INTERNATIONAL MOLYBDENUM ASSOCIATION

May 2010

Hazard Identification/Assessment of Molybdenum Disulfide (MoS_2)

in preparation for Notification to the EU Inventory (EU CLP Regulation)

Substance identification (according to European Chemical Substances Information System, ESIS):

EC Name	EINECS No.	CAS No.
molybdenum disulphide (MoS_2)	215-263-9	1317-33-5
molybdenite (MoS_2)	215-172-4	1309-56-4

The Molybdenum Consortium (MoCon), an initiative of the International Molybdenum Association (IMOA), is currently preparing a number of REACH registration dossiers of molybdenum substances for its members. In this context, a comprehensive work and research programme relating to physico-chemical, human health and environmental hazard and risk assessment is ongoing.

On the one hand, molybdenum disulfilde (MoS_2) as a **naturally-occurring**, non-chemically modified ore concentrate is exempt from REACH registration, in accordance with Annex V of the REACH Regulation. On the other, IMOA has been made aware by CONCAWE that petro-chemical refining processes produce a **chemically-manufactured** MoS2 that will require REACH registration (as it does not meet the Annex V criteria for exemption). It is in this context that the IMOA Molybdenum Consortium for REACH has prepared this current document.

MoCon has always included MoS_2 to some extent in its research programme, to assess potential hazardous properties required by the EU CLP regulation and to prepare the notification of MoS_2 to the C&L inventory.

At this point in time, the following conclusion is derived:

Phys-Chem: No hazard identified
Human Health: No hazard identified
Environment: No hazard identified
Overall conclusion:
MoS_2 does not meet the criteria for classification under the CLP-Regulation.
MoS_2 is not a hazardous substance.

Initial information on the stability/solubility of MoS_2:

Molybdenum disulfide is the chemical form in which the metal molybdenum is found in natural ore bodies as the mineral molybdenite. This fact already initially indicates a high stability of this compound under ambient/natural conditions, including low solubility and low reactivity. MoS2 can be designated as chemically inert under normal conditions.

MoCon has recently conducted experimental investigation on the solubility of MoS_2 (water solubility test in accordance with OECD guideline 105, conducted in accordance with GLP principles). A sample of MoS_2 ("Technical Fine Grade", purity min 98%, median particle size ca. 4.6 µm) was suspended in distilled water at a loading of 2 g/L. Analytical samples were taken daily, separated from the undissolved solid and analysed for the concentration of dissolved molybdenum. During the 8-day study period, concentrations of dissolved molybdenum were below 100 µg/L. This was re-calculated (based on stoichiometry) and rounded to a conservative maximum water solubility of MoS_2 under these laboratory test conditions of 200 µg/L.

Furthermore, MoCon has recently conducted in-vitro "bioaccessibility" testing on MoS_2 (same sample characteristics as above). The test programme included the following five artificial physiological media: phosphate-buffered saline (pH 7.4), Gamble's solution (pH 7.4), artificial lysosomal fluid (pH 4.5), artificial gastric fluid (pH 1.5) and artificial sweat (pH 6.5). The test item was mixed with the freshly made solutions at a solid to liquid ratio of 0.1 g/L. Two exposure periods (2h and 24h) were used after which the undissolved solid material was separated from the supernatant. Subsequently, the solutions were analysed for the dissolved molybdenum concentration. Very low concentrations of dissolved molybdenum were measured from below background to ca. 20 µg/L, depending on medium and exposure time. Between 0.001% and 0.04% (mass) of the added sample amounts dissolved in this test. The solubility of MoS_2 in artificial biological fluids under these laboratory test conditions was shown to be negligible.

Preliminary assessment of physico-chemical hazard classification:

At this point in time, the available information indicates no need for a hazard classification of MoS_2 because of physico-chemical hazards (such as explosiveness, flammability, auto-flammability, oxidising properties or corrosion to metals). That said, an in-depth assessment of flammability is currently ongoing (see below).

MoS_2 is used on an industrial scale to produce Roasted molybdenum concentrate. The overall mechanism for the transformation of MoS_2 to RMC involves a complex series of oxidation reactions.[1] The overall reaction is exothermic, but requires a high activation energy (heating to at least 400°C in air).

