How to assess the hazardousness of waste?
Proposal of an analytical protocol for the determination of elements and substances in waste

Pierre HENNEBERT, Arnaud PAPIN
pierre.hennebert@ineris.fr
Institut National de l’Environnement Industriel et des Risques, FR

WASCON 2012
Why to assess the hazardousness of waste?

The hazardousness of waste must be assessed for regulatory compliance, i.e.:
- Safe handling and management (a.o. Seveso regulation applies to waste treatment facilities)
- Determination of some recycling/reuse potential:
  - Not hazardous character for reuse of waste in natural environment
  - Not hazardous or hazardous for other uses

Non-hazardous waste are NOT waste that fulfill the acceptance criteria for inert or non-hazardous waste landfill !!
Hazardous waste are NOT waste that fulfill the acceptance criteria for hazardous waste landfill !!!
Two different approaches in waste characterisation:

**RISK**
- Waste
- Leaching, Scenario, Evolution
- Risk of emission of substances
- Long term behavior

**HAZARD**
- Waste
- Analysis elements and substances
- Intrinsic hazard
- Regulatory classification

Risk = hazard + transfer/exposure + target
A hazardous waste is …

… a waste classified as hazardous in the European List of Waste
… a waste that exhibit at least one HP1 – HP15 property!
(HP : hazardous property, formerly H1 – H15)

Discussion are ongoing among EU Member States to align the definition of hazardous properties to chemical legislation (Classification, Labeling and Packaging of substances and mixtures regulation – CLP 2008), according to the Global Harmonized System of the UN.

Technical definitions of the HP and concentration limits of substances are in consultation up to end of May 2012:

http://ec.europa.eu/environment/waste/framework/list.htm
Example : HP4 irritant

If the sum of the concentrations of all substances classified H314 Cat.1A exceeds or equals 1%, the waste shall be classified as hazardous according to HP4.

\[ \sum c \text{H314 Cat. 1A} \geq 1\% .\]

If \( \sum (c \text{H318}) \geq 10\% \), the waste shall be classified as hazardous according to HP4.

\( \sum (c \text{H315} + c\text{H319}) \geq 20\% \), the waste shall be classified as hazardous according to HP4.

The hazardous substances and their concentrations must be known…
Option 2

Definition to be included in Annex III to Directive 2008/98/EC

HP14 'Ecotoxic': wastes which present or may present immediate or delayed risks for one or more sectors of the environment.

\[ \sum (M \times c_{Aquatic\text{ Acute}\ 1}) \geq 25\% \]

\[ \sum (M \times 10 \times c_{Aquatic\text{ Chronic}\ 1}) + \sum (c_{Aquatic\text{ Chronic}\ 2}) \geq 25\% \]

The hazardous substances and their concentrations must be known...

The properties of the substances can be found at

Number of substances with aquatic toxicity properties in the CLP Annex 3.2 Table VI.

<table>
<thead>
<tr>
<th>Category of substances</th>
<th>H sentence</th>
<th>Number of substances in CLP Annex VI Table 3.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquatic Acute 1</td>
<td>H400</td>
<td>1207</td>
</tr>
<tr>
<td>Aquatic Chronic 1</td>
<td>H410</td>
<td>1080</td>
</tr>
<tr>
<td>Aquatic Chronic 2</td>
<td>H411</td>
<td>600</td>
</tr>
<tr>
<td>Aquatic Chronic 3</td>
<td>H412</td>
<td>432</td>
</tr>
<tr>
<td>Aquatic Chronic 4</td>
<td>H413</td>
<td>254</td>
</tr>
<tr>
<td>With specified M factor</td>
<td></td>
<td>211</td>
</tr>
<tr>
<td>Total individual substances</td>
<td></td>
<td>4467</td>
</tr>
</tbody>
</table>
How to assess hazardousness of waste? (simplified…)

