparison of Chemical and Mineralogical Approaches for Defining the Composition of a Hypothetical Copper Concentrate

Chemical Approach	Mineralogical Approach																																				
<p>Many Safety Data Sheets for O&amp;Cs are rather dated, and may not reflect recent advances in analytical chemistry and mineralogy. It is not uncommon to see constituents described only in terms of major cations and anions on a dry weight basis, with little information on their mineralogical forms. For example, the reported composition of a hypothetical copper concentrate in a conventional SDS could resemble the following:</p> <table border="1"> <tr><td>Iron (Fe)</td><td>25%</td></tr> <tr><td>Copper (Cu)</td><td>35%</td></tr> <tr><td>Arsenic (As)</td><td>3%</td></tr> <tr><td>Sulfur (S)</td><td>34%</td></tr> <tr><td>Antimony (Sb)</td><td>2%</td></tr> <tr><td>Lead (Pb)</td><td>1%</td></tr> </table> <p>With this limited characterization, errors in classifying the concentrate could result from assumptions that the more toxic constituents (lead, arsenic, copper) could be available in free, dissociated form (more readily bioavailable).</p>	Iron (Fe)	25%	Copper (Cu)	35%	Arsenic (As)	3%	Sulfur (S)	34%	Antimony (Sb)	2%	Lead (Pb)	1%	<p>Through consultation with geochemists and mineralogists familiar with the ore body, and possible additional analytical investigation, the same hypothetical concentrate could be described in mineralogical terms:</p> <table border="1"> <thead> <tr> <th><i>Mineral</i></th> <th><i>Percentage</i></th> <th><i>Chemical Formula</i></th> </tr> </thead> <tbody> <tr><td>Tennantite</td><td>5.2%</td><td><math>Cu_{11}FeAs_4S_{13}</math></td></tr> <tr><td>Luzonite</td><td>7.0%</td><td><math>Cu_3AsS_4</math></td></tr> <tr><td>Enargite</td><td>1.6%</td><td><math>Cu_2AsS_4</math></td></tr> <tr><td>Tetrahedrite</td><td>7.6%</td><td><math>Cu_4Fe_3SbS_{13}</math></td></tr> <tr><td>Galena</td><td>2.2%</td><td><math>PbS, PbS_2</math></td></tr> <tr><td>Chalcopyrite</td><td>75.2%</td><td><math>CuFeS_2</math></td></tr> <tr><td>Water</td><td>1.2%</td><td><math>H_2O</math></td></tr> </tbody> </table> <p>The mineralogical approach offers several advantages over the chemical approach. First, it provides toxicologists with relevant metal speciation information needed for accurate GHS classification. Most minerals have discrete CAS numbers and, for certain endpoints, have existing toxicological data searchable under that CAS number.</p> <p>Secondly, this approach illustrates that the constituents may be materials that are tightly complexed in a natural mineral matrix, only slightly soluble, and essentially non-bioavailable. General information on the properties of the mineral (stability, solubility, pH, particle size) can often complement the toxicological data by dimensioning the likelihood of breakdown to free metal ions or exposure through various routes.</p> <p>Thirdly, this approach underscores that the constituents of ores and concentrates are naturally-occurring mineral products extracted from the ground. Recognition of their natural origin and nature reveals them to be somewhat less onerous than a mixture of chemicals including, in this case, copper, arsenic and lead.</p>	<i>Mineral</i>	<i>Percentage</i>	<i>Chemical Formula</i>	Tennantite	5.2%	$Cu_{11}FeAs_4S_{13}$	Luzonite	7.0%	$Cu_3AsS_4$	Enargite	1.6%	$Cu_2AsS_4$	Tetrahedrite	7.6%	$Cu_4Fe_3SbS_{13}$	Galena	2.2%	$PbS, PbS_2$	Chalcopyrite	75.2%	$CuFeS_2$	Water	1.2%	$H_2O$
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Historical SDSs typically list compositions chemically (e.g., freely dissociated metal anions or cations that may not actually exist in the mineral). These reflect early, non-specific analytical procedures (e.g., atomic absorption spectrophotometry). More recent advances in analytical chemistry (e.g., Microprobe assays and advanced X-ray crystallography) are available to define more precisely the structure and composition of O&Cs in mineralogical form. Compositions which are defined mineralogically in SDSs provide toxicologists with more relevant data which help to minimize overly stringent classifications. Example 2.1 compares chemical and mineralogical approaches for defining the composition of a hypothetical copper concentrate.

### Guidance on characterizing O&Cs in Safety Data Sheets

Generic entries for a set of common characterization parameters are shown in an example Substance ID Template available upon request from ICMC or Euromines.

Representative samples should be characterized to estimate the typical concentration of each listed constituent. Often, historical analytical data can assist in establishing typical concentration ranges. For each type of ore or concentrate, data from all available examples should be used including data from ores or concentrates containing at least one metal (e.g., data from Cu/Au ores can be included



in developing entries for the 'Cu ore' Substance ID Template).

Any constituent present in any single ore or concentrate in concentrations greater than 0.1%w/w should be listed in the Substance ID Template, however not all will necessarily need to be listed in the Safety Data Sheet.

Constituents known to be Classified, or containing a metal substance with generic entries in Annex VI of the EU-CLP (e.g., Luzonite  $\text{Cu}_3\text{AsS}_4$ , Galena  $\text{PbS}$ , Tetrahedrite  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ) should be listed separately if their concentrations range above 0.1%w/w or above their specific thresholds as listed in Annex VI of the EU-CLP regulation in any single ore or concentrate.

For each listed constituent, the maximum concentration reported for any single ore or concentrate should be entered as the maximum of the %-range for that constituent. Where information is only available for a group of constituents (E.g., '70% made up of the following minerals,...'), the maximum concentration for the group can be attributed to each of the individual constituents.

Finally, a quick 'summation-check' should be performed to refine the listed typical concentrations such that the total %w/w of all listed constituents equals 100%w/w. This reinforces the credibility of the data upon which the classifications are made.

In characterizing the composition of O&Cs, consideration should be given to the mineralogy of the ore body, and the effects of typical transport, handling and use (e.g., beneficiation, concentration, storage, weathering) on chemical speciation. The product (physical form) as it is shipped and/or handled should be described. For example, if water is present (or intentionally added to suppress dust) it might allay concerns over flammability, explosivity, or respiratory exposure. It could, however, raise other concerns such as corrosivity or potential leaching. The goal is to communicate the realistic hazards of the product through typical handling and use.

### Documenting current classifications (E.g., in the EU)

Some current EU chemical classifications are comparable to some GHS classifications, but not all. The EU classifications can be useful guide toward sound GHS classifications, but must be supplemented with robust toxicological data for accurate self-classification of an O&C.

Euromines and ICMM have recommended the use of Substance ID Templates to characterize the mineralogical composition and the physical-chemical form of the O&C constituents. They may also enable identification of classified constituents that drive GHS classification for particular endpoints.

The Substance ID Templates contain the O&C composition, the speciation of constituents to the extent possible, and existing conventional classifications. From this initial characterization, certain endpoints with robust toxicological databases (e.g., eye/skin irritation), and direct reference to EU classifications, may be readily classified. Subsequent efforts for bridging and read-across can then be focused on the remaining endpoints.

The generic 'Substance ID Templates' developed by Euromines, are supplemented by 'lookup' classification tables and automated IT tools being developed by individual commodity associations. These tools enable broad comparisons of GHS classifications with existing EU classifications, where direct comparisons across health endpoints exist. They have been used to identify some of the major drivers for O&C classification (e.g. As, Pb and Sb-bearing minerals).

However, Euromines and ICMM caution that these tables currently only reflect 'EU harmonized classifications', and that self-classification of O&Cs using all available supplemental data is mandatory under GHS. In the large part, many EU classifications are evolving, or have been superseded by more recent interpretations of hazard. It must be remembered that self-classification requires interpretation of a current and complete toxicological database for each endpoint to ensure accurate GHS classification. Classification tables and associated tools should therefore be used for broad guidance only.



### Assembling best available toxicological data for self-classification of O&C

Self-classification of O&Cs should be based upon a complete and current database for each endpoint.

As stated previously, accurate GHS classifications cannot be based on conventional classification schemes alone. They must reflect current toxicological data and understanding. The early compilation of accessible data for the O&C, and its specific constituents, is an essential step in accurate GHS classification. From an initial data review, certain data-rich GHS endpoints may be quickly resolved, and a data gap analysis can be performed for others. Resource databases for compiling (eco)toxicological data are widely available and should be used to organize data for further evaluation. However, an unpublished literature search commissioned by ICMM during 2008 revealed that scientific data concerning the toxicology of metal-bearing minerals is scarce.

