UN/SCEGHS/21/INF.5

Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals **24 May 2011**

Twenty–first session
Geneva, 27–29 June 2011
Item 2 (e) of the provisional agenda
Updating of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) – Miscellaneous proposals

Background information and an overview of ongoing projects to define methods for assessing alloys and other inorganic matrix-type substances

Transmitted by the International Council on Mining and Metals (ICMM)

Introduction

1. While several jurisdictions are introducing the hazard assessment rulings for substances, the application of the GHS hazard assessment system for mixtures is only now gaining momentum. The inorganic sector noted some years ago the special situation of matrix type substances, such as alloys, for which the hazards of the mixture do not correspond to those of the constituent elements. In some cases these hazards can be very different.

2. In recent years, through the MERAG and HERAG projects[1] the metals industry has consequently been developing suitable hazard and risk assessment approaches for alloys. These approaches were discussed briefly at the twentieth session of this Committee at which members expressed interest and requested further information. This paper is intended to provide an overview of the concepts developed to date and stimulate discussion on the potential development of a specific assessment scheme in line with the GHS mixture ruling and guidance.

Background

3. In general, a metal alloy consists of a metal or a metalloid base element, constituting the largest percentage of the material and one or several intentionally added elements to achieve specific and improved mechanical, physical or chemical properties compared to its individual alloy constituents.

4. Alloying with specific components provides the alloy with unprecedented properties. The addition of even minor amounts of alloying elements may have significant beneficial effects on the mechanical, metallurgical, physical and chemical performance of

[1] MERAG – Metals Environmental Risk Assessment Guidance, ICMM 2007; HERAG – Health Risk Assessment Guidance, ICMM 2007. See www.icmm.com for further details.

the alloy. These changes in the intrinsic properties make it difficult to translate from the properties of the constituent elements to those of the alloy. These properties may include the corrosion resistance and metal release rate – and hence the related toxicity of the alloy. As a result, the properties of alloys are in need of evaluation based on their specific characteristics, and not on those of the individual constituent metals.

5. The fact that alloys largely exhibit different properties and consequently have different hazard/risk profiles from their individual metal components was recognised in 2002 when the United Nations established the GHS. There are indeed several regulatory frameworks that already require robust assessment of alloys, for example the United Nations Globally Harmonised System of Classification and Labelling GHS (2003, 2005, 2007, 2009) and, in the European Union the Registration Evaluation and Authorisation of Chemicals Regulation REACH (2006) and the CLP Regulation (2008). Between them these require hazard identification, classification and exposure scenarios to be developed and circulated through the supply/use chain for mixtures and their use in downstream applications.

6. While significant progress has been made through industry initiatives, the current lack of internationally validated approaches for assessing alloys means that compliance with such regulatory systems in a manner that describes accurately the actual hazard these materials may pose is challenging.

Potential ways forward

7. The hazard assessment of special inorganic matrix type mixtures and in particular alloys has already been investigated during the Validation Management Group on the validation of the Transformation Dissolution protocol for the Environmental assessment of metals and metal compounds.

8. Based on this experience, industry developed subsequently a hazard assessment strategy scheme under the MERAG program demonstrating how such mixtures could be assessed under GHS for the environmental endpoint.

9. However, unlike the environmental hazard classification scheme for alloys, the development of a health assessment scheme would require significant technical discussion given the complexity of endpoints and the use of bio-elution tests. Industry has advanced well with internal validation of a draft health assessment strategy for alloys and aims to finalise this evaluation in 2011 (under HERAG).

10. A summary of the approaches developed to date through the MERAG and HERAG projects is given in the Annex.

Recommendation

11. To ensure that the GHS hazard assessment strategy and guidance provides adequate identification of the hazards of metallic alloys and other inorganic matrix-type materials, ICMM requests that the Sub-Committee considers providing a mandate to the Organisation for the Economic Co-operation and Development (OECD) to develop specific guidance for the hazard assessment of special inorganic matrix type mixtures. This could be based on the experience developed to date with alloys and the commitment of industry to provide a proposal for the environment in 2011 and on health in 2012.

