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) [6], 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 [7]. 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.

Key words:
Water-reactivity – Reaction with Water – Flammable Substance Classification

1. INTRODUCTION

A suitable evaluation of the hydro-reactivity of powders or other chemical compounds is crucial to correctly assess the risks associated to handling, storage and transport of key emerging materials, like nanopowders [1 and 2] or complex hydrides as hydrogen storage materials [3, 4 and 5].

The characterization of substances which in contact with water emit flammable gases up to the point that an intrinsic hazard has to be considered is usually performed according to the test method UN N.5. This method is defined in the UN Manual of Test and Criteria for the Transport of Dangerous Goods [6]. The UN N.5 test method is also designated as the appropriate test method to classify and label such substances according to the new CLP regulation [7] (Classification, Labeling, and Packaging). This is the European enforcement of the GHS (Global Harmonized System) developed at the UN level, in order to harmonize classification of hazardous materials throughout the world. It should also be noted that the UN N.5 test method approach is a possible candidate to determine an additional hazard statement, the EUH029 "Contact with water liberates toxic gases", for which there is no test method in the GHS and for which no international standard exists.

In the context of CLP, the UN test N.5 is the experimental method adopted with respect to the newly implemented physico-chemical hazard class of "substances and mixtures which in contact with water emit flammable gases". Hazard statements associated to this class are codified as H260 "In contact with water releases flammable gases which may ignite spontaneously" and as H261 "In contact with water releases flammable gases" depending on pertinent observations in the experiments.

In practice, experience shows that the implementation of this test method leads to technical issues with respect to metrology. This is even pointed out in an official application guidance recently issued by the European Chemical Agency [8]. The relating difficulties generate significant uncertainties of the results, since in some

difficult experimental cases the absolute error can be on the same order of magnitude as the threshold of classification adopted in the standard. Moreover, variations in experimental results from one laboratory to another for a same test sample may arise due to potential variations in testing apparatuses. These difficulties are especially due to the fact that some basic environmental parameters, such as sample mass, temperature, sample/liquid mass ratio, nature of aqueous medium and dead volume, are not fixed in the standard test method as described in the current version of the Manual of Test and Criteria [6]. Although the influence of some of these parameters has been partly identified in the past, no research has been published to date with the aim of proposing test protocol improvements.

The present work is a contribution in that direction.

This issue has also been the subject of lengthy discussions in the past between experts belonging to the IGUS group [9]. Particularly, a Round-Robin test was organized by the German Federal Institute for Materials Research and Testing (BAM) in 2007 and more recently in 2011 [10]. This work is still underway, under the mandate of UN, in the Sub-Committees of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System. Work on test method UN N.5 was initiated in the 2009-2010 biennium work program, then more recently registered again in the 2011-2012 biennium work program [11]. In this context, technical reports were provided by several experts (from France, Germany and USA), also confirming metrology issues have to be solved, in particular before considering any expansion of use of the test regarding the evaluation of water-reactive chemicals in terms of toxic emissions [12, 13 and 14].

Based on a parametric experimental study, this article seeks to highlight the qualitative and whereas possible quantitative influence of various parameters on the results of the application of the UN N.5 test method. In addition, this study also compares the results obtained according to the use of two different volumetric flow meters. At last, some guiding principles have been identified that can lead to an improved test method.

2. CLASSIFICATION SCHEMES OF SUBSTANCES WHICH IN CONTACT WITH WATER EMIT FLAMMABLE GASES

The characterization of substances which in contact with water emit flammable gases can be done according to at least three referenced test protocols, namely:

- The UN N.5 test, from UN Recommendations for the Transport of Dangerous Goods [6],
- The EC A.12: test Flammability (contact with water), described in the European Regulation No 440/2008 [15]. This reference was used for the classification according to the 67/548/EEC Directive [16],
- A former French technical standard referenced NF T 20-040 [17] and recently cancelled.

2.1 PRINCIPLE OF THESE TESTS

The objective of all mentioned test procedures is to determine whether or not the reaction of a substance with water leads to the emission of a dangerous amount of flammable gases. The methods are applicable for testing a solid or a liquid substance or mixture in its commercial form at ambient temperature (20 °C).

The first three steps in the procedure are the same for all three methods and are carried out to identify a violent reaction by bringing the substance into contact with water under different conditions. The final step consists in determining the rate of emission of flammable gas.

The comparison of the three standards, regarding the 4^{th} step, reveals some differences. Major differences are linked to the reactant quantities, as shown in Table 1.

During the 4^{th} step, the overall volume of gas evolved may be measured by any suitable means. The gas flow rate is calculated over 7 hours at 1 hour intervals. If the gas flow rate is erratic or increases after 7 hours, the measuring time is extended to a maximum of 5 days. If the chemical nature of the gas is unknown, the flammability of the gas should be tested.

2.2 EVALUATION CRITERIA AND LABELING

A material shall be considered as a substance which in contact with water emits flammable gases if:

- A spontaneous ignition of the gas occurs at any stage of the test, or
- There is a release of a flammable gas at a rate greater than 1 $l.kg^{-1}.h^{-1}$.

The classification is assigned according to criteria given in Table 2.

3. SCIENTIFIC BACKGROUND

When water reactive materials come in contact with water, the resulting hydrolysis initial reaction mechanism drives the production of heat, flammable, toxic or oxidizing gas. Examples of these water reactive substances are:

- Alkali metals, like sodium (Na), potassium (K) or lithium (Li),
- Anhydrous metal halides, for example aluminium chloride ($AlCl_3$) or stannic chloride ($SnCl_4$),
- Alkali metal hydrides and alkali metal amines, such as sodium amine ($NaNH_3$),
- Calcium carbide (CaC_2),
- Halides of nonmetals, like boron trichloride (BCl_3) or silicon tetrachloride ($SiCl_4$),
- Inorganic acid halides, such as thionyl chloride ($SOCl_3$),
- Metals alkyls, such as lithium, aluminum or magnesium alkyls,
- Metal hydrides, for example of aluminum (AlH_3) or sodium (NaH),
- Organic acid halides and anhydrides of low molecular weight, like acetyl chloride and acetic anhydride.

In the case of substances which emit flammable gases when wet, several other reaction mechanisms can be involved, e.g. oxidation of metals like aluminum [18 and 19] or magnesium [20], to produce hydrogen and a metal oxide.

Analysis of significant influential parameters was previously provided in the literature, but mainly limited to the study of the water reactivity of aluminum and aluminum hydrides. Below is a brief overview of previously studies available in the literature:

- The reaction temperature: the rate of hydrogen production from reaction of aluminum-metal oxide powders with water is strongly dependant on temperature [21]. The reaction can be practically stopped by cooling down the flask containing the reactants. Then the reaction can be restarted by warming the flask to its initial temperature.
- The quality of the mixing of the reactant powder with water: when a fraction of aluminum powder is caked in a corner of the flask and is effectively isolated from water, this part of the powder remains unreacted at the end of the test [21]. On the contrary, if the flask position is adjusted to avoid caking, the completeness of the reaction increases,

- The protective oxide layer at the surface of aluminum is remarkably stable in many oxidizing environments, due to the continuous film of aluminum oxide that rapidly grows on surface exposed to oxygen, water or other oxidizers [5]. The same fact was observed for magnesium: under ordinary atmospheric conditions, the reaction is terminated because of the formation of an insoluble hydroxide film [19]. By contrast however, one researcher has recently reported [21] an experimental result indicating that the rate of hydrogen production reveals no significant difference for both aged or freshly prepared aluminum-metal oxide powders samples in contact with water, even if, for the fresh sample, the reaction continues a bit further than for the aged one,
- The pH of aqueous solution: aluminum oxide film dissolves in alkaline solutions; corrosion is rapid, producing soluble alkali-metal aluminate and hydrogen [19]. Moreover, aluminum is amphoteric and can react with mineral acids to form soluble salts and evolve hydrogen.

  In the case of magnesium, the rate of corrosion in aqueous solutions is strongly influenced by the pH: magnesium is resistant to alkalis but is attacked by acids that do not promote the formation of insoluble films. Chlorides are usually corrosive even in solution having pH values above that required to form magnesium hydroxides. Magnesium is resistant to pure alkalis in solution of pH 10.2 or greater. However, at elevated temperatures, a reaction can still occur,
- The presence of impurities: it has been reported in [18] that, in general, impurities increase the oxidizability of aluminum and, in particular, contact with mercury or its salts.

This literature review suggests some parameters of interest, the influence of which has been characterized in details as part of the parametric experimental study reported in this paper. We can cite:

- Reaction temperature,
- Sample mass, powder/liquid mass ratio, inner volume of the conical flask used. All these parameters influence the quality of the mixture between the powder and water and the wetting of the powder by the water. Moreover, the confinement of the reaction is also dependent of these parameters,

- Chemical nature and pH of the aqueous medium: distilled water, seawater and aqueous solutions of sodium hydroxide and hydrochloric acid were used.

Moreover, in order to highlight the uncertainties due to the thermal expansion of gases produced, the overall inner volume of conical flask and dropping funnel was also varied as a potentially important parameter.

In this work, the reaction with water of only two metals, aluminum and magnesium, was studied. These metals present partial similarities in that hydrogen is released on contact with water. However, the results presented below may not be directly applicable for other reaction mechanisms, such as the reaction of calcium carbide or sodium monosulfide with water, since they produce respectively acetylene and hydrogen sulfide, both flammable gases. These two reactions are describes in [20].

Finally, some authors have thoroughly investigated the reaction of aluminum with water. In particular, three steps have been identified in the description of the overall reaction process: the induction period, the fast reaction phase and the slow reaction final period [21]. Moreover, a detailed physicochemical mechanism was proposed in [22].

4. EXPERIMENT

4.1 MATERIALS

The characteristics of both aluminum and magnesium powders selected for this work are detailed in Table 5.

4.2 APPARATUS

The experimental apparatus consists mainly of an assembly of two pieces of glassware: a conical flask and a dropping funnel. Different volumes were tested. Related configurations are specified in Table 6.