When data are available for the O&C, those data should be preferentially considered for classification purposes. In practice, this is typically relevant for relatively few acute health endpoints (e.g. eye or skin irritation).

Conventional criteria for assessing data quality, such as Klimisch Criteria, are widely applied in the selection and prioritization of the most reliable data for hazard classification purposes. Accurate and credible classifications often require the professional judgment of trained toxicologists. For this reason, the data and rationale used to support a classification decision should be transparent. With the likely abundance of new data resulting from REACH, the basis for current classifications in the near-term should be well documented. This may include a synopsis of the data upon which classification decisions were based (and the date), existing data gaps, and the rationale for using other classification conventions (e.g., bridging, read-across) principles for classification or justifying no classification. It is considered unlikely however that REACH will generate new scientific data concerning the toxicology of metal-bearing minerals due to its focus on marketed organic substances.

### 2.3 Guidance on classification of O&Cs for physical-chemical endpoints

GHS lists sixteen physical-chemical endpoints. Some of these endpoints may conceivably not apply to O&Cs, as many relate only to liquids, gases, or organic substances and mixtures (Table 2.1 gives a brief summary).

The EU-CLP ultimately requires companies to test for physical-chemical endpoints, but below is a brief outline of some of the categories that may be more obviously applicable to O&Cs.

#### Flammable Solids

Some physical forms of O&Cs may be classified as 'Flammable Solids', as examples cited by the EU for this endpoint include 'powders of metals or metal alloys'. A flammable solid is 'a solid which can be readily combustible, or may cause or contribute to fire through friction' (2007 EU GHS). Some O&Cs in fine granular or powdered form can be flammable in the presence of an ignition source.

The U.S. Occupational Safety and Health Administration (OSHA) and National Fire Protection Association (NFPA) offer some guidelines on the relevant particle size and conditions under which combustion may occur, i.e.<sup>6</sup>,

'Combustible dust is defined by NFPA 654 as: 'Any finely divided solid material that is 420 microns or smaller in diameter and presents a fire or explosion hazard when dispersed and ignited in air.'

*Different dusts of the same chemical material will have different ignitability and explosibility characteristics, depending upon many variables such as particle size, shape, and moisture content. Additionally, these variables can change while the material is passing through process equipment. For this reason, published tables of dust explosibility data may be of limited practical value. In some cases, dusts will be combustible even if the particle size is larger than that specified in the NFPA definition, especially if the material is fibrous.*

*The amount of dust accumulation necessary to cause an explosive concentration can vary greatly. This is because there are so many variables – the particle size of the dust, the method of dispersion, ventilation system modes, air currents, physical*

<sup>6</sup> As cited by the U.S. Occupational Safety and Health Administration at [www.osha.gov/dts/shib/shib073105.html](http://www.osha.gov/dts/shib/shib073105.html) (accessed 1 July 2009).



*barriers, and the volume of the area in which the dust cloud exists or may exist. As a result, simple rules of thumb regarding accumulation ... can be subjective and misleading.'*

### Classification criteria

The classification criteria for flammable solids is based on burning rate in a standard test method described in the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria* (Test Method N.1, Part III, sub-section 33.2.1). The test is performed using a mould to form a powder train of 250mm length, 20mm width and 10mm height on an impervious, low heat-conducting base plate. The powder train is ignited at one end with a microburner and burning time over a distance of 100mm is monitored.

Two hazard categories are described. Metal powders with a burning time less than or equal to 5 minutes in the test are classified as Category 1 flammable solids. Powders with a burning time >5 minutes and <10 minutes are classified as Category 2.

Interpreting the data from this test with respect to O&Cs presents several challenges. Shipments of bulk ores may contain relatively little mass in the particle size range described above, although the percentage of fine particles may increase due to attrition during shipping. Concentrates may contain a higher percentage of fines, but as noted above many variables affect whether a suspension of those particles may present explosive conditions.

### Hazard communication

Both classification categories carry the GHS flame symbol and the accompanying hazard statement, 'flammable solid'. Category 1 and 2 flammable solids are distinguished by the signal words, 'danger' and 'warning', respectively.

### Explosives

The EU defines explosivity as:  
*'An explosive substance (or mixture) is a solid or liquid substance (or mixture of substances) which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings. Pyrotechnic substances are included even when they do not evolve gases.'*

The classification of substances and mixtures as explosives, and further allocation to a division, is a relatively complex procedure and as for all phys-chem endpoints O&Cs should be evaluated on a case by case basis. It is referenced in Part I of the *UN Recommendation on the Transport of Dangerous Goods, Manual of Tests and Criteria*. The EU test method and criteria for explosivity can be found in the Official Journal of the European Communities, under Directive 92/69/EEC (O.J. L383 A, Section A.14, Explosive Properties).

### Corrosive to Metals

The definition of corrosivity is: *'a substance or mixture which by chemical action will materially damage, or even destroy, metals.'* (GHS Guidance, Chapter 2.16).

The criterion is the corrosion rate of the O&C on steel or aluminum exceeding 6.25 mm per year at a test temperature of 55° C. The corrosion test is described in Part III, sub-section 37.4, of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*.

A single category is identified under this endpoint and as for all phys-chem endpoints O&Cs should be evaluated on a case by case basis. It carries the Corrosion symbol and the signal word, 'Warning'. The Hazard Statement is: 'May be corrosive to metals'.



**Table 2.1:** Relevance of the 16 GHS physical-chemical endpoints to O&Cs

Physical-Chemical GHS Endpoints (UN, 2007)	Relevant to Ores and Concentrates (O&Cs)?	Rationale
Explosives	Yes, for fine powders	Dust explosions have been known to occur in underground mines
Flammable Gases	No	O&Cs are not gases
Flammable Aerosols	No	O&Cs are not aerosols
Oxidizing Gases	No	O&Cs are not gases
Gases Under Pressure	No	O&Cs are not gases
Flammable Liquids	No	O&Cs are not liquids
Flammable Solids	Yes, for fine powders	Powders of metals and alloys can be flammable under certain circumstances (e.g., tungsten carbide, pyrrhotite)
Self-Reactive Substances and Mixtures	No	O&Cs are heterogeneous in composition and sourced from naturally-occurring minerals, and unlikely to be thermally unstable and susceptible to undergo a strongly exothermic decomposition (with or without the presence of air)
Pyrophoric Liquids	No	O&Cs are not liquids
Pyrophoric Solids	No	O&Cs are exposed to air during mining and concentration processes therefore unlikely to ignite within five minutes of coming into contact with air
Self-Heating Substances and Mixtures	Yes	Some O&C can react with air without an external energy supply to self heat
Substances and Mixtures which, in contact with water, emit flammable gases	No	While certain metals (e.g., sodium) can react vigorously with water, most O&Cs will not meet the specific criterion that the mixture (O&C) produces flammable gases upon contact with water
Oxidizing Liquids	No	O&Cs are not liquids
Oxidizing Solids	No	O&Cs are relatively stable and would not be expected to oxidize in a rapid manner in bulk form
Organic Peroxides	No	O&Cs do not contain peroxides
Corrosive to Metals	Yes	Some O&Cs may release aqueous discharges with low (<2) pH in the transport chain

## 2.4 Guidance on classification of O&Cs for human health endpoints

A conceptual outline of the approach suggested for hazard identification and classification of O&Cs for human health endpoints is given in Figure 2.

The scheme starts with the collection of existing data on the composition and mineralogy of the O&C to be classified. In case specific data for some toxicological endpoints are available for the O&C itself the O&C can be classified as being a single substance for those endpoints.

