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Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Transport of Dangerous Goods **3 July 2012**

Forty-first session
Geneva, 25 June – 4 July 2012
Item 10 (b) of the provisional agenda
Issues relating to the Globally Harmonized System of Classification and Labelling of Chemicals: Criteria for water-reactivity

Classification of Water-Reactive Substances

Report of the Working Group – 3 July, 2012

Submitted by the Chairman of the Working Group in Relation to Agenda Item 10(b)

Toward the improvement of UN N.5 test: contributing work from France

Presentation from the expert from France

UN SCETDG/GHS (41th session/23th session)

Outline

- Ref documents
  - INF 8 (Germany) & INF 38 (USA) 40th session of TDG subCommittee and doc 2012/46 (F) + INF 4 (F)
- Current N.5 test
- Problems of gas release rate measurements
- Factors influencing the gas release rate
- Results of an INERIS parametric study
- Guiding proposal for discussion

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Background

- In relation with activities of sub-committees of TDG/GHS, a new focus on UN N5 was considered useful for a while
  - New data welcomed on UN N5 test by subcommittees TDG/GHS
- France Contribution to this relates to two initiatives:

1) Round robin testing with UN N5 testing of water-reactives materials under the leadership of BAM with a reference material
2) Parametric study carried out by INERIS under the auspices of the Ministry of Ecology (TDG mission)

- This presentation deals only with point 2)

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Current N.5 test protocol

- Use : to qualify the flammability hazard resulting from aptitude of water-reactive materials to emit flammable gases
- Regulatory uses :
  - Classification in 4.3 according to TDG Regulations
  - Classification and labeling issues according to CLP in the EU or to GHS and related texts elsewhere
  - Open discussions for consideration of use regarding EUH029 (toxic gas release)
- Overall N5 Test procedure basic infos (according to UN Manual of tests and criteria) :
  - “no specific lab equipment requested” mentioned in 33.1.4.2.
  - Three preliminary tests (33.4.1.4.3. 2 - 3 - 4) : no real issues with those
  - Fourth test (33.4.1.4.3.5) to quantify the gas release rate at 20 °C /atmospheric pressure
  - Sample mass: up to 25 g to produce 100 to 250 ml of gas
  - quantity of water: not specified
- Reasons for concern:
  - Potential inaccurracies up to different classifications for same samples

Current N.5 test additional given specifications

- Gas release rate is measured for 7 hours on an hourly basis
- If the gas release rate is variable or increasing after 7 hours, the test shall be prolonged up to 5 days
- Should the nature of the gas be unknown, than a flammability test needs to be done

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Current N.5 test : results implications

CLP /GHS	TDG Regulation	
phys-chem hazard, CLP, section 2.12	Packing group	Criteria
Release of flammable gas when wet Cat 1	I	Vigorous reaction or ignition or Maximum rate of gas release greater than 10 l/kg/min
Release of flammable gas when wet Cat 2	II	Not PG I and Maximum rate of gas release greater than 20 l/kg/hr
Release of flammable gas when wet Cat 3	III	Not PG I or PG II and Maximum rate of gas release greater than 1 l/kg/hr
Not classified in CLP according to such hazard	Not 4.3	Rate of gas release less than 1 l/kg/hr

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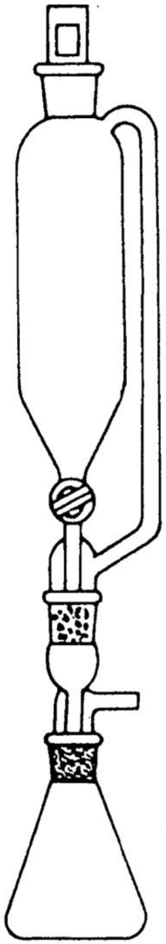
INERIS test conditions before dedicated study

- Volume of system: > 700 ml
- Standard sample mass: 10 g
- Two techniques for gas release rate measurement:
  - volumetric with burettes and a stop watch or
  - automatically with a SYSTAG Flow measurement system

