Case Study - Chronic Classification of a Nickel Matte Based on Transformation/ Dissolution Characteristics [With Solutions]

Submitted by: Australia

Workshop on Metals Risk Assessment
Cebu, Philippines
28-29 August 2015

Case study - Chronic classification of a nickel matte based on Transformation/Dissolution characteristics [with solutions]

Problem Statement: Metals and metals compounds are classified under the EU CLP at the chronic level based on the loading cutpoints of 1, 0.1 and 0.01 mg/L. The lower two loadings are unattainable under normal laboratory conditions (for comparison, a single eyelash can weigh approximately 0.075 mg and the 0.01 mg/L loading is equivalent to 1 mg of the substance in a 100 L barrel).

Scientific Issues: Aquatic hazard classification proposals are mandatory for producers, importers, and users of chemical substances to secure and expand on their markets within the European Union (EU). The EU has modified the UN GHS to arrive at their Classification, Labeling and Packaging (CLP) regulation. The EU CLP framework retains the Acute 1 and the Chronic 1 levels of the basic UN GHS scheme, but omits the Acute 2 and 3, while retaining the Chronic 2, 3 and 4 levels. As in the basic GHS scheme, under the EU CLP, the acute and chronic categories are applied independently. The basic UN GHS appears to be structured for the hazard classification of highly toxic, synthetic organic chemicals and has chronic concentration cutpoints of as low as 0.01 mg/L. For metals and metal compounds, if chronic ERV data are available, the cutpoints in the EU CLP are the same as in the basic UN GHs strategy, with the provision that metal substance loadings of 1, 0.1 and 0.01 mg/L that deliver metal concentrations exceeding the selected chronic ERV will classify the substance for chronic levels 3, 2 and 1 respectively. This applies in the case of evidence of rapid environmental transformation, such as speciation change to a less harmful
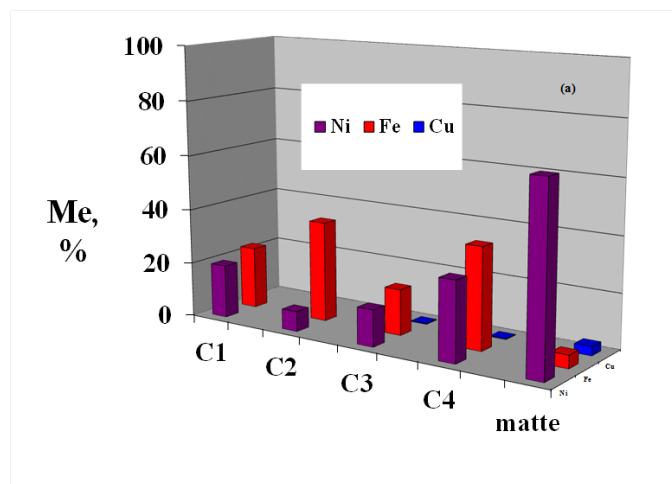
form or precipitation over 28 days. If there is no evidence of rapid environmental transformation, then the scheme calls for chronic classifications 2 and 1 if loadings of 1 and 0.1 mg/L, respectively, exceed the selected chronic ERV. Because of practical difficulties in obtaining such low mass loadings, extrapolation of Transformation/Dissolution (T/D) data to lower loadings in a precautionary way is proposed in the EU CLP guidance document (EU 2013).

Current risk assessment: Loading cutpoints of 0.1 and 0.01 mg/L are not attainable under normal laboratory conditions and so a method of extrapolation and scaling of T/D data was developed (Skeaff and Beaudoin, 2014) in order to meet the chronic hazard classification requirements as set out in the EU CLP.

Example: Using T/D kinetic data from Ni matte (M143) (data from Skeaff and Beaudoin, 2014)

I- Derivation of UN GHS hazard classification outcomes
II- Derivation of EU CLP hazard classification outcomes

I-   Derivation of UN GHS hazard classification outcomes

Step 1

- Test the Ni matte at the 100, 10 and 1 mg/L loading in triplicate with procedural blanks following the procedure set out in the T/D Protocol.

