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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 **17 June 2013**

Forty-third session
Geneva, 24–28 June 2013
Item 11 (b) of the provisional agenda
Issues relating to the Globally Harmonized System of Classification
and Labelling of Chemicals: criteria for water-reactivity

Criteria for water-reactivity - HM-14 Project status report

Submitted by the expert from the United States of America

Introduction

1. During the 42nd session of the Sub-Committee a status report was provided describing work underway under a contract managed by the U.S. Transportation Research Board (TRB). The intent is to keep the Sub-Committee informed of the work to develop a revised N-5 test method and to provide the opportunity for experts to comment on the work. Since the last session significant progress has been made to develop a test method, apparatus and general approach for characterizing water reactive materials. To date, our research indicates that it is possible to develop a revised test method that provides accurate results for both water reactive substances that evolve flammable gasses on contact with water, and for water reactive materials that evolve toxic gasses. A comprehensive status report that summarizes the work completed to date is provided as an Annex to this information paper. In addition, a number of experts participated in a teleconference where the status report was described in specific detail and questions were addressed by the principal investigator. The expert from the United States and a representative working with the principle investigator under contract with TRB will be prepared to address any questions regarding progress to date as described in the status report.

2. With developed apparatus and general approach, water reactive substances that emit flammable gasses are reasonably straightforward to test. Water reactive materials that emit toxic gasses are also easily accommodated by the apparatus and general procedure, but create some challenges in interpreting the results because of the wide range of type and magnitude of reactivity they demonstrate. There are important qualitative differences in the way various materials react. Some materials react in predictable fashion, with steady or slightly falling rates of reaction. In other cases, the reaction rates vary more significantly over time, demonstrating distinct phases of reaction. Yet other reactions can be very fast, but transient, with rates over 5 seconds very different (10 x) from rates over several minutes. In yet other cases, a transient and rapid release of gas is observed, followed by rapid absorption of gas by the reaction products. This wide qualitative variation in reactivity will need to be considered when developing classification criteria. Input from experts on this topic would be welcome.

3. The work has advanced to a point where the principal investigator believes that resources involving other test laboratories and experts can be leveraged to further the research including refinement of the test method, characterization of water reactive substances and enhancing an understanding of the range of reactivity as it relates to consideration of appropriate classification criteria that may be considered by regulators in

the future. The principle investigator plans to identify interested parties and begin to work directly to coordinate technical assessment and testing efforts to validate a proposed test method and results. Delegations interested in collaborating in this work are invited to contact the principal investigator directly as the work is not managed by the Expert from the United States but rather by the investigator as stipulated under the terms of the TRB contract in place.

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HMCRP

HM-14

Test Procedures and Classification Criteria for Release of Toxic Gases from Water-Reactive Materials

TRANSPORTATION RESEARCH BOARD
NAS-NRC
LIMITED USE DOCUMENT

Preliminary Reporting for UNSCOE TDG
(2013-05-30)

ScienceSmith Consulting, Inc. & Alliance Technologies, LLC

1. SUMMARY

HMCRP HM-14 - "Test Procedures and Classification Criteria for Release of Toxic Gases from Water-Reactive Materials"

Title:	Preliminary Reporting for UNSCOE TDG
Summary:	This document has been prepared to serve as the basis for a briefing of the UN Subcommittee of Experts on the Transport of Dangerous Goods, Forty-third session, to occur in Geneva, 24–28 June 2013. It provides a snap-shot of experimental progress to date, focusing more on outcomes than specific experimental or technical details. Results presented here show that the project team has arrived at a simple, convenient, and versatile apparatus and approach to measuring the rate of gas production when a water reactive substance (WRS, evolving a flammable gas) or a water reactive material (WRM, evolving a toxic gas) is combined with water. The apparatus is a closed, heavy wall, glass vessel capable of leak-tight combination of water reactive liquids and/or solids with water. The apparatus accommodates addition of water to water reactive materials/substances or *vice-versa*. Gas evolution is determined by monitoring the pressure change in the closed vessel (with appropriate safety precautions); the pressure/volume response is calibrated with standard additions of gas, making it intrinsically as accurate as the standard gas aliquot (i.e. it is not necessary to test a standard material to calibrate the response). The apparatus appears to be yielding a dynamic range of up to 10^6:1, with as good as 5 % relative standard deviation (best case) for replicate measurements. Experience is showing that a good *general* approach using the apparatus comprises: • An assessment, based on chemical knowledge and experience with the WRM/WRS in question, of the amount of gas likely to be produced. • Range-finding experiments based on that assessment. • Evaluation of the optimal order of addition (WRM/WRS to water, or vice-versa), and the extent to which having excess water present may affect the result. • After establishing the reactivity in trial runs, conducting several replicate runs under conditions that yield a readily measureable evolution of gas over a reasonable period of time. However, it appears that there will not be a single set of universally applicable test conditions that will yield valid results for all possible materials. . It is also, as yet, unclear what algorithm should be used to extract a single characteristic metric for gas evolution rate (for instance: does one use the highest average rate over some period of time vs. highest transient rate observed vs. main sustainable rate observed, etc.; how should results be averaged and reported for replicate runs, how many replicates should be used, etc.); nor is it clear that a single algorithm will suffice for all materials. These topics will be addressed in ongoing work, and input from UN experts is solicited.

	To illustrate some of the issues: - While reaction of sodium borohydride with water yielded, in our hands, a reproducible and fairly steady rate of gas production of 111(6)[1] l/kg-hr at a w/w ratio of water to sodium borohydride of ~ 8, reaction of a -200 mesh Mg powder with water at a w/w ratio of ~ 4 yields an initial rate[2] of 106(12)[1] l/kg-hr, an intermediate rate of 22 (4)[1] l/kg-hr, and (sometimes) a longer term rate of ~6 l/kg-hr. In both cases, adding solid to water yielded the most consistent & informative results. - Meanwhile reaction of the same Mg powder with salt water (3.5 % NaCl, w/w), yielded a more sustained rate of 65-80 l/kg-hr.[3] - While reaction of Mg and sodium borohydride with water (both yield hydrogen) tolerated excess water, reaction of dimethyldichloro silane needed to be measured without excess water present. It was also most appropriate to add water to the dimethyldichloro silane, rather than adding dimethyldichloro silane to water. - While reaction of dimethyldichloro silane gave a fairly well defined rate of gas production of ~ 515-615 l/kg-hr, reaction between acetyl chloride and water yielded a less well defined, but much higher, rate of between 50 and 500 l/kg-min. - As a further complication, aluminum trichloride, at all conditions tested, initially and immediately produced gas (within 5 seconds of contact) then proceeded (within fractions of a minute) to re-absorb all the gas formed. Thus, on a time-frame of seconds, gas production rates as high as 3000 l/kg-min were observed; on a time frame of minutes, gas evolution was not detectable. So, while the project has successfully demonstrated a generally applicable apparatus and procedure for characterizing and measuring rates of gas production from the reaction of WRM and WRS with water, challenges remain in developing a single universally applicable metric for these materials. The underlying issue is the wide range and character of the materials and reactivity in question.
Date:	May 30, 2013
Revision:	2013-05-30a
Prepared by:	Gregory M. Smith, Ph.D., Managing Principal ScienceSmith Consulting, Inc. Jonathan Chun, Chief Technology Officer & William Pointsett, Senior Chemist Alliance Technologies, LLC

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[1] The value reported is a mean of several measurements, the sample standard deviation is given in parentheses.

[2] First 100 seconds.

[3] There was some evidence of a very brief, initial period of faster gas production, but overall the reported rate was clearly the characteristic rate for the materials.

2. INTRODUCTION & SUMMARY

Introduction. This document has been prepared as part of Project HM-14, which is funded by the United States' National Academy of Sciences Transportation Research Board. HM-14 was commissioned with the following overall mandate:[4]

> "The objective of this research is to identify test procedures and classification criteria for water-reactive materials (WRMs) that take account of the potential release of toxic gases during transport."

Work with project HM-14 is currently within Phase II, Task 4 of the project, which is chartered to:

> "Conduct the work plan approved in Task 3. Identify key parameters affecting test outcomes and prescribe a revised test procedure applicable to substances that evolve both toxic and flammable gases."

Part of phase II, Task 6 calls for the project team to:

> "As directed by the project panel, present these findings for consideration by various regulatory bodies for further input."

This report provides the basis for a briefing of the UN Subcommittee of Experts on the Transport of Dangerous Goods, Forty-third session, to occur in Geneva, 24-28 June 2013, in accordance with this task of the project charter.

Summary Findings.