Experimental set-up (INERIS)



Volumetric measuring device

Device used to measure the rate of gas release

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Gas release rate measurements issues regarding the volumetric method (use of a burette)

⇒ Temperature and pressure differences in the test volume lead to significant)potential errors even *after* correction or using a *parallel blank reference apparatus used without sample*

⇒ For 700 ml dead volume with 10 g of sample :

⇒ Variation of 1 °C or 8 mm Hg (Atmospheric pressure)

⇓

Error of ~ 0.25 liters/kg/hr in gas release rate

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List of identified influencing factors :

- Mass of sample, mass of water (sample/water ratio)
- Particle size of sample
- Duration of test
- Stirring (yes/no)
- Pressure - composition of the atmosphere (air, nitrogen, argon)
- Water chemistry (distilled water, tap water, sea water), pH
- Water solubility of released gaseous products
- Temperature - thermal insulation - self-heating

INERIS parametric study main characteristics

- Al powder – Mg powder
- Use of INERIS experimental device
- Test program targeting :
  - Influence of sample mass
  - Influence of temperature (fixed by a thermostatic bath)
  - Influence of sample / liquid ratio (at a fixed temperature)
  - Influence of the chemical nature and pH of the liquid
  - Influence of the overall volume of conical flask and dropping funnel
- Results
  - Full details available in recent paper by Janès et al in the Journal of Loss Prevention in the Process Industries (2012)

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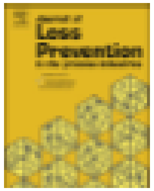
Journal of Loss Prevention in the Process Industries

journal homepage: www.elsevier.com/locate/jlp



Towards the improvement of UN N.5 test method for the characterization of substances which in contact with water emit flammable gases

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ABSTRACT

This paper deals with a sensitivity analysis of main parameters affecting the measurement of the gas flowrate emitted during testing substances for their potential to emit flammables gases in dangerous quantities where in contact with water, according to the UN N.5 test procedure. UN N.5 is described in the Manual of Tests and Criteria of United Nations (part of the Orange Book) (ONU Manual of Test and Criteria, 2008), serving both applications of international transport regulations as well as classifications of dangerous substances according to Globally the Harmonized System (GHS) and the derived regulation applying in the EU known as "CLP" Regulation (Regulation (EC) No 1271/2008). The main reason that justifies the present research is that the measurement of emitted gases is highly critical in the final classification resulting from the interpretation of the test results. Moreover, that idea has been raised to adapt the UN N.5 test protocol for classifying, in the future, substances that by contact with water would emit dangerous quantities of toxic gases.

Experiments have been carried out to cover the analysis of the influence of ambient temperature, overall volume of glassware, nature of aqueous media, mass sample and sample-to-liquid mass ratio, since such parameters are not fixed within any defined range in the UN N.5 test procedure. The influence of the flow rate measuring device was also considered. Results confirm that the above mentioned parameters may play a significant role to such an extent as to finally alter the final classification resulting from the testing. Guiding principles have also been derived from our measurements and observations towards an improved and more robust UN test protocol in the future.

