CONCLUSIONS OF CHARACTERISATION AND TRANSFORMATION/DISSOLUTION WORK PERFORMED ON PMC PM REFINABLES

28 April 2010

Introduction and objectives

This paper documents and summarises the main outcomes of the different characterisation programmes conducted on the PM Refinables with the aim of arriving at a refined (tiered) hazard classification proposal. It further states and concludes for each Refinable group some concerns for further clarification and the potential to improve or confirm the hazard classification proposal. The latter is than translated into further information gathering suggestions for PMC Members. These recommendations include a combination of Transformation/Dissolution (T/D) testing, additional characterisation work, particle size distribution or powder surface measurements and determining the physical forms the material is produced and used as, as intermediate, to allow defining the appropriate classification category.

Table 1 below provides an overview on the substances that underwent characterisation work at Outotec Research Oy and 24h T/D pre-tests at ECTX.

Table 1. Overview of analysis/tests conducted in tier 1

N°	Refinable group	Characterisation @ Outotec	T/D pre-test @ ECTX
1a	Doré pure	Done	Done
1b	Doré impure	Done	Done
2	Matte, PM refining	Done	Done
3a	Boro-silicate slags, PM refining	Done	Done
3b	Phosphate slags, PM refining	Done	Done
3c	Silicate slags, PM refining	Done	Done
3d	Borate slags, PM refining	Assumed to be similar to boro-silicate slag	Done
4	Slimes and sludges, PM refining	None; assumed to be metal oxides, chlorides (soluble + classified)	
5.1	Residues, FeCuPbNi matte leaching	Elemental analysis + characterisation available from Members	Done
5.2	Residues, Cu speiss acid leaching	Done	Done
6.1	Ag electrolyte	None; assumed in acid (HNO_3) phase	
6.2	Au electrolyte	None; assumed in acid (HCl) phase	
7	Flue dusts, PM refining	None; assumed to be mainly metal oxides (soluble + classified)	
8	Residues, PM refining cementation and reduction	None; assumed to be mainly metal oxides and chlorides (soluble + classified)	
9.1a	Materials for reclaim, PM without support	None; assumed to be metallic	
9.1b	Materials for reclaim, PM with metallic support	None; assumed to be metallic	
9.1c	Materials for reclaim, PM with carbon support	None; assumed to be metallic + C (C drives the classification)	
9.1d	Materials for reclaim, PM with ceramic support	Done	Done
9.2	Materials for reclaim, bricks, crucibles, trays, etc.	None; assumed to be metallic	
9.3	Materials for reclaim, PM production by-products (e.g. PM sweeps)	None; assumed to be mainly metallic oxides (soluble + classified)	
10	PGM rich Lead bullion	None; read-across from information from Pb Consortium	

Classification approach for PM Refinables

The summation rule is the general applicable rule to derive the hazard classification for the environmental and health endpoints. In the absence of (eco-)toxicity data on the Refinable ("mixture") itself, the