Results presented here relate a simple, convenient and versatile apparatus and approach to measuring the rate of gas production when a water reactive substance (WRS, evolving a flammable gas) or a water reactive material (WRM, evolving a toxic gas) is combined with water. The apparatus is a closed, heavy wall, glass vessel capable of leak-tight combination of water reactive liquids and/or solids with water. The apparatus accommodates addition of water to water reactive materials/substances or *vice-versa*. Gas evolution is determined by monitoring the pressure change in the closed vessel (with appropriate safety precautions); the pressure/volume response is calibrated with standard additions of gas, making it intrinsically as accurate as the measurement of the standard gas aliquot (i.e. it is not necessary to test a standard material to calibrate the response). The apparatus appears to be yielding a dynamic range of up to 10^6:1 with as good as 5 % relative standard deviation (best case) for replicate measurements.

Experience is showing that a good *general* approach using the apparatus comprises:

- An assessment, based on chemical knowledge and experience with the WRM/WRS in question, of the amount of gas likely to be produced.

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[4] See http://apps.trb.org/cmsfeed/TRBNetProjectDisplay.asp?ProjectID=3138.

- Range-finding experiments based on that assessment.
- Evaluation of the optimal order of addition (WRM/WRS to water, or vice-versa), and the extent to which having excess water present may affect the result.
- After establishing the reactivity in trial runs, conducting several replicate runs under conditions that yield a readily measureable evolution of gas over a reasonable period of time.

However, it appears that there will not be a single set of universally applicable test conditions that will yield valid results for all possible materials. It is also, as yet, unclear what algorithm should be used to extract a single characteristic metric for gas evolution rate (for instance: does one use the highest average rate over some period of time vs. highest transient rate observed vs. main sustainable rate observed, etc.; how should results be averaged and reported for replicate runs, how many replicates should be used, etc.); nor is it clear that a single algorithm will suffice for all materials. To illustrate some of the issues:

- While reaction of sodium borohydride with water yields a reproducible and fairly steady rate of gas production of 111(6)[5] l/kg-hr at a w/w ratio of water to sodium borohydride of ~ 8, reaction of a -200 mesh Mg powder with water at a w/w ratio of ~ 4 yields an initial rate[6] of 106(12)[5] l/kg-hr, an intermediate rate of 22 (4)[5] l/kg-hr, and (sometimes) a longer term rate of ~6 l/kg-hr. In both cases, the solid was added to water, for the best results.
- Meanwhile reaction of the same Mg powder with salt water (3.5 % NaCl, w/w), yielded a more sustained rate of 65-80 l/kg-hr.
- While reaction of Mg and sodium borohydride with water (both yield hydrogen) tolerated excess water, reaction of dimethyldichloro silane needed to be measured within a limited range, with not too much excess water present. It was also most appropriate to add water to the dimethyldichloro silane.
- While reaction of dimethyldichloro silane gave a fairly well defined rate of reaction of ~ 515-615 l/kg-hr, reaction between acetyl chloride and water yielded a less well defined, but much higher, rate of between 50 and 500 l/kg-min.
- As a further complication, aluminum trichloride, at all conditions tested, initially and immediately produced significant quantities of gas (within 5 seconds of contact) then proceeded (within fractions of a minute) to re-absorb all the gas formed. Thus, on a time-frame of seconds, gas production rates as high as 3000 l/kg-min were observed; on a time frame of minutes, gas evolution was not detectable.

Thus, while it is proving possible to develop a generally applicable apparatus and procedure for characterizing and measuring rates for the reaction of WRM and WRS with water, challenges

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[5] The value reported is a mean of several measurements, the sample standard deviation is given in parentheses.

[6] First 100 seconds.

remain in developing a single universally applicable metric for these materials. The underlying issue is the wide range and character of the materials and reactivity in question.

Report Structure.

Subsequent sections of this document address:

3. Context & Terminology
4. Results
5. Conclusions.

3. CONTEXT & TERMINOLOGY

Before discussing the results, some additional context and terminology should be reviewed.

The context for this work includes both the United Nations (UN) *Globally Harmonized System of Classification and Labeling of Chemicals* (herein, the GHS) and the UN *Model Regulations for the Transport of Dangerous Goods* (herein the, "Model Regulations"). Test N.5 from the UN *Manual of Tests and Criteria* (which accompanies the Model Regulations) is the only formal UN test procedure currently used for classifying water reactive materials. This test is used to classify substances that are regulated in transport on the basis of their reaction with water and their evolution of flammable gases. These materials are grouped in hazard Division 4.3, as, "Substances which in contact with water emit flammable gases."

Because of the need to differentiate between water reactive substances which emit flammable gases in contact with water and other substances (herein, "materials") which emit nonflammable toxic gases in contact with water, the former will be referred to as water reactive substances (WRS), and the latter as water reactive materials (WRM).[7]

4. RESULTS

Background. Prior to beginning the experimental work, a comprehensive review of pre-existing work, reported testing, general technical literature, and UN discussions on this was conducted. A number of industry stakeholders and other experts were also consulted for input.

Key themes or ideas that emerged from this included:

- <u>Simplicity of apparatus was valued</u>; though, successful function of the test supersedes this. <u>Single-use or disposable apparatus would also be valued</u> because clean-up needs would be minimized.
- <u>There are several possible techniques that could be used to measure gas evolution</u>. Candidate methods of gas measurement include:
    - Displacement of fluids (but, problematic as noted above).
    - Displacement of a syringe plunger or other volumetric mechanism.
    - Via electronic mass-flow meter.

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[7] This is done, among other reasons, to be consistent with the HM-14 proposal solicitation.

  - Via capture in a gas sampling bag.
  - Via pressure increase within a closed volume.
- However, many of the preceding can be problematic with the toxic gasses produced by WRM. In particular, and in contrast to flammable gasses, many of the gasses encountered with WRM have appreciable solubility in water, hydrocarbons, and even the materials under test themselves. As a further complication, the most commonly produced toxic gas is HCl (see below, which can be corrosive to equipment.
- Overall, typical gasses evolved include:
  - From WRS:
    - Hydrogen
    - Light hydrocarbons
  - From WRM:
    - HCl (by far, the most common example for previously identified WRM)
    - H_2S
    - PH_3
    - HF
    - NH_3
    - Other HX (HBr, HI…), including HCN.
- The ability to manage the reaction would be important − there is a large possible dynamic range of results, from 1 l/kg-hr up to more than 600 l/kg-hr. While some reactions could be very slow and mild, the most highly reactive materials could have rapid and energetic reactions with water.
- The test should be as easily reproduced as possible, and ideally be a test that DG producers and shippers could conduct in house; failing that, it should be as straight-forward as possible for execution in chemical testing laboratories, such as third party analytical services & testing vendors.

From this, it was determined that a successful approach would need to

- Enable work on scales that varied from very small amounts (≤ 0.1 g) to larger amounts (up to 10 g or more) of water and/or WRM/WRS, and from very short times (10's of seconds) to longer times (an hour or more) to accommodate the likely range of reactivity.
- Enable work with either water or the WRM/WRS as the limiting reagent, to enable the control of energetic reactions, and to minimize interference from gas solubility in excess water.
- Minimize fluids present (other than water and the materials under test), to reduce the impact of gas solubility in those fluids.
- Utilize the simplest possible apparatus.
- Have a simple and straight-forward mechanism for determining the rate at which gas is produced which, at the same time, could be universally applied to a wide variety of gasses.

Apparatus. As experimental work proceeded, several points emerged very quickly:

- Establishing a reliably leak-tight apparatus that could measure from 1-100 ml of gas evolution over time-frames varying from a few minutes to an hour or more would require specialized equipment. Unfortunately, single use/disposable apparatus had to be eliminated from consideration. This also made mechanical (i.e. syringe plunger displacement) methods of measuring gas problematic.
- No type of fluid displacement would be suitable for measuring the gas evolution.
- Mass-flow meters posed problems in selection of suitable dynamic range and calibration.

Consequently, effort quickly focused on a custom fabricated vessel that could accommodate addition of water to the WRM/WRS or vice-versa, and which could tolerate both solid and liquid WRM/WRS. The method of choice for measuring gas evolution rapidly became monitoring pressure change in a closed vessel.

Before describing the specific apparatus used, the latter point bears some discussion. With a potentially rapid reaction between WRM/WRS and water, and likely formation of gas within a closed vessel, consideration had to be given to pressure relief and the structural integrity of the vessel. At the same time, a steel vessel would be very inconvenient (and not necessarily compatible with all materials); also, other than burst-disks, it can be difficult to reliably seal relief valves, unless they operate at fairly substantial cracking pressures. Ultimately (see below) a heavy-walled glass vessel equipped with a simple low pressure relief system (< 50 kPa gauge) was selected. This has proven (see below) to be quite useful, but an important prerequisite for any experimental work is careful consideration of the total amount of gas that can be evolved from a given combination of WRM/WRS and water. Initial reactions need to be conducted with sufficiently small amounts of WRM/WRS and/or water that unacceptably high pressures cannot be developed. Only after the behavior of the reaction is clearly established, can limits on the amounts of reagents used be (cautiously) relaxed (to some extent).