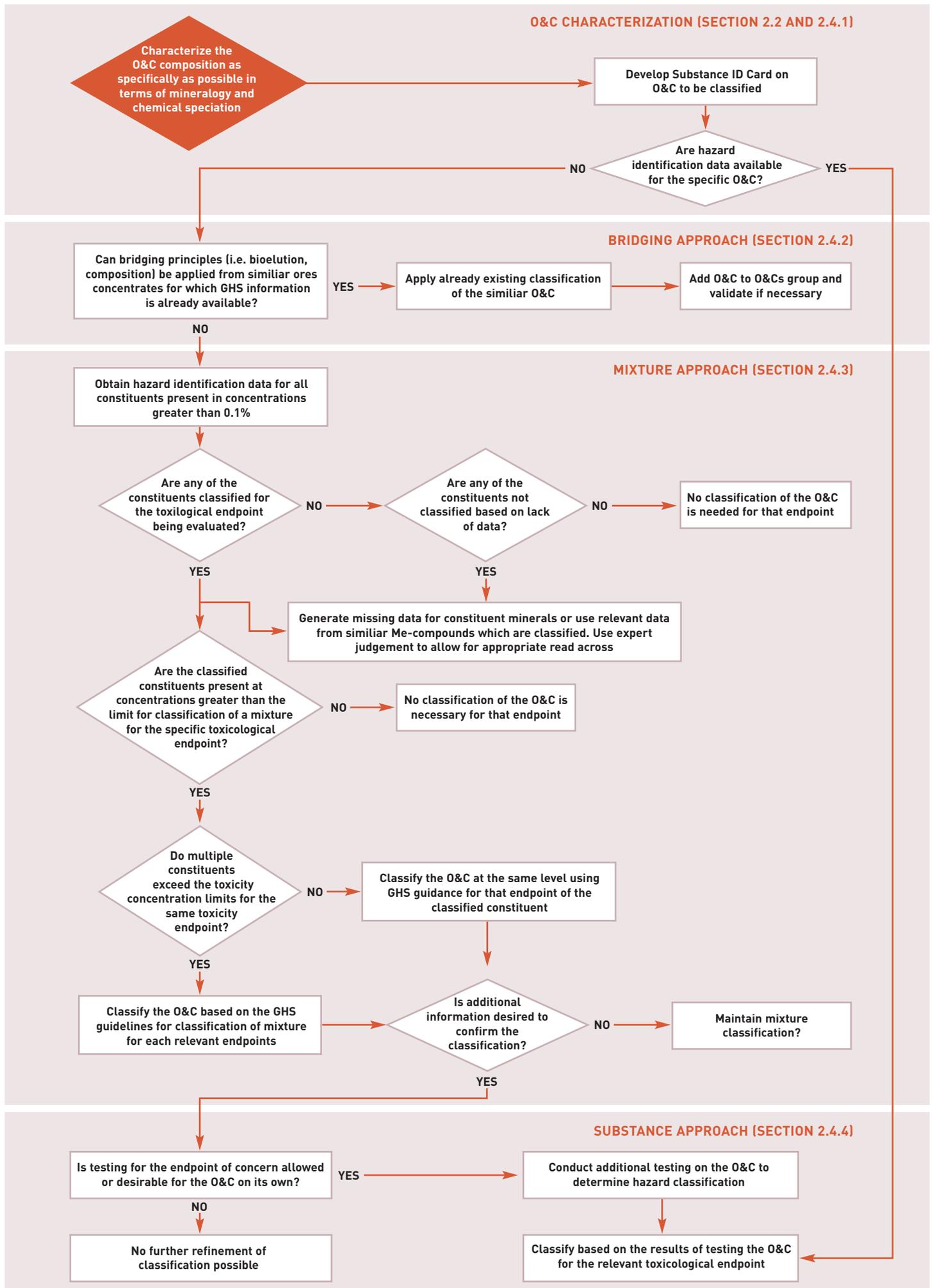
If no hazard data are available but other relevant data are available for the O&C under consideration an evaluation can be made to determine if the O&C behaves in a similar way as other O&C groups for

which the GHS classification process has already been completed. If 'sufficient' evidence is available to apply bridging principles, the already existing GHS information from the O&C peer group can be applied.

When bridging principles can not be applied the default approach in which an O&C is considered as a simple mixture<sup>7</sup> can be used. Subsequently the hazard classification is derived based on the hazard profiles of the constituents present in the O&C. In case the obtained classification needs to be refined additional testing could be performed to generate new data on the O&C and a specific classification can be derived according to the substance approach.

<sup>7</sup> In which the constituent substances retain their own intrinsic properties.

Figure 2: Conceptual overview for the hazard evaluation of O&Cs for human health endpoints





### 2.4.1 O&C Characterization

In the first step of the scheme shown in Figure 2 all of the data for composition, physico-chemical, speciation, and toxicological endpoints for the ore or concentrate should be collected. Data (of sufficient quality and relevance to the ore or concentrate) should be entered into the Substance ID Template for that ore or concentrate. More details on how to characterize the ore or concentrate are explained in the O&C characterization section of the document (Section 2.2). The steps set out in each of the subsequent approaches should be followed for each human health toxicological endpoint individually for the ore or concentrate being classified.

### 2.4.2 Guidance on the Bridging Approach

Typically for O&Cs, available data on a particular O&C or its specific constituents are limited for many GHS endpoints. As a result, GHS classifications for O&Cs rely on extrapolations of toxicological properties from surrogate substances with similar physical, chemical and toxicological properties. These bridging and read-across approaches are strongly emphasized in current GHS guidelines for self-classification of substances and mixtures, (which would include O&Cs). However, the heterogeneity and variability of O&Cs raise unique challenges in this regard. Each toxicological endpoint has its own specific rules on bridging, and specifically to the concentration limits that impact the final hazard classification

#### Identifying surrogates for Read-Across

Ideally, a surrogate for an O&C shall have a similar composition and physical form as the O&C being classified. Major constituents will be present in similar concentrations. Constituents should ideally have the same chemical class (form) and demonstrate similar physical, chemical and toxicological behavior.

For human health endpoints, composition data and/or bioelution study results (reflecting bio accessibility, see also 2.4.4) may be used in certain cases to establish similarity of O&Cs. Bioelution studies may, for example, confirm similar constituent metal ion release from different O&Cs in relevant fluids. Relevant simulated biological fluids and associated routes of exposure could include:

1. Gastric fluid (oral route of exposure)
2. Intestinal fluid (oral route of exposure)

3. Lysosomal fluid (as a worst-case related to respiratory cancer)
4. Lung interstitial fluid (inhalation route of exposure)
5. Lung lavage/alveolar fluid (inhalation route of exposure)
6. Artificial sweat (dermal route of exposure)

Additional guidance on bioaccessibility testing including the composition of the relevant fluids and protocols as well as the limitations of this type of *in vitro* testing can be found in the Draft HERAG Alloys Fact Sheet, currently being drafted and available from ICMM.

As relevant data is collected for the O&C, the data should be compiled and grouping performed for O&Cs with similar physico/chemical properties. Within each of these groups, the bridging principle can be applied so that read across can be performed between O&Cs of the same group. As more data is collected for more O&Cs, these can be added to each group and more groups created as necessary.

### 2.4.3 Guidance on the Mixture Approach for classification

If relevant toxicological data is not available for the specific ore or concentrate being classified or similar O&Cs then the next step in hazard classification should be the evaluation of the individual constituents of the ore or concentrate using the Mixture Approach. In this approach, O&Cs are treated as mixtures of their constituents and evaluated for the toxicological properties of each individual constituent. Using this approach, relevant hazard identification data (e.g. *in vitro*, *in vivo*, and human data) and/or classification data for the toxicological endpoint being assessed should be gathered for all of the constituents that exist in concentrations greater than 0.1% in the ore or concentrate being classified. It is important that the speciation of the constituent be characterized (see Section 2.2) as fully as possible since this may affect the classification of the constituent and subsequent classification of the ore or concentrate.

In case any of the constituents are not classified based on the lack of data the generation of new data or the use of relevant data from similar metal compounds which are classified should be considered. Based on expert judgment on the toxicity profiles and bioavailability (using



bio-elution tests to provide surrogate information) appropriate read-across can be allowed.

The constituent-concentration that warrants classification of an O&C is dependent on the toxicological endpoint of concern. The specific concentration limit for classification of the O&C is dependent on human health toxicological endpoint, the level of classification of the constituents (i.e. category), and the concentration of those constituents.

If none of the constituents is present above the concentration limit appropriate for mixtures for the toxicological endpoint of concern, then no classification of the O&C is necessary. If only one of the constituents is present in the specific O&C above the concentration limit for the toxicological endpoint being evaluated then the mixtures guidance for that endpoint should be consulted to determine at what level classification is appropriate. If more than one of the constituents present in the specific O&C is above the concentration limit for the toxicological endpoint being evaluated then the O&C should be classified according to the GHS/EU-CLP guidelines for each specific human health toxicological endpoint. Depending on the amount of data for each classifiable constituent, an additivity approach or other endpoint-specific mixture classification criteria should be applied for the specific toxicological endpoint (located in the mixtures section of the Draft HERAG Alloys Fact Sheet, currently being drafted and available from ICM, for each toxicological endpoint).

Once a classification is derived using the Mixtures Approach, it may be desirable to confirm the classification that was determined using a (minimal) testing strategy. This can be done using the Substance Approach. If no additional information is desired to confirm the classification then the classification derived using the Mixture Approach can be applied.