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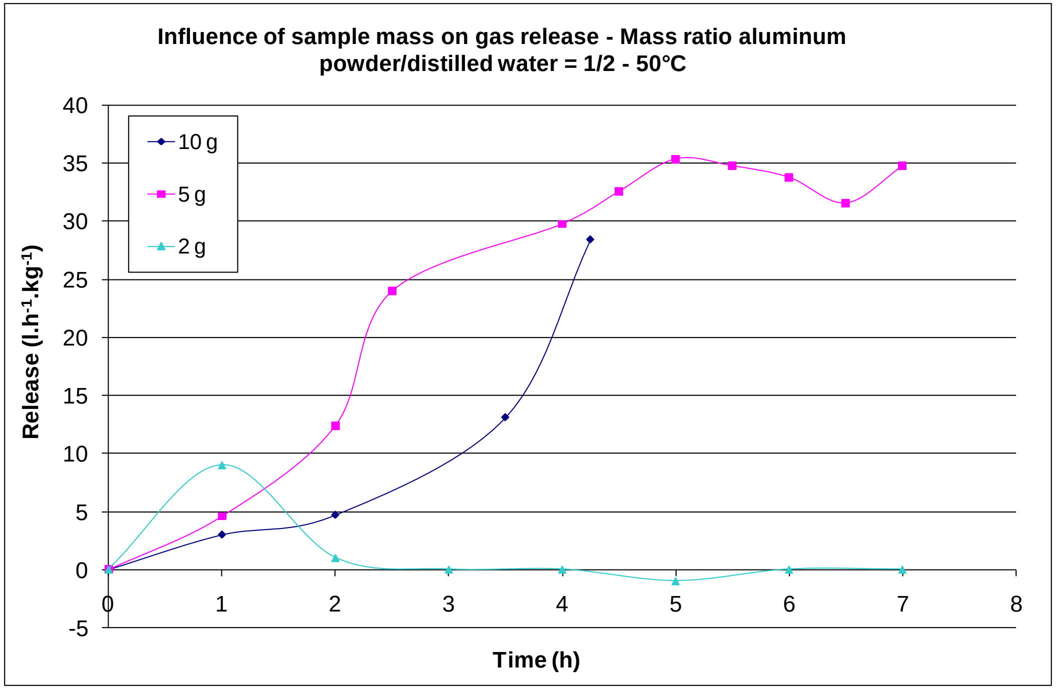
Results : 1. Influence of sample mass



The sample mass:

- must be sufficient to obtain a significant gas release
- must be adjusted to keep within the overall capacity of gas volume measurement system

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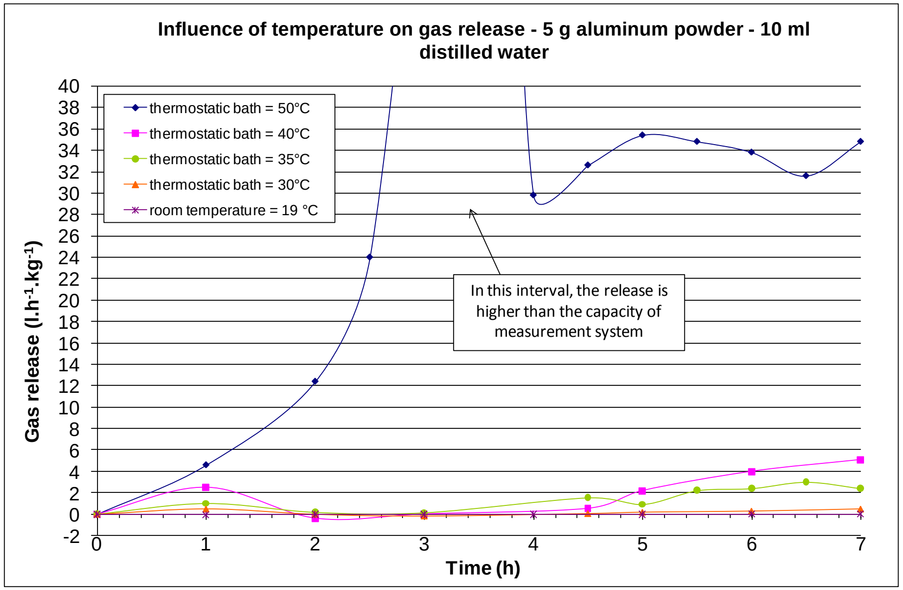
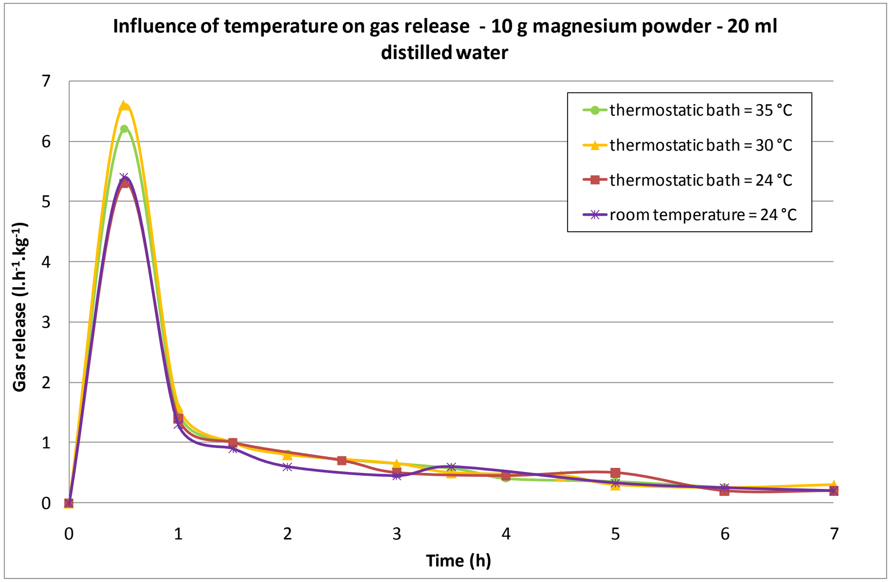
Results: 2. Influence of ambient temperature