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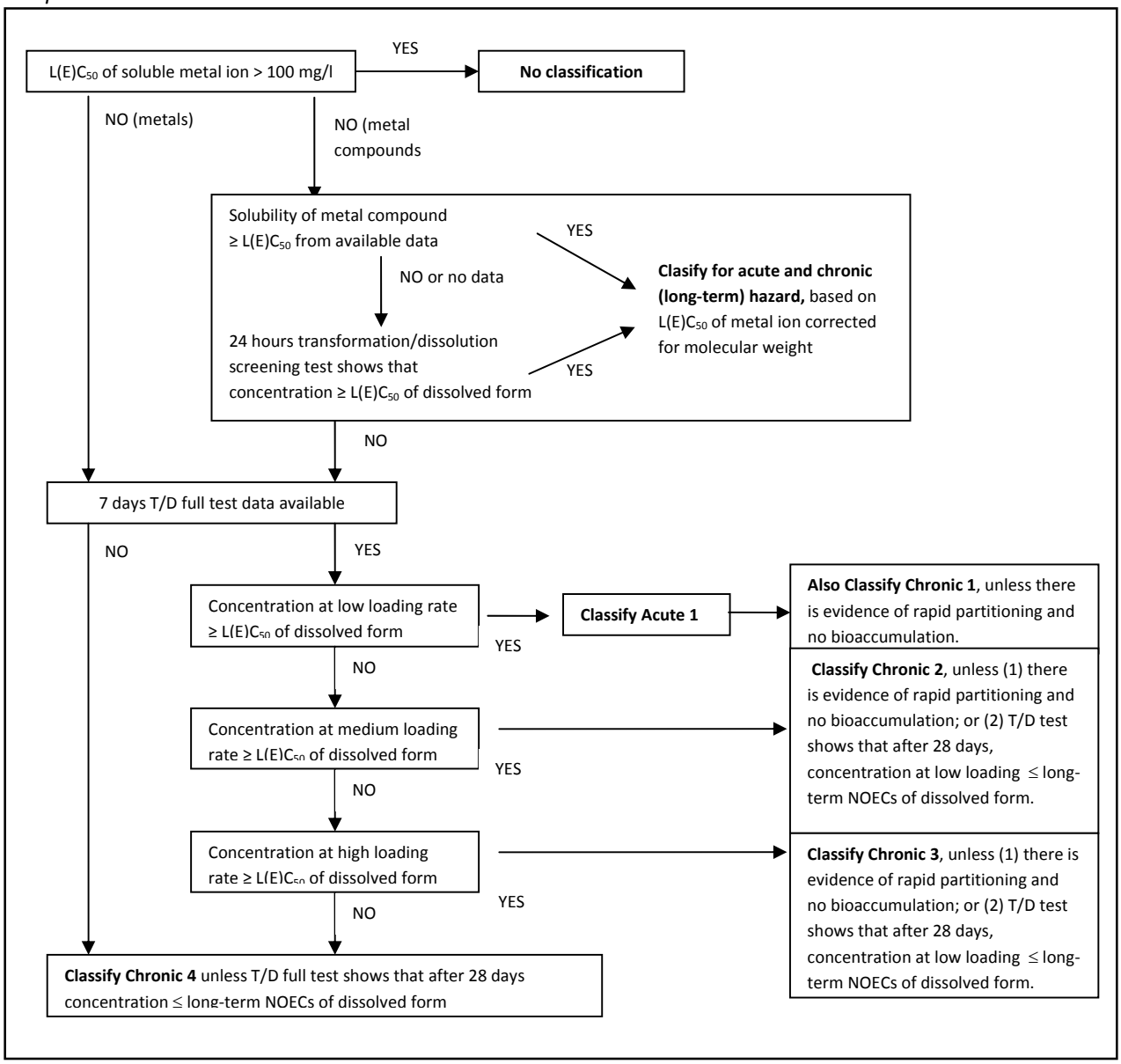
concentration of each constituent classified for each hazard categorisation (e.g.: acute 1 ecotox, carcinogenicity category 1, sensitisation, etc.) are summed up and compared with the classification trigger applicable to mixtures (e.g.: 0,1 % for the sum of all carcinogens category 1a) and 1b) under CLP). Where the sum is higher or lower than the trigger, the Refinable is classified for that classification endpoint or not, respectively.

Extract from Chapter 4, Annex 4 of the CLP guidance: Figure IV.5.1 *Classification strategy for metals and metal compounds*



Complementary, CLP foresees a specific approach for the environmental classification of metals, sparingly metal compounds and soluble metal compounds. The amount and release rate of the toxic metal ion measured by the Transformation/Dissolution protocol (T/D) allows refining the environmental classification. (cf. Chapter 4, Annex 4 of the (guidance to) the CLP regulation and especially by scheme IV.5.1 (see above)).

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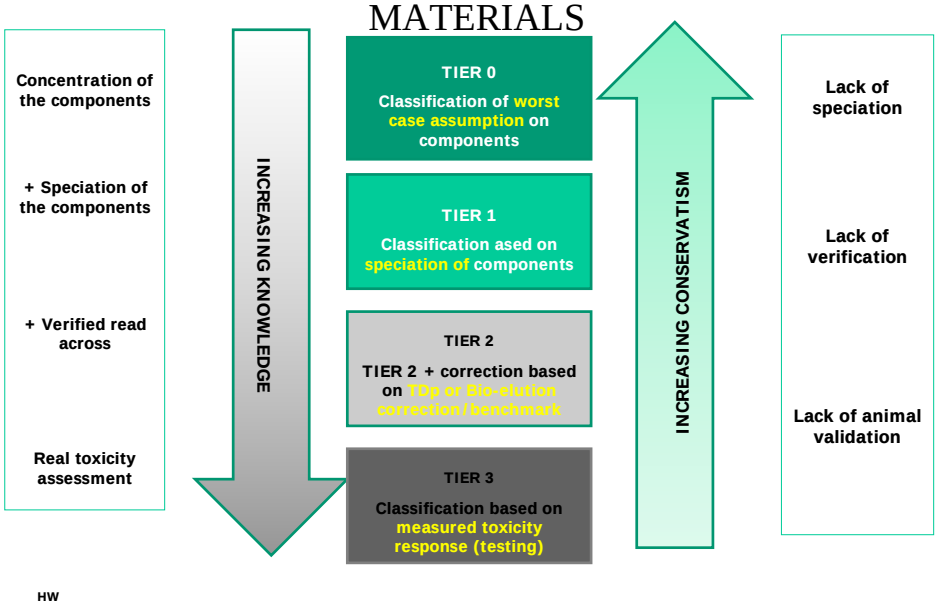
The summation and T/D refining approach has been applied to the PM Refinables based on the available and generated information. The less information on the exact composition and on the release rate and equilibrium in water of the Refinable, the more conservative the classification assumptions are. This is further illustrated below:

- *TIER 0: worst case classification based on the maximum elemental concentration range as listed in the Refinables ID cards using the classification of the most bio-available form (usually the oxide or the sulphate form)*
- *TIER 1: refined classification based on the maximum compounds/minerals concentration ranges as defined by the PMC Members using the classification of the expected or most probable species (based on process e.g.: metallic form)*
- *TIER 2: refined classification based on the species and released amounts confirmed by testing (mineralogical characterisation and T/D) and using the elemental concentration range of the tested "reference sample"*

SCHEMATIC OVERVIEW of the TIERED CLASSIFICATION APPROACH FOR COMPLEX MATERIALS



The mineralogical characterisation and T/D pre-tests were conducted on certain PM Refinables to reach an early stage of TIER 2 classification refinement. Some PM Refinables where not analysed or tested as their composition was reasonably well known or so variable that worst case assumptions had to be used to classify them.

The tiered classification approach was carefully considered by the PMC and suggestions for further work confirmation/refinement were agreed upon as follows:

1. Particle size distribution and N-BET analysis to confirm the relevance of the proposed classification for the physical form in which the PM Refinable is manufactured/imported (e.g.: massive, dusty lumps, dry or wet powder, etc.). Several Refinables were indeed milled to obtain forms that could be tested but such forms are not always representative of the form they are manufactured or imported in.
2. Repetition of characterisation and/or 24h T/D pre-tests that did not yield conclusive results in the first round of tests (e.g.: Group 1A, pure doré; Group 2: matte, PM refining)

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3. Additional T/D tests to confirm or refine the proposed environmental classification. The additional T/D tests are so-called "Full" tests that are required to confirm or refine the results obtained through the 24h 100mg/l T/D pre-test:
    - over a longer period (7 or 28 days) in order to avoid a default Chronic 4 environmental classification (see figure IV.5.1 of CLP guidance)
    - with lower dose level testing (1 and 10 mg/l) in order to consider the relevance of lower environmental classification categories (e.g.: Chronic 1 or 2) to avoid the worst case classification Acute 1/Chronic 1
    - analysing a refined set of elements which were measured in the 24h T/D pre-test and trigger the classification
4. Bio-accessibility test in artificial sweat to confirm or refine the proposed classification as skin sensitiser.

The discussion for each Refinable group below summarises the outcome of all test work so far and suggests next steps.

SUMMARY RESULTS AND RECOMMENDED FURTHER WORK AS PER INFORMATION AVAILABLE OR GENERATED AND THE AGREED TIERED APPROACH (TIERS 0 TO 2)

1. DORE

1a Doré pure: TIER 2

Physical form tested: irregular "spring or stripe type" sawed particles (+/- 1 mm) obtained as per sampling recommendations (in line with technical requirements for the evaluation of massives)

- All constituents in metallic form except Cu-Pb oxides
- CMR below classification level (TIER 2) → no need for defining actual As valence
- Very high Ag concentration but very low release/availability → results repeatable and consistent
- Cu reasonably high but highly available and classifiable at low and high pH in pre-screening test

Concerns:

- Tested form may have influenced release rates - not representative of form of the material placed on the market (i.e. bars/ingots). One possible explanation is that Cu-Pb oxides included in the matrix are regularly surfacing (less the case for Doré impure)
- Cu could trigger a higher environmental classification category in the full T/D test
- How to explain the difference in Ag release between the 24h T/D pre-test on doré and the Full T/D test on Ag powder?