#### 2.4.4 Classification by the Mixture Approach corrected for (bio)availability

Bioavailability considerations may have an influence on hazard classification, for instance in justifying a read-across because of a lack of bioavailability or/and to correct the default approaches to take into consideration the bioavailable, active concentration. An illustrative example of the consideration of bioavailability is given below.

For example:

For **acute health effects**, classification is based on comparison of Acute Toxicity Endpoint of the mixture (ATE<sub>mix</sub>) with the acute toxicity category ranges defined in GHS. ATE<sub>mix</sub> is derived through the use of an additivity formula and the ATE's for the individual relevant ingredients present in the O&C at  $\geq 1\%$ . An ATE for an individual ingredient is expressed as an LD<sub>50</sub> (oral and dermal exposure) or an LC<sub>50</sub> (inhalation exposure).

Bioaccessibility information may be used to derive an adjusted ATE<sub>mix</sub>. The classification procedure is then the following (this is described in more detail for alloys in the fact sheet currently under development):

1. Assess whether there is any constituent with a  $LD_{50} \leq 5000$  mg/kg present above 1% of O&C?
2. If yes, derive bioaccessibility data for source metal-bearing minerals and O&C and use either the boundary/breakpoint or the trend analysis approach to estimate unknown toxicity value for the constituent metal-bearing minerals of the O&C
3. Assess now if there is any constituent with an adjusted  $LD_{50} \leq 5000$  mg/kg present in the O&C?
  - a. If no constituents have an estimated toxicity value below the upper limit of classification, no classification is necessary
  - b. If only one constituent has an estimated toxicity value below the upper limit of classification, classify based on that constituent (ATE<sub>mix</sub> = adjusted LD<sub>50</sub> of single metal)
  - c. If more than one constituent has an estimated toxicity value below the upper limit of classification, use the additivity formula described in the GHS (UN 2007) to derive ATE<sub>mix</sub>



For **health endpoints other than acute toxicity**, classification is based on cut-off concentration limits. Mixtures that contain a classifiable ingredient at a concentration above the cut-off limit receive the same classification as the ingredient. Bioaccessibility can be taken into account to characterize the 'active' concentration of metal in the O&C and propose a correction of the default approach by using relative bioaccessibility (this is again described in more detail for alloys in the fact sheet under development):

1. Assess whether there is any constituent above cut-off limits
2. If yes, derive bioaccessibility data for source metal-bearing minerals and O&C and derive relative bioaccessibility (RB) ratio of target O&C constituent compared to source constituent (constituent ion release from the target O&C divided by the constituent ion release from the source constituent, calculated on a per unit mass basis)
3. Compare RB to cut-off and classify accordingly

#### **Important note**

These proposed approaches are currently being tested and exemplified. Examples and recommendations for verification of the proposed approaches will be included as soon as data will become available

### **2.4.5 Guidance on the Substance Approach for classification**

The Substance Approach is based on data derived from the O&C being classified, treating it as a substance rather than a mixture of its constituents. This approach may be used if either data is available for the O&C for the toxicological endpoint being evaluated (Step 2 in Figure 1) or confirmation of the classification derived using the Mixture Approach is desired (Step 5 in Figure 1). If relevant and quality data is available for the O&C for the toxicological endpoint being evaluated, then that data should be used for classification for that endpoint.

If testing is allowed and desired then data can be generated by testing the specific O&C using relevant testing protocols (e.g. OECD guideline tests) for the toxicological endpoint of concern, and classification can be performed using that data in the context of the GHS criteria.

#### **Conclusion**

The suggested way forward, following a number of workshops with experts from the ICMM membership, is to use a stepped approach covering:

##### **Tier 1**

Apply the Excel-based tools developed by ARCHE to derive the classification for O&Cs using the mixture rules. Information on speciation and concentration is the minimum input requirement. Tier 1 information should be gathered for as many O&C streams as possible.

##### **Tier 2**

Physchem, T/Dp Environment and pilot Bio-elution tests for Human Health for declassification or validation under certain conditions (i.e., bio-elution studies in metals can benchmark against other substances). The pilot Bio-elution tests should be performed on one 'typical' and one 'reasonable worst case' sample for each main-metal concentrate.

##### **Tier 3**

If pilot Bio-elution testing confirms that current classifications are overly conservative, individual companies should carry out similar testing on their own O&Cs.



## 2.5 Guidance on classification of O&Cs for environmental endpoints

A conceptual outline of the approach suggested for hazard identification and classification of O&Cs for environmental endpoints is given in Figure 3.

The scheme begins with the collection of existing data on the composition and mineralogy of the O&C to be classified. If specific hazard data are available for the O&C itself, it can be classified as a single substance.

In case no hazard data are available but other relevant data are available for the O&C under consideration an evaluation can be made to determine if the O&C behaves in a similar way as other O&C groups for which the GHS classification process has already been completed. If 'sufficient' evidence is available to apply bridging principles the already existing GHS information from the O&Cs peer group can be applied.

When bridging principles cannot be applied the default approach in which an O&C is considered as a simple mixture<sup>8</sup> could be used. Subsequently the hazard classification is derived based on the hazard profiles of the constituents present in the O&C. If the obtained classification needs to be refined, additional testing could be performed on the O&C and an O&C-specific classification can be derived according to the substance approach.

### 2.5.1 O&C Characterization

In the first step of the scheme all of the data for composition, physico-chemical, speciation, and toxicological endpoints for the ore or concentrate should be collected. Data (of sufficient quality and relevance to the ore or concentrate) should be entered into the Substance ID Card for that ore or concentrate. More details on how the characterize the ore or concentrate are explained in the O&C characterization section of this document (Section 2.2). The steps set out in each of the following sections should be followed for environmental endpoints individually for the ore or concentrate being classified.

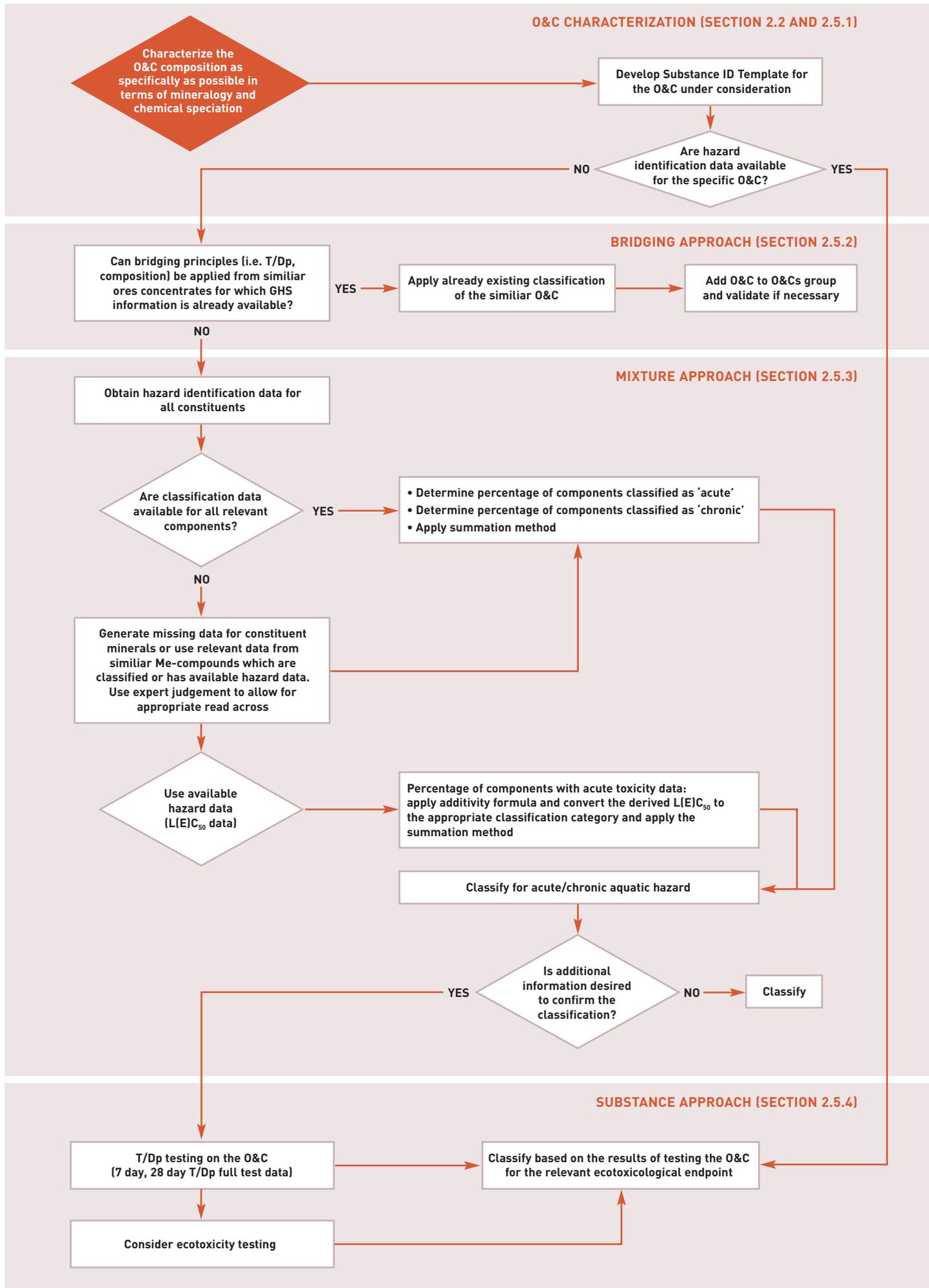
### 2.5.2 Guidance on the Bridging Approach