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Annex

Summary of ongoing work on hazard and risk assessment of alloys in the metals/minerals industry

(Material extracted from the ongoing drafting of the MERAG/HERAG Alloys Fact Sheet)

Introduction

Alloys are defined as "…*a metallic material, homogeneous on a macroscopic scale, consisting of two or more elements so combined that they cannot be readily separated by mechanical means*" (REACH, 2006; UN GHS, 2009).

Alloys are a prominent and diverse group of materials. While some metals are used as engineering materials or in consumer products in their elemental form or as simple mineral compounds, the majority of metals in commerce are used in the form of alloys. While they appear on the market in large volumes and mainly in the massive form, powder forms and even ultra fine or nano forms also exist.

Several regulatory frameworks require assessment of alloys, for example, in the European Union, REACH (2006) and CLP (2008). Between them these frameworks require hazard identification, classification and exposure scenarios to be developed and circulated throughout the supply/use chain for mixtures and their use in downstream applications.

However, alloys may largely exhibit different properties from their individual metal components and consequently have different hazard/risk profiles. This aspect was recognised by the UN GHS, the EU CLP. The EU REACH designated alloys as a form of "special preparation" referring to a potential difference in properties from their constituents and recognising that specific assessment methods, tools and new exposure scenarios will be required.

The work carried out up to date by the metals sector has aimed to collect existing knowledge and experience on alloys, in order to provide possible consolidated hazard and risk assessment guidance on:

(i) the properties of alloys and how these might influence the hazard profile

(ii) hazard identification and classification of the alloy: environment and health, including preliminary guidance on how the hazard profile of the alloy and the differences of it versus its constituents could be assessed using pragmatic tools like the Transformation Dissolution protocol and bio-accessibility tests

(iii) grouping in order to plan for appropriate testing strategies

(iv) developing relevant REACH exposure scenarios for alloys

A brief overview of the items relevant to hazard assessment and classification is provided here below. More detailed text can be found in the draft MERAG/HERAG alloys fact sheet.

(i) What do we know about alloys properties?

In general, a metal alloy consists of a metal or a metalloid base element, constituting the largest percentage of the material and one or several intentionally added elements to achieve specific and improved mechanical, physical or chemical properties compared to its individual alloy constituents.

The addition of even minor amounts of alloying elements may have significant beneficial effects on performance of the alloy. These changes, sometimes radical, in the intrinsic properties, may make translation of properties, such as corrosion resistance and metal release rates, of individual elements to the alloy (and hence their related toxicity), inaccurate and irrelevant. As a result, the properties of alloys need by preference an evaluation based on their alloy specific characteristics, and not on the individual constituent metals.

Like metals, alloys will interact with the environment forming surface oxides and other corrosion products. Corrosion[2] and surface properties play an important role in the potential release of alloys to the environment. Metal release is described as the amount of metal that is released or dissolved from surface oxides or corrosion products on metals or alloys per unit of surface area and time unit (Leygraf and Graedel, 2002). While corrosion and oxidation are naturally occurring, primarily electrochemical processes, the process of metal release/dissolution is usually combined, electrochemically and chemically induced.

The extent of corrosion and metal release/dissolution depends on a combination of interacting parameters including material characteristics, surface properties, exposed surface and prevailing environmental and exposure conditions:

Surface oxidation and corrosion products often act as a barrier to the metal release. Those products are strongly related to parameters such as surface composition and material properties. The barrier capacities influence the rate of further corrosion/oxidation and determine the corrosion resistance of the alloy.

Prevailing environmental and exposure conditions will largely influence the metal release process for metals and metal alloys. For example, severe acidic conditions and the presence of halogen ions (e.g. chlorides) will be the most corrosive conditions for many engineering alloys. Under these conditions, the protective ability and re-passivating properties of surface oxides can indeed be hindered. Neutral and more alkaline conditions are more severe for other metals and metalloids such as molybdenum and silicon.

The degree of alloying may influence noticeably the extent of metal release, which from metallic alloys can be significantly different in comparison with their pure metal constituents. This is demonstrated e.g. by molybdenum, which as an alloy constituent in stainless steel is resistant to very extreme environmental conditions, and not as metal.