Recommendation:

- Prepare asap sample in same way as Doré impure and repeat 24h T/D pre-test to allow comparison with Doré impure
  → if results comparable, no further T/D work
  → if results very different, further T/D work:
    - 1 mg/l 7 d and 28 d, analysing Cu and Ag
    - 100 mg/l 7 d, analysing only for Ag (and Cu?)
    - eventually 10 mg/l 7 d, analysing Cu (or Ag) depending on results of 1 and 100 mg/l
- Investigate difference between release of Ag from doré in 24h T/D pre-test vs release of Ag from Ag powder full T/D test

1b Doré impure: TIER 2

Physical form tested: small droplets (+/- 1 mm) (in line with technical requirements for the evaluation of massives).

- All constituents in metallic form, except Sb-Cu oxides
- CMR below classification level (TIER 2) → no need for defining the actual species of CMR compounds

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- High Ag concentration but very low release/availability → results repeatable and consistent
- Cu concentration somewhat higher than Doré pure, but lower release/availability

Concern:

- Unclear whether release is related to the form of the sample or due to the different preferential corrosion
- Would no environmental classification remain at 100 mg/l 7 d T/D test?
- How to explain the lower release/availability of Cu compared to pure Doré?

Recommendation:

- T/D 1 mg/l 7 - 28 days for Ag and Cu
- T/D 100 mg/l 7 days for Cu and Ag:
  - If negative → no classification confirmed
  - If positive (classified) → conduct 10 mg/l T/D test for classifying element (e.g.: Cu)
- Investigate difference between release of Ag from doré in 24h T/D pre-test vs release of Ag from Ag powder full T/D test

1 Doré: GENERAL

- Should be handled as one group. Selection of reference sample for tests to be performed on doré will depend on outcomes of repeated 24h T/D pre-test on new pure doré sample and comparison with results obtained for impure doré
- Need to investigate difference between release of Ag from doré in 24h T/D pre-test vs release of Ag from Ag powder full T/D test

2. MATTE

2 Matte Refining: TIER 2

The Lead Registrant confirmed the material was not representative of what is placed on the market.

Recommendation:

- Prepare new sample and obtain PSD + N-BET
- Repeat characterisation analysis at Outotec
- Repeat 24 h T/D pre-test at ECTX and depending on results:
  - If negative, perform a 100 mg/l 7 days T/D test to confirm absence of classification
  - If positive, perform a 1 mg/l 7-28 days T/D test analysing classifying elements (e.g.: Pb)

3. SLAGS

3a Boro-silicate slags: TIER 2

Physical form tested: fine bluish/greenish powder. Tested form smaller than what is placed on the market (dusty massive lumps).

- Na-Cu-silicate matrix with Ag metallic embedded but also in the free metallic form
- High Cu concentration and release compared to other slags, reasonably low content and release of Pb
- CMR below classification level (TIER 2) → no need for defining the actual species of CMR compounds (probably in oxide form; only amorphous Si)
- B oxide concentration below "development toxicity limit" (special concentration limit of 5% for Borates); release of very high but not classified

Concerns:

- Release of Ag triggering classification as ecotox at 24h; release of Cu could trigger classification at 7days → Acute 1/Chronic 1 to aquatic environment classification

Recommendation:

- Accept classification but consider PSD and N-BET results to confirm classification based on size

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3b phosphate slags: TIER 2

Physical form tested: grey granules

- Large quartz and metal phosphate fraction
- High Ag, low Cu, and very low B concentrations
- CMR elements in phosphate form, so very high solubility (triggering CMR classification) but no crystalline silica
- High release of Ag (more than in boro-silicate slag, where Ag is presumably trapped in the quartz matrix)
- Despite very high concentration, Pb release not sufficient to trigger classification at 24h (7d ?)

Concerns:

- The tested form was fine but was it reasonably representative of the 1 mm default diameter for massive forms? Other slags were finer.

Recommendation:

- 1 mg/l 7 d and 28 d T/D analysing Ag and Pb:
  - If positive, no further test
  - If negative, test 10 mg/l

3c silicate slags: TIER 2

Physical form tested: Fine brownish/yellowish powder. Tested form smaller than what is placed on the market (dusty massive lumps).