[1] Gupta, C.K.: Extractive Metallurgy of Molybdenum. CRC Press, 1992. ISBN 0-8493-4758-0

Based on this information, MoS_2 does not need to be considered as an oxidising substance in the sense of the CLP regulation, as it does not yield oxygen to or supports combustion of other substances.

Spontaneous self-ignition or explosion have not been observed, which is in agreement with the high activation energy needed to start reaction with oxygen.

To assess whether hazard classification for flammability is required, IMOA/MoCon is currently conducting a standard laboratory test (EU Testing Method A.10). When the results are available, this issue will be assessed further.

Preliminary assessment of human health hazard classification:

At this point in time, the available information indicates no need for a health hazard classification of MoS_2 for any local, general systemic or specific organ effect after acute or repeated exposure. This assessment is specifically supported by the poor to negligible solubility of MoS_2 and its chemical inertness. Molybdenum is an essential nutrient element and molybdenum compounds are of low general toxicity towards human health. Metallic/inorganic molybdenum compounds have not been subjected to hazard classification before.

The sole exception is molybdenum trioxide, MoO_3, which was classified in in the 1st ATP to the EU CLP Regulation (in accordance with the GHS hazard classification system) as a Carcinogen Category 2, with the hazard statement H351: "Suspected of causing cancer *via inhalation*.", as well as for eye and respiratory irritation. The carcinogenicity classification is based on experimental data in laboratory animals (male and female rats and mice), in which *some evidence of carcinogenic activity* was observed (mice only). There are no human case reports or epidemiological data in support of this classification. It is believed that the effects caused by MoO_3 in the laboratory animals are very specific to MoO_3 particles and the fact that the moderately soluble MoO_3 reacts slightly acidic upon dissolution. Local irritation in the lung due to acidity and particle shape is the postulated cause for the observed results regarding carcinogenicity. The same acidity effect may be the background for the current classification of MoO_3 as an eye and respiratory irritant.

Available studies on other molybdenum compounds not showing this acidic reaction (e.g. molybdenum metal, molybdenum dioxide, sodium- and ammonium molybdates) do not show toxicological effects.

Based on this, the classifications for MoO_3, which are for substance specific, local effects, should not be read-across to any other molybdenum compound.

Preliminary assessment of environmental hazard classification:

At this point in time, the available information identifies no requirement for an environmental hazard classification of MoS_2, based on the poor to negligible solubility of and its chemical inertness, as explained below.

In accordance with the EU and UN-GHS rules, metals and metal compounds are classified for aquatic hazard mainly based on their i) intrinsic toxicity and ii) solubility.

i) Regarding intrinsic toxicity:

To be considered as a hazardous substance, the Ecotoxicological Reference Value (ERV) (EC50 or LC50) for that substance has to be:

- lower than 100 mg/L to qualify for an *acute* classification
- lower than 1 mg/L to qualify for a *chronic* classification.

Acute/chronic classification of a substance is required when the lowest acute value is below 100 mg/L for relevant standard species that are generally considered for classification purposes (algae, invertebrates, fish). For the MoCon substances, for compounds relevant for read-across, the lowest acute data points are all over 100 mg/L, so no acute classification is required.

As commented, to qualify for a chronic classification, the ERV has to be lower than 1 mg/L. The value of **39.9 mg/L is the lowest reliable chronic value for molybdenum** (34d-EC10 for the fish *Pimephales promelas*), and is therefore the ERVchronic for this element, so no chronic classified is required

ii) Regarding solubility:

In the case of sparingly soluble substances such as molybdenum disulfide, the approach for environmental classification is the one shown on the next page in Figure 1 (Annex 9 of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS)), where the Transformation/Dissolution protocol (T/D P) is applied.