Overall, in view of the above, it is imperative to treat alloys as unique materials of disparate intrinsic properties and not as simple mixtures of the pure constituents (Herting et al 2005, 2008; Goidanich et al, 2008). This requires consequently separate assessments of their different and distinctive hazard profiles for man and the environment. Such assessments will demand detailed knowledge of physico-chemical bulk and surface properties, release rates and equilibrium in relevant media, and the chemical speciation and bioavailability aspects of the released metals.

These unique alloys properties were presented and further discussed at an EU workshop in 2009 and more information on the outcomes of this workshop can be made available.

(ii) Hazard identification and classification guidance

(a) Environment

The environmental hazard identification and classification of alloys builds further upon the concepts and experience already developed for the classification and labelling of metals and sparingly soluble inorganic metal compounds, i.e. the classification is based on the level of metal ion that may be present in solution following the addition of an alloy to a standard aqueous medium defined by the OECD (Transformation Dissolution protocol (OECD 2001).

[2] Corrosion is defined as the *"…chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties"* (ASM, 1987)

The aim of the MERAG/HERAG alloys fact sheet is to highlight the various alloys-specific considerations that should be taken into account while conducting the hazard identification and classification of alloys and providing guidance on how to classify alloys in a pragmatic way.

The conceptual outline of the proposed alloy classification strategy builds further on the scheme used to assess the environmental hazards of metals (Chapter IX, X of the UN GHS) and is given in Figure 1. It follows a tiered approach and is in line with the general regulatory context in which testing should only be considered in case no other existing data are available that provide for an adequate reliable classification. It also recognises that alloys have unique release characteristics and that in many cases it is relevant to develop real data sets in order to obtain a more appropriate classification.