- if there is a possibility of self-heating when material is transported in bulk, it seems relevant to perform another test at a higher temperature

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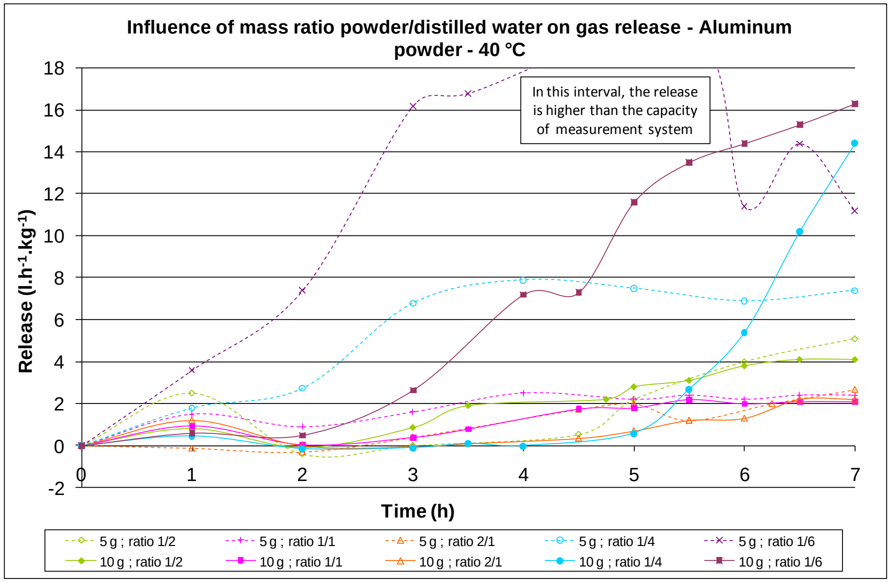
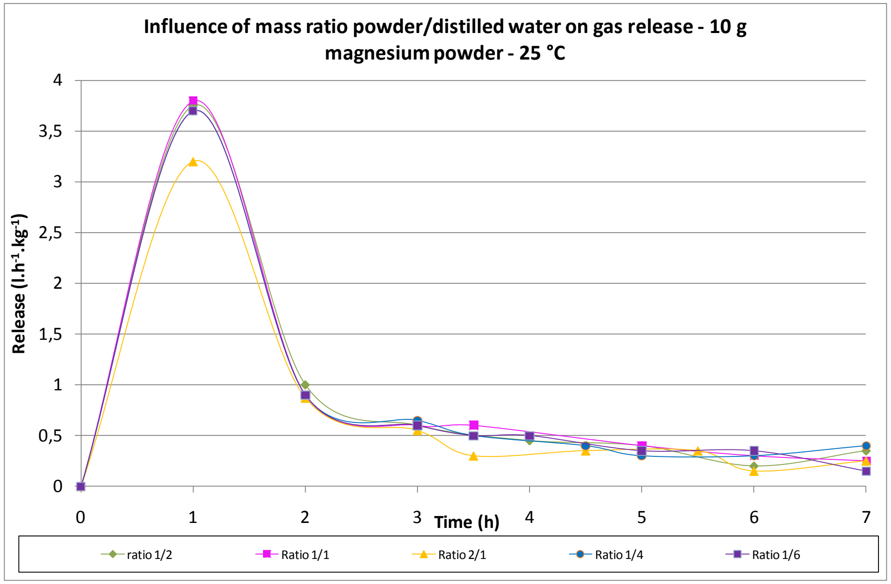
Results: 3. Influence of sample / liquid ratio (Al)