- Is there sufficient information to get a European Waste Code?
- Can an absolute entry (H, non H) in the List of Waste be assigned?
- Is it a (used) product material? Use the product hazard statements, the labels, the safety data sheet
- Does the origin or nature of waste provides sufficient evidence for characterisation?
- Is it explosive (HP1), oxidising (HP2), flammable (HP3)? : Test!
- Does it contain some decisive substances? Substances, concentration: Test!
- Do you have results of biotests (human toxicity HP4 to HP11 & HP13, aquatic toxicity HP14)?
- Does it produces acute toxic gas (HP12)? (test to be developed…)
- Does it yield another hazardous substance (HP15)? Test!
- Perform (exhaustive) chemical analysis and compute HP4 to HP11, HP13, HP14: This proposal
Characterisation and classification of waste: 4 modules

1. Exhaustive determination of substances in waste
   1.1 Analytical protocol: this presentation
   1.2 Speciation of (mineral) elements in substances: speciation of the mineralogy – various methods; not discussed here

   In absence of experimental/observed mineralogical data, the mineralogy is calculated from the elemental composition by stoechiometry.

   The « worst case » (most dangerous substance) is used, and depends on the Hazardous Property that is classified.

   The conversion of elements content into mineral species content with defined hazard properties is an unresolved problem in routine practice of waste characterisation: selective extraction, leaching at different pH, inverse geochemical modelling, litterature should be used.

2. Database of properties of substances: CLP + Reach process
3. Regulation rules (Seveso, Hazardous properties, …)
4. Classification by computation for each regulation (including hazardous property)
Module 1: An analytical protocol for the determination of elements and substances in waste

An analytical protocol uses a combination of quantitative methods, screening methods and measure of pools of unresolved composition, to reach for most samples an analytical mass balance of at least 90%:

- New parameters: unresolved pools of probably higher molecular weight organic substances supposed to be less bioactive and less hazardous ("non extractible organic compounds"), "unidentified volatile compounds" and "unidentified semi-volatile compounds".

- Screening ICP methods for major elements

- Screening GC MS methods are used for volatile and semi-volatile organics.

- Classical quantitative analysis for heavy metals and compounds particularly hazardous and subject to regulation (chromium(VI), cyanides, organo-halogens, PCB …).
Conceptual scheme of waste composition

Laboratory Sample 100%

Total Organic Carbon

Total Petroleum Hydrocarbon

Suspended Solids

Soluble Fraction

Non-extractible organic compounds 550 °C
Unidentified Semi-volatile
Semi-volatile
Unidentified volatile
Volatile

Metals S P As Hg
Ash content - Metals
Water

Loss on ignition 550 °C
(including carbonate, organic O N S Cl F, cyanides)

Ash content 550 °C
(including mineral O N Cl F)

CO3
Organic O N S Cl F
CN
The analytical protocol …

- Is under discussion at AFNOR as experimental standard « XP X30-489 Characterization of waste — Determination of the content of elements and substances in waste”

- Has been applied to 32 industrial samples for impact assessment of different options of classification (protocol and report available: Classification of industrial waste for hazard properties HP4, HP6, HP8, HP13 and HP14 criteria based on substance concentrations, and impact assessment of options for HP14 on classification of various wastes, composts, sediments and soils. Study report 10/03/2012 INERIS-DRC-12-125740-03014A.

- Has been applied today to > 150 samples
- Is used in the French regulation, and practiced « in routine » by 3 laboratories
- Is submitted to Waste Management and is detailed in the proceedings
Results: exemple of mass balance