Keeping the preceding consideration in mind, careful experimentation with a number of approaches led to development of the apparatus shown in Figures 1 through 3 below. This vessel can be pre-charged with solid or liquid WRM/WRS, or liquid WRM/WRS can be injected via syringe through a septum to the fully assembled apparatus. Likewise, water can either be pre-charged or injected via syringe after assembly. Thus, it is straight-forward to add water to pre-charged solid or liquid WRM/WRS samples, and liquid WRM/WRS samples can be added to pre-charged water. Solid WRM can be added to pre-charged water via a solids-addition fixture (see Figure 3).

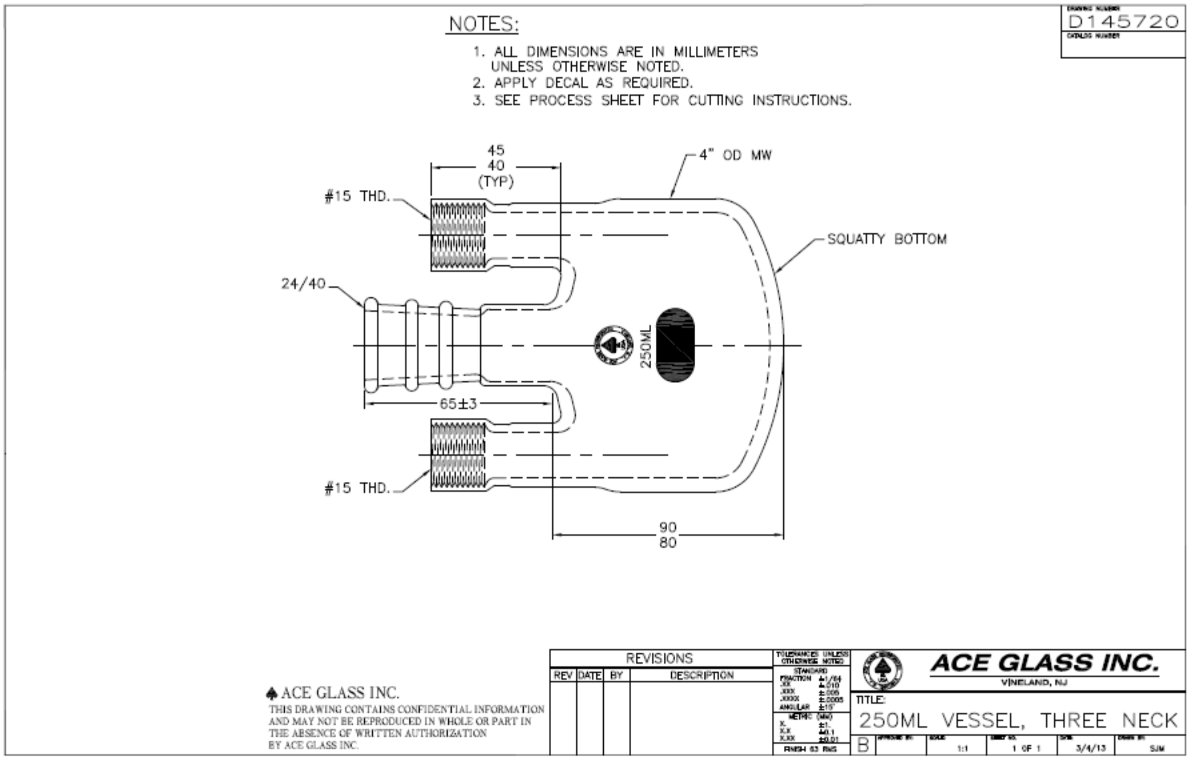

Figure 1 – Vendor drawing of the reaction apparatus, as obtained.

Figure 2 – Reaction apparatus, configured for manual data acquisition (left) and electronic data acquisition (right). In both cases the center port is fitted with a septum to allow fluid injection.

Figure 3. Reaction apparatus configured for addition of solids to water. The image on the left is prior to combining solid and water, the image on the right is after.

Overall, the apparatus comprises the following components:

- A heavy-wall glass vessel, nominally 250 ml in capacity, with two #15 Ace-Thred joints and a 24/40 ground glass joint.
- An 0-ring sealed plug for one # 15 Ace-Thred joint (this joint is used used for adding solids in advance, and other general-purpose functions).
- An adapter for the other #15 Ace-Thred joint (1/4″ NPT) to accommodate a pressure transducer (or mechanical pressure gauge).
- The pressure and temperature transducer (or, alternatively, a timer and appropriate pressure gauge).
- A friction-fit, o-ring seal PTFE thermometer adapter equipped either with a GC style septum seal or a PE solids addition tube and bulb fabricated from a disposable pipette.
- A micro-stir-bar.

A heavy wall glass vessel is used to provide more resistance to pressure than a standard wall vessel; pressure relief is provided by the friction-fit adapter in the center opening; experience shows that this will be ejected at pressures between 30 and 50 kPa gauge, which is well within the strength of the vessel (see Figure 4, below; the abrupt drop in pressure at around 8 minutes is due to the release of pressure via the center opening). While the fitting is ejected with an audible pop, and enough force to hit the ceiling of the hood, it is not violent and falls with no more force than had it been dropped from a meter or so of height.

As it developed, the use of pressure measurements to determine the volume or rate of gas evolution turned out to be very simple and reliable.

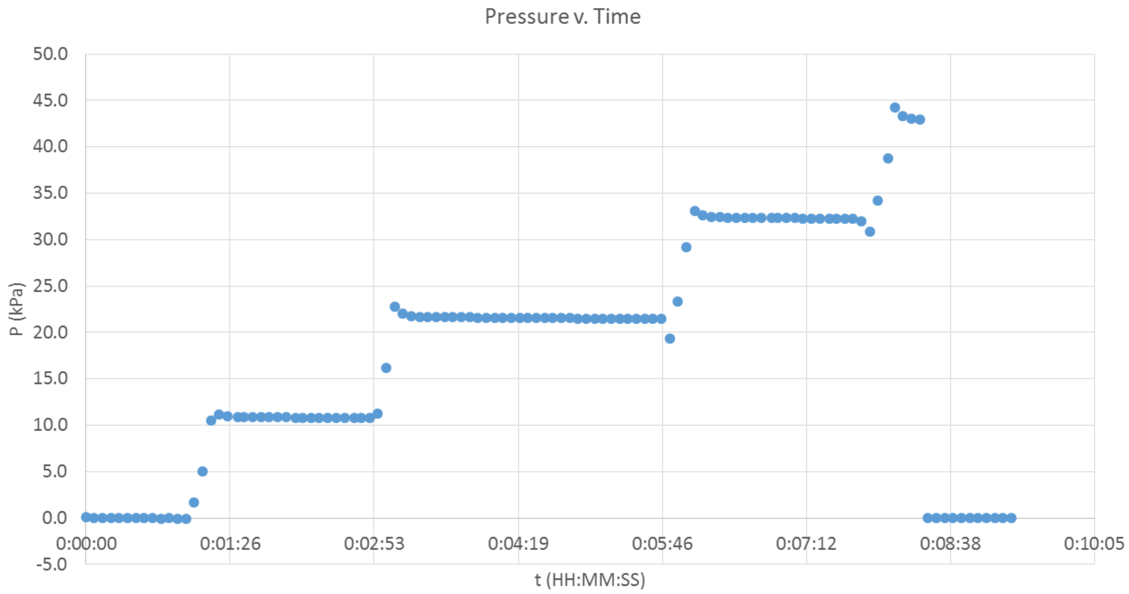

Figure 4. Calibration of Flask 1 using 50 ml additions of nitrogen and the pressure transducer.