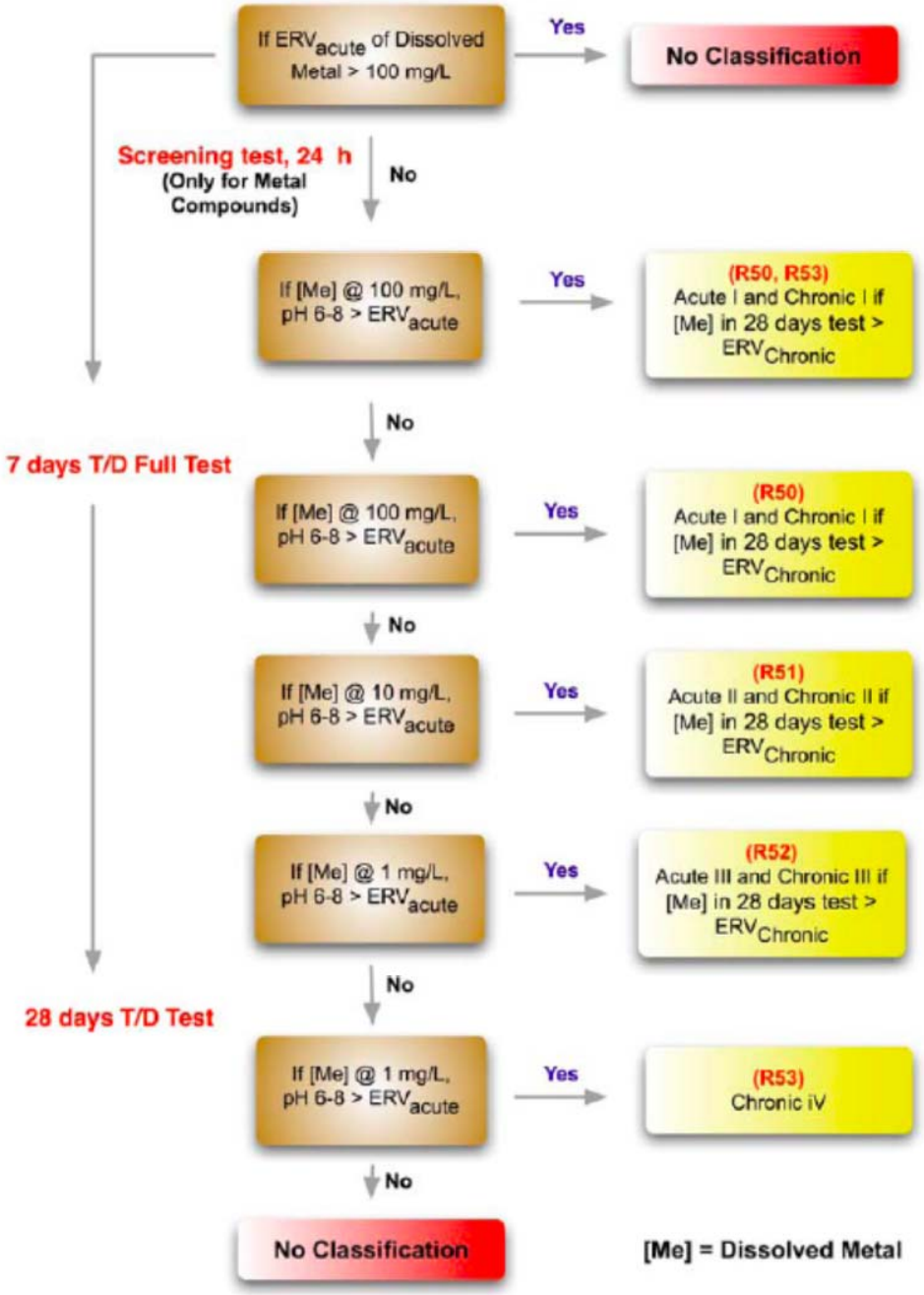
Before the start of any T/D testing program, it is first necessary to assess if the molybdenum substance is hazardous or not and then evaluate the need for T/D testing of the substance taking into account its solubility.

In terms of the solubility of molybdenum disulfide (< 200 ug/L), simply from an inspection of the acute and chronic ERV values (i.e. > 100 mg Mo/L and 39.9 mg Mo/L respectively) and taking into account that very low solubility and the loading that would be used in the Transformation/dissolution test (see Figure I), we can safely conclude that NO Chronic or Acute Classification is assignable.

Environmental Hazard Assessment Conclusion:

Given the very low solubility of molybdenum disulphide, and taking into account that all reliable acute values are situated well above the chronic ERV of 39.9 mg/l, it can be concluded that no environmental classification is required for molybdenum or molybdenum compounds, including molybdenum disulphide (read-across approach).

Figure 1.- Classification of Sparingly Soluble Substances using the Dissolution Transformatio Protocol.



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