- Quite different from one product to another
- Role of containment, wettability of material

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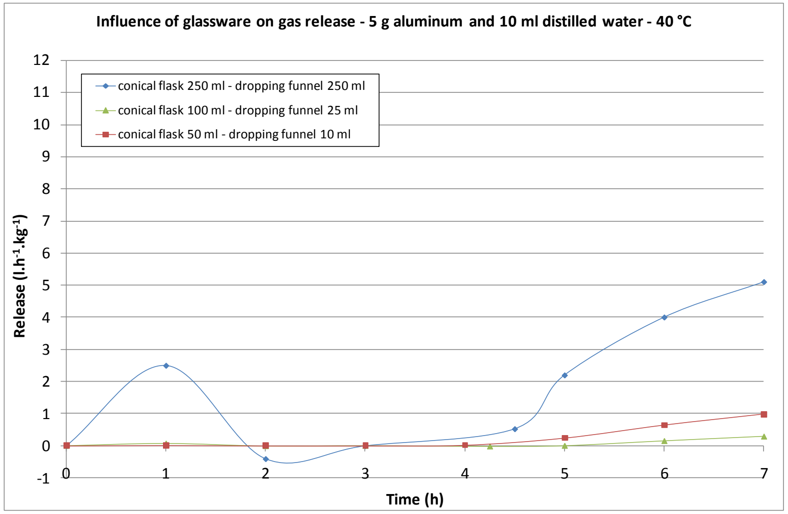
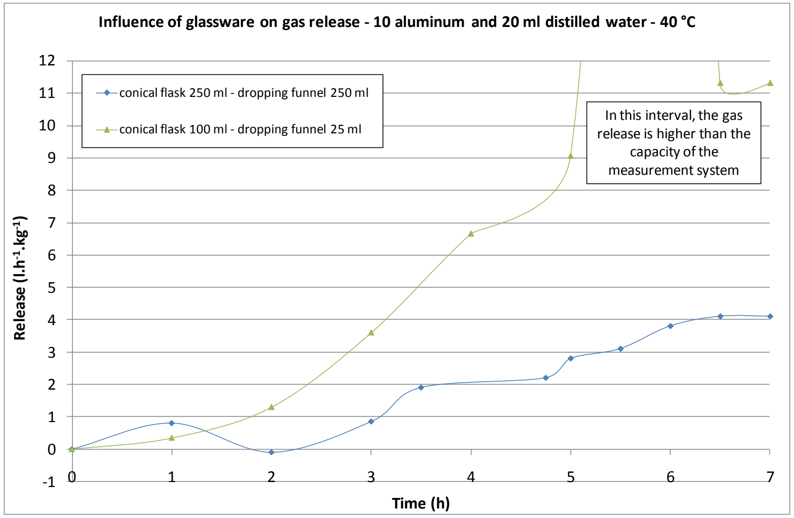
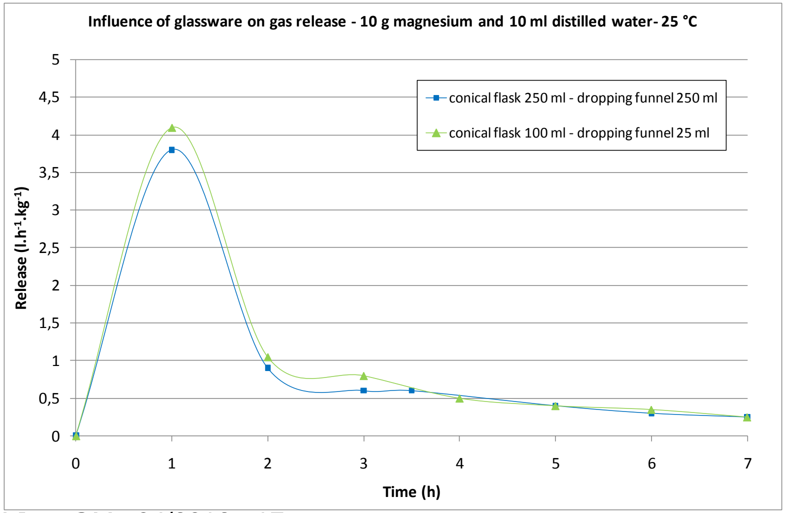
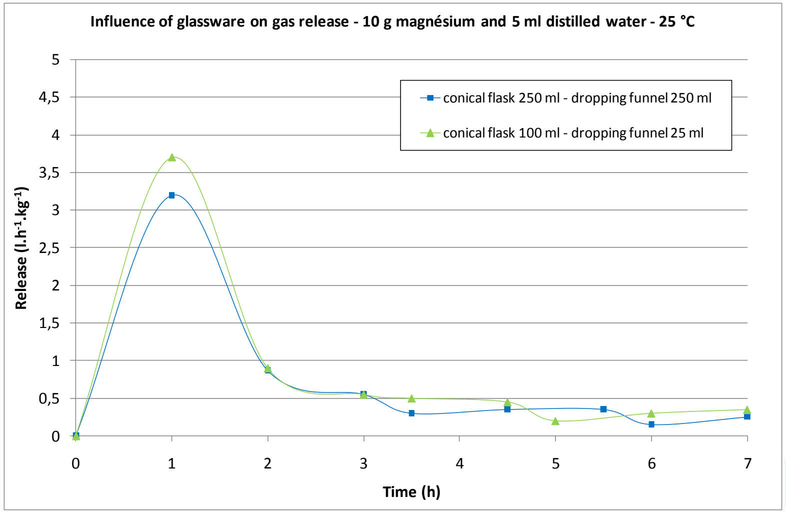
Results: 4. Influence of the overall volume of conical flask and dropping funnel