The volume of gas release was measured by two means:

- A home-made built-in metering system consisting of water-filled burettes, allowing gas volume to be measured at atmospheric pressure,
- A commercially available automatic flow meter “Gas flow meter FM4/04”, supplied by SYSTAG [23].

For tests using the first system, a control apparatus was used in combination with the experimental device, in order to overcome variations due to temperature or pressure variations.
In the case of most experiments, the flask containing the reactants was placed in a thermostated bath, at a specified temperature.

4.3 TEST PROCEDURE

The various test parameters taken into account in this study were:

- Sample mass,
- Temperature,
- Powder/liquid mass ratio,
- Chemical nature and pH of the liquid phase (aqueous medium): distilled water, seawater sampled on May 25, 2010 at Malo-les-Bains (France, North Sea) at pH 6, solutions of sodium hydroxide at pH 10.78 and pH 11.90 and a solution of hydrochloric acid at pH = 1.25 were used,
- Inner volume of the conical flask and the dropping funnel.

Both gas measurement systems were used.
The tables 3 and 4 list the tests performed and their experimental conditions.
In this study, we have limited the time span of the experiment to the first seven hours for practical reasons even though that in some cases the tests should have been extended to several days, since the rate of gas release was not constant at the end of the first day.

5. RESULTS AND DISCUSSION

5.1 INFLUENCE OF THE TEMPERATURE

As described in [21], Figures 1 and 2 highlight the following points:

- Regarding the aluminum powder, no significant release was observed at room temperature at 30 °C. However, over 35 °C the threshold for classification is exceeded. The higher the temperature was observed, the greater volume of the gas was released. The gas flow was particularly high at 50 °C,
- In the case of the magnesium powder, the threshold was already exceeded at room temperature. There is no significant difference between the results obtained at 24 °C, with and without thermostatic bath. We observed that the

gas flow was increasing as a result of a related temperature rise due to the exothermic reaction.

These results show that the classification of a given substance according to the measurements made according to the UN N.5 test may be very temperature sensitive. This is an important point, because the sample temperature is dependent on several factors:

- Room temperature: the variation range may be wide (if not regulated), and different depending on the location (hot or cold country) where the tests are carried out,
- The intensity and exothermicity of the reaction between the powder and the liquid,
- A possible self-heating effect due to lack of cooling and control of the sample temperature.

5.2 INFLUENCE OF THE SAMPLE MASS

As shown in figure 3, the experiment involving a sample mass of only 2 g of aluminum powder shows a lower gas release compared to test series using 5 and 10 g. The gas flow rate measured with 5 g sample mass was surprisingly higher than the one obtained with 10 g sample mass.

This latter result might be related to uncertainties of the method. Moreover, the influence of the parameter “sample mass” is certainly not independent of the conical flask volume. For a given conical flask volume and shape, heat losses from sample to the outside may be more or less important from one sample mass to another leading to thermal runaway or not. The sample shape for a given mass will render the hottest region in the sample more or less thermally insulated from the flask surface.

Difficulties were encountered during these tests: for the highest masses of powder, the overall volume of gas released was too large for the capacity of the metering system. Therefore, the system had to be purged between two measurements.

These results indicate that the sample mass must be adjusted so as to obtain a significant gas release but on the other hand not to exceed the capacity of the measuring system.

5.3 INFLUENCE OF THE SAMPLE/LIQUID MASS RATIO

In the case of aluminum, it in shown in figure 4 that significantly higher gas flow rates were observed for powder/distilled water mass ratios 1/6 and 1/4 than for mass ratios 1/2, 1/1 and 2/1. A plausible explanation lies in the efficiency of wetting of the powder that is likely to reveal better when there is a larger amount of liquid. The contact between the powder and the water is effective in 250 ml conical flask for ratios 1/4, 1/6 and 1/2. In other cases, the observed lower gas emission rate could be related to the fact that the contact between the powder and water is not optimal.

In the case of the magnesium powder, the gas was emitted at the same rate in all cases, regardless of the powder/liquid mass ratio tested, with one exception (mass ratio 2/1), as shown in figure 5. The 2/1 ratio led to a lower rate than the others. Again, the best explanation is that there is a potentially poorer contact between the powder and water. In all other cases, the wetting of the powder with distilled water is very good: all of the powder is wetted and covered with water.

This result clearly differentiates the behavior of magnesium compared to aluminum and could explain at least partially the very different profiles obtained for these two materials.

5.4 INFLUENCE OF THE CHEMICAL NATURE AND pH OF THE AQUEOUS PHASE

In the case of aluminum, the oxidation mechanism seems quenched by seawater. As is shown in figure 6, the only test result showing a significant gas release was observed at a temperature of 50 °C. This somewhat higher degree of rate of gas release kept however much lower than those obtained with distilled water at the same temperature, but the final trend (at the end of test) was still an indication of a potential increase tendency of the rate of gas release.

Contrary to aluminum, magnesium reacts violently with seawater, as it shown in figure 7. For this test, the gas flow exceeded the capacity of the measuring system and the test was terminated prematurely.

For the aluminum powder, the results are highly dependent on temperature, as the figure 8 shows. Indeed, at 20 °C, the reaction only starts after a few hours. The maximum gas flow is half that obtained at 40 °C. However, under these conditions the measured flow rate at 20 °C is comparable as that measured at 40 °C with distilled water. The acidity of the medium therefore increases the reaction rate. In the second test at 40 °C in the acidic aqueous solution, the reaction also occurred

earlier. It also appeared that the powder/liquid mass ratio had an influence on the shape of the curve. The curve showed a higher gas release rate during the "decreasing phase" for the 1/2 ratio compared to the ¼ ratio, but the maximum release rate was similar.

In the case of magnesium, the reaction obtained during the preliminary test was very intense: bubbles appeared instantaneously.

In the case of aluminum powder, figure 9 shows that the results were highly dependent on temperature and pH. No significant reaction was observed at a temperature of 20 °C. However, at 40 °C and pH 11, the reaction starts after a few hours and reached a rate of emission comparable to that obtained with distilled water at 40 °C. As a response to an increase in pH, the reaction observed at 40 °C became very intense after a few hours and exceeded the capacity of the measurement system.

In the case of magnesium powder, the reaction at 25 °C and pH 12 gives rise to a reaction similar to that obtained with distilled water, as shown in figure 10.

No general rule can be established regarding the use of seawater versus distilled water. Indeed, it was observed that the reaction with aluminum powder is less intense when seawater is used compared with the use of distilled water. The contrary was observed for the magnesium powder. This might be a very important issue for maritime transport transportation.

Tests at different pH levels also showed significant differences depending on temperature and the powder tested. These behavioral differences could be explained by the decomposition of the metal oxide layer on the surface of the particles by sodium hydroxide, depending on temperature, pH and nature of the oxide: MgO or Al_2O_3. These results are in accordance with the literature [19].

5.5 Influence of the overall volume of conical flask and dropping funnel

The free volume of the glassware is likely to influence the measured gas flowrates due to thermal expansion of gases when the ambient temperature varies during the test. In order to reduce this free volume, two other conical flask and dropping funnel volumes were used.

Moreover, our tests also show that the conical flask volume influences the quality of the powder wetting, as well as the powder/liquid mass ratio.

5.5.1 ALUMINUM POWDER

The results shown in figures 11 and 12 highlight the fact that the gas flowrates are highly dependent on test conditions. The full range of powder/liquid mass ratios could not be explored because of the limitation imposed by the volume of the glassware.

Regarding the wetting efficiency of the aluminum powder by distilled water, a summary of observations is presented in Table 6. These results confirm the link between the quality of the powder wetting by the liquid and the peak gas flow measured.

5.5.2 MAGNESIUM POWDER

Distilled water mixes very easily with magnesium powder. This can explain the fact that results are not dependent on the glassware volume used or on the powder/liquid mass ratio, nor on the sample mass. There is no significant difference between the maximum gas release shown in figures 13 and 14.

5.6 FLOW MEASUREMENT SYSTEMS COMPARISON

Gas flow measurements derived from the two volumetric gas flow measurement systems described previously are compared, as an example, in figure 15. The results obtained are in good agreement when the gas release is low. This is the case of powder/liquid mass ratios of 2/1 and 1/1. However, for other mass ratios, discrepancies between results become quite significant. This suggests that the water-filled burette system is not completely impervious to hydrogen. This point however needs to be investigated further by additional tests.

5.7 SUMMARY OF IMPORTANT IDENTIFIED FACTORS

The influence of important factors is summarized below.

- Sample mass

The sample mass must be sufficient to obtain a significant gas release, but not too great as to exceed the capacity of the gas volume measurement system. The tests show that a mass of 10 g is appropriate in most cases.

- Temperature

Given the importance of this factor on the results, if there is a possibility of self-heating when the material is transported in bulk, it seems pertinent to perform another test at a higher temperature. This should also be applied if the product is transported in a hot environment. In any case, reporting results as a function of

ambient temperature or using efficient temperature regulation would help achieving more consistent results between laboratories.

- Free volume of the glassware

The free volume of the glassware is likely to influence the measured gas flow due to thermal expansion of gases when the ambient temperature varies throughout the test. Indeed, in the worst cases, the thermal expansion of gases alone creates an uncertainty which can exceed the classification threshold criterion. Free volume of the glassware should then be reduced as much as possible. Moreover, the conical flask volume influences, as well as the powder/liquid mass ratio, the quality of the powder wetting. Thus, defining the overall volume of the test apparatus would help in limiting the scattering of results between laboratories.

- Quality of sample wetting by the liquid phase

There is a strong link between the quality of wetting and the measured flow releaserate. The two substances tested showed very different behaviours according to their actual wettability. Indeed, intimate contact between water and aluminum was not very easy to obtain, while magnesium and water mix very well in all cases. As the best compromise, we suggest to use a 100 ml conical flask in combination with a 25 ml dropping funnel. Moreover, the most efficient sample/liquid mass ratios observed proved to be 1/2 and 1/4.