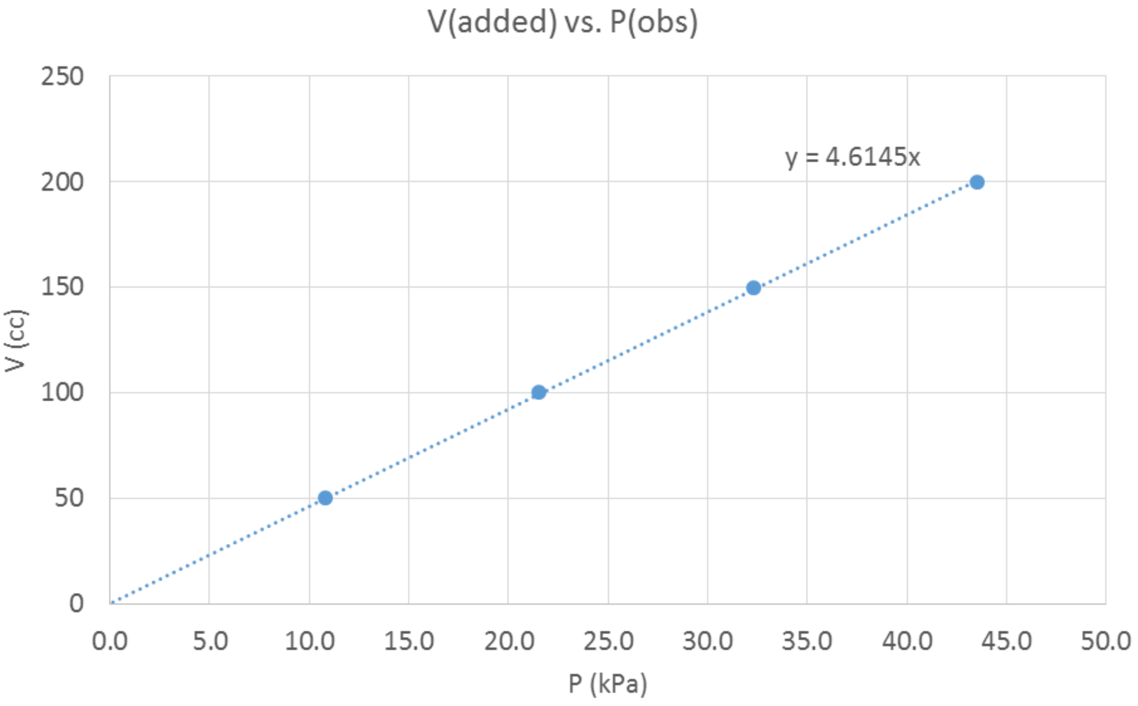

Figure 5. Calibration curve for Flask 1 using 50 ml additions of nitrogen and the pressure transducer.

Table 1. Calibration results.

Flask	1	2	3
	(ml/kPa)	(ml/kPa)	(ml/kPa)
Nitrogen	4.62	4.44	4.27
Air	4.59	4.47	4.27
	V_{flask}	V_{flask}	V_{flask}
	(ml)	(ml)	(ml)
Nitrogen	467	450	433
Air	465	452	433

The use of a data-logging pressure and temperature transmitter was also found to be very convenient. In this case, a turnkey system was available from Omega (a well-known vendor of temperature, pressure and other sensors and instrumentation); this was extremely convenient. Manual logging can be done, and in fact has been demonstrated as part of this project (see Figure 2), but the instrumental method is preferred.[8]

The use of a pressure-volume relationship to calibrate the pressure response in terms of gas produced is shown above in Figures 4 & 5 and Table 1. Ideal gas-law considerations make it clear that this linear relationship is to be expected. To give an example: adding 100 ml of gas to a closed vessel with 100 ml internal volume at ambient pressure will double the total pressure within the vessel from 1 atmosphere to 2 atmospheres absolute, or from 0 atmospheres to 1 atmospheres gauge. Thus, the gauge pressure is directly proportional to the volume of gas produced.

Since atmospheric pressure is nominally 101.325 kPa, it's easy to show (for instance) that the volume of the apparatus assembled with flask 1 is 101.325 kPa * 4.6 ml/kPa = 466 ml. Note that calibration of the syringe used for adding the gas is easily done by mass using DI water and an accurate thermometer. Likewise, if necessary, knowledge of temperature and ambient pressure can be used to compute absolute amounts of gas.[9] That has not been done for this work, as the

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[8] It should be noted in passing, however, that the Omega pressure transducer has been found to be subject to corrosion by the HCl formed in many of the reactions reported here. Best practices for cleaning the pressure transducer between runs, as well as possible alternatives, remain under investigation. In the meantime, a backup transducer is a good investment.

[9] Also, the standard conditions used by compressed gas vendors, which are normally used for reporting 'standard liters' (as distinct from IUPCA standard conditions), correspond closely to ambient lab conditions.

volume of gas under ambient laboratory conditions with normally graduated laboratory apparatus (i.e. gas-tight syringes), given likely experimental error, should be adequate.

Further, note that the ability to construct the calibration curve shown in Figure 4 demonstrates that the apparatus is leak-tight; as will be shown below, this was also borne out by the experimental runs. Achieving this was not trivial; a number of trial apparatus and approaches, using more off-the shelf parts and equipment, were attempted and rejected prior to setting upon the apparatus and approach discussed here.

Procedure. While the procedure is still being refined, and a full protocol suitable for use with an arbitrary unknown compound is still under development, the following general procedure is emerging:

- Begin with an assessment, based on chemical knowledge and experience with the WRM/WRS in question, of the amount of gas likely to be produced. For instance, a reaction between magnesium powder and water would be expected to produce hydrogen and $Mg(OH)_2$. Complete reaction of 0.100 g of magnesium with water would yield ~200 ml of hydrogen gas at 22 °C and 101.325 kPa ambient pressure. Likewise, complete reaction of 0.100 g of water with magnesium would produce ~ 134 ml under normal lab conditions.
- Use that knowledge to set up some range-finding experiments. For instance, 1.0 g of water could be added all at once to 0.05 g of Mg. Even with complete reaction, the resulting 100 ml of gas would only pressurize the vessel to ~ 22 kPa gauge.
- As part of the range-finding experiments determine the optimal order of addition (WRM/WRS to water, or vice-versa); also establish the extent to which having excess water present may affect the result (for more on this, see discussions below).
- After establishing the reactivity in trial runs, conduct several replicate runs under conditions that yield a readily measureable evolution of gas over a reasonable period of time.

Example results. Tests have been conducted, to date, with a modest set of materials. Much of the testing to date was done to validate equipment, and develop or test the generalized procedure above. The following sections omits that developmental work, and focuses instead on some initial materials characterization obtained to date. This work shows (a) that the apparatus works well, but (b) the wide variety of reactivity encountered will demand careful though in establishing a generalized procedure capable of arriving at a valid metric for an arbitrary water reactive material or substance.[10]

Mg Powder.

Magnesium powder has frequently been used as a standard for testing WRM. Conveniently, one of the industry experts contacted during this project was from a company that manufactured magnesium powder (ESM Group) and generously supplied samples. These were ESM SMT -70 and -200 mesh powders. The -200 mesh powder was more reactive; further, trial experimentation established that the results were not highly sensitive to the mass of water, so long as it was present in sufficient quantities, and that the clearest results were obtained by adding the Mg powder to the water. Consequently only results from adding the -200 mesh powder to excess water are reported here.

Examples of the pressure vs. time results when 200 mesh Mg powder is added to ~ 4x its mass of water are shown in Figures 6 and 7 below. Note that experience has shown that if the temperature in the lab varies during the run, it can affect the results. Consequently, all the pressure vs. time results shown here are corrected for any change in temperature to yield a pressure that corresponds to the temperature at the start of the reaction. Further, note that when the water is pre-charged into the reactor, the reactor head-space is allowed to come to equilibrium, so that the vapor pressure of water is accounted for.

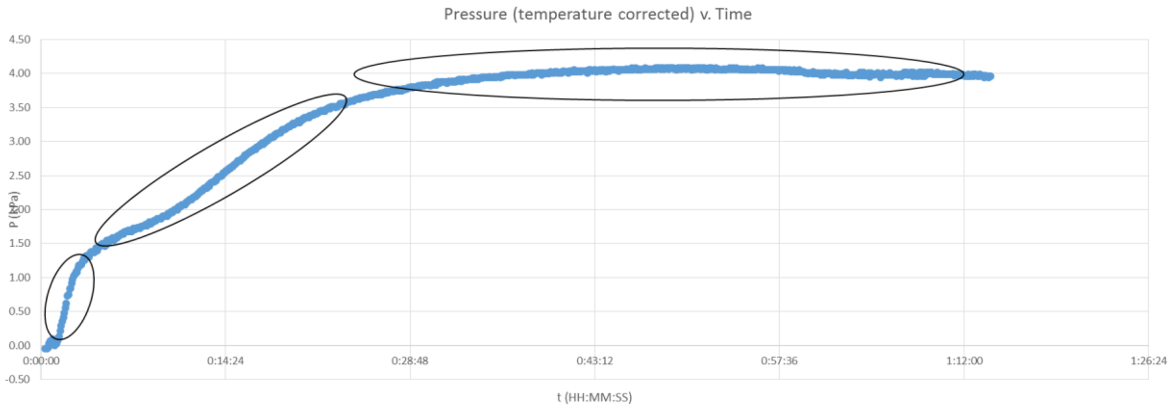

Figure 6. Reaction between 1.2 g of -200 mesh Mg powder and 5.0 g water (Mg added to water). The blue line is the experimental result. The ovals indicate three distinct regions of the reaction, which are discussed in the text.