- Mixed silicates and oxides, Pb and As in combined oxide above classification level (= CMR); no crystalline silica
- Low Ag concentration, high Cu, and almost 50 % Pb content; high Cu and Pb release probably due to oxide and free metal form, respectively but possibility of refining classification (release < 100x TRV)

Concerns:

- High classification level (CMR-STOT, …) and low potential for improvement for HH endpoints

Recommendation:

- 1 mg/l at 7 d and 28 d T/D analysing Cu and Pb:
  - If result at 7 days is positive: confirm environmental classification
  - If result at 7 days is negative: stop test and repeat 7 days test with 10 mg/l loading

3d borate slags: TIER 2

Physical form tested: fine greyish powder. Tested form smaller than what is placed on the market (dusty massive lumps).

- Content of CMR elements not yet performed, awaiting elemental analysis from sample provider.
- Very high Zn (at pH 6) but less than 100 x TRV; very high B release and reasonably high Pb at both pH.

Concerns:

- Composition assumed to be similar to boro-silicate but release of Zn in T/D indicates different profile

Recommendation:

- Conduct characterisation at Outotec
- 1 mg/l at 7 d and 28 d T/D analysing Zn (and Pb):
  - If result at 7 days is positive: confirm environmental classification
  - If result at 7 days is negative: stop test and repeat 7 days test with 10 mg/l loading

3 Slags: GENERAL

- Can be handled as one group with differentiated classifications based on process/flux applied
- Selection of reference sample for tests to be performed on slags will depend on outcomes of remaining characterisation and further T/D tests and comparison with results obtained for each

4. SLIMES AND SLUDGES

4. Slimes and sludges: TIER 1

Not tested at Outotec and ECTX
Physical form: fine dry or wet powdery material

- Highly variable group (intermediates resulting from refining of Ag, Au and PGM)
- Assumed to be in oxide and chloride form
- High concentration of CMR materials (Co, Ni, Pb, As, …) above classification levels
- Pt concentrations above level of respiratory and skin sensitization (also Ni)
- Ni and Cd above STOT RE classification levels
- Long series of metal ions above environmental classification level

Concerns:

- Highly hazardous group including CMR, Env (acute 1), STOT RE and Resp./Skin sensitizer elements
- Possibility of considering a separate classification sub-group category for Au slimes and slimes which do not contain any of the CMR and/or respiratory sensitizers above the maximum levels

Recommendation:

- Classify and derive classification clusters for different profiles in the group
- Obtain elemental and expected species (based on input material and process) for Au and non-CMR slime from relevant Members and consider need for T/D test subsequently

5. LEACHING RESIDUES

5.1 Residues from FeCuPbNi matte leaching: TIER 2

Physical form tested: fine black powder

- Mineralogical composition provided by two Members; no need for further characterisation at Outotec
- T/D test performed on one sample: high release of Pb, Cu, Ni and Ag sufficient to trigger classification

Concerns:

- Need to confirm sameness and classification within the group

Recommendation:

- 1 mg/l at 7 d and 28 d T/D analysing Pb, Cu, Ni, and Ag

5.2 Residues, Cu speiss acid leaching: TIER 2

Physical form tested: fine grey powder, reasonably representative

- Very high in Cu sulphides and Anglesite (PbSO4)
- Very high CMR levels, Ni in arsenide form and Sb-As oxides
- No crystalline silica and Chromates in 3+ form
- Release of As, Cu, and Ni very high at both pH levels due to accessible forms
- Release of Pb low (confirmed by poorly soluble anglesite form)

Concerns:

- High release levels of Ni-Cu-As trigger CMR and environmental classification

Recommendation:

- Accept classification

6. ELECTROLYTES

6.1 Spent Ag electrolyte: TIER 1

Physical form: (nitric) acid solution

- Very high Ag and Cu concentration leading to environmental classification

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- Reasonably high Pb concentrations (above CMR classification level)
- Pt levels above classification level for skin/eye corrosivity/irritation and respiratory sensitisation
- No further characterisation or T/D work required since metals dissociated in acid solution and assumed to be fully bio-available (manufacturers to confirm)

Concerns:
- Highly bio-available material expressing all hazard properties of constituents (CMR-Env. Acute 1-Irrit.-resp. sensitization-STOTre)

Recommendation:
- Accept classification
- Compare with chemical stability plots

6.2 Spent Au electrolyte: TIER 1

Physical form: (chlorhydric) acid solution
- Very high dissociated Au concentrations. Hazard properties unknown so far
- No CMR materials above classification limit
- Pt levels above classification level for acute toxicity (cat 4), eye corrosivity/irritation and respiratory sensitization
- No further characterisation or T/D work required since metals dissociated in acid solution and assumed to be fully bio-available (manufacturers to confirm)