- Nature of the liquid and pH

Given the influence of composition and pH of the liquid, it seems important to specify the pH of the distilled water used during the test. Moreover, in the case of maritime transport, it appears also pertinent to perform an additional test using seawater. Indeed, seawater can either stop the reaction or magnify it depending on the sample.
The results obtained with an acid and a base raise the question of the influence of the thickness of the oxide layer or the coating layer on the surface of the sample tested. If such a layer is likely to be affected by the conditions of transport or of storage, an additional test with an acid or a base would be suitable, if an acidic or caustic environment may affect accident scenarios.

- System used for measuring gas flow

The difference between the results obtained with the two gas flow measuring systems is of particularly importance. The differences observed could be related to hydrogen leakage, most likely in the system with water-filled burettes, because of

longer flexible connections. It would be necessary to conduct additional tests to confirm these results.

6. CONCLUSION

A systematic study of the influence of important parameters relevant to the UN N.5 test protocol has been performed. This internationally standardized test method is used to classify substances and compounds with respect to their ability to emit dangerous quantities of flammable gases when wet.

The test results show that some of these parameters may greatly influence final data obtained from using the test protocol as is.

From the present work, the following principles can be cited in order to move forward and to propose a more robust test protocol.

A first order improvement would be to define the ambient temperature range in order to establish controlled laboratory conditions.

Moreover, it appears important to define some experimental conditions which are not specified in the standardized protocol, e.g.:

- The use of a 100 ml conical flask and a 25 ml dropping funnel,
- The use of a sample mass of 10 g and a sample/liquid mass ratio of 1/2 or 1/4.

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

- Bulk storage or transport, substances capable of self-heating in contact with water would be tested with a thermostatic bath at 40 °C,
- Maritime shipment: test with seawater,
- In case of possible destruction of oxidation layer or coating layer: test with an acidic or a basic solution.

Another more specific difficulty of the test method described in this paper is the possible solubility of emitted gases in water, as would be the case for example for acetylene generated by the reaction between carbide calcium and water.

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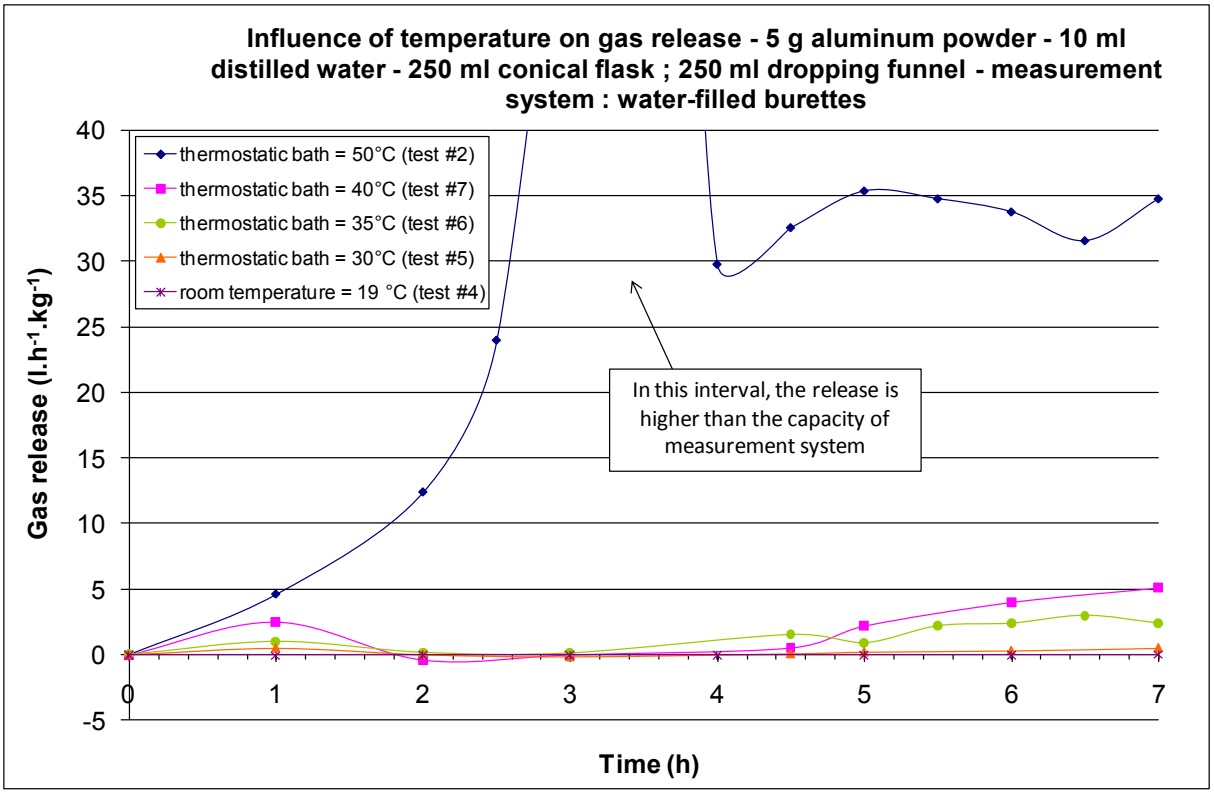

