Guidance Document

Transport Classification of Lead Metal Ingots

20th May 2024

Executive Summary

Lead metal is not a dangerous good entry listed in Chapter 3.2 of UN Model Regulation or Table A of Chapter 3.2 of ADR 2023.

The aquatic hazard classification for metals in massive forms can be derived directly comparing the dissolution data from the Transformation Dissolution protocol (T/Dp) tests carried out on the insoluble/sparingly soluble metal and the corresponding ecotoxicity reference values (ERVs) of the soluble metal ion derived from acute and chronic aquatic toxicity test data specified under 2.2.9.1.10.3 of ADR. Here we assess the transport classification for commercially available lead metal ingots, using the *Critical Surface Approach (CSA)*, a method developed specifically to assess sparingly soluble inorganic substances and that helps assess substances that cannot be directly tested using the standardized T/Dp protocol due to size and shape.

The assessment demonstrates that typical lead metal ingots that are shipped by road, rail or sea do not meet the classification criteria to be assigned to the entry for UN 3077 Environmentally Hazardous Substance.

Background

The carriage of dangerous goods by road, rail, inland waterway, sea, and air is regulated internationally by European agreements, directives, and regulations.

Lead metal is not a dangerous good entry listed in Chapter 3.2 of UN Model Regulation or Table A of Chapter 3.2 of ADR 2023. It is therefore the responsibility of the consigner to establish whether the product being transported, in this case lead metal ingots, meet any of the criteria for classification as dangerous goods. This paper describes how lead metal ingots may be assessed for environmentally hazardous properties using available aquatic toxicity test data and information on releases of the toxic lead ion using the Transformation Dissolution Protocol (T/Dp) test developed for metals and metal compounds.

Properties of Lead Metal Ingots

There are a small number of generally traded shapes and weights for lead ingots that are transported. Ingots are generally shaped so that they may be easily handled by lifting by "ears" at each end. It is usual for lead ingots to be stacked and strapped into bundles, often weighing approximately 1 tonne, to facilitate handling by fork-lift trucks and other mechanical lifting and handling devices. Typically, lead ingots arising from recycling of wastes containing lead, known as secondary lead, historically tended to be produced in 25 kg, whilst ingots produced out of "new" lead originated from lead bearing ores, known as primary lead, tended to be heavier, typically 40-50 kg. There are variations from manufacturer to manufacturer, and weight and dimensions may be tailored to specific customer demands.

In the present assessment for classification, the critical surface approach (CSA) has been applied to two typical and commercially available lead metal ingot examples (Vedanta, Hindustan Zinc, 25 kg; Bergsoe, Boliden, 45 kg) that are registered at the London Metal Exchange (LME) and traded in Europe (Table 1). Other forms of lead metal ingots shipped may be assessed as to whether they meet the criteria for classification as environmentally hazardous substances (UN 3077) using equivalent methodology.

Table 1: Specifications of lead ingots used in the present assessment.

Specifications	Lead ingots	
	Vedanta (Hindustan Zinc)[1]	Bergsoe (New Boliden)[2]
Dimensions	535 mm x 85 mm x 75 mm	627 mm x 121 mm x 84 mm
Weight	25 kg	45 kg
Purity	99.99 % Pb	99.97 % Pb
Brand name	Vedanta	BERA

1: https://vedanta-zincinternational.com/wp-content/uploads/2021/04/Pure-Lead-2.pdf
2:https://www.boliden.com/48e712/globalassets/operations/products/lead/lead-bergsoe-product-sheet-2018.pdf

Aquatic Toxicity Tests Applicable for Classification

<u>Acute classification</u>

According to the general definition of 'acute aquatic toxicity' given in the regulatory criteria (UN Globally Harmonised System for Classification and Labelling of Chemicals, 10th Revised Edition, Annex 9; ADR 2023 section 2.2.9.1.10.2.3; EU CLP Regulation EU 1272/2008, Section 4.1.2.7.1), a fish 96h-LC50 (OECD 203 or equivalent), a crustacea species 48h-EC50 (OECD 202 or equivalent), and/or an algal species 72h- or 96h-EC50 (OECD 201 or equivalent), will be used to determine the acute toxicity classification. These species are considered as surrogates for all aquatic organisms. Data on other species (such as duckweed *Lemna*) may also be considered if the test methodology is suitable. The EC50 values obtained from aquatic plant growth inhibition tests are normally treated as acute values for classification purposes. The standard species/endpoints for each of the three taxonomic groups are:

- 3-4 days Algae EC50 growth rate (e.g. *R. subcapitata*, *C. vulgaris*, C. *reinhardtii*)
- 48 hours Invertebrates/Crustacea first instar juveniles L(E)C50 mortality or immobilization (e.g. *D. magna*)
- 96 hours Fish – juveniles (0.1-5g) LC50 mortality (e.g., P*. promelas*, *O. mykiss*, *S. fontinalis*, *D. rerio*, *C. carpio*)
- For vascular plants (e.g. *Lemna* spp.), EC50 values obtained from tests consistent with OECD TG 221 and US EPA 850:4400 are retained for the database. The observational acute endpoint is the change (50% effect) in the number of fronds produced and the test duration is 7 days.

Standard endpoints that can be used for classification purposes have been defined for each taxonomic group. Mortality is the acute effect that is considered for crustaceans and fish (LC50), whereas inhibition of growth rate is the relevant effect for algae (ErC50); effect on biomass can be used for algae when no data on growth rate are available.

Acute ERV for Lead

Reliable acute aquatic data for soluble lead compounds were found for six species:

- the invertebrates *C. dubia* (n=17) and *D. magna* (n=4);
- the fish species *O. mykiss/S. gairdneri* (n=12), *P. promelas* (n=24) and *P. reticulata* (n=1);
- the green alga *R. subcapitata* (n=9);
- the aquatic plant *L. minor* (duckweed) (n=1).

The ecotoxicity data for the soluble lead compounds are combined to derive acute ecotoxicity reference values (ERVs) to allow a comparison of the toxicity data with solubility data to allow classification as described in section A9.7.1 of the UN GHS.

Table 2: Overview of Acute Environmental Reference Values (ERVs) for Soluble Lead (ARCHE, 2024).

Species	Assessed parameter (most sensitive)	Reported values represent the dissolved fraction					
		pH: 5.51-6.50		pH: 6.51-7.50		pH: 7.51-8.50	
		Lowest value	Geomean[1] (n>3)	Lowest value	Geomean[1] (n>3)	Lowest value	Geomean[1] (n>3)
Crustaceans							
C. dubia	Mortality	73.56 µg Pb/L n=3			121.3 µg Pb/L n=6		125.3 µg Pb/L n=9
D. magna	Mortality					337.1 µg Pb/L n=3	
Fish							
O. mykiss	Mortality				445.1 µg Pb/L n=8	127.0 µg Pb/L n=2	
P. promelas	Mortality	40.8 µg Pb/L n=3			241.1 µg Pb/L n=10		500.1 µg Pb/L n=11
P. reticulata	Mortality	1990.0 µg Pb/L n=3					
Algae							
R. subcapitata	Growth rate	72.0 µg Pb/L n=3			32.5 µg Pb/L n=5	20.5 µg Pb/L n=1	
Aquatic plants							
L. minor	Root growth rate					221.7 µg Pb/L n=1	
Acute ERV		**40.8 µg Pb/L**		**32.5 µg Pb/L**		**20.5 µg Pb/L**	

[(1)]: geometric mean was used to derive the datapoint when n>3; otherwise, the lowest value was selected.
Values in green indicate the lowest value used for ERV for a specific pH-band.

Chronic classification

According to the general definition of 'chronic aquatic toxicity' that is outlined in the UN Globally Harmonised System for Classification and Labelling of Chemicals, 10th Revised Edition, Annex 9, ADR 2023 section 2.2.9.1.10.2.4, and 2nd ATP to the CLP (EC Regulation, 2008; EU Regulation, 2011), NOEC or other equivalent ECx (e.g. EC10) values should be used, and should be determined according to the following Standard Guidelines:

- For fish, chronic or long-term tests with fish that are initiated with fertilized eggs, embryos, juveniles, or reproductively active adults. Tests should be consistent with OECD Test Guideline 210 (Fish Early Life Stage), the fish life-cycle test (US EPA 850.1500), or equivalent. Observational endpoints may include hatching success, growth (length and weight changes of the surviving fish), spawning success, and survival.
- For daphnids, tests, consistent with OECD TG 211 (duration: 21 days) and/or OECD TG 202 Part II (duration: 14 days) are recommended and retained.
- For algae, NOEC and EC10 values derived from 72- or 96-hour toxicity tests are generally considered as chronic data and used for classification (ECHA, 2015). Growth endpoint (ErC10) is preferred over biomass (EbC10) when available, as specified in the CLP Regulation 'EC 1272/2008 and 2nd ATP to the CLP).
- For vascular plants (e.g. *Lemna* spp.), NOEC/EC10 values obtained from tests consistent with OECD TG 221 and US EPA 850:4400 can be used for classification if no algal data are available. The observational endpoint in international protocols is the change in the number of fronds produced; test duration is 7 days.

Chronic ERV for Lead

Reliable chronic aquatic data for soluble lead compounds were found for twelve species:

- the invertebrates *C. dubia* (n=36), *D. magna* (n=3),
- the fish species *A. sinensis* (n=1), *A. transmontanus* (n=5), *C. carpio* (n=2), *I. punctatus* (n=3), *L. macrochirus* (n=2), *D. rerio* (n=1), *O. mykiss* (n=17), *P. promelas* (n= 12), *S. salar* (n=1), *S. fontinalis* (n=3) and *S. namaycush* (n=3);
- the green alga *R. subcapitata* (n=9);
- the aquatic plant *L. minor* (duckweed) (n=2).

The ecotoxicity data for the soluble lead compounds are combined to derive chronic ecotoxicity reference values (ERVs) to allow a comparison of the toxicity data with solubility data to allow classification as described in section A9.7.1 of the UN GHS.

Table 3: Overview of Chronic Environmental Reference Values (ERVs) for Soluble Lead (ARCHE, 2024).

Species	Assessed parameter (most sensitive)	Reported values represent the dissolved fraction					
		pH: 5.51-6.50		pH: 6.51-7.50		pH: 7.51-8.50	
		Lowest value	Geomean[1] (n>3)	Lowest value	Geomean[1] (n>3)	Lowest value	Geomean[1] (n>3)
Crustaceans							
A. rectangula	Gross reproductive rate			40.2 µg Pb/L n=1			
C. dubia	Reproduction	33.3 µg Pb/L n=1			12.0 µg Pb/L n=9		49.0 µg Pb/L n=11
D. magna	Mortality			9.0 µg Pb/L n=1		78.0 µg Pb/L n=2	
D. birgei	Net reproductive rate			13.3 µg Pb/L n=1			
H. azteca	Length					8.2 µg Pb/L n=1	
Fish							
A. sinensis	Abnormalities					129.0 µg Pb/L n=1	
A. transmontanus	Mortality					26.0 µg Pb/L n=2	
C. carpio	Mortality	17.8 µg Pb/L n=1					
I. punctatus	Weight			98.2 µg Pb/L n=1			
L. macrochirus	Length			70.0 µg Pb/L n=1			
O. mykiss	Scoliosis/growth			18.9 µg Pb/L n=1		55.4 µg Pb/L n=1	
P. promelas	Mortality	29.3 µg Pb/L n=1			32.0 µg Pb/L n=4	174.4 µg Pb/L n=1	
S. salar	Mortality	48.0 µg Pb/L n=1					
S. fontinalis	Weight			39.4 µg Pb/L n=1			
S. namaycush	Mortality			72.0 µg Pb/L n=1			
Algae and Aquatic plants							
R. subcapitata	Growth rate	25.5 µg Pb/L n=3			8.0 µg Pb/L n=5	6.2 µg Pb/L n=1	
L. minor	Root growth rate					85.0 µg Pb/L	

						n=2	
Chronic ERV		**17.8 µg Pb/L**		**8.0 µg Pb/L**		**6.2 µg Pb/L**	

(1): geometric mean was used to derive the datapoint when n>3; otherwise, the lowest value was selected. Values in green indicate the lowest value used for ERV for a specific pH-band.