In Figure 6, when Mg powder is added to water, there appear to be three regions. An initial faster reaction, a slower mid-term reaction, and finally period of slower reaction. In some cases, (above) gas production appeared to subside completely; in others (Figure 7, below) it appeared to continue.

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[10] Note, however, that WRS (which produce flammable gasses) are generally easier to address: the hydrogen or light hydrocarbons produced do not have appreciable solubility in water, so using excess water is generally applicable.

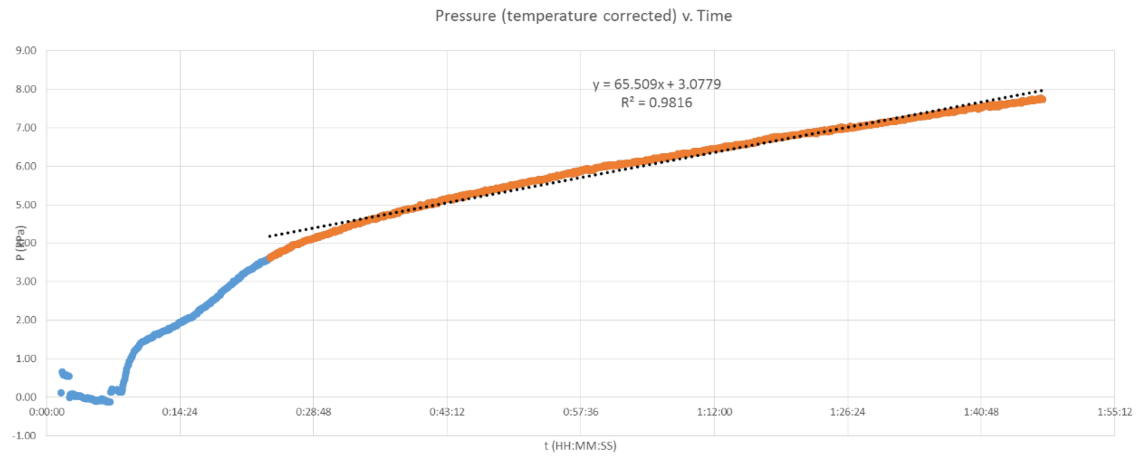

Figure 7. Reaction between 1.9 g of -200 mesh Mg powder and 8.2 g water (Mg added to water).

In Figure 7, for the three different relatively linear ranges, it is very straight-forward to extract a rate of reaction (one example is shown in Figure 7). The fitted line, given the data acquisition configuration used here, yields a slope in units of kPa/day. With the calibration data and simple unit conversions, this can be converted to (for instance) a rate of gas evolution in units of ml/hour; that value, divided by the mass of WRM/WRS used, in grams, yields a rate of gas evolution normalized to the mass of WRM/WRS in units of liters/kilogram/hour (l/kg-hr).[11]

Figure 8 shows an example of the rate calculation for the initial burst of hydrogen production (in yet another run).

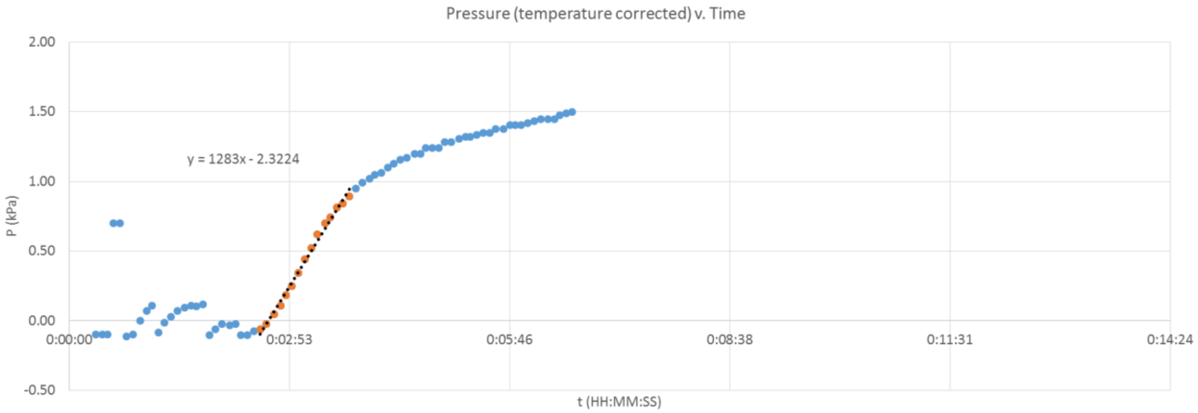

Figure 8. Detail of the reaction between 2.0 g of -200 mesh Mg powder and 8.0 g water (Mg added to water). The rate shown (1283 kPa/day) is based on the first 100 seconds of hydrogen production. The choppy region prior to that represents venting of the reactor to equalize pressure within the vessel with ambient before adding the Mg powder.

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[11] For the purposes of this report, all gas volumes are as found at ‘ambient conditions’. These were typically near ambient (i.e. 22 °C and 1 atmosphere), and roughly correspond to ‘standard liters’ as commonly used within the context of compressed gas vendors (e.g. CGA). These results could be corrected to arbitrary standard conditions if desired, but it is probably not necessary given the level of precision possible in this work.

The results from 4 test runs with the -200 Mg powder are tabulated in Table 2.

Table 2. -200 Mg powder results.

ESM-SMT -200 Mesh Mg Powder	Initial (l/kg-hr)	Mid-term (l/kg-hr)	Long Term (l/kg-hr)
Run 1 (1.2 g Mg/5.0 g water)	104	23.8	6.2
Run 2 (1.9 g Mg/8.2 g water)	101	26.4	6.5
Run 3 (2.1 g Mg/8.0 g water)	96	16.4	N/A
Run 4 (2.0 g Mg/8.0 g water)	123	19.7	N/A
Mean	106	21.6	N/A
Sample Std. Dev.	12	4	N/A

The results with Mg show an important finding from this work so far: <u>it is not always obvious which rate from the experiment should be used to characterize the material</u>. Even for the rates shown above, some judgment was exercised in which region of the curve to fit in order to extract a rate. In this case, the manufactures' own testing (procedure not disclosed) of this material suggested a rate of ~ 15 l/kg-hr.

Sodium Borhydride Powder

Another convenient and well known WRS is sodium borohydride ($NaBH_4$, SBH). A sample of this (Rohm & Haas material, supplied via Sigma-Aldrich in 2009) was on hand and used for testing.

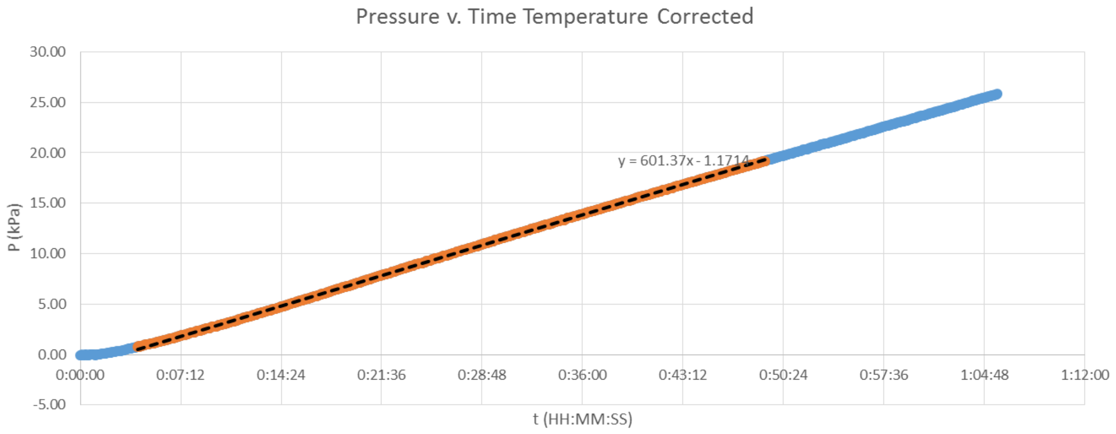

Figure 9. A typical reaction between the SBH on hand and water, when solid SBH (0.99 g) is added to water (7.97 g). The rate of pressure increase in the linear range shown corresponds to a rate of 112 l/kg-hr.