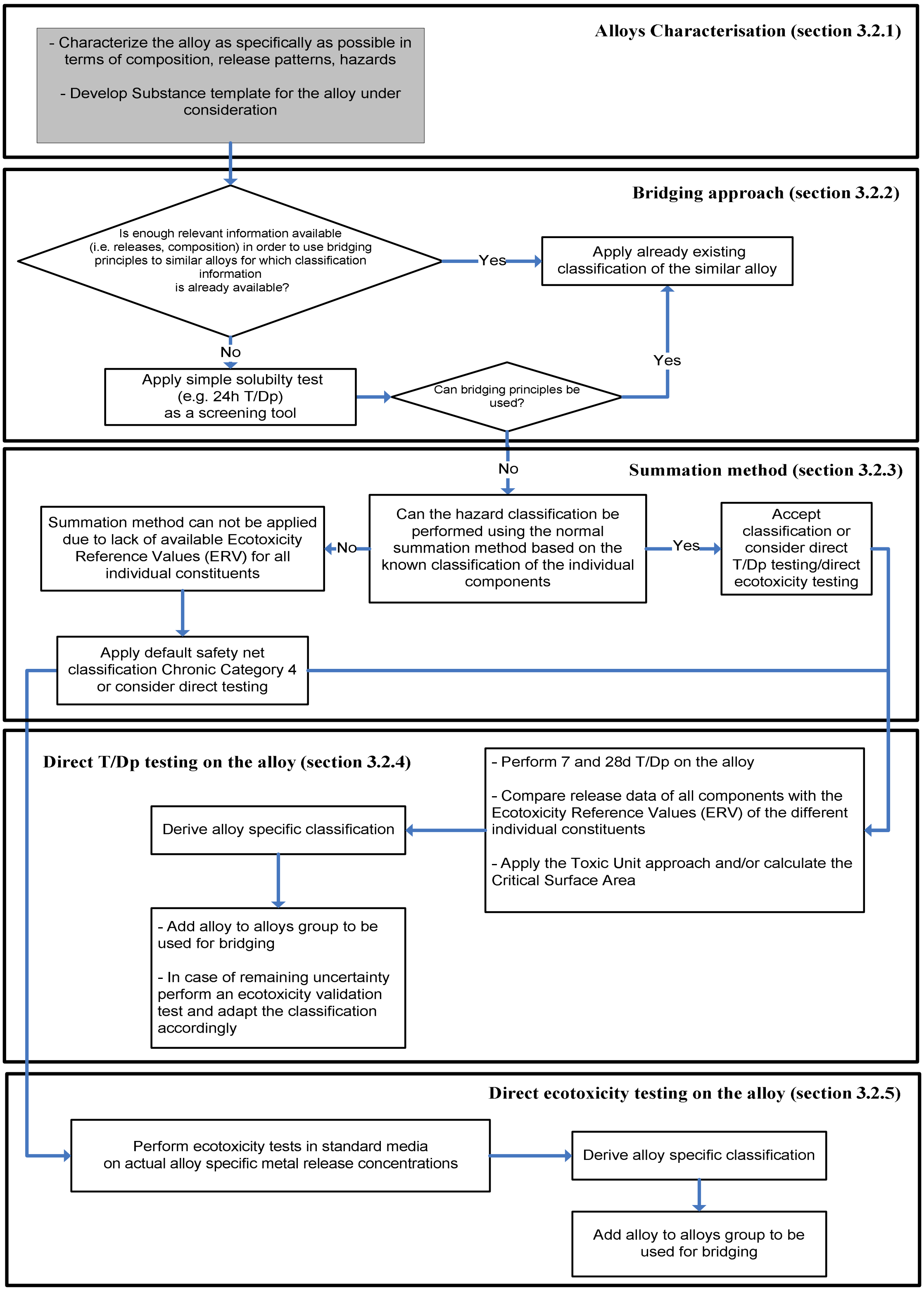

Figure 1: Conceptual overview for the hazard evaluation for alloys * the summation method can not be used in cases where metal releases from the alloy are higher than the constituting single metal forms.

Main assumptions and concepts used in the tiered approach are briefly summarized here below.

Step 1: alloys characterization

In the first step of the scheme, relevant data is compiled for the alloy that needs to be classified. This process has three elements: 1) defining the alloy composition; 2) estimating releases under conditions relevant for the aquatic environment; and 3) assembling the best available ecotoxicological hazard data that is available for the alloy itself or its constituents.

Step 2: bridging approach

Given the vast number of alloys that exist, testing all alloys is deemed impractical. Instead it is advocated to evaluate if bridging principles3 can be applied in order to justify read-across4 of the hazard classification or no classification from a peer alloy group displaying similar dissolution behaviour (i.e. similar releases rate of metals).

Step 3: summation method (default approach)

The use of the summation method is used as the default approach in case the metal release of the alloy are similar or lower compared to the constituting single metal forms. For this approach the alloy is considered as behaving as a simple mixture and the classification of the alloy is based on summation of the classification of its individual components.

Step 4: classification based on the results of transformation/dissolution tests

For the environment, the principles used to assess the hazard properties for metals (e.g. release rate and equilibrium as a function of surface properties) can be taken forward in almost exactly the same way for alloys. Indeed, recognising that the metallic ion dissolved in aqueous solution is the main driver for environmental aquatic toxicity expression, the tool to measure the release rate and equilibrium developed for metals, i.e. the Transformation Dissolution protocol (TDp) (OECD, 2001), can equally be used for assessing the release rates of metals from alloys. This information can subsequently be used to classify the mixture under CLP by applying the “Toxic Unit (TU) concept” on the released metal fractions, recognising their individual hazard profiles. By using the TU concept, all released hazardous metals are taking into account. By default, strict additivity is assumed and the alloy should be classified or further evaluated if Σ TU ≥ 1 whereby ‘M factors’ are included in the assessment where appropriate. In case of doubt on the validity of the strict additivity assumption it is recommended to perform an ecotoxicity validity test.

In line with the implementation of the third revision of the GHS into the CLP guidance the classification should be conducted in 2 ways:

(1) using the surrogate approach in absence of appropriate chronic toxicity reference data; or

(2) using chronic reference data when available.

The scheme below describe an example of the proposed classification strategy for reactive alloys based upon available and appropriate chronic toxicity data for the soluble form of the constituents.