Critical surface area approach

To facilitate classification, aquatic toxicity test data derived with soluble metal compounds (the ERV) must be compared with solubility data (release of the metal ion) from a sparingly soluble metal.

The details of the Critical Surface Area (CSA) concept to determine hazard classification of sparingly soluble inorganic substances, were laid out initially by Skeaff et al. (2000) and in the MERAG (Metal Environmental Risk Assessment Guideline) fact sheet on classification (MERAG 2007). This approach has been recognized in ECHA CLP[1] and GHS[2] guidance.

The CSA applied to metallic substances relies on the fact that the release of metal ions to the media is a function of the area exposed to the solvent, independent of the mass. To use this methodology for aquatic hazard classification it is necessary to undertake transformation and dissolution testing (T/Dp) on the metal in massive form as outlined in GHS Annex 10 (UN Globally Harmonised System for Classification and Labelling of Chemicals, 10th Revised Edition). This test guidance was designed to determine the rate and extent to which metals can produce soluble available ionic and other metal bearing species in aqueous media under a set of standard laboratory conditions representative of those generally occurring in the environment.

T/Dp data is available for lead metal in massive form (1mm sphere) at loadings of 1mg/L and 0.1mg/L at pH 6, 7 and 8. It is not possible to experimentally derive transformation dissolution test data at pH 5.5, the lowest pH recommended in the UN GHS for 28-day testing to account for possible long-term effects in acidic lakes. Therefore, a linear extrapolation of experimental test data obtained in the pH range 6-8 was applied to estimate soluble available lead ions that can be formed at pH 5.5.

[1] CLP Guidance Version 5, 2017, IV.5.6, pp 612.
[2] GHS, 7th edition, 2017, section A9.7.5.4, pp 489

Table 4: Overview of pH dependent T/Dp data available for lead metal massive (1 mm).

Lead Massive (1 mm)	Loading	Time	Pb released, µg/L			
			pH = 5.5*	pH = 6	pH = 7	pH = 8
Acute test	1 mg/L	7 days	--	5.1	2.0	0.28
Chronic test	1 mg/L	28 days	52.1*	14.2	2.0	0.66
	0.1 mg/L	28 days	5.21	1.42	0.02	0.066

* ECHA Committee for Risk Assessment calculated Pb release at pH 5.5 for a 1 mm diameter default massive for 1 mg/L loading in 28 days [ECHA, 2021]

Assessing the critical surface area for default lead metal massive (1 mm)

If the specific surface area (SSA) and the density of the substance is known, then the CSA (critical surface area) can be calculated using the metal release data (dissolved Pb as mg/L) obtained from transformation dissolution protocol (T/Dp) tests and ecotoxicity reference values (ERVs) at the corresponding pHs. The specific CSA (mm^2/mg) necessary to trigger a classification as environmentally hazardous is the surface area loading (SAL; mm^2/L) or specific surface area (SSA, mm^2/mg) at which the concentration (mg/L) of Pb ions released to the test media is equal or greater than the acute or chronic ERV (mg/L) at a given pH in a 7-day or 28-day T/Dp test, respectively.

The following steps were used to calculate the CSA for lead massive (1 mm):

1) First, the surface area (SA) of a Pb sphere with 1 mm (i.e., 0.1 cm) diameter was calculated using the formula: $SA = 4\pi r^2$ = 4 * 3.14* 0.1/2* 0.1/2 = 0.0314 cm^2;
2) the volume (v) of a Pb sphere with 0.1 cm diameter was calculated using the formula: $SA = 4/3\pi r^3$ = 4/3 * 3.14* 0.1/2* 0.1/2*0.1/2 = 0.000523 cm^3
3) From the sphere volume and lead density (d) of 11.35 g/cm^3, the mass (m) of the sphere was calculated: m = v * d = 5.9398 mg
4) Finally, the specific surface area (SSA) per unit mass was calculated: SA/m = 0.529 mm^2/mg. **Therefore, lead massive (>1mm) can be defined as having a SSA of <0.529 mm^2/mg to trigger classification as environmentally hazardous.**
5) Using this worst-case SSA and the available T/Dp data for lead dissolution (Table 4) and lead acute and chronic ERVs (Tables 2 and 3), the corresponding specific CSAs for a default lead massive (1mm) were calculated (Table 5). The relationship between lead releases during T/Dp tests and surface loadings (mm^2/L) follow a linear trend (Figure 1).