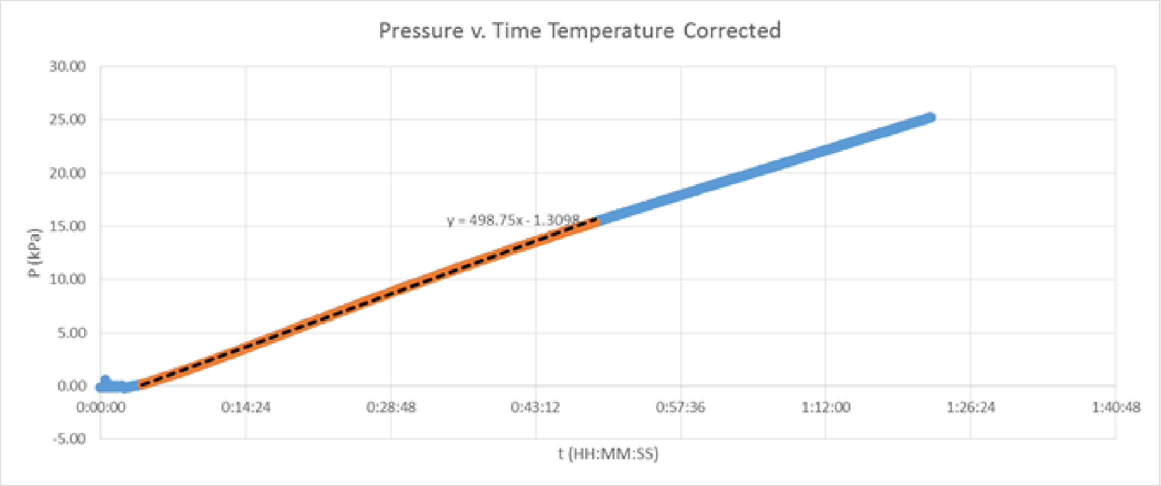

Figure 10. A typical reaction between the SBH on hand and water, when solid SBH (0.94 g) is added to water (8.03 g). The rate of pressure increase in the linear range shown corresponds to a rate of 105 l/kg-hr. This reaction shows some evidence of diminishing rate with time, at times in excess of 1 hr.

Unlike the Mg powder, this yielded an obvious and fairly steady rate of reaction − at least over the first hour or so. As the reaction proceeds further, the rate does appear to fall off slightly (which is consistent with expectations, based on chemistry knowledge).

In some cases, anomalous behavior can be observed (Figure 11). In this case, a rate could still be extracted, but the project team suspects that the apparatus began to leak as the pressure increased. This was not observed frequently, and the apparatus was more leak resistant using the septum for addition of liquids, vs. the thermometer adapter and PE pipette. The solids addition apparatus is functional, but it does require care and attention to detail to maintain a leak-tight system.

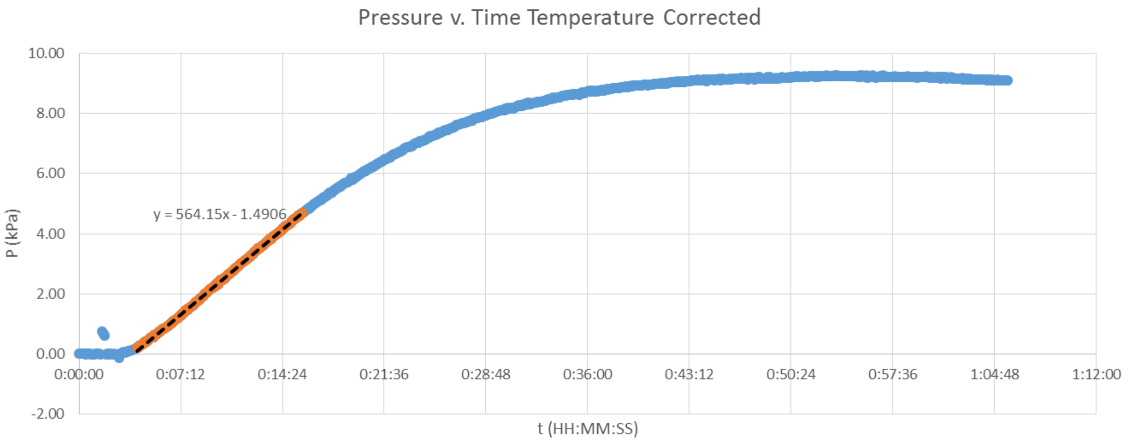

Figure 11. An atypical reaction between the SBH on hand and water, when solid SBH (0.92 g) is added to water (8.16 g). The rate of pressure increase in the linear range shown corresponds to a rate of 117 l/kg-hr. In comparison to Figures 8 and 9, it appears that this experiment failed to remain leak-tight above 9 kPa gauge pressure.

Table 3 tabulates the results shown in Figures 8-10 above.

Table 3. Results for SBH on hand (SBH added to water).

SBH (g)	Water (g)	Ratio	Rate (l/kg-h)
SBH added to water			
0.99	8.0	8.0	112
0.94	8.0	8.5	105
0.92	8.2	8.9	117
mean			111
sample standard deviation			6

Note that, prior to conducting experiments with the amounts reported in Table 3, smaller scale experiments were conducted with water added to SBH, to establish under controlled conditions that the rate of reaction and amount of gas produced was manageable. Those results were less clear than the results above, but did indicate that the observed rate tended to increase with increasing ratio of water to SBH (at least, up to the 8:1 water:SBH ratio used here), and established that the rate would be in a measureable range with 1 g of SBH and 8 g of water. Rates observed in those experiments ranged from a low of ~ 65 l/kg-hr when water was limited to highs of ~ 200 l/kg-hr for portions of some experiments.

Also, it is known[12] that the rate of reaction of SBH with water is dependent on pH (increasing at lower pH) and that it has an overall complex dependence on conditions, including a strong dependence on temperature. As a result, the interpretation of the results given here should be limited to the following conclusion:

- For the SBH tested here, when SBH is added to water with water present in an 8:1 water:SBH mass ratio, the rate of gas production is 111(6) l/kg-hr.[5]

Different conditions of test (different temperatures, different water:SBH ratios) may well yield different results.

In this context, it should be noted that while these results would put this SBH powder in PG II for Division 4.3 materials (20 l/kg-hr < gas evolution rate ≤ 10 l/kg-min), SBH is currently placed in PG I within the Dangerous Goods table (UN 1426). Though the project team feels that

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[12] This assertion is based on a combination of published reports and personal experience of the project principal investigator. Dow Chemical has published online an overview of SBH properties (http://www.dow.com/assets/attachments/industry/pharma_medical/chemical_reagents/reducing_agents/sodium_borohydride_digest.pdf) which includes a discussion of the stability of SBH in water; this indicates that the stability is strongly pH dependent, and that both the dissolution of SBH and the ongoing hydrolysis of SBH raise the pH, which inhibits the rate of reaction somewhat. Unpublished work by G. Smith while employed by Millennium Cell in 2003 indicated that the rate of hydrolysis of base-stabilized (3 wt % NaOH) aqueous solutions of SBH was complex, with rates of spontaneous hydrogen generation first increasing, then decreasing, as SBH concentration increased.

the test method is sound, given the preliminary nature of the test and the uncertain status of the SBH sample used, this data should not be relied upon for transport classification.

For the purposes of HM-14, the key findings from this experiment, are

- Rates as high as 200 l/kg-hr are readily measureable.
- Relative standard deviations (RSDs) for experiments with an initial steady rate of reaction are on the order of 5 %. These can be compared to RSDs of 11 % for the initial rate with -200 mesh Mg powder and 18 % for the intermediate rate with -200 mesh Mg powder.

Dimethyldichloro silane

While Mg powder and SBH were convenient materials to test, and in particular they were used to evaluate the ability to use the solids addition apparatus, dimethyldicholoro silane (DMDCS) is representative of the broad class of WRM which produce HCl on contact with water; and, like many of them (e.g. SiCl4, TiCl4, $SOCl_2$, $POCl_3$…) is a liquid.

As a liquid WRM, and one which produces a water soluble gas on contact with water, DMDCS represents more of a challenge in testing. First of all, any change in pressure due to hydrogen gas needs to be differentiated from the vapor pressure of the material itself (or from water); secondly, care needs to be taken to ensure that the presence of water is not suppressing gas formation.

As with all materials, experiments with DMDCS began with some exploratory runs. In one of these, Figure 11, 0.0548 g of water was added all at once to 1.0512 g of DMDCS pre-charged to the apparatus.