The Ni matte (from hereon M143) has the following composition:

Wt%

	Ni	Fe	S	Cu	Co	As	Totals
M143	66.7	4.7	30.7	3.25	0.84	0.33	106.5

For the purpose of this example, I will only be discussing the T/D results generated at pH 6.

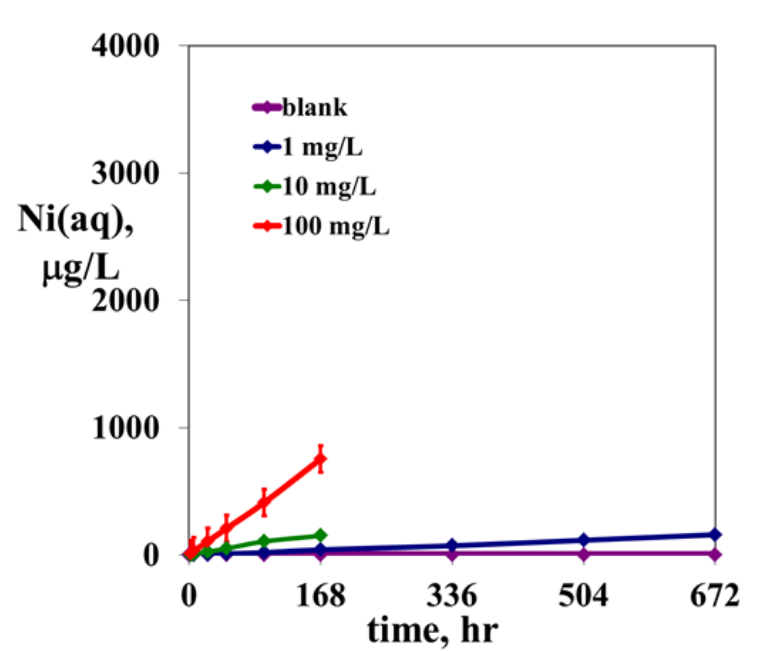The acute and chronic ERVs for comparison with T/D data are as follows:

	Ni	Cu	Co
Acute	120 (pH 6)	29	90.1
Chronic	2.4	8	4.9

Test M143 at each of the 100, 10 and 1 mg/L loadings in triplicate (n=3) with 2 procedural blanks (n=2) for the 100 and 10 mg/L loadings and one (n=1) for the 1 mg/L loading. Collect solution subsamples a 0, 24, 48, 96 and 168 h in triplicate and single samples at 2 and 6 h. For the 1 mg/L loading continue sampling at 336, 504 and 672 h. ** Note in this example we did extend the 10 and 100 mg/L loadings to 672 h in order to verify the extrapolated data** After filtering the T/D solutions, analyse the solutions for Ni, Cu and Co.

Step 2

- Derive the net average T/D reaction kinetic data, expressed as Me(aq) and plot as a function of time. For multi-component systems, using the accepted ERV, calculate the acute and chronic TU. For the 1 mg/L loading, the 168 h concentration of the acute TU was 0.35, so the Ni matte

would not classify as Acute 1 under the GHS. For the 10 mg/loading, the 168 h TU was 1.3 so the Ni matte would classify as GHS Acute 2-CHronic 2.

Me(aq) is calculated as the difference between the average total dissolved concentrations among all 3 test jars and the average concentrations in the blanks. Standard deviation and the percentage coefficient of variance is also calculated.

TU values are calculated as:

$$TU = \sum_{Me=1}^{n} TU_{Me} \tag{1}$$

where the TU_{Me} of metal component Me is:

$$TU_{Me} = \frac{Me(aq)}{LC50_{Me}} \qquad (2),$$

As noted above, Me(aq) is the net average metal concentration at a specified time, in this case 168 hr, and $LC50_{Me}$ is the acute ERV of the metal. Applied to the 18Ni300 alloy, we used:

$$TU = TU_{Ni} + TU_{Cu} + TU_{Co} \qquad (3)$$

From the figure above you can see concentrations of Ni(aq) increase almost linearly with no suggestion of an approach to limiting concentrations after 672 h.