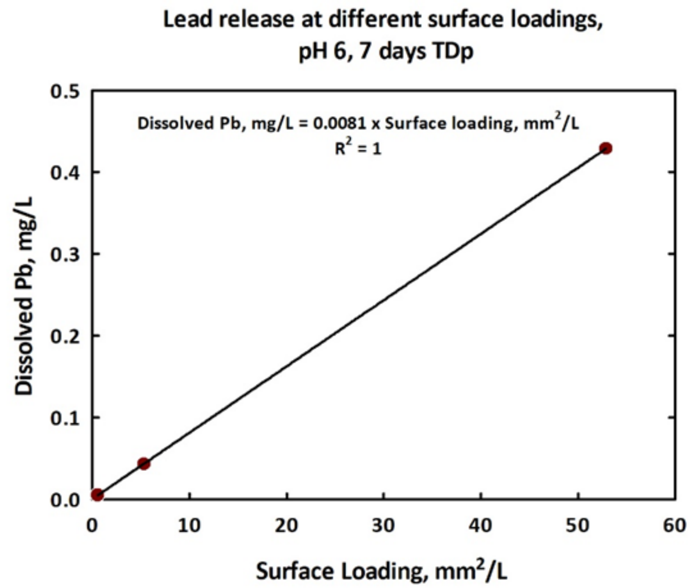

Figure 1. Relationship between dissolved Pb in 7 days and the surface loading in transformation dissolution tests with lead metal massive at a mass loading of 1, 10, and 100 mg/L (surface loading of 0.529, 5.286, and 52.863 mm^2/L respectively) at pH 6 (Rodriguez, 2009).

Therefore, CSA (mm^2/L) for acute and chronic cut-offs (1 or 0.1 mg/L) that releases lead ions equal to the acute or chronic ERV could be calculated from the simple relationship:

$$CSA = (SAL/TDp)*ERV,$$

where SAL (mm^2/L) is the initial surface area loading for 1 or 0.1 mg/L mass loading,

T/Dp (mg/L) is the Pb release during the transformation dissolution test at a given pH, and

ERV (mg/L) is the acute or chronic ERV for lead.

6) The CSA (mm^2/L), i.e., the surface area loading that will deliver the ERV for the soluble lead ion, is transformed into specific CSA (mm^2/mg) by dividing the acute and chronic classification cut-off loadings (1 or 0.1 mg/L) and then applying necessary adjustments for units. To derive the environmental classification of ingots i*t is the specific CSA (mm^2/mg) that will be directly compared with the SSA (mm^2/mg) of metal ingots (25-45 kg) for which experimental TDp testing is not possible.*

Table 5: Specific critical surface areas (CSA) of lead metal massive (1 mm) to release lead ions equivalent to ecotoxicity reference values (ERVs) for acute and chronic aquatic hazards.

TDp & ERV Comparison	**pH**	**Mass loading mg Pb/L**	**Initial surface area loading mm²/L**	**Pb release in solution mg/L**	**Chronic ERV mg/L**	**Specific surface area for 1 mm cut-off (SSA), mm²/mg**	**Specific critical surface area (CSA), mm²/mg**
Acute							
Same pH	T/Dp pH 6; ERV pH 6	1	0.529	0.0051	0.0408	0.529	4.232
Same pH	T/Dp pH 7; ERV pH 7	1	0.529	0.002	0.0325	0.529	8.596
Same pH	T/Dp pH 8; ERV pH 8	1	0.529	0.00028	0.0205	0.529	38.730
Worst case	T/Dp pH 6; ERV pH 8	1	0.529	0.0051	0.0205	0.529	**2.126**
Chronic							
Same pH	T/Dp pH 6; ERV pH 6	1	0.529	0.0142	0.0178	0.529	0.663
		0.1	0.0529	0.00142	0.0178	0.529	6.631
Same pH	T/Dp pH 7; ERV pH 7	1	0.529	0.002	0.008	0.529	2.116
		0.1	0.0529	0.0002	0.008	0.529	21.16
Same pH	T/Dp pH 8; ERV pH 8	1	0.529	0.00066	0.0062	0.529	4.969
		0.1	0.0529	0.000066	0.0062	0.529	49.694
Worst case	T/Dp pH 6; ERV pH 8	1	0.529	0.0142	0.0062	0.529	0.231
		0.1	0.0529	0.00142	0.0062	0.529	2.310
Worst case	TDp pH 5.5; ERV pH 8	1	0.529	0.0521	0.0062	0.529	**0.063**
		0.1	0.0529	0.00521	0.0062	0.529	0.630