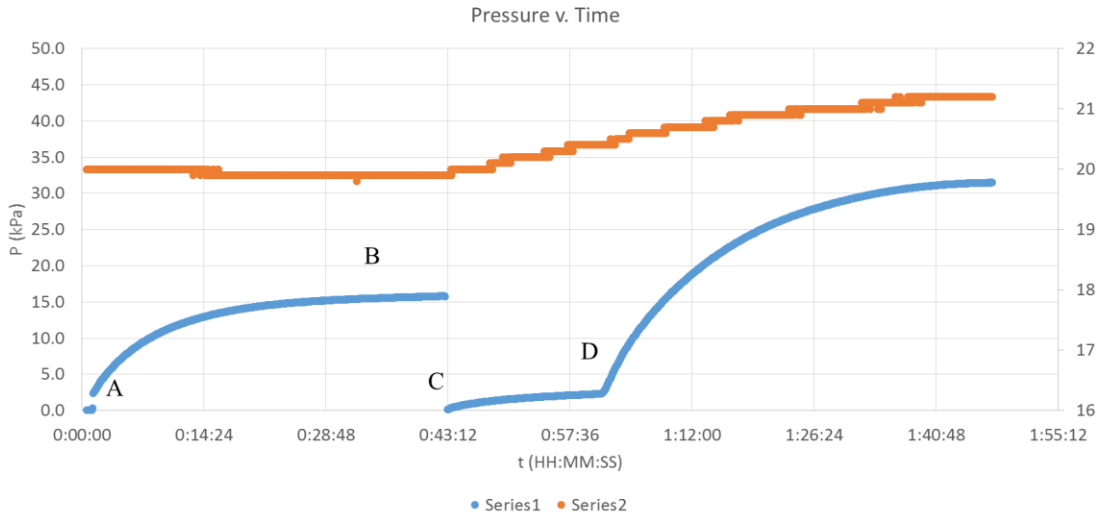

Figure 12. Uncorrected data shown observed pressure and temperature vs. time for a run where 0.055 g water was added all at once to 1.05 g HMDCS. The lettering indicates specific parts of the experiment: (A) HMDCS added via syringe to closed vessel; pressure increases and then levels off (B) as some HMDCS evaporates (b.p. 70 ˚C), (C) vessel vented, (D) water added all at once,

In this case, Figure 12 shows both the uncorrected pressure data and the temperature as recorded during the run. Figure 12 also shows an issue that needs to be addressed with liquid WRM. Namely, even in the absence of water they produce measureable amounts of gas simply from evaporation. With this apparatus, it is easy to correct for that simply by venting the apparatus. Eventually, a near-equilibrium is established where part of the atmosphere within the vessel has be replaced by sample vapor, yet the total pressure within the vessel remains near 1 atm absolute (i.e. near zero gauge pressure). After that, water can be added and reaction monitored. In some cases, it is necessary to account for the vapor pressure of water as well; in this case, however, that is not necessary as gas evolution is immediate and obvious.

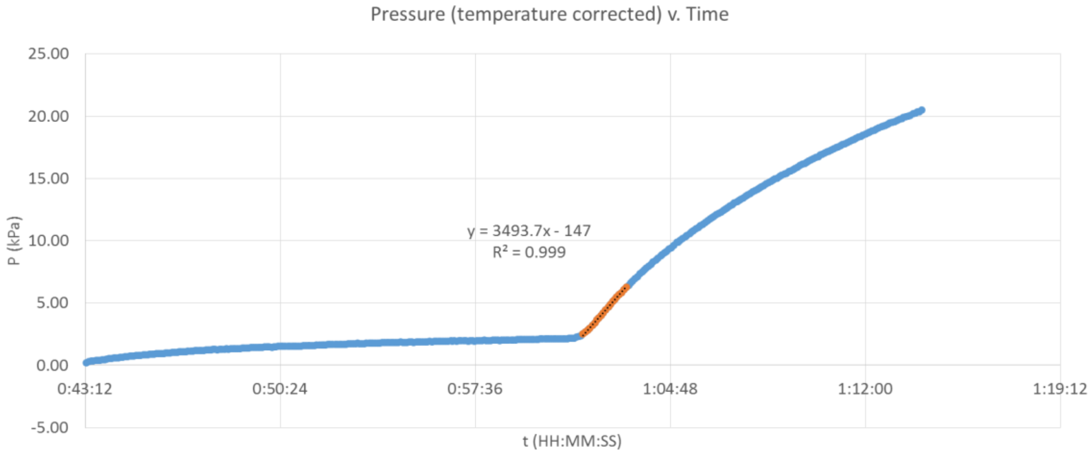

Figure 13. Detail from the addition of 0.0548 g water to 1.0512 g DMDCS. The line shown is fit to the first 100 seconds of reaction, and yields a rate of 615 l/kg-hr or 10.3 l/kg-min.

Figure 13 shows that, with water not present in excess (0.37 moles water/mole DMDCS), a gas production rate of ~ 10 l/kg-min (based on mass of DMDCS) is observed. The water used here was limited both to keep the reaction manageable, and to minimize the impact of sequestration of HCl within liquid water remaining present in the vessel.

In passing, note that the total observed pressure change (Figure 12) of ~ 30 kPa corresponds to production of ~ 130 ml of gas; This appears to represent an extent of reaction near 90 %; the theoretical production of gas (2 moles HCl per mole water) in this reaction is ~ 150 ml.

Several additional reactions were conducted, with varying amounts of water and DMDCS.

Table 4. Results for DMDCS (water added to DMDCS).

DMDCS	water	water/ DMDCS	slope	ml/kPa	Rate (DMDCS)	Rate (water)
g	g	mol/mol	kPa/day		(L/kg-hr)	(L/kg-hr)
1.078	0.0515	0.342	3357.9	4.62	600	12,551
2.0831	0.104	0.358	4395.9	4.27	375	7,520
1.0512	0.0548	0.373	3493.7	4.44	615	11,794
0.5966	0.0536	0.644	1602.1	4.62	517	5,754

0.5762	0.0877	1.090	1624.5	4.44	522	3,427
0.5662	0.1781	2.253	1023.8	4.44	335	1,063
0.543	0.4888	6.449	--	--	--	--
0.5399	0.5094	6.759	--	--	--	--

The reactions with the highest water/DMDCS mole ratio do not report a rate. The reason for this is illustrated in Figure 14.

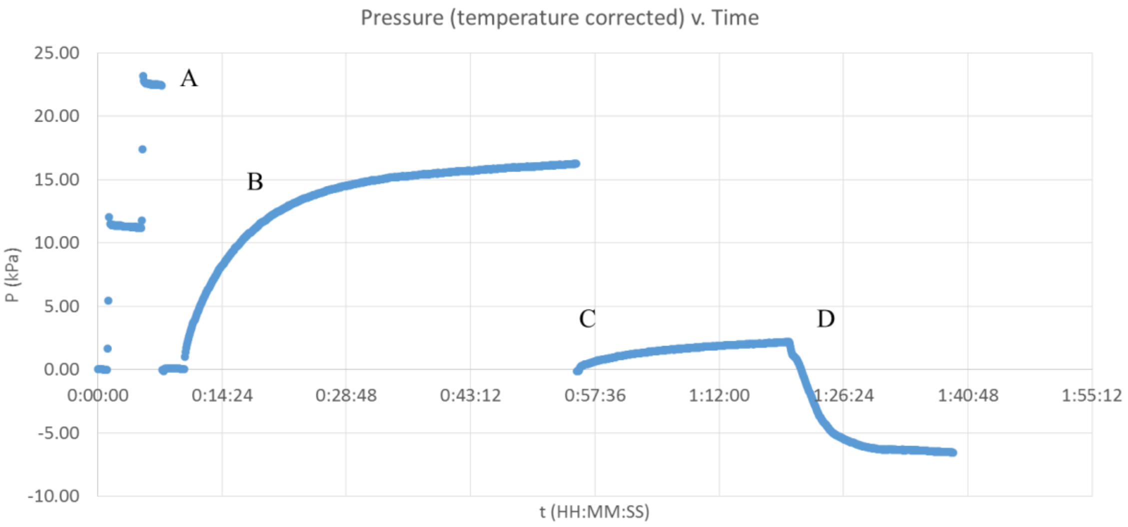

Figure 14. Addition of 0.49 g water to 0.54 g DMDCS. (A) in-situ calibration check, (B) DMDCS added (C) vented to reduce pressure (D) water added.

Apparently, when too much water is added reaction occurs (removing DMDCS from the apparatus and the vapor phase, while HCl that is produced is held in solution rather than released to the gas phase.

Another trend apparent from the data in Table 4 is the fact that the observed slope (total rate of gas production) tracks the amount of DMDCS present much better than it tracks the amount of water present. Correspondingly, the rate of gas evolution expressed per unit mass of DMDCS (up to the point where gas starts being absorbed by excess water) is more nearly constant than the rate relative to the amount of water. This actually came as a surprise as, prior to experimental work, the project team had felt that the rate might better be expressed per kg of water present than per kg WRM/WRS.