Figure 1: Influence of temperature on gas release – aluminum powder

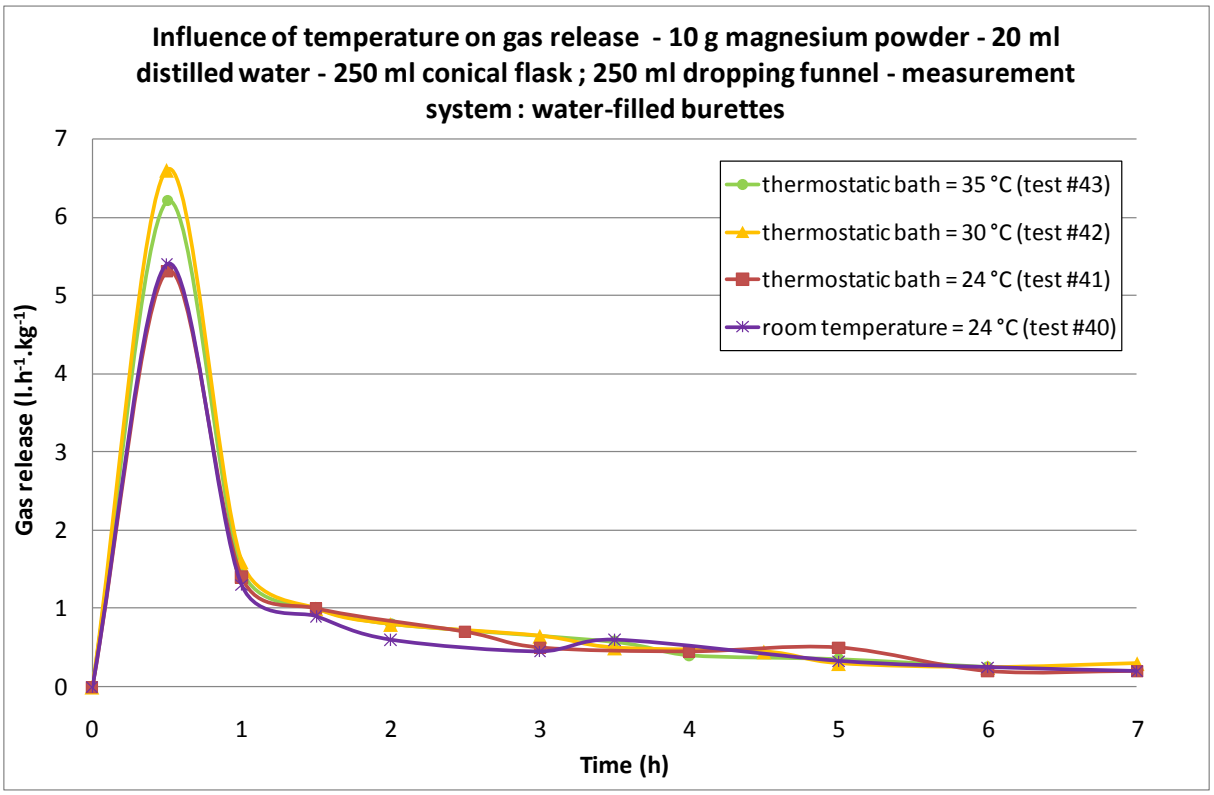

Figure 2: Influence of temperature on gas release – magnesium powder

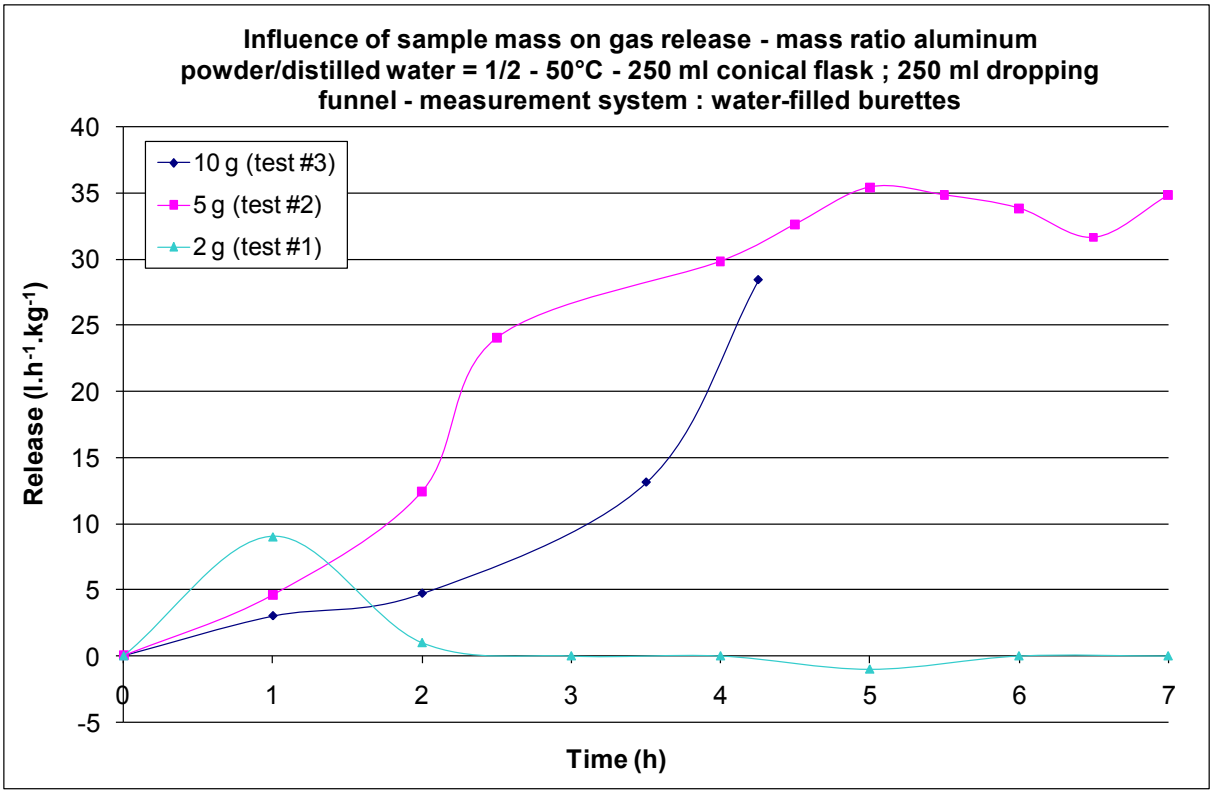

Figure 3: Influence of sample mass on gas release

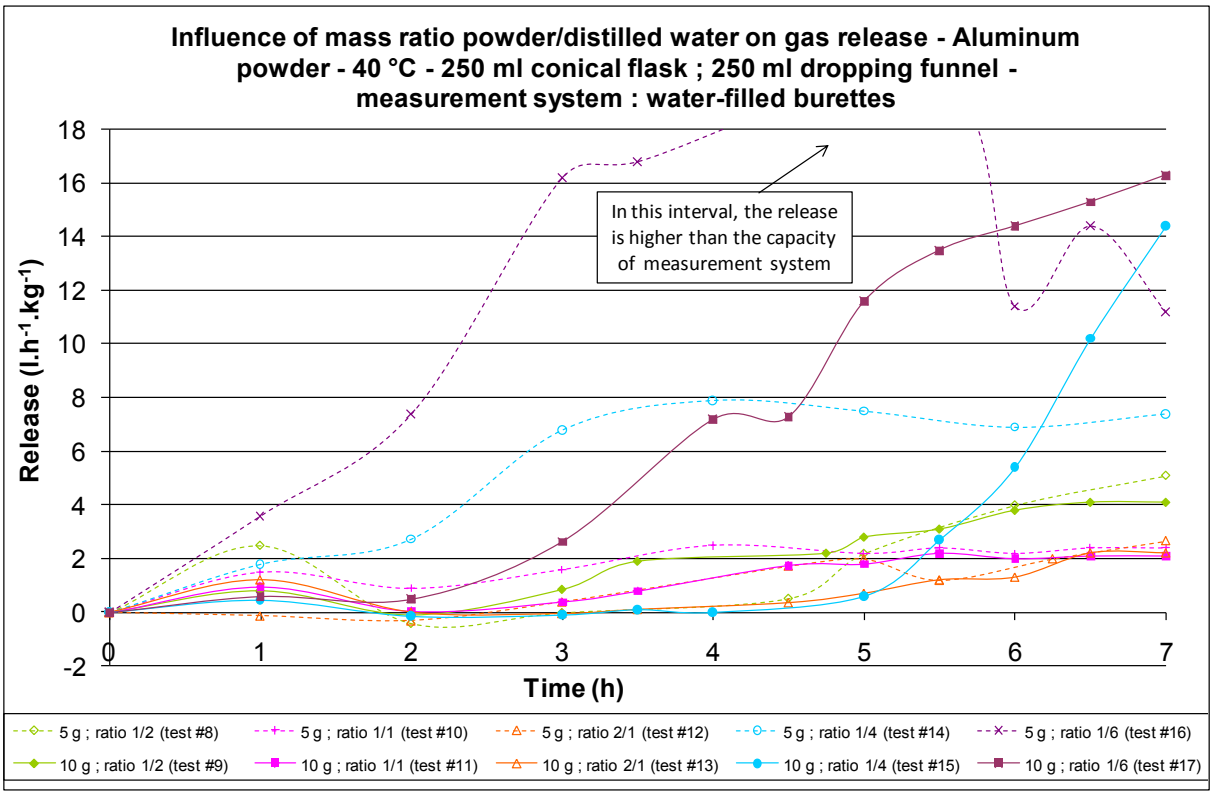

Figure 4: Influence of mass ratio powder/distilled water, aluminum powder

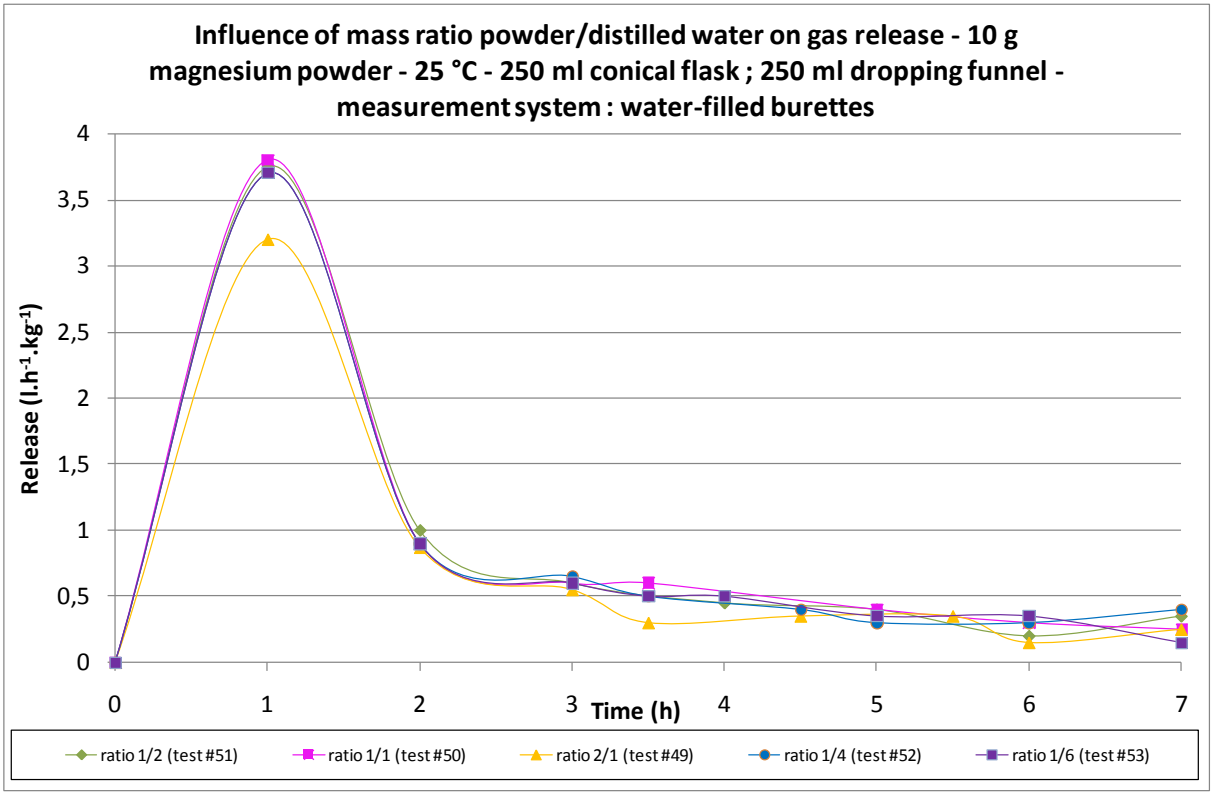

Figure 5: Influence of mass ratio powder/distilled water, magnesium powder

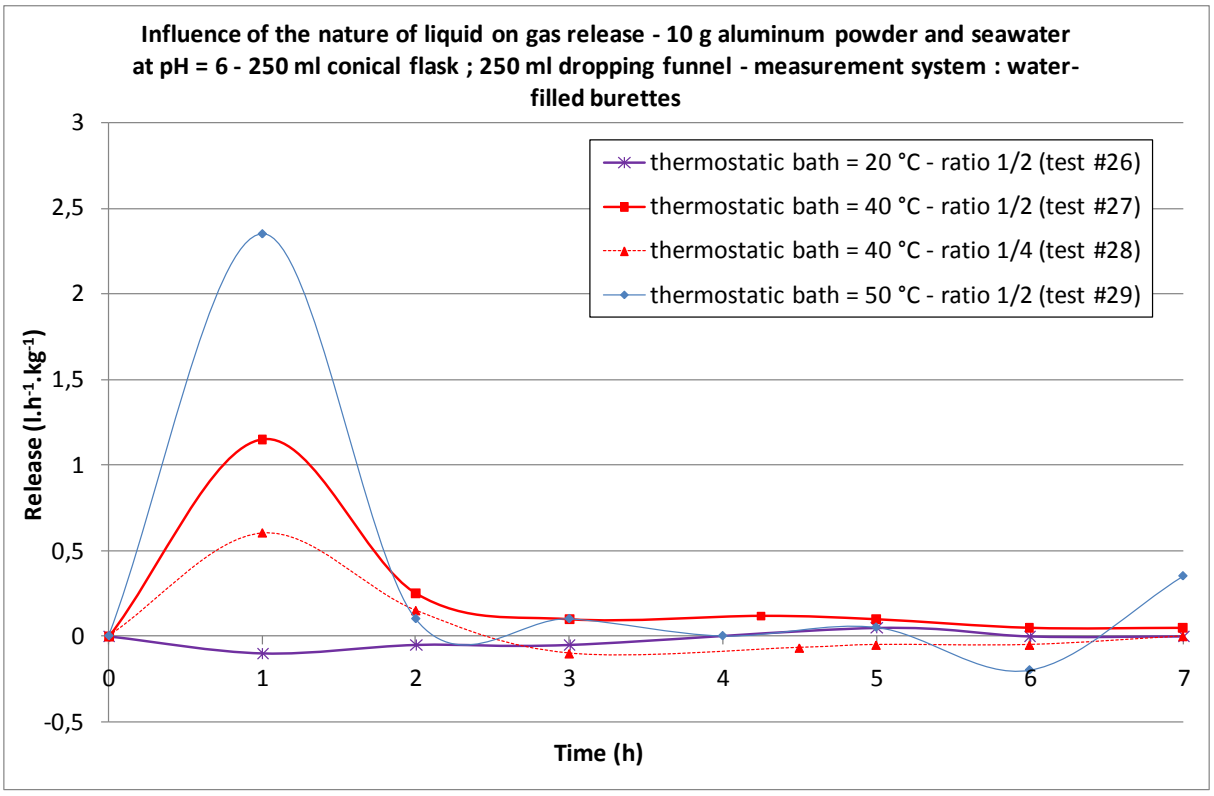

Figure 6: Influence of the nature of the liquid on gas release, aluminum and seawater