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[3] bridging is the use of data of similar tested alloys and its individual hazardous ingredient substances to classify an alloy for which such data are not available

[4] read-across is the use of hazard specific information for one substance to predict the same hazard for another substance

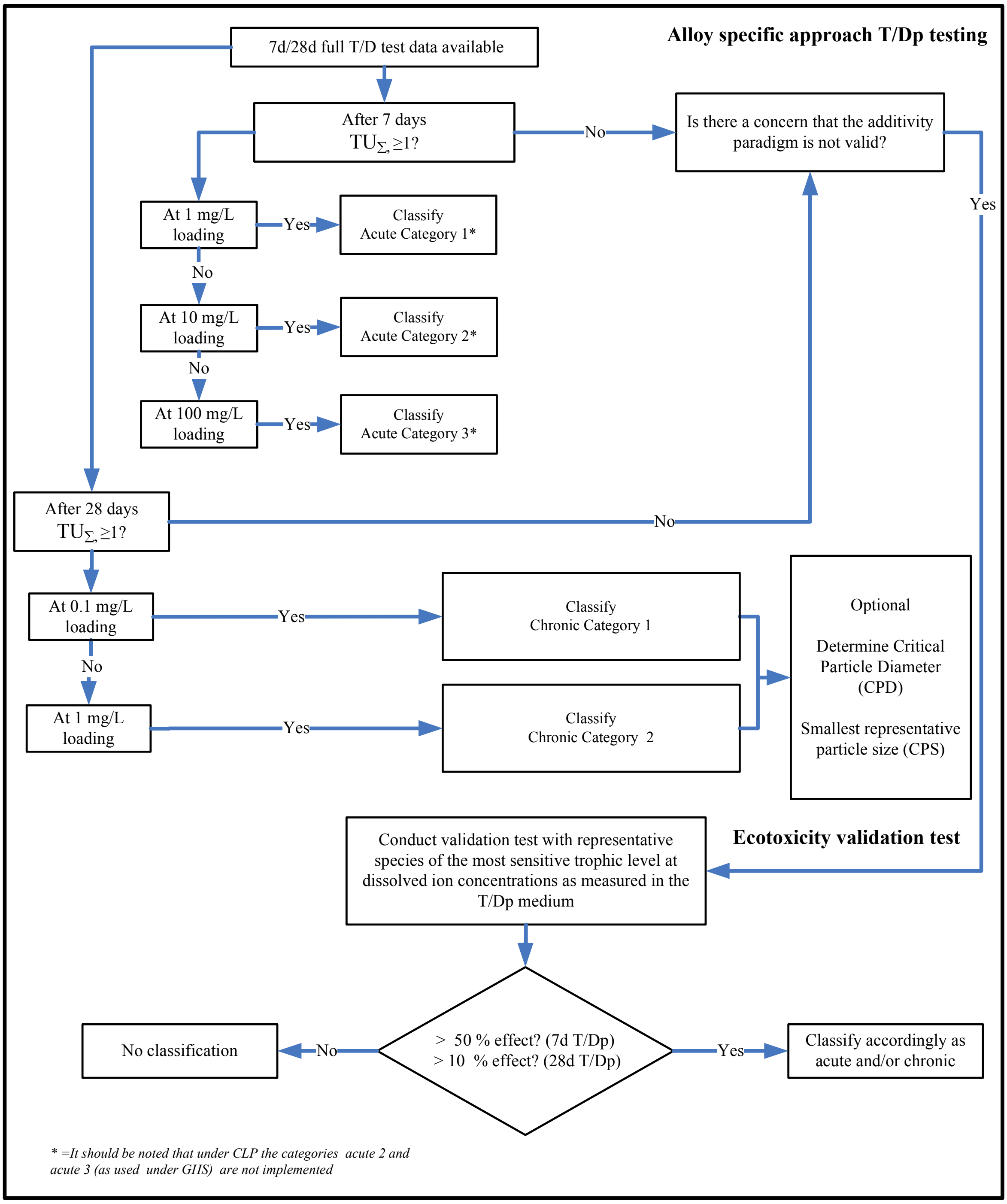


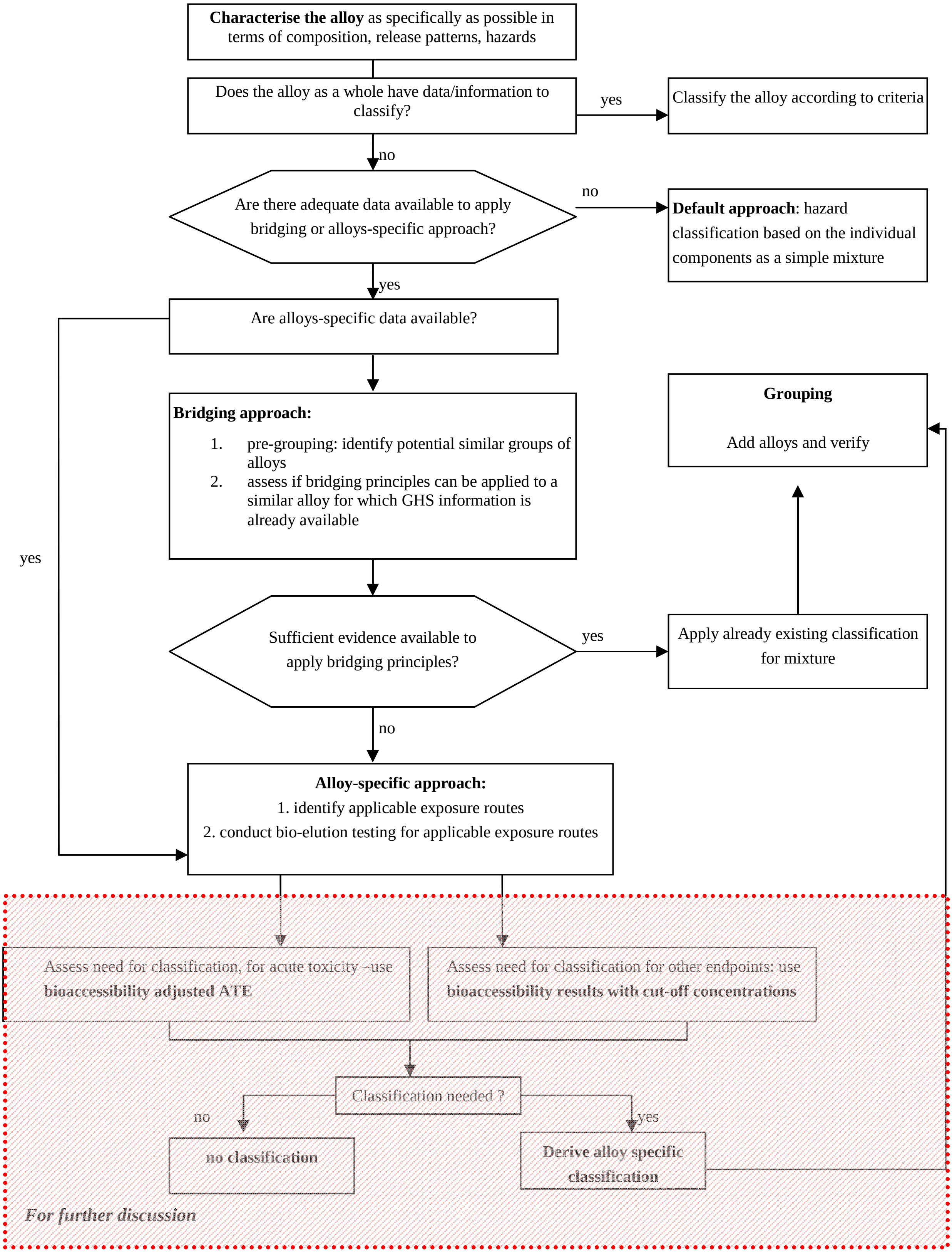
Figure 2: Classification strategy for reactive alloys based on chronic data and for which no rapid degradation is demonstrated (UN GHS 2009)

Step 5: Direct testing

In rare cases where hazard data are not available for all individual constituents, or different hazard properties for the alloy are to be expected due to combined or antagonistic effects, the approach can be taken to test the alloy as it is a substance. Given that nominal testing is not recommended because the loading is highly influenced by the surface of the material added, it is recommended to conduct the ecotoxicity tests at the concentrations obtained during the TD testing after 7 days (acute) or 28 days (chronic). The testing should be conducted by spiking soluble metal salts up to these concentrations.

(b) Human health

For human health hazard identification and classification, an overall framework has been proposed, starting from the collection and evaluation of available data and followed by three further tiers of evaluation depending on the sufficiency of these data.