Concentrations were as follows for the 100 mg/L loading (note that in this case we do have 672 h data for the 100 and 10 mg/L loading as these were extended to verify the extrapolated values) :

Time	Ni(aq) µg/L	Cu(aq) µg/L	Co(aq) µg/L
168 h	754	2.2	14
672 h	3020	12.9	54

Concentrations were as follows for the 10 mg/L loading:

Time	Ni(aq) µg/L	Cu(aq) µg/L	Co(aq) µg/L
168 h	151	0.66	2.82
672 h	753	6.7	13

Concentrations were as follows for the 1 mg/L loading:

Time	Ni(aq) µg/L	Cu(aq) µg/L	Co(aq) µg/L
168 h	40.5	0.18	0.66
672 h	159	3	2

Acute TU calculation for the 1 mg/L loading: (40.5/120) + (0.18/29) + (0.66/90.1) = 0.35

Acute TU calculation for the 10 mg/L loading: (151/120) + (0.66/29) + (2.82/90.1) = 1.3

For the 1 mg/L loading, the 168 value of the acute TU was 0.35, so the Ni matte would not classify as Acute 1 under the GHS. For the 10 mg/L loading, the 168 h TU was 1.3 so the Ni matte would classify as GHS Acute 2-Chronic 2.

II- Derivation of EU CLP hazard classification outcomes

Step 1

- Using the T/D kinetic data for the 10 and 100 mg/L loadings from 0 to 168 h do a regression analysis and then extrapolate the data to 672 h to yield a Ni(aq) value at t = 672 h. Also do a regression analysis of the 1 mg/L loading 0 to 672 h dataset to derive a Ni(aq) value at t = 672.

  Note that this extrapolation and scaling was only done using the Ni(aq) values as contributions from Co(aq) and Cu(aq) were minor in comparison.

  Develop 2 sets of data for Ni(aq) as a function of time. The first set is for the regression analysis on the complete 0 to 672 h data set yielding concentrations for Ni(aq) of 2860, 745 and 156 µg/L for the 100, 10 and
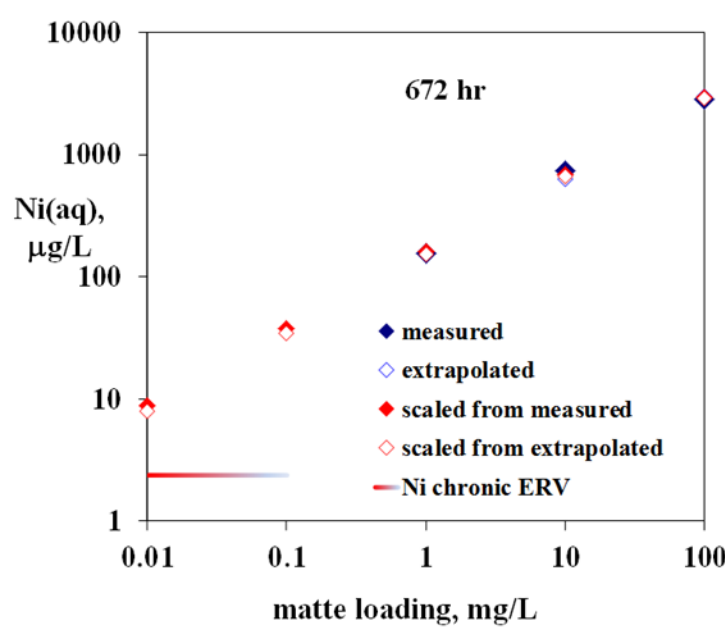
1 mg/L loadings, respectively , for t = 672 h. These are referred to as measured values.

For the second data set, using the 10 and 100 mg/L loading data, regression fit the nearly zero-order reaction kinetic concentrations of measured Ni(aq) as a function of time over the period 0 to 168 hr. Using the regression equation, extrapolate to 672 hr to obtain Ni(aq) values of 2980 and 630 µg/L. These are referred to as extrapolated values.

- Applying a regression analysis to the 672 h Ni(aq) values for the 100, 10 and 1 mg/L loadings, derive a log-log linear plot and then evaluate Ni(aq) at 0.1 and 0.01 mg/L.