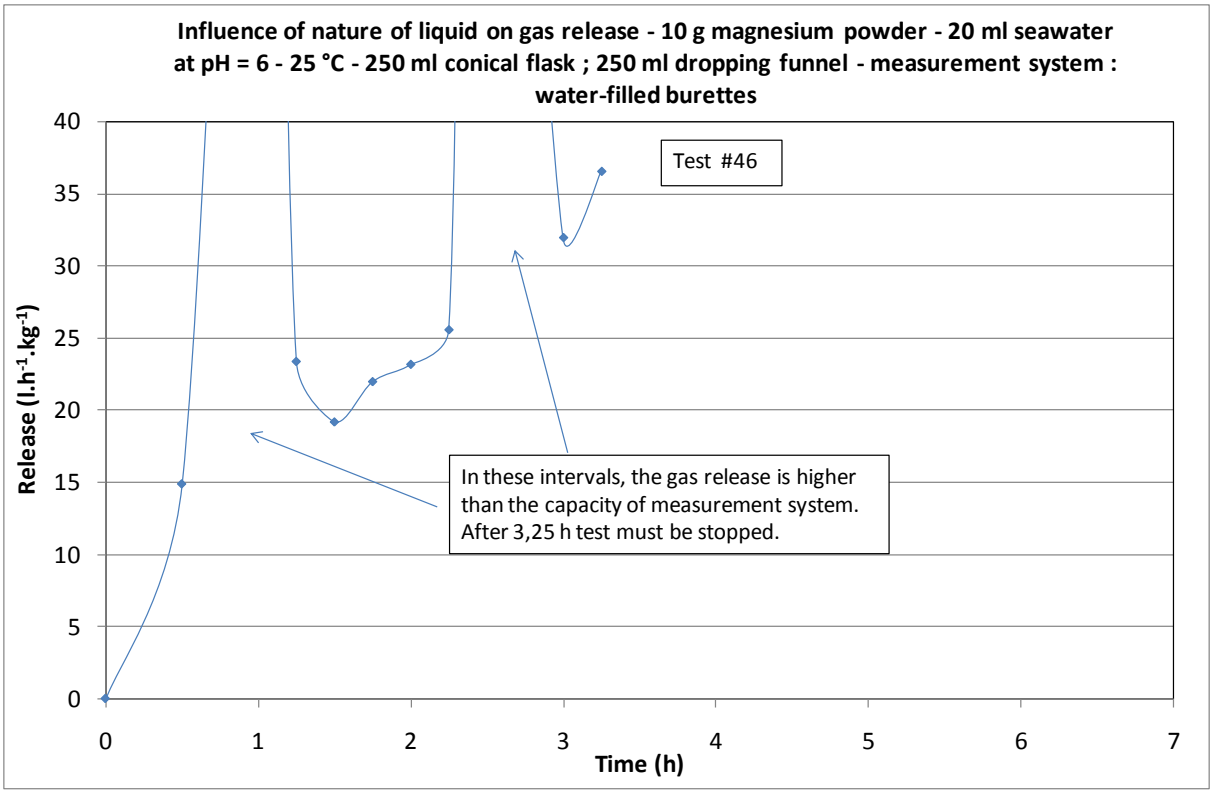

Figure 7: Influence of the nature of the liquid on gas release, magnesium and seawater

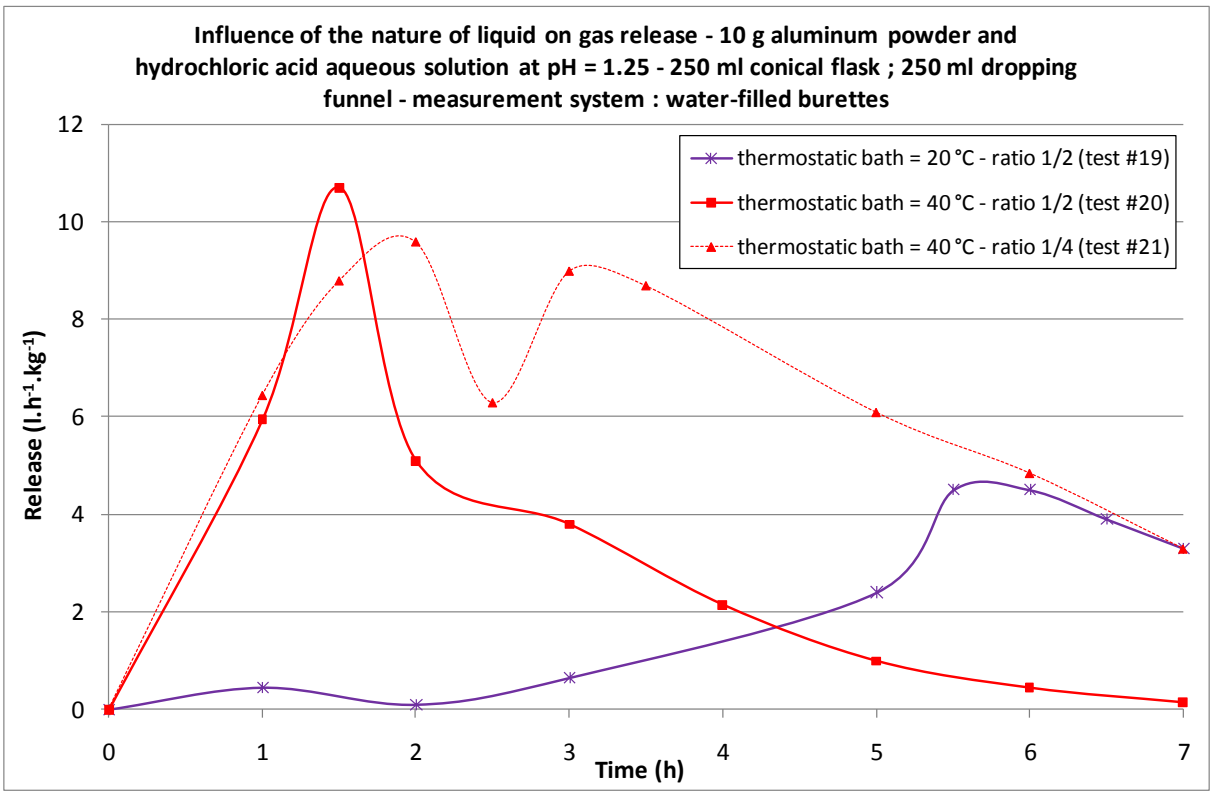

Figure 8: Influence of the nature of the liquid on gas release, aluminum and hydrochloric acid at pH = 1.25

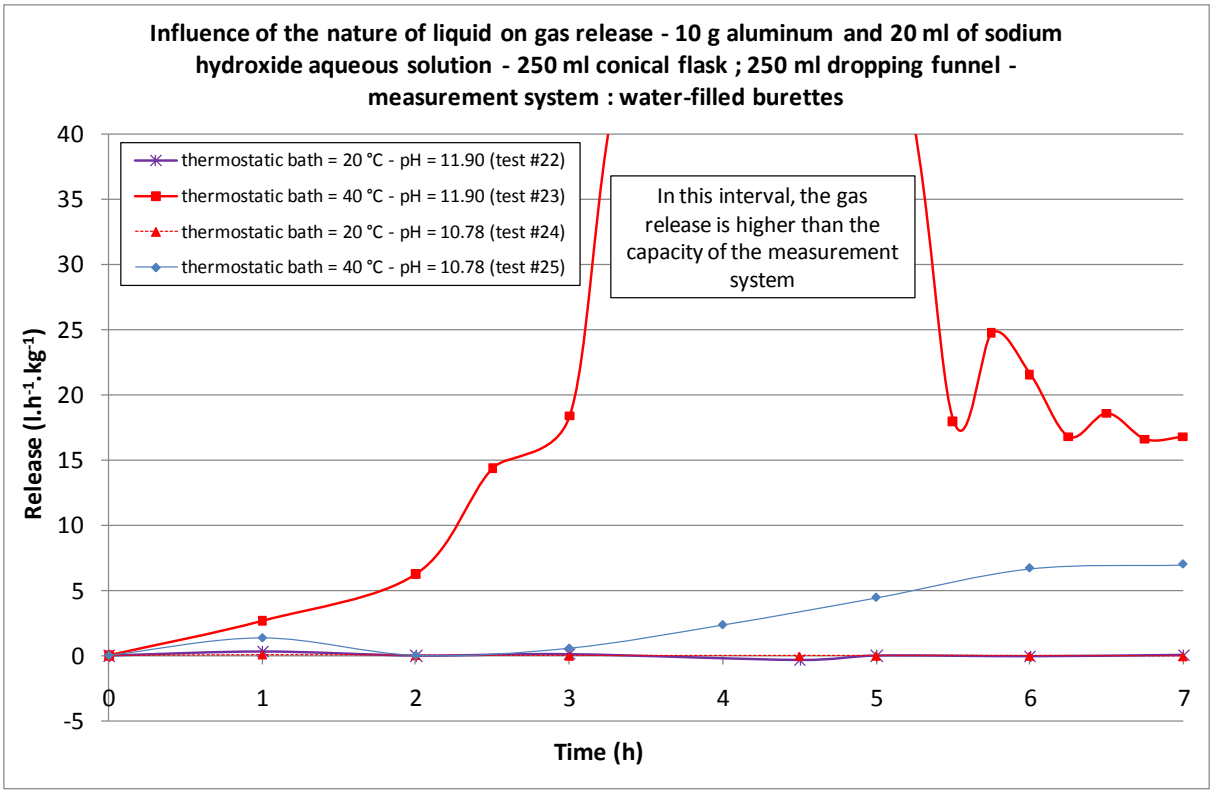

Figure 9: Influence of the nature of the liquid on gas release, aluminum and sodium hydroxide acid at pH = 10.78 and 11.90