Values highlighted in yellow indicate the worst-case scenario pH and ERVs to estimate the CSA for lead metal ingots

Calculating the Specific Surface Area for Typical Lead Metal Ingots

Lead metal ingots are cuboid in shape and thus the total surface area (TSA) of an ingot is the sum of the areas of its six rectangular faces. The specific surface area (SSA) of a lead ingot can be easily calculated from its length (*L*), width (*W*) and thickness (*T*) with the following two steps:

1) Measure the length, width, and thickness of the ingot in cm or mm and calculate the total surface area (TSA) with the equation:

   TSA (mm^2) = 2*(L*W) + 2*(W*T) + 2*(T*L)

2) Measure the weight (kg converted to mg) of the ingot and then calculate the SSA by dividing TSA with the ingot weight (*wt*):

   SSA_{ingot} ((mm^2/mg) = TSA/*wt*

According to this formula, the SSA calculated for the ingots Vedanta (25kg) and Bergsoe (kg) with dimensions reported in Table 1 are 0.00736 mm^2/mg and 0.00616 mm^2/mg, respectively.

Assessment of Environmental Classification of Lead Metal Ingots using the Critical Surface Area

The relationship between lead releases into solution during T/Dp tests (mg/L) and surface area loadings (mm^2/L) follows a linear trend (Figure 1).

Thus, the environmental classification of an ingot can be derived by comparing the specific surface area of the ingot (SSA_{ingot}) with the specific critical surface area of the default 1 mm massive (CSA) relative to the acute and chronic ERVs (See Table 5).

Acute Classification of metal ingots:

SSA_{ingot} (mm^2/mg) > specific CSA (mm^2/mg) at 1 mg/L ➔ Acute 1

SSA_{ingot} (mm^2/mg) < specific CSA (mm^2/mg) at 1 mg/L ➔ No Classification

Chronic Classification of metal ingots:

SSA_{ingot} (mm^2/mg) > specific CSA (mm^2/mg) at 1 mg/L ➔ Chronic 2

SSA_{ingot} (mm^2/mg) > specific CSA (mm^2/mg) at 0.1 mg/L ➔ Chronic 1

SSA_{ingot} (mm^2/mg) < specific CSA (mm^2/mg) at 1 mg/L ➔ No Classification

As highlighted in Table 5, the smallest specific critical surface areas (CSA) for a 1 mm massive sphere of lead are 2.126 and 0.063 mm^2/mg for acute and chronic ERVs respectively, both corresponding to the classification cut-off of 1 mg/L mass loading and the worst-case TD/p pH of 6 (7 day, acute, T/Dp) and 5.5 (28-day, chronic, T/Dp) representing highest lead ion in solution.

The SSA_{ingot} calculated for the ingots Vedanta (0.00736 mm^2/mg) and Bergsoe (0.00616 mm^2/mg) are much smaller than these critical surface area values. Therefore, neither of these ingots will meet the criteria to be considered dangerous goods per UN 3077 Environmentally Hazardous Substance**.**

Conclusion

The most common form of lead metal shipped by land, sea or rail is ingots weighing 25 – 45 kg. These have a calculated specific surface are (SSA) less than 0.0074 mm^2/mg. This is significantly less than that of the default lead massive sphere with 1 mm diameter, which has an estimated SSA of 0.529 mm^2/mg.

The critical surface area approach for classification of metals highlights that a typical lead metal ingot would not meet the UN GHS criteria for classification as an acute or long-term hazard for the aquatic environment and is a not Environmentally Hazardous Substances (UN 3077) for transportation.

References

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