Characterise the alloy as specifically as possible in terms of composition, release patterns, hazards
Does the alloy as a whole have data/information to classify?
yes
Classify the alloy according to criteria
no
Are there adequate data available to apply bridging or alloys-specific approach?
no
Default approach: hazard classification based on the individual components as a simple mixture
yes
Are alloys-specific data available?
yes
Bridging approach:
1. pre-grouping: identify potential similar groups of alloys
2. assess if bridging principles can be applied to a similar alloy for which GHS information is already available
Grouping
Add alloys and verify
Sufficient evidence available to apply bridging principles?
yes
Apply already existing classification for mixture
no
Alloy-specific approach:
1. identify applicable exposure routes
2. conduct bio-elution testing for applicable exposure routes
Assess need for classification, for acute toxicity –use bioaccessibility adjusted ATE
Assess need for classification for other endpoints: use bioaccessibility results with cut-off concentrations
Classification needed ?
no
no classification
yes
Derive alloy specific classification
For further discussion

The default approach, to be applied when few or no alloy-specific data are available, follows the rules of GHS: additivity formula for acute toxicity classification and cut-off concentration/limit approaches for the other toxicological endpoints.

Use of bridging principles should be considered for the classification of alloys for which toxicological data are available to group those alloys with similar alloys for which classification is possible.

If sufficient and reliable alloy toxicity data are available for classification, some refinement to the classification approach could be proposed. One of the tools that could potentially allow some refinement of the hazard identification and classification of alloys is bioaccessibility testing. The latter has already been incorporated into decision-making in some regulatory areas. However, further testing on a broader range of alloys and a structured validation effort is needed before a bioaccessibility-based approach to hazard classification can be implemented.

(iii) Grouping

Given the vast number of alloys, and the desire to avoid unnecessary testing, it is worthwhile considering grouping alloys with similar release characteristics and subsequently read-across when appropriate. Alloys are already grouped in numerous national and international standards (AFNOR, AISI, DIN, ASTM, JISI, UNS, etc.) based on their chemical composition. In addition they can also be grouped in respect to their technical performance (e.g. hard metals, stainless steels, …). These types of groupings, however, are in most cases less useful for hazard identification and classification purposes. Instead, for most alloys, (eco)toxicity will depend primarily on the rate of metal release and concentration in the environment or human body fluids under biologically relevant conditions. These release rates and concentrations can however not necessarily be adequately predicted based solely on the bulk composition of the alloy.

A stepwise approach has been proposed in the MERAG/HERAG draft, starting with an understanding of the technical performance of the alloy group under consideration. A second key step is delivered by basic thermodynamic information (Pourbaix diagrams) indicating when a constituent of an alloy would be stable in a given medium, and when it would not. A third step is provided by assessing information regarding the release rate and concentration from simple solubility data for the relevant components of the alloys. The information gathered in these 3 steps, in combination with information on surface properties and corrosion science, should form a sufficiently solid basis for grouping to define for which benchmark alloys a hazard profile should be developed and which others could be read-across to this benchmark alloy in a precautionary way. This information, combined if need be with a comprehensive testing programme using artificial biological fluids (human classification) or the use of transformation dissolution tests (environmental classification), can enable robust decisions to be taken regarding the likely behaviour of alloys in the context of classification and potential for risk.

(iv) Others

The MERAG/HERAG fact sheet also proposes a generic approach to the drafting of exposure scenarios/safety data sheets for alloy producers. As the composition of an alloy can involve a significant number of constituents, the alloy producer may receive a significant amount of information about the constituents (as forwarded by the registrants of the constituents) from which it will be difficult to identify and to extract ***key and relevant information*** that he should use and communicate further down the supply chain. To ensure overall safe use, it is vital to have comprehensive information in respect of their content, proposed approaches, methodologies and language. A workflow is proposed, starting from the collection and evaluation of the data, and moving on to the assessment of the classification of the alloy and the identification of the driver of the exposure scenario (the lead substance) that will trigger the risk management measures to be put in place and communicated. When alloys data are available, some refinements of the proposed risk management measures can be considered.

While this part is more related to REACH, the proposed approach can be used outside the EU and may be encountered for example in alloys Safety Data Sheets circulated outside the EU.

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