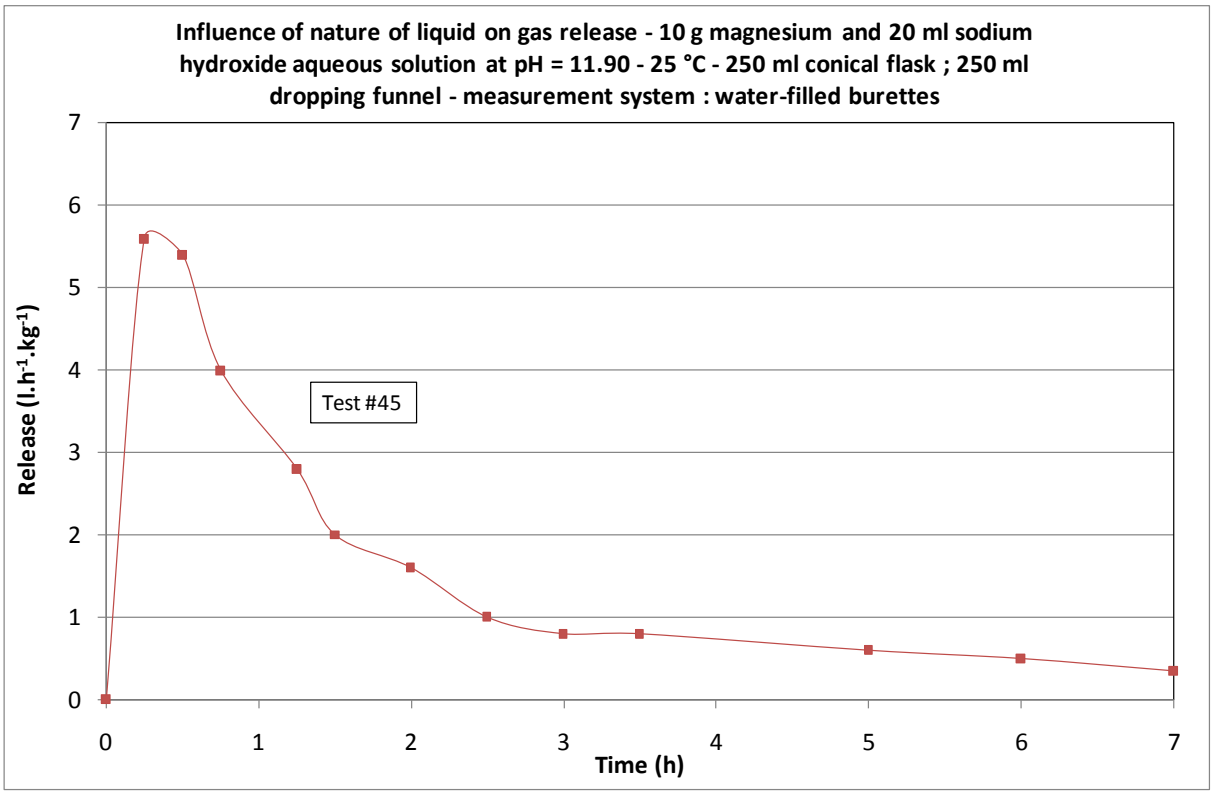

Figure 10: Influence of the nature of the liquid on gas release, aluminum and sodium hydroxide acid at pH = 11.90

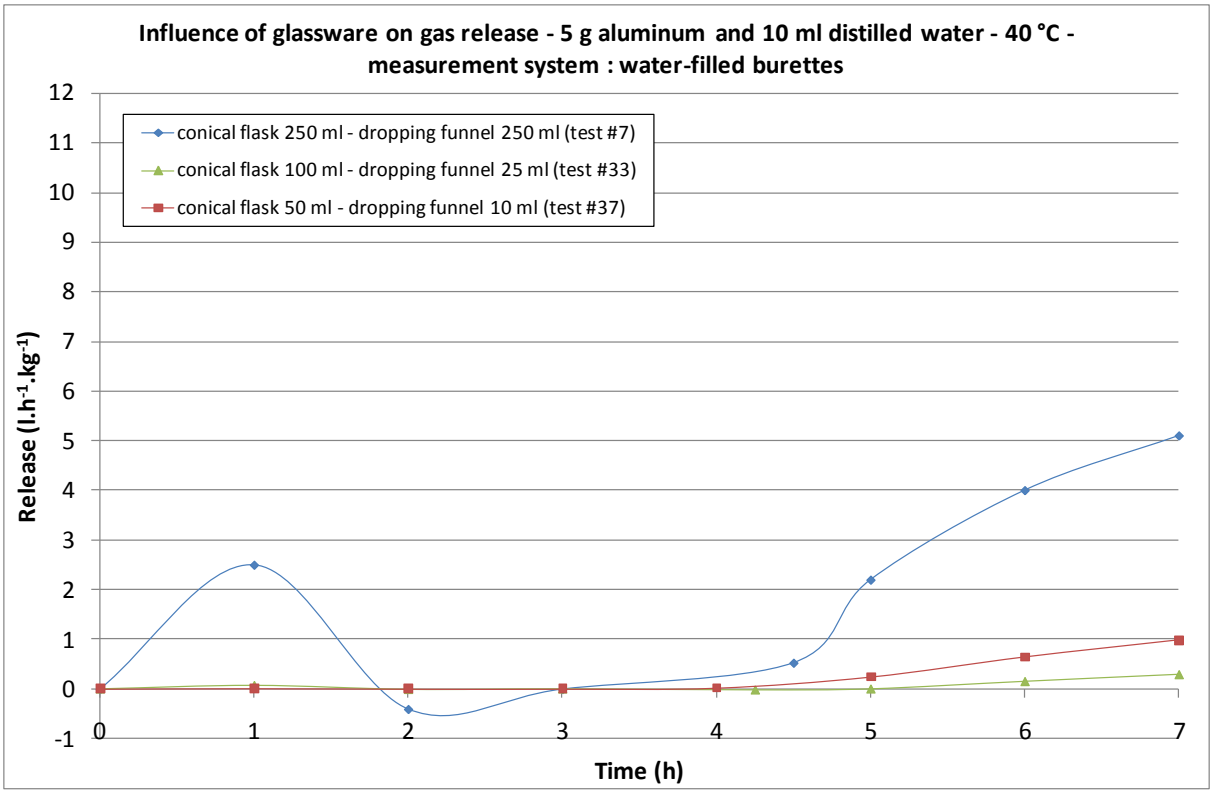

Figure 11: Influence of glassware on gas release, 5 g aluminum, and mass ratio 1/2

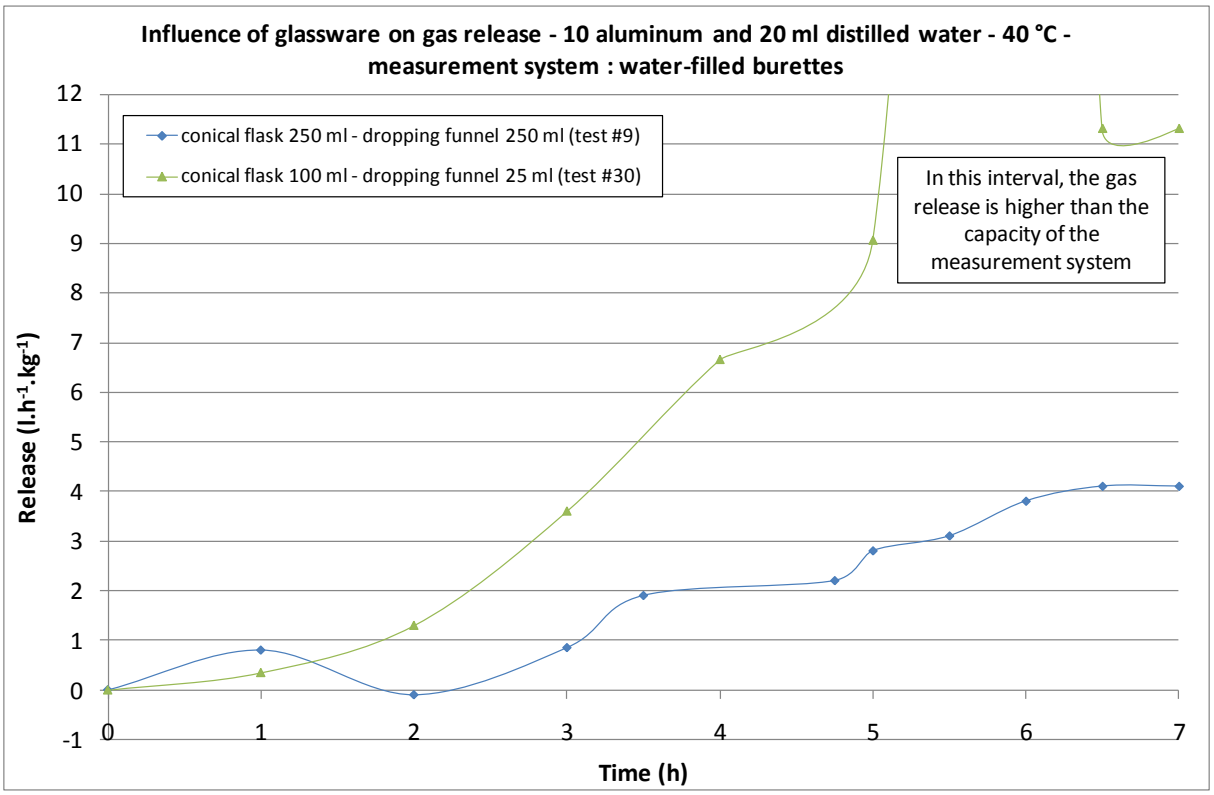

Figure 12: Influence of glassware on gas release, 10 g aluminum, and mass ratio 1/2