  Using the measured values, with a log-log plot of Ni(aq) vs loading scale down to loadings of 0.1 and 0.01 mg/L to obtain Ni(aq) values of 38 and 8.8 µg/L for loadings of 0.1 and 0.01 mg/L respectively.

  Using the extrapolated values, with a log-log plot of Ni(aq) vs loading scale down to loadings of 0.1 and 0.01 mg/L to obtain Ni(aq) values of 35 and 7.9 µg/L for loadings of 0.1 and 0.01 mg/L respectively.

- As the concentration for the 0.01 mg/L loading for 672 h was greater than the chronic ERV of 2.4 µg/L for dissolved Ni, the Ni matte would classify as Chronic 1 under the EU CLP.

The Ni(aq) values for the 0.01 mg/L loading from both the measured and extrapolated data sets would classify this Ni matte as Chronic 1 under the EU CLP, assuming rapid environmental transformation for dissolved Ni.

If Annex 9 of the UNGHS were revised for consistency with the basic GHS, then acute and chronic classification would be derived independently and the substance would classify as GHS Acute 2 Chronic 1.
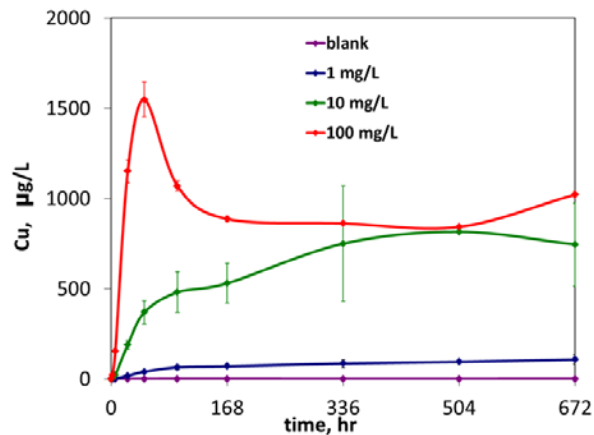
Discussion questions:

1. Can the use of extrapolated and scaled data be justified for chronic hazard classification of metals and metal compounds?

It is not practical to measure loadings of 0.1 and 0.01 mg in the lab.

The reason behind extending the duration of the T/D test for the 100 and 10 mg/L loadings was to be able to compare the measured 672 h concentrations of Ni(aq) with those derived from extrapolation of the 0 to 168 h concentrations to 672 h. This revealed that the 2 sets of Ni(aq) concentrations were not statistically different. Also, using both measured and extrapolated values to derive the log-log plot to scale to 0.1 and 0.01 mg/L loadings yielded common chronic classification outcomes. From measured values the Ni(aq) concentration for the 0.1 and 0.01 mg/L loading was 38 and 8.8 µg/L and the Ni(aq) concentration for the 0.1 and 0.01 mg/L loading was 35 and 7.9 µg/L for the extrapolated dataset.

2. Are there any examples where this approach may not be valid?

It is important to always verify the fit of the data to the regression curve. We used the F-statistic or Fstat as a measure to determine the extent to which a given equation represents the data. The higher the Fstat, the more efficiently a given equation models the data. There are cases, when one observes a spike in Me(aq) concentrations, for example in Cu(aq) in a marine T/D media for the 100 mg/L loading. This is due to the formation of transient more soluble species. This data set could be more challenging to regression fit.

3. Should this approach be validated and how?

This approach could be validated but would need the involvement of at least three labs in a round-robin type exercise.

4. How would you conduct a sensitivity analysis with respect to the chronic classification outcomes taking into account the possible errors in extrapolation and scaling?

How might error or uncertainties effect the chronic classification outcome for the Ni matte? Using the 672 h extrapolated values and calculating the upper and lower confidence limits we get:

Ni(aq) μg/L			
Loading mg/L	Predicted from regression	+95% confidence limit	-95% confidence limit
100	2983	3080	2723
10	630	704	623
1	156	161	142
	Predicted from scaling		
0.1	38	37	33
0.01	8.82	8.41	7.44

This demonstrates that variations in the extrapolated 672 h values of Ni(aq) within ±95% confidence limits will not affect the EU CLP chronic classification outcomes of the Ni matte.