As explained in detail in Section 2.3 it is worthwhile considering grouping ores and concentrates with similar characteristics and read-across the hazard classification when appropriate, e.g., based on compositional information. Using this methodology for classification processes, however, may be debatable as grouping of ores and concentrates has to be done in such a way that within a specific group the displayed exposure behavior is similar (e.g., release rate of the assessed metals in the ore/concentrate), and this cannot be predicted merely on the composition of the ore/concentrate. Ideally, once data becomes available for a number of O&Cs within a particular peer group, it can be assessed to identify any 'clustering' of results within different classification categories. It may be possible to then identify concentration 'envelopes' that correspond to the different classification categories, such that defensible read-across of hazard classifications can be proposed for O&Cs whose composition clearly falls within those 'envelopes'. Expert judgment is therefore required for the allocation of an ore/concentrate to a specific peer group. In general, bridging principles for environmental endpoints could include:

- Concentration of the constituent metal-bearing minerals;
- Physicochemical properties of the ore/concentrate;
- Relevant ecotoxicological data on the metal(s) or the metal-bearing minerals;
- Metal release studies (transformation/dissolution data).

<sup>8</sup> In which the constituent substances retain their own intrinsic properties.

Figure 3: Conceptual overview for the hazard evaluation of O&Cs for environmental endpoints





### 2.5.3 Guidance on the Mixture Approach for classification (summation method)

If relevant toxicological data is not available for the specific ore or concentrate being classified or for a similar O&C, then the next step in hazard classification should be the evaluation of the individual constituents of the ore or concentrate using the Mixture Approach. O&Cs can be considered as complex substances containing many constituents, and therefore the general rules for the classification of mixtures – based on the classification of the individual elemental components – can be applied. For the environmental classification the Mixture Approach consists of applying the summation method.

The summation method is based on the classification of the individual constituents of the O&C. It is a simple calculation approach in which the classification of a mixture is based on the summation of the classification of its elemental components. The summation method is outlined in detail in GHS and in the EU-Regulation 1272/2008 on classification, labeling and packaging of substances and mixtures ('EU-CLP-Regulation').

The summation method considers the contribution of all relevant elemental components of the O&C that are classified as Acute/Chronic Category 1, Category 2, Category 3 and Category 4. Category 4 implies the incorporation of default classifications for constituents for which the data do not allow classification under the criteria that are defined in the EU-CLP, but for which there are nevertheless some grounds for concerns. The underlying toxicity criteria among the different categories differ by a factor of 10, and this factor of 10 is also reflected in the classification procedure based on the summation methodology.

These rules stipulate that in general a more stringent classification of a mixture always overrides a less stringent classification, i.e. once a specific Chronic Category classification has been determined for a given mixture, there is no need anymore to evaluate the classification criterion for less stringent Chronic categories. E.g., the classification procedure for an O&C is already completed if the result of the classification is Chronic Category 1.

Step-wise guidance on how to apply this method for the environmental classification of O&Cs is given here below and in the case provided in Example 2.2.

### Summation method

#### Step 1: Acute Category 1 classification

The composition of the O&C can be defined in two ways:

1. by the individual elemental components of the O&C (e.g., S, Si, As, Cu,...) O&C, with each element having its specific classification;
2. by the different minerals, each having a specific classification. This mineral specific classification is based on its elemental composition, unless a specific classification for a mineral is already available.

In those cases where no classification is available for any of the minerals in the O&C, the method based on the elemental composition is preferred as it avoids the intermediate step of deriving mineral-specific classifications.

The first step of the classification procedure considers all components that are classified as Acute Category 1 (DSD: R50). If the sum of these components is greater than 25% by weight the whole mixture is classified as Acute Category 1 (DSD: R50). For ores and concentrates, this is the sum of the w/w % of all individual components (elements or minerals, depending on the approach) that are Acute Category 1. The classification of a mineral can be derived from the classification Table that is given in the Substance ID Template, i.e. the classification that is associated a pure mineral (i.e., and O&C containing only 1 mineral).

In general, when a mixture contains components that are classified as Acute/Chronic Category 1, attention must be paid to the fact that such components may contribute to the toxicity of the mixture even at very low concentration levels. In order to prevent that the presence of such components would lead to an 'under-classification' of the mixture, multiplying factors (M-factors) are applied of the w/w% of such highly toxic components.



These M-factors (as shown in Table 2.2) increase by an order of magnitude with corresponding decrease of the acute toxicity ( $LC_{50}$ ) of the component, starting with an M-factor of 1 for components with an  $LC_{50}$  ranging between 0.1 and 1 mg/L.

**Table 2.2**

L(E)C <sub>50</sub> value	Multiplying factor
0.1 < L(E)C <sub>50</sub> ≤ 1 mg/L	1
0.01 < L(E)C <sub>50</sub> ≤ 0.1 mg/L	10
0.001 < L(E)C <sub>50</sub> ≤ 0.01 mg/L	100
(continue in factor 10 intervals)	

### Step 2: Chronic Category 1, 2, 3, 4 classification

Firstly, all components classified as Chronic Category 1 are considered. If the w/w% sum of these components (already multiplied by their corresponding M-factor in the Substance ID Template) is equal to or greater than 25%, the O&C is classified as Chronic Category 1. If the result of the calculation is indeed a Chronic Category 1, the classification procedure is completed as no more stringent classification can be obtained.

In cases where the O&C is not classified as Chronic Category 1, classification as Chronic Category 2 is considered. An O&C is classified as Chronic Category 2 if 10 times the (M-factor corrected) w/w% sum of all mineral components classified as Chronic Category 1 plus the w/w% sum of all mineral components classified as Chronic Category 2 is equal to or greater than 25%. If the result of the calculation is indeed a Chronic Category 2, the classification procedure is complete.

In those cases where the O&C is not classified either Chronic Category 1 or Chronic Category 2, classification of the O&C as Chronic Category 3 is considered. An O&C is classified as Chronic Category 3 if 100 times the (M-factor corrected) w/w% sum of all mineral components classified as Chronic Category 1 plus 10 times the w/w% sum of all mineral components classified as Chronic Category 2 plus the w/w% sum of all mineral components classified as Chronic Category 3 is equal to or greater than 25%. If the result of the calculation is indeed a Chronic Category 3, the classification procedure is complete.

If an O&C is not classified in Chronic Category 1, 2, 3 following this procedure, classification of the mixture as Chronic Category 4 is considered. An O&C is classified as Chronic Category 4 if the sum of the percentages of mineral components classified as Chronic Category 1, 2, 3 and 4 is equal to or greater than 25%.

These different classification steps for O&C are summarized in Table 2.3.

Example 2.2 (page 18) illustrates the classification of an O&C for which the typical concentration levels and classification of the different constituents are available. It should be noted, however, that it is possible to develop a tool that automatically derives the classification of an O&C. Such a tool would be based on a database containing the human and environmental classification for each O&C compound (element or possibly mineral), and would automatically derive both the human and environmental classification based on the O&C composition.