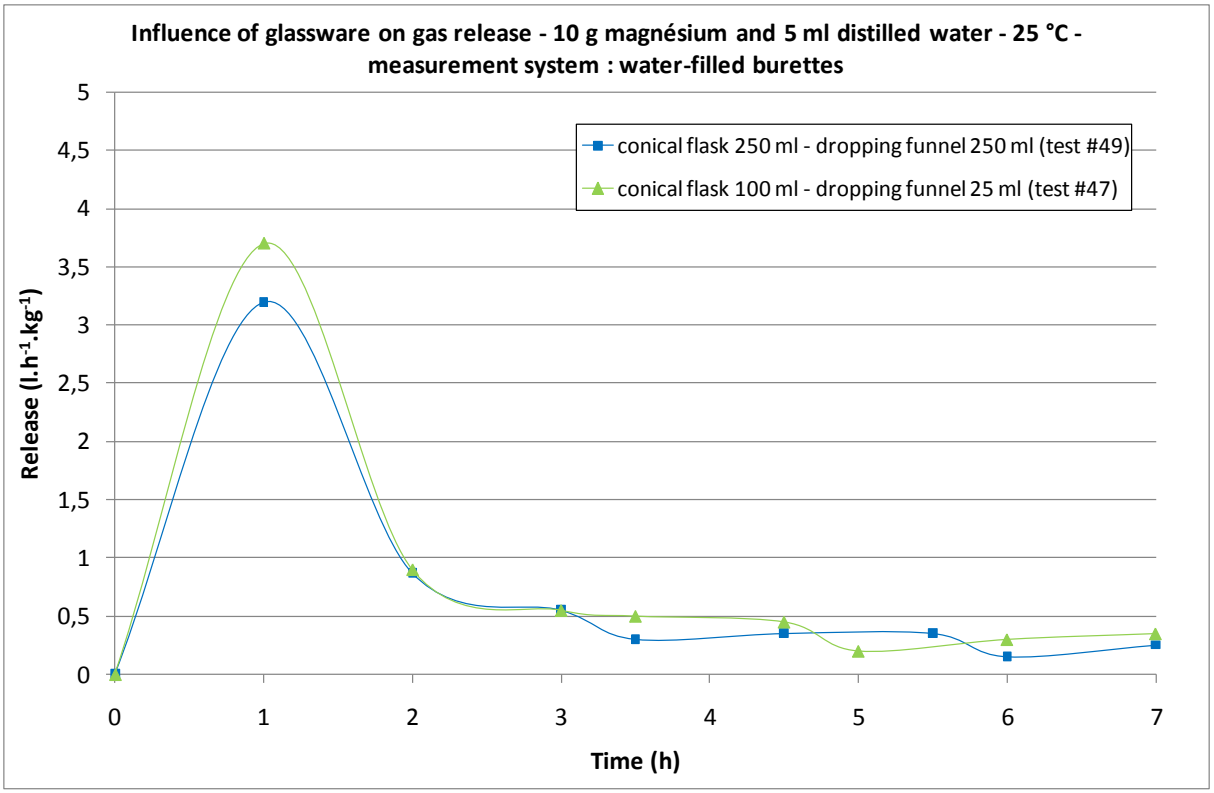

Figure 13: Influence of glassware on gas release, 10 g magnesium, and mass ratio 2/1

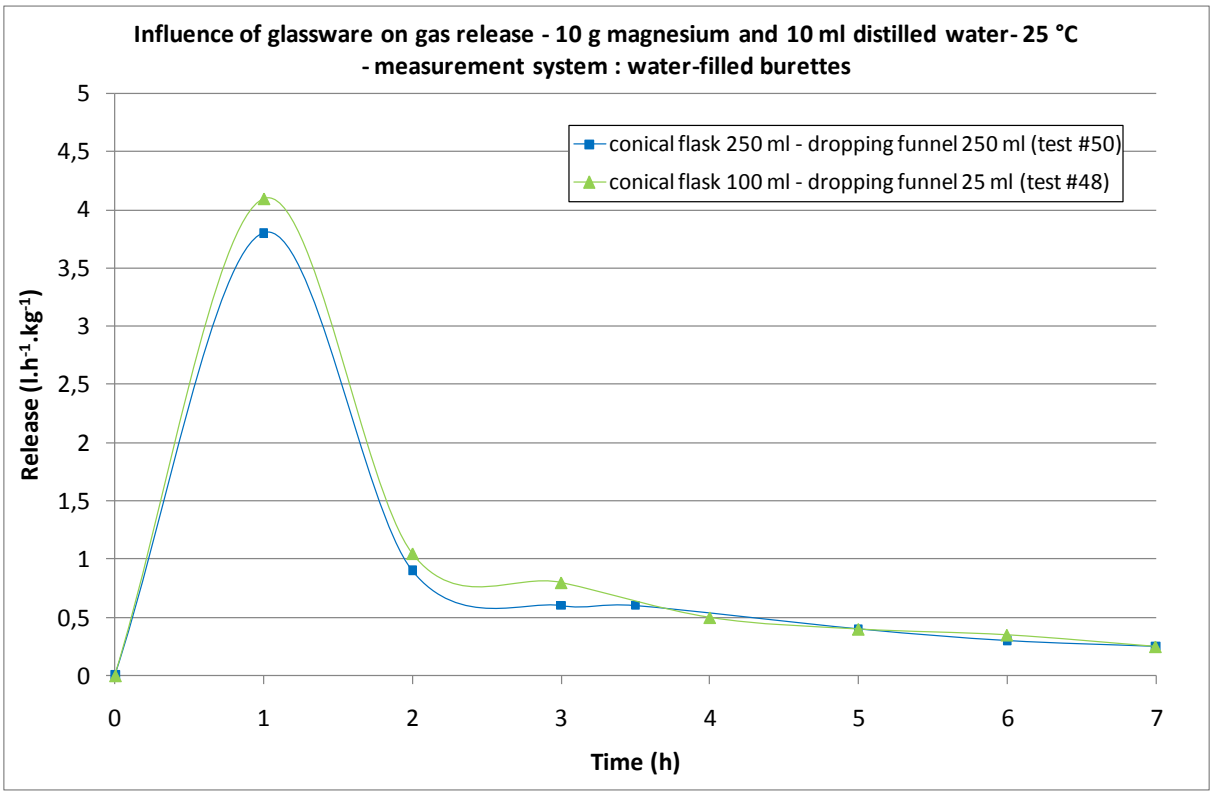

Figure 14: Influence of glassware on gas release, 10 g magnesium, and mass ratio 1/1

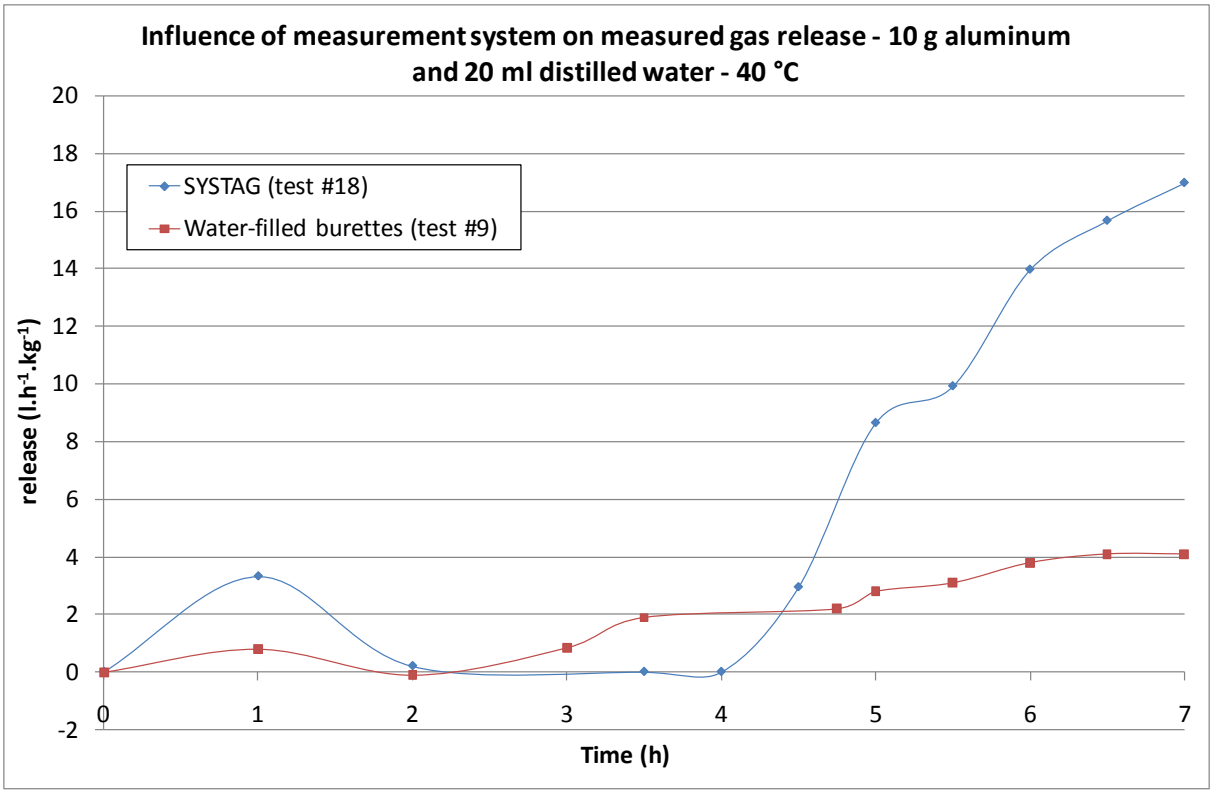

Figure 15 : Influence of measurement system on measured gas release, 10 g aluminum and mass ratio 1/2