± 7 000 results and groups for the 32 samples and the two laboratories

<table>
<thead>
<tr>
<th>Substances/group (% m)</th>
<th>Example of Industrial bottom ash</th>
<th>Lab1</th>
<th>Lab2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total mass</td>
<td></td>
<td>97.26</td>
<td>95.83</td>
</tr>
<tr>
<td>Non-extractible organic compounds (pool)</td>
<td></td>
<td>9.60</td>
<td>5.30</td>
</tr>
<tr>
<td>Semi-volatile organic compounds (sum of -)</td>
<td></td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>Volatile organic compounds (sum of -)</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total Petroleum Hydrocarbons (TPH)</td>
<td></td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>Ash content – Metals (sum of -)</td>
<td></td>
<td>44.64</td>
<td>58.98</td>
</tr>
<tr>
<td>Metals (sum of -)</td>
<td></td>
<td>42.36</td>
<td>31.52</td>
</tr>
</tbody>
</table>

Important differences between laboratories…
Comparison of results between labs
Comparison of results between labs

Volatile and semi-volatile organic compounds, cc > 0.1 %
Results: mass balance for solid samples

<table>
<thead>
<tr>
<th>Teneur en substance pour bilan de masse (% m)</th>
<th>Lab1</th>
<th>Lab2</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 : APC Bicarbonate</td>
<td>126.00</td>
<td>99.96</td>
</tr>
<tr>
<td>S2 : APC Lime</td>
<td>98.70</td>
<td>99.83</td>
</tr>
<tr>
<td>S3 : MSWI fly ash</td>
<td>99.40</td>
<td>99.59</td>
</tr>
<tr>
<td>S4 : APC residue industrial waste #1</td>
<td>91.21</td>
<td>99.81</td>
</tr>
<tr>
<td>S5 : APC residue industrial waste #2</td>
<td>92.31</td>
<td>99.80</td>
</tr>
<tr>
<td>S6 : Industrial waste bottom ash</td>
<td>97.26</td>
<td>95.83</td>
</tr>
<tr>
<td>S7 : Metallic dust from aluminum industry</td>
<td>95.05</td>
<td>101.35</td>
</tr>
<tr>
<td>S8-DON : Packages and materials</td>
<td>64.91</td>
<td>80.04</td>
</tr>
<tr>
<td>S8-GEO : Packages and materials</td>
<td>75.60</td>
<td>89.60</td>
</tr>
<tr>
<td>S8-SAR : Packages and materials</td>
<td>104.59</td>
<td>91.34</td>
</tr>
<tr>
<td>S8-SCO : Packages and materials</td>
<td>84.52</td>
<td>100.50</td>
</tr>
<tr>
<td>S8-TRI : Packages and materials</td>
<td>40.88</td>
<td>67.45</td>
</tr>
<tr>
<td>S9-GEO : Pasty waste</td>
<td>100.03</td>
<td>85.24</td>
</tr>
<tr>
<td>S9-SCO : Pasty waste</td>
<td>100.80</td>
<td>79.41</td>
</tr>
<tr>
<td>S18 : Solid recovered fuel</td>
<td>98.61</td>
<td>94.39</td>
</tr>
</tbody>
</table>
## Results: mass balance for liquid samples