**Table 2.3**

Sum of components classified as:	Ore/Concentrate is classified as:
Acute Category 1 x M ≥ 25%	Acute Category 1
Chronic Category 1 x M ≥ 25%	Chronic Category 1
(M x 10 x Chronic Category 1) + Chronic Category 2 ≥ 25%	Chronic Category 2
(M x 100 x Chronic Category 1) + (M x 10 x Chronic Category 2) + Chronic Category 3 ≥ 25%	Chronic Category 3
Chronic Category 1 + Chronic Category 2 + Chronic Category 3 + Chronic Category 4 ≥ 25%	Chronic Category 4

**Example 2.2: Classification of a 'hypothetical' copper ore for environmental effects**

The following composition of a hypothetical copper ore was assumed:

Tennantite	3%
Luzonite	4%
Enargite	0.9%
Tetrahedrite	4.2%
Lead sulphide	1.2%
Chalcopyrite	41.8%
Other	44.9%

**Elemental-based classification**

Tennantite contains 20.3% of As (R50/R53; Chronic 1); other elements are Cu and S (*no classification*)

Luzonite and enargite both contain 19.0% of As (R50/R53; Chronic 1); other elements are Cu and S (*no classification*)

Tetrahedrite contains 29.2% of Sb (R51/R53; Chronic 2); other elements are Cu and S (*no classification*)

Lead Sulphide contains 86.6% of Pb (R50/R53; Chronic 1); other element is S (*no classification*)

Chalcopyrite contains no classified elements

- Arsenic content (%) in the hypothetical copper ore:  $3 \times 0.203$  (tennantite contribution) +  $4 \times 0.190$  (luzonite contribution) +  $0.9 \times 0.19$  (enargite-contribution) = 1.54% of a R50/R5 (Chronic 1) compound
- Antimony content (%) in the hypothetical copper ore:  $4.2 \times 0.292$  (tetrahedrite content) = 1.23% of a R51/R53 (Chronic 2) compound
- Lead content (%) in the hypothetical copper ore:  $1.2 \times 0.866$  (lead sulfide contribution) = 1.04% of a R50/R53 (Chronic 3) compound

Based on the information in the Classification IT tool (excel based), the following environmental classifications for the different minerals have been put forward (classification reflecting 100% of the mineral in the ore):

Tennantite, Luzonite, Enargite, Tetrahedrite; R51/R53 or Chronic 2 Category

Lead sulphide: R50/R53 or Acute1/Chronic1 Category

Chalcopyrite and other minerals: no classification

**Step 1: Determination of category-specific w/w%**

The information on the hypothetical ore that were provided in the previous section has been entered into an automated software tool (excel based) including the M-factor for each element that has an R50/53 or Acute1/Chronic Category 1 classification. In this specific case there are two R50/53 or Acute1/Chronic Category 1 components (Arsenic and Led) both having an M-factor of '1'. The corrected w/w% for this category is the original w/w% multiplied by the M-factor.

Once the w/w% for all other mineral components has been to be added to the excel sheet, a summation of all the w/w% fractions is made for each classification category, and these summation values are used to calculate the classification of the O&C automatically (Table 1).

- Sum of R50/R53 (Chronic 1) compounds = 1.54% + 1.04% = 2.58%
- Sum of R51/R53 (Chronic 2) compounds = 1.23%

**Step 2: Classification of the ore**

The total category-specific values that are derived in the excel sheet are used to classify the ore (Table 1)

**Table 1: Classification methodology for O&C**

Sum of components classified as:	Ore/Concentrate is classified as:
Acute Category 1 x M ≥ 25%	2.58% ≥ 25% ? No = > no Acute Category 1
Chronic Category 1 x M ≥ 25%	2.58% ≥ 25% ? No = > no Chronic Category 1
(M x 10 x Chronic Category 1) + Chronic Category 2 ≥ 25%	(10 x 2.58%) + 1.23% = 25.8% + 1.23% = 27.1% ≥ 25% ? Yes = > Chronic Category 2 / R51/R53
(M x 100 x Chronic Category 1) + (M x 10 x Chronic Category 2) + Chronic Category 3 ≥ 25%	Not required as a more severe classification has been determined
Chronic Category 1 + Chronic Category 2 + Chronic Category 3 + Chronic Category 4 ≥ 25%	Not required as a more severe classification has been determined

According to the rules of this element-based summation method the hypothetical ore is classified as a R51/R53 or Chronic Category 2.



### Use of the additivity formula in combination with the summation method

For self-classification, adequate data for mineral constituents in the O&C that are not (yet) classified, should be taken into account. 'Adequate' data refers to specific toxicity data that are available for these compounds, and for which the combined toxicity can be calculated using the additivity formula that has been described in the EU-CLP-regulation. The toxicity value that is derived with this method is then used to assign an acute/chronic classification category to this portion of the ore/concentrate. This classified portion is then subsequently used in applying the summation method. The classification of this portion as far as it is known should, however, already be given in the Substance ID Template.

### 2.5.4 Guidance on the Substance Approach for classification

If information is available on release behaviour, and it justifies (significant lower or significant higher release rates) deviation from the proportional availability rule as mentioned above, then an O&C specific approach is warranted. In this approach the O&C is treated as a substance rather than a mixture of its constituents. This approach may be desired for confirmation of the classification derived using the Mixture Approach (in this case the classification is based on using the critical surface area-toxic unit (CSA-TU) approach) or if data is available for the O&C for the ecotoxicological endpoint being evaluated (derived from direct testing).

### 2.5.4.1 CSA-TU approach

Most of the concepts (e.g., T/Dp, critical surface area/critical diameter) that have been developed for the classification and labeling of metals and sparingly soluble metal compounds can in this regard be used and extended to O&Cs. The T/Dp is an operationally defined procedure (Skeaff et al, 2008, GHS Annex 10) in which weighed quantities (1, 10, 100 mg/L) of the metal bearing substance (in this case an ore or concentrate) are added to an aqueous medium and agitated for a defined period of time (24 hours, 7 days, or 28 days). The rate and extent at which metal ions are released is a measure of the reactivity of the O&C.

A brief overview of some potential scenarios for further refinement of the classification of an O&C based on T/Dp is given below:

- The O&C is not particularly reactive (soluble metal compounds are not present in the aqueous medium above the detection limit) under the conditions of the 28 day T/Dp. In that case a null classification (no classification) is justified
- Results that are available from a 28 day T/Dp experiment show that metal concentration in the aqueous medium is less than the long-term NOEC of the dissolved metal form. In that case the (default safety net) classification can be removed
- The O&C is reactive under the condition of the T/Dp and several metals can be identified as a critical component on the basis of release and toxicity considerations. In this case the classification can be conducted following the Critical Surface Area/Toxicity Unit (CSA-TU) approach.

The use of the Critical Surface Area-Toxic Unit approach was first demonstrated by Skeaff (2008) who extended the general concepts of Critical Surface Area (CSA) and Critical Particle Diameter (CPD) developed for metals and metallic compounds to alloys. In a similar way this can be done for a complex metal containing material such as O&Cs.

Within the CSA-TU approach the dissolved concentrations of all constituents is taken into account using the Toxic Unit (TU) approach as originally developed for multi component metal solutions by Anderson and Weber (1975). The TU approach normalizes the measured individual metal concentrations towards their respective toxicities ((L(E)C<sub>50</sub> or NOEC/EC<sub>10</sub>)) assuming that the joint effect of the metals is additive. This is a conservative assumption since in the majority of



cases the toxicity of multi component metal solutions have shown to be less than additive (Norwood and Borgmann, 2003). In general, for an n-component O&C, the sum of the toxic units,  $TU_{\Sigma}$  for each component, Me, is given by Equation-1 (Skeaff et al, 2008):

**Equation-1**

$$TU_{\Sigma} = \sum_{Me=1}^n TU_{Me}$$

Where the  $TU_{Me}$  component is

**Equation-2**  $X = 10 \text{ or } 50 \%$

$$TU_{Me} = \frac{C_{Me}(aq)}{L(E)C_x}$$

**Equation-3**

$$TU_{\Sigma} = \frac{C_{Me,1}(aq)}{L(E)C_{1,x}} + \frac{C_{Me,2}(aq)}{L(E)C_{2,x}} + \dots + \frac{C_{Me,n}(aq)}{L(E)C_{n,x}}$$

In case of the use of  $L(E)C_{50}$  values and assuming complete concentration addition the 50% response of a mixture of chemicals is obtained when the sum of TU of all individual constituents equals unity. Therefore if  $\sum TU \geq 1$  the alloy should be classified or further evaluated (see ecotoxicity validation step).

In the CSA-TU approach the TU are plotted as a function of the O&Cs surface area loading (Figure 4).

The critical surface area loading (CSA) can be derived from the  $TU_{\Sigma} = 1$  line which can be easily translated into a Critical Particle Diameter (CPD).

In Figure 5, a more detailed scheme is given on the CSA-TU strategy and the ecotoxicity validation test.