Reactant	CE A.12 [15]	ONU N.5 [6]	NF T 20-040 [17]
Sample mass	10 g	Up to 25 g (volume of emitted gas should be from 100 to 250 ml)	
Liquid volume	10 to 20 ml	Unspecified	

Table 1: Requirements concerning the reactant quantities according to selected standards

Transport of Dangerous goods [6]	Division 4.3		
	Packing Group I	Packing Group II	Packing Group III
European Regulation CLP [7]	Substances or mixtures which in contact with water emit flammable gases		
	Category 1	Category 2	Category 3
European Directive 67/548/EEC [16]	Substances which, in contact with water, evolve highly flammable gases in dangerous quantities		
Criteria	Any substance or mixture which reacts vigorously with water at ambient temperatures and demonstrates generally a tendency for the gas produced to ignite spontaneously, or which reacts readily with water at ambient temperatures such that the rate of evolution of flammable gas is equal to or greater than 10 litres per kilogram of substance over any one minute.	Any substance or mixture which reacts readily with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 20 litres per kilogram of substance per hour, and which does not meet the criteria for Category 1.	Any substance or mixture which reacts slowly with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 1 litre per kilogram of substance per hour, and which does not meet the criteria for Categories 1 and 2.

Table 2: Classification criteria depending on the standard

Test #	Parameters investigated								Gas flow measurement system
	Liquid used	Dropping funnel volume (ml)	Conical flask volume (ml)	Thermostatic bath	Temperature (°C)	Powder mass (g)	Liquid mass (g)	Powder/ liquid mass ratio	
1	Distilled water	250	250	Yes	50	2	4	1/2	Water-filled burettes
2	Distilled water	250	250	Yes	50	5	10	1/2	Water-filled burettes
3	Distilled water	250	250	Yes	50	10	20	1/2	Water-filled burettes
4	Distilled water	250	250	No	Ambient = 19	5	10	1/2	Water-filled burettes
5	Distilled water	250	250	Yes	30	5	10	1/2	Water-filled burettes
6	Distilled water	250	250	Yes	35	5	10	1/2	Water-filled burettes
7	Distilled water	250	250	Yes	40	5	10	1/2	Water-filled burettes
8	Distilled water	250	250	Yes	40	5	10	1/2	Water-filled burettes
9	Distilled water	250	250	Yes	40	10	20	1/2	Water-filled burettes
10	Distilled water	250	250	Yes	40	5	5	1/1	Water-filled burettes
11	Distilled water	250	250	Yes	40	10	10	1/1	Water-filled burettes
12	Distilled water	250	250	Yes	40	5	2,5	2/1	Water-filled burettes
13	Distilled water	250	250	Yes	40	10	5	2/1	Water-filled burettes
14	Distilled water	250	250	Yes	40	5	20	1/4	Water-filled burettes
15	Distilled water	250	250	Yes	40	10	40	1/4	Water-filled burettes
16	Distilled water	250	250	Yes	40	5	30	1/6	Water-filled burettes
17	Distilled water	250	250	Yes	40	10	60	1/6	Water-filled burettes
18	Distilled water	250	250	Yes	40	10	20	1/2	Systag
19	Hydrochloric acid	250	250	Yes	20	10	20	1/2	Water-filled burettes

	aqueous solution pH=1,25								
20	Hydrochloric acid aqueous solution pH=1,25	250	250	Yes	40	10	20	1/2	Water-filled burettes
21	Hydrochloric acid aqueous solution pH=1,25	250	250	Yes	40	10	40	1/4	Water-filled burettes
22	Sodium hydroxide aqueous solution pH=10,78	250	250	Yes	20	10	20	1/2	Water-filled burettes
23	Sodium hydroxide aqueous solution pH=10,78	250	250	Yes	40	10	20	1/2	Water-filled burettes
24	Sodium hydroxide aqueous solution pH=11,90	250	250	Yes	20	10	20	1/2	Water-filled burettes
25	Sodium hydroxide aqueous solution pH=11,90	250	250	Yes	40	10	20	1/2	Water-filled burettes
26	Seawater pH=6	250	250	Yes	20	10	20	1/2	Water-filled burettes
27	Seawater pH=6	250	250	Yes	40	10	20	1/2	Water-filled burettes
28	Seawater pH=6	250	250	Yes	40	10	40	1/4	Water-filled burettes
29	Seawater pH=6	250	250	Yes	50	10	20	1/2	Water-filled burettes
30	Distilled water	25	100	Yes	40	10	20	1/2	Water-filled burettes

31	Distilled water	25	100	Yes	40	10	10	1/1	Water-filled burettes
32	Distilled water	25	100	Yes	40	10	5	2/1	Water-filled burettes
33	Distilled water	25	100	Yes	40	5	10	1/2	Water-filled burettes
34	Distilled water	25	100	Yes	40	5	5	1/1	Water-filled burettes
35	Distilled water	25	100	Yes	40	5	2,5	2/1	Water-filled burettes
36	Distilled water	25	100	Yes	40	5	20	1/4	Water-filled burettes
37	Distilled water	10	50	Yes	40	5	10	1/2	Water-filled burettes
38	Distilled water	10	50	Yes	40	5	5	1/1	Water-filled burettes
39	Distilled water	10	50	Yes	40	5	2,5	2/1	Water-filled burettes

Table 3: List of tests performed on aluminum

Test #	Parameters investigated								Gas flow measurement system
	Liquid used	Dropping funnel volume (ml)	Conical flask volume (ml)	Thermostatic bath	Temperature (°C)	Powder mass (g)	Liquid mass (g)	Powder/ liquid mass ratio	
40	Distilled water	25	100	No	Ambient = 24	10	20	1/2	Water-filled burettes
41	Distilled water	25	100	Yes	24	10	20	1/2	Water-filled burettes
42	Distilled water	25	100	Yes	30	10	20	1/2	Water-filled burettes
43	Distilled water	25	100	Yes	35	10	20	1/2	Water-filled burettes
44	Hydrochloric acid aqueous solution pH=1,25	25	100	Yes	25	10	20	1/2	Water-filled burettes
45	Sodium hydroxide aqueous solution pH=11,90	25	100	Yes	25	10	20	1/2	Water-filled burettes
46	Seawater pH=6	25	100	Yes	25	10	20	1/2	Water-filled burettes
47	Distilled water	25	100	Yes	25	10	5	2/1	Water-filled burettes
48	Distilled water	25	100	Yes	25	10	10	1/1	Water-filled burettes
49	Distilled water	250	250	Yes	25	10	5	2/1	Water-filled burettes
50	Distilled water	250	250	Yes	25	10	10	1/1	Water-filled burettes
51	Distilled water	250	250	Yes	25	10	20	1/2	Water-filled burettes
52	Distilled water	250	250	Yes	25	10	40	1/4	Water-filled burettes
53	Distilled water	250	250	Yes	25	10	60	1/6	Water-filled burettes

Table 4 : List of tests performed on magnesium

	Aluminum powder	Magnesium powder
Reference	No commercial reference	Magnesium powder, supplied by Fisher Scientific Ref.: M/0050/53
Median size distribution (volume distribution)	80 µm	200 µm
Note	Material was crushed to reduce size distribution down to 80 µm under cryogenic nitrogen, and then stored under air atmosphere.	-

Table 5: Characteristics of materials tested

Experimental device	Dropping funnel volume	Conical flask volume
Device n°1	250 ml	250 ml
Device n°2	25 ml	100 ml
Device n°3	10 ml	50 ml

Table 6: Volumes of dropping funnel and conical flask used

Wetting efficiency	Glassware volume	Test configuration (powder mass – powder/liquid ratio)	Peak gas flow measured during the 7 first hours ($L.h^{-1}.kg^{-1}$)
Very good: all the powder is wetted by the liquid. At the end of the test, all the powder reacted	250 ml conical flask and 250 ml dropping funnel	10 g – 1/4 10 g – 1/6	14 to 17
	100 ml conical flask and 25 ml dropping funnel	10 g – 1/2	Overflow of measurement capacity
Good: the major fraction of the powder is wetted by the liquid. Almost all the powder reacted et the end of the test.	250 ml conical flask and 250 ml dropping funnel	5 g – 1/2 10 g – 1/2 5 g – 1/4	4 to 8
	100 ml conical flask and 25 ml dropping funnel	5 g – 1/4	1 to 3
	50 ml conical flask and 10 ml dropping funnel	5 g – 1/2	1 to 3
Poor: only a small fraction of the powder is wetted by the liquid. The major fraction of the powder remains intact at the end of test.	250 ml conical flask and 250 ml dropping funnel	5 g – 2/1 10 g – 2/1 5 g – 1/1 10 g – 1/1 5 g – 1/6	2 to 4
	100 ml conical flask and 25 ml dropping funnel	5 g – 2/1 10 g – 2/1 5 g – 1/1 10 g – 1/1 5 g – 1/2	< 1
	50 ml conical flask and 10 ml dropping funnel	5 g – 2/1 5 g – 1/1	< 1

Table 7: Comparison of the maximum flow measured with the quality of aluminum powder wetting