Results: 4. Influence of the overall volume of conical flask and dropping funnel, conclusions

- Free volume of the glassware is likely to influence the gas flow due to thermal expansion of gases (when the ambient temperature is changing): free volume of the glassware should be reduced as much as possible

- Conical flask volume influences the quality of the powder wetting

- There is a strong link between the quality of wetting and the gas release rate measured

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Influence of the chemical nature and pH of the liquid

- Seawater can stop the reaction (aluminum), but can also magnify it (magnesium)
- Results obtained with the acid and basic solutions raise the question of the influence of the thickness of the oxidation layer or the coating layer on the surface of the sample tested

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Proposal for discussion

5. The experts from France suggest the following modification principles in the subsequent UN N.5 test protocol.

(a) It appears important to define some experimental conditions which are not specified in the standardized protocol, e.g.:

(i) The use of a 100 ml conical flask and a 25 ml dropping funnel;

(ii) The use of a sample mass of 10 g and a sample/liquid mass ratio of 1/2 or ¼;

(b) It is recommended that other factors not mentioned in the current protocol be taken formally into account, depending on the conditions of storage or transport (further work needed):

(i) Bulk transport, substances capable of self-heating in contact with water would be tested with a thermostatic bath at 40 °C;

(ii) Maritime shipment: test with seawater;

(iii) In case of possible destruction of oxidation layer or coating layer: test with an acidic or a basic solution;

(c) Finally, the work group should encourage complementary work on the issue of water solubility of gases.

Thank you for your attention