**Figure 4:** Determination of critical surface area loading from regression line of  $\log TU_{\Sigma}$  versus  $\log$  surface area loading (adapted from Skeaff et al, 2008)

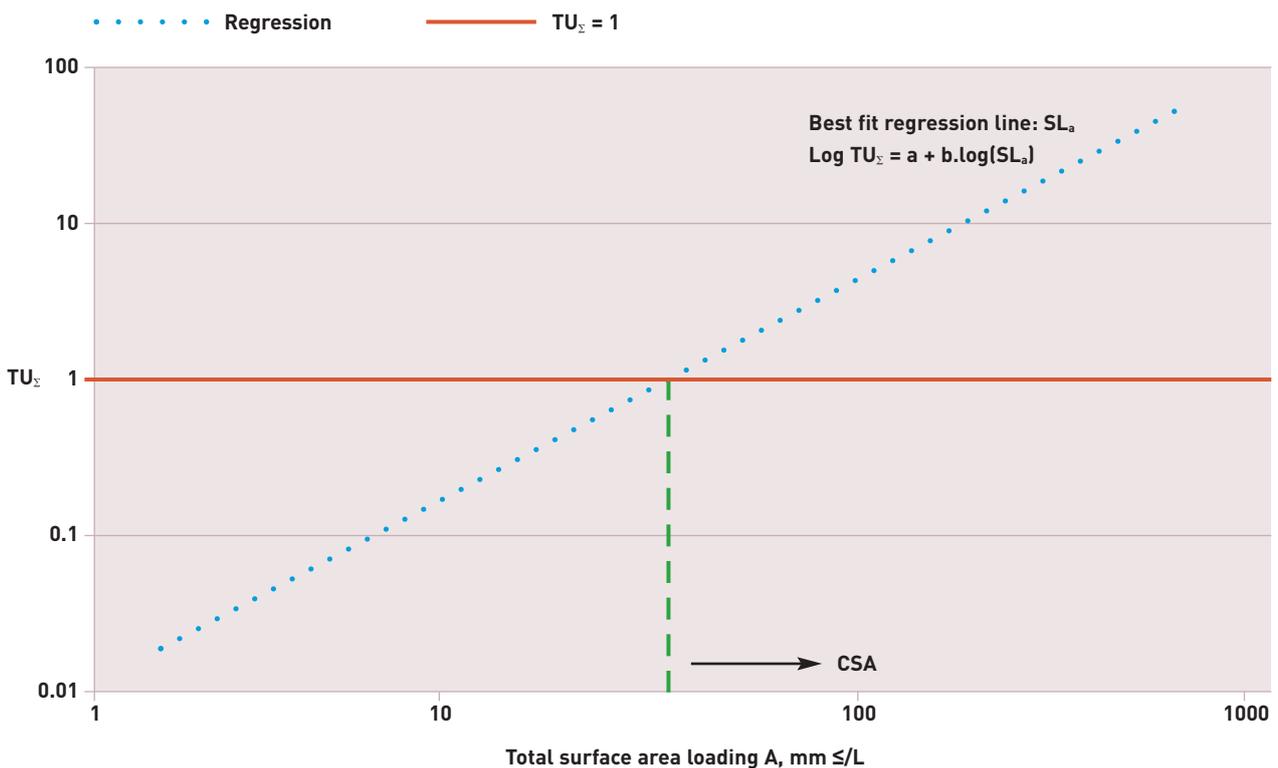
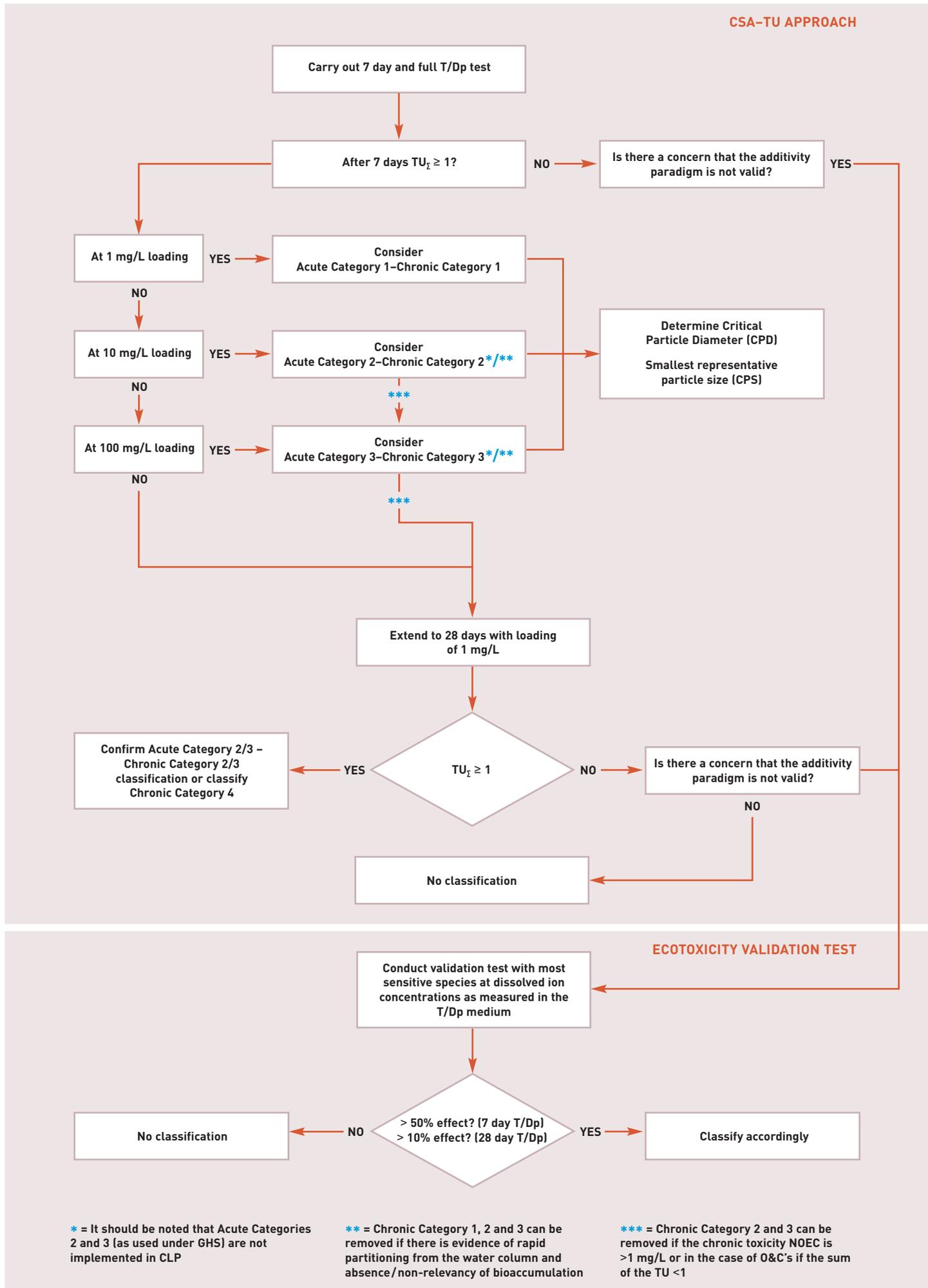


Figure 5: Classification strategy for reactive O&Cs





### 7-day Transformation Test

If the  $TU_x$  after a period of 7 days (or earlier) exceeds one, then the default classification for the O&C is replaced by the following classification as given under the GHS scheme:

- (i) if the summation of the toxic units of the mixture at the low loading rate (1 mg/L) is greater than or equal to 1, then classify Acute Category 1. Classify also as Chronic Category 1 unless there is evidence of both rapid partitioning from the water column and no bioaccumulation.
- (ii) If the summation of the toxic units of the mixture at the medium loading rate (10 mg/L) is greater than or equal to 1, then classify Acute Category 2 (note that Acute Category 2 is not applicable under the EU-CLP regulation). Classify also Chronic Category 2 unless there is evidence of both rapid partitioning from the water column and no bioaccumulation.
- (iii) If the summation of the toxic units of the mixture at the high loading rate (100 mg/L) is greater than or equal to 1, then classify Acute Category 3 (note that Acute Category 3 is not applicable under the EU-CLP regulation). Classify also as Chronic Category 3 unless there is evidence of both rapid partitioning from the water column and no bioaccumulation.

The 7-day Transformation Test could be extended to 28 days in order to remove the Chronic Category 4 default classification and/or to remove Chronic Category 2 and 3.

### 28-day Transformation Test

In the absence of 28-day Transformation Test, a default Chronic category 4 classification is applied. If the process described in previous paragraph results in the classification of Chronic category 1, no further assessment is required as the O&C will be classified irrespective of any further information. In all other cases, further data may have been generated through the dissolution/transformation test for 28 days in order to show that the classification may be amended. If  $TU_x$  after a period of 28 days (or earlier) is higher or equal to 1, classify as Chronic 4. If it is lower than 1 and there is concern that the additivity paradigm is not valid a validation test should be run with the most sensitive species.