Concerns:
- Highly bio-available material expressing all hazard properties of constituents (Env. Acute 1-Irrit.-resp. sensitization-Acute tox cat 4)

Recommendation:
- Accept classification

7. FLUE DUST

7. Flue dust: TIER 1

Physical form: fine powdery material
- Expected to be in the oxide form
- High concentration of CMR materials (Ni, Pb, As, …) above classification levels
- Pt concentrations above level of respiratory and skin sensitization (also Ni)
- Cu and Pt levels above classification limit for eye damage and irritation
- Ni and Cd above STOT RE classification levels
- Sn levels above STOT SE !!!
- Long series of metal ions above environmental classification level

Concerns:
- High hazard group material including CMR, Env (acute 1), STOT SE/RE and Resp./Skin sensitizer)

Recommendation: STOP at TIER 1
- Accept classification but confirm species triggering STOT classification with manufacturers

8. RESIDUES, PM REFINING CEMENTATION AND REDUCTION

8. Residues, PM refining cementation: TIER 1

Physical form: fine dry or wet powdery material
- Expected to be in the oxide or chloride form
- Ag and As concentrations above classification limits for skin corrosion/irritation
- High concentration of CMR materials (Ni, Pb, As, …) above classification levels
- Pt concentrations above level of respiratory and skin sensitization (also Ni)

- Cu and Pt levels above classification limit for eye damage and irritation
- Ni above STOT RE classification levels
- Long series of metal ions above environmental classification level

Concerns:
- High hazard group material including CMR, Env (acute 1), STOT RE, Skin corrosion/damage and Resp./Skin sensitizer)

Recommendation : STOP at TIER 1
- Accept classification

9. MATERIALS FOR RECLAIM

9.1a Materials for reclaim, PM with or without support: TIER 1

Secondary sources of precious metals on metallic (non-PM), ceramic, carbon support or no support (PM only)
Physical form tested: spent mixed catalyst on ceramic support crushed into a fine powder; defining a representative sample would be very difficult given the wider variety in composition of the material

- CMR's above classification limits for As, Pb, Ni,…
- High release of Ag (and Cr) (in line with composition?); increased solubility at pH 8 for Ni and Co (expected)
- When with C support, consider classification of C

Concerns:
- Elemental analysis
- Cr speciation

Recommendation:
- Can be handled as one group with differentiated classifications based on type of support
- Refine for CMR based on info on elemental composition by the manufacturers
- 1 mg/l 7 and 28 d T/D analysing Ag, Ni and Co
- Bio-accessibility test in artificial sweat (if result negative: may remove sensitization classification)

9.2 Materials for reclaim, PM in bricks, crucibles and trays: TIER 1

PM contained in bricks, crucibles, trays, etc. used during refining of precious metals (metallic + other forms trapped in matrix)
Physical form: usually lumps of crushed bricks, crucibles and trays which may also contain a dusty/powdery fraction

- CMR's above classification limits for As, Pb, Ni,…
- Cr in bricks likely to be 3+
- Metal concentrations are often high but form/solubility unknown (assumed to be metallic → acute 1/chronic 1 environmental classification likely

Concerns:
- Large variability in elemental analysis, need to confirm Cr and other metals' species/classification

Recommendation:
- Refine for CMR based on info on elemental composition by the manufacturers
- 24 h T/D pre-test

9.3 Materials for reclaim, PM production by-products: TIER 1

PM contained in production by-products such as precious metal sweeps.
Physical form: usually dusty materials

- CMR's above classification limits for As, Pb, Ni,…
- Cr in sweeps likely to be 3+
- Metal concentrations are often high, assumed to be in metallic and oxide form

Concerns:
- Large variability in elemental analysis, need to confirm Cr and other metals' species/classification

Recommendation:
- Accept classification but confirm CMR composition with each manufacturer

10. PGM RICH Pb BULLION

10. PGM rich Lead Bullion: TIER 1

Massive metallic material, similar to Pb Consortium in composition but resulting from a different process and hence, richer in PGM content

- CMR's above classification limits for Pb, Ni,…
- Skin sensitization for Ni content

Concerns:
- Availability of info from the Pb Consortium, Ni sensitivity, Env. solubility

Recommendation:
- Obtain info from the Pb Consortium
- Depending on information of Pb Consortium, conduct bio-elution test in artificial sweat to refine sensitisation classification triggered by Ni and 24 h T/D pre-test analysing Pb, Cu, Ag, Ni, Sb, and As to refine environmental classification

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