<table>
<thead>
<tr>
<th>Substance Description</th>
<th>Lab1</th>
<th>Lab2</th>
</tr>
</thead>
<tbody>
<tr>
<td>S9-SAR: Pasty waste</td>
<td>104.76</td>
<td>96.06</td>
</tr>
<tr>
<td>S10: Engine oil</td>
<td>90.28</td>
<td>84.67</td>
</tr>
<tr>
<td>S11: Hydraulic oil</td>
<td>87.36</td>
<td>82.83</td>
</tr>
<tr>
<td>S12-SON: Hydrocarbon</td>
<td>23.01</td>
<td>70.39</td>
</tr>
<tr>
<td>S13-SCO: Hydrocarbon</td>
<td>95.79</td>
<td>112.73</td>
</tr>
<tr>
<td>S13-SON: Hydrocarbon</td>
<td>97.27</td>
<td>97.24</td>
</tr>
<tr>
<td>S14-PCX: Halogenated solvent</td>
<td>62.17</td>
<td>27.25</td>
</tr>
<tr>
<td>S14-SAN: Halogenated solvent</td>
<td>96.58</td>
<td>83.63</td>
</tr>
<tr>
<td>S14-SAR: Halogenated solvent</td>
<td>71.97</td>
<td>89.06</td>
</tr>
<tr>
<td>S15: Non-halogenated solvent</td>
<td>66.45</td>
<td>57.88</td>
</tr>
<tr>
<td>S16-CHI: Waste water</td>
<td>101.47</td>
<td>95.92</td>
</tr>
<tr>
<td>S16-DUC: Waste water</td>
<td>99.18</td>
<td>96.83</td>
</tr>
<tr>
<td>S16-GEO: Waste water</td>
<td>100.11</td>
<td>97.20</td>
</tr>
<tr>
<td>S16-HOM: Waste water</td>
<td>99.41</td>
<td>101.40</td>
</tr>
<tr>
<td>S16-SAR: Waste water</td>
<td>88.42</td>
<td>97.39</td>
</tr>
<tr>
<td>S16-SCO: Waste water</td>
<td>97.70</td>
<td>90.69</td>
</tr>
<tr>
<td>S17: Liquid recovered fuel</td>
<td>47.00</td>
<td>66.18</td>
</tr>
</tbody>
</table>
Conclusion over protocol

Despite discrepancies for some parameters, a quite satisfactory analytical balance of 90 % is reached for 20 samples (63 % of the samples), with for most of the unsatisfying results identified reasons.

A detailed report is available:

Caractérisation des déchets industriels en vue de la détermination de leur potentiel de danger dans un objectif de classement SEVESO : résultats de la campagne d’analyses. Rapport d’étude 07/04/2011 N° INERIS DRC-11-118161-04055A

(http://www.ineris.fr/centredoc/ineris-campagne-analyse-d%C3%A9chets.pdf)
Module 1 : 1.2 Speciation of mineral elements in substances

A preliminary stoechimetric approach is proposed: the amount of each element is distributed in one or more substances screened from the CLP annex for each HP as « worst case » substances.

A report and an Excel® sheet are available (in French) (mail to flore.rebischung@ineris.fr): Reconstitution d’une spéciation des éléments totaux en minéraux dans les déchets en vue de la détermination d’un potentiel de danger dans un objectif de classement SEVESO. Principes et mode d’emploi de l’outil de calcul. Rapport d’étude 10/08/2011 N° INERIS-DRC-11-118157-06170A (http://www.ineris.fr/centredoc/ineris-sp%C3%A9ciation-d%C3%A9chets-seveso.pdf)

This point is not satisfactorily resolved in routine and a guideline about the speciation of elements in waste is needed…
General Conclusion

A protocol for the determination of elements and substances in waste is considered as validated but can be improved (edible oil, polymers, quantification of mineral elements and organic substances, mass balance for chlorinated solvents, …).

It is currently applied in France. It will be formally adopted as a French standard in Sept 2012, and will be proposed as a work item to CEN TC 292 in June 2012.

It is allows the computation of most of the Hazard Properties with one analytical run, and can sometimes avoid numerous specific tests. It is the only feasible and exhaustive determination of (human) toxicity HP of waste.

The true speciation of elements in minerals with known hazard properties is critical and is an unsatisfactorily resolved problem in routine analysis. A stoechimetric approach is available. A working group starts at AFNOR and this subject will be proposed as a work item to CEN TC 292.
Acknowledgements

This work was supported by the Ministry for Ecology, France (www.ecologie.gouv.fr). The continuous support of Mr Eric Gaucher and Ms Pauline Langeron was much appreciated.


The protocol uses partly methods of analysis of (identified) organic compounds practiced by Holcim (cement) and Micropolluants Technologie (laboratory) companies. The contributions of Mr François David (Research and Development Manager, SGS Multilab) and Christophe Allamelle (Development Engineer, Eurofins laboratory) were essential to this work. The work of Mrs Pauline Molina (treatment of samples) was greatly appreciated.
Thank you !!!