### Ecotoxicity validation test

The option to perform an ecotoxicity test has been embedded in the CLP classification strategy (CLP, 2009) for alloys and complex metal containing materials (e.g. ores, concentrates and slags). An ecotoxicity validation step may be important for O&Cs where binding of the metal to abiotic and biological binding sites will be in many cases competitive. Therefore the 'additivity' paradigm is not necessarily valid and additional information may be relevant. This validation test should be conducted with the most sensitive species in the situation where  $TU_x$  is smaller than 1. According to the CLP guidance testing directly in the T/Dp medium is not recommended<sup>9</sup> because the composition of this medium is unlikely to meet the requirements for standard test media to ensure proper survival and reproduction. Therefore, ecotoxicity tests should preferentially be conducted in standard media dosed at metal concentrations equivalent to the concentration level actually measured in the T/Dp medium.

The GHS annex 10 provides specific guidance for purposes such as data validation where it is stated that it may be appropriate to use the aqueous medium from a completed transformation test directly in an OECD 202 and 203 daphnia and fish ecotoxicity test (GHS, 2007). The GHS annex 10 provides also specific guidance for the modification of T/Dp media for use of the completed transformation medium in an OECD 201 algae ecotoxicity test. If the  $CaCl_2 \cdot 2H_2O$  and  $MgSO_4 \cdot 7H_2O$  concentrations of the transformation medium have been reduced to one-fifth of the ISO 6314 medium (i.e. to sustain lower pH levels) micronutrients can be added.

Both options have advantages and disadvantages and expert judgement is needed on a case by case basis.

If the validation test indicates acute (>50% effect) or chronic (>10% effect) effects the O&Cs should be classified accordingly. If no effects are observed the O&C should indeed not be classified.

<sup>9</sup> Although the GHS annex 10 provides specific guidance for purposes such as data validation where it is stated that there might be cases where it may be appropriate to use the aqueous medium from a completed transformation test directly in an OECD 202 and 203 daphnia and fish ecotoxicity test. (GHS, 2007). The GHS annex 10 provides also specific guidance for the modification of T/Dp media for use of the completed transformation medium in an OECD 201 algae ecotoxicity test. If the  $CaCl_2 \cdot 2H_2O$  and  $MgSO_4 \cdot 7H_2O$  concentrations of the transformation medium have been reduced to one-fifth of the ISO 6314 medium (i.e. to sustain lower pH levels) micronutrients can be added.

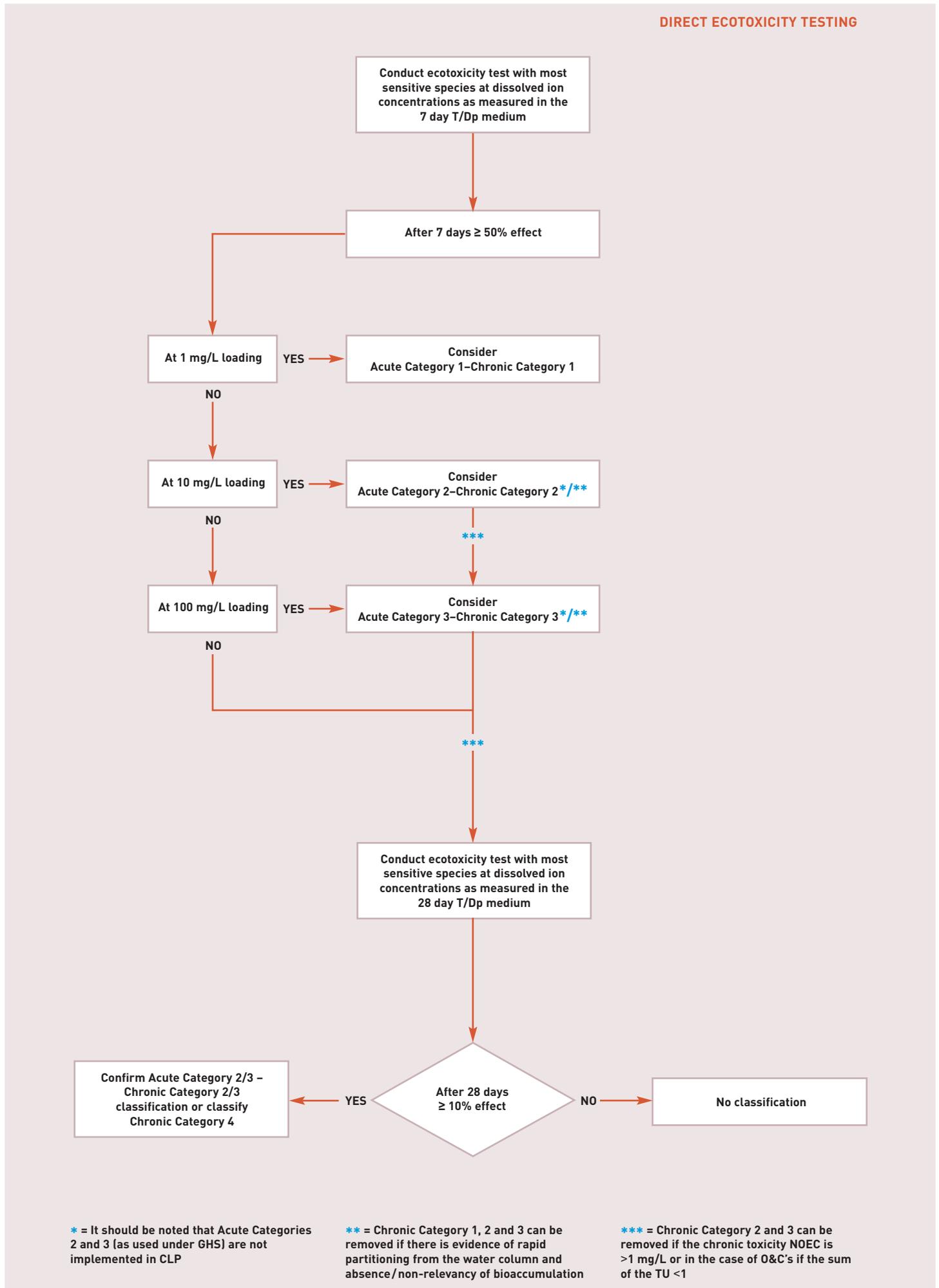


#### 2.5.4.2 Direct testing approach

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In case hazard data are not available for all individual constituents the approach taken should be to test the O&C as it is a substance. Similar to the ecotoxicity validation test acute and chronic ecotoxicity tests should be conducted in standard media dosed at metal concentrations equivalent to the concentration level actually measured in the 7 day–28 day T/Dp medium or by using the T/Dp medium as such if the medium sustains the survival of the organisms. The O&C can then be classified directly on the outcome of the performed ecotoxicity tests as depicted in Figure 6.

Figure 6: Direct testing strategy



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# Acknowledgements



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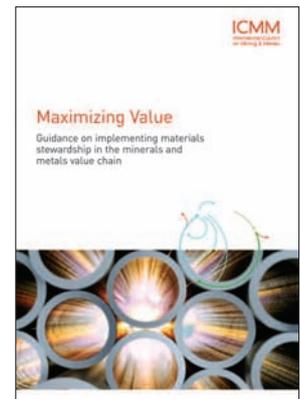
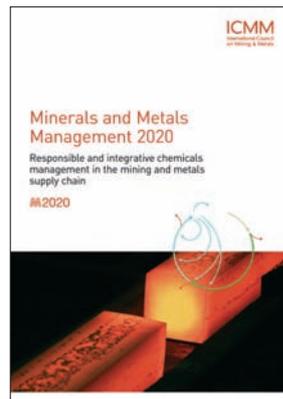
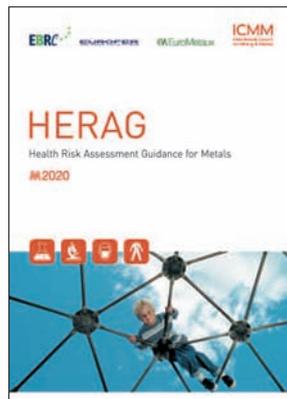
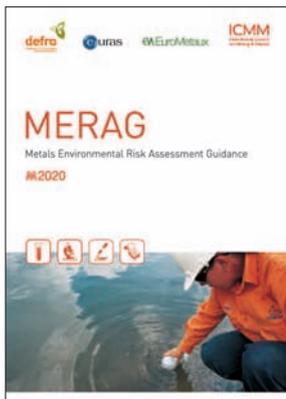
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