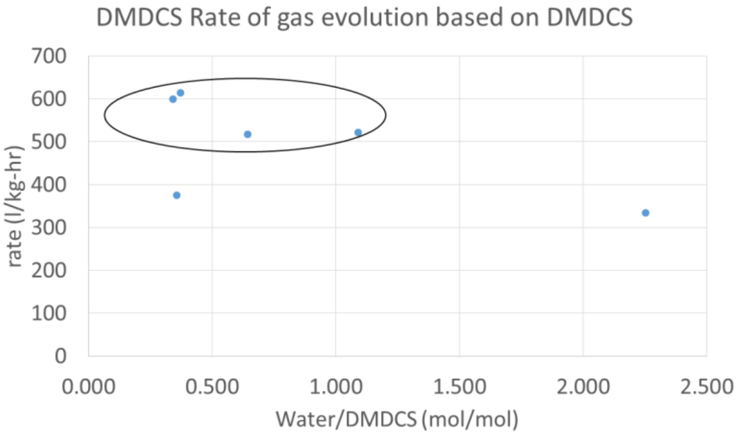

Figure 15. Plot of observed rates, based on mass of DMDCS present, vs. mole ratio of water to DMDCS. The fact that the rate is somewhat independent (for ratios up to 1.0) of water to DMDCS ratio, suggests that results should be reported on the basis of l/kg$_{WRM}$-hr, which has been conventional practices for WRS (current division 4.3 materials). Further, the circled region indicates that the intrinsic rate for this material is 500-600 l/kg-hr.

It will probably be necessary to conduct some additional replicate runs, aiming for slightly larger DMDCS charges, but the data above (Table 4, discarding the 375 and 335 l/kg-hr results) suggests that the rate of reaction for DMDCS with water is 560 (50) l/kg-hr.[13]

For the purposes of HM-14, the key findings from this experiment are:

- <u>In some cases, it will be better to add water to WRM/WRS</u> − particularly with volatile liquids.
- When doing this, <u>even though the water is limiting, in at least some cases the rate should still be expressed per kg of WRS/WRM</u>.
- Even with the limited replicates (i.e. at fully identical conditions), relative standard deviations on the order of 9 % are observed (compare to 5 % RSD for SBH, and 11 % for the initial rate with -200 mesh Mg powder).

Acetyl Chloride

Dimethyldicholorosilane (DMDCS) was chosen as a material representative of the broad class of WRM which product HCl on contact with water; it was also chosen as a material expected to have rapid, but manageable reactivity, and to represent reactive liquid metal halides (e.g. $SiCl_4$ and $TiCl_4$). Acetyl chloride ($CH_3C(O)Cl$) is an organic acid chloride, and another material that should yield HCl on contact with water. It turns out to be substantially more reactive than DMDCS.

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[13] Mean reported, sample std. dev. in parentheses.

Figure 16 again shows the as-observed temperature and pressure data for a reaction, this time for the reaction of 0.1117 g water with 1.1248 g Acetyl chloride.

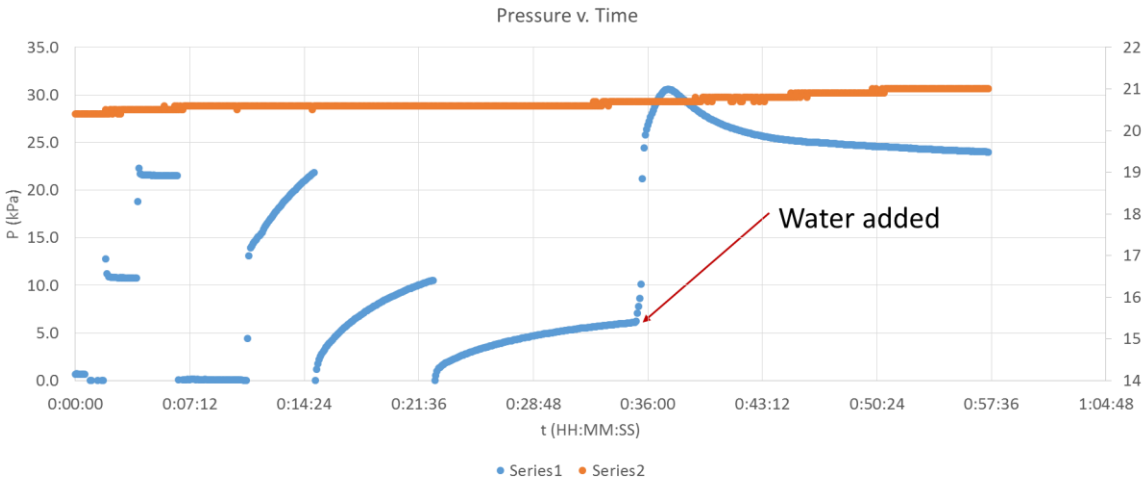

Figure 16. Plot of observed temperatures and pressures for the reaction of 0.11 g water with 1.1 g Acetyl chloride. As in Figure 13, the in-situ calibration tests are shown. The increase in pressure due to the vapor pressure of acetyl chloride − and the related need to vent the reaction − is also apparent.

In Figure 16, it is clear that reaction occurs very rapidly. If acetyl chloride reacts with water to yield HCl and acetic acid, then the theoretical yield of HCl is 150 ml at 21 °C. For the apparatus used, that would correspond to ~ 30 kPa of pressure increase; from the addition of water to the peak pressure observed, the change in system pressure is ~ 25 kPa, so apparently reaction was nearly complete. Though, it is not 100 % clear what accounts for the pressure subsiding afterwards. That might be due to absorption of some of the HCl formed by the liquids present, or it may be that reaction as rapid as this created heated gas, which changed volume (shrank) as it cooled (without affecting the observed temperature in the relatively massive pressure/temperature transducer).

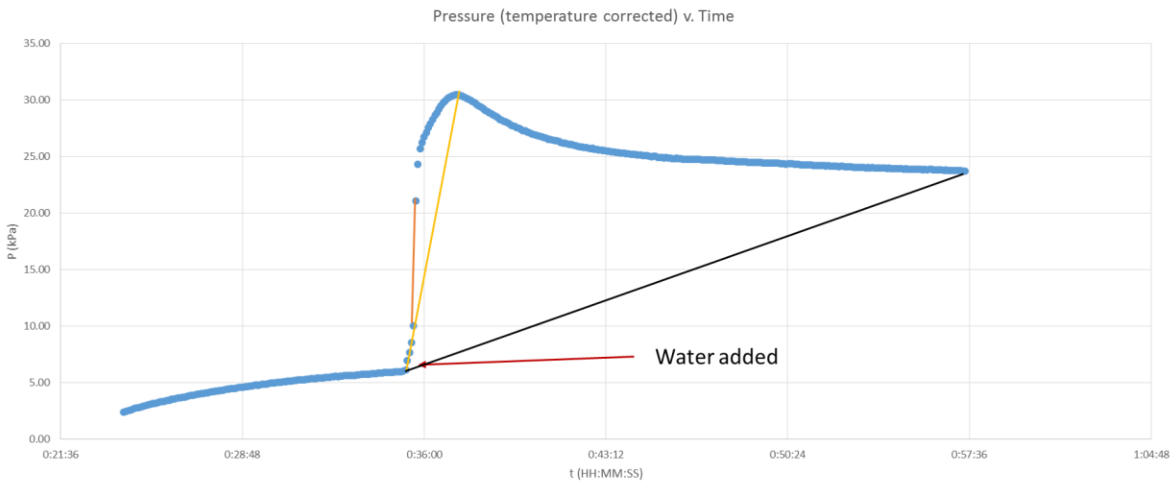

Figure 17. Temperature corrected pressure trace for 0.11 g water with 1.1 g Acetyl chloride. For the orange segment (fasted 5 second interval), the rate is 544 l/kg-min; for the yellow segment it is 48 l.kg-min; for the fastest minute, the rate is 89 l/kg-min.

As was the case with the Mg powder, it is not immediately clear what to use as the reaction rate to characterize this reaction. It is also not clear whether additional experiments can be conducted with this material. Acetyl chloride had sufficient volatility that 1 g was a practical minimum for experimentation: 0.5 g aliquots tended to evaporate nearly completely within the apparatus (particularly given the need to vent the reaction). The mole ratio of water to acetyl chloride in the experiment shown was 0.4 mole water per mole acetyl chloride, while smaller amounts could be used, they are not expected to be qualitatively different. Conversely, larger amounts will likely exceed the capacity of the apparatus.

The key findings from this experiment, for the purposes of HM-14, appear to be

- Acetyl chloride is_at or near the upper limit of reactivity for this approach, with a maximum rate of gas production in contact with water well in excess of 100 l/kg-min.
- In at least some cases, concerns about complex behavior and/or re-adsorption of gasses are valid.

Aluminum Chloride

The first solid WRM tested was aluminum chloride ($AlCl_3$, anhydrous). Aluminum trichloride is reported to very rapidly react with water to (ultimately) form $Al(OH_2)_6Cl_3$, a coordination compound that is the hydrated form of $AlCl_3$ found in solution. That reaction would not, actually, yield any net HCl gas.

In fact, results consistent with that − but nevertheless very interesting − were observed. As usual, initial experiments adding a limited amount of water to the WRM were conducted (for safety and to limit the extent of gas dissolution in the water. Figure 18 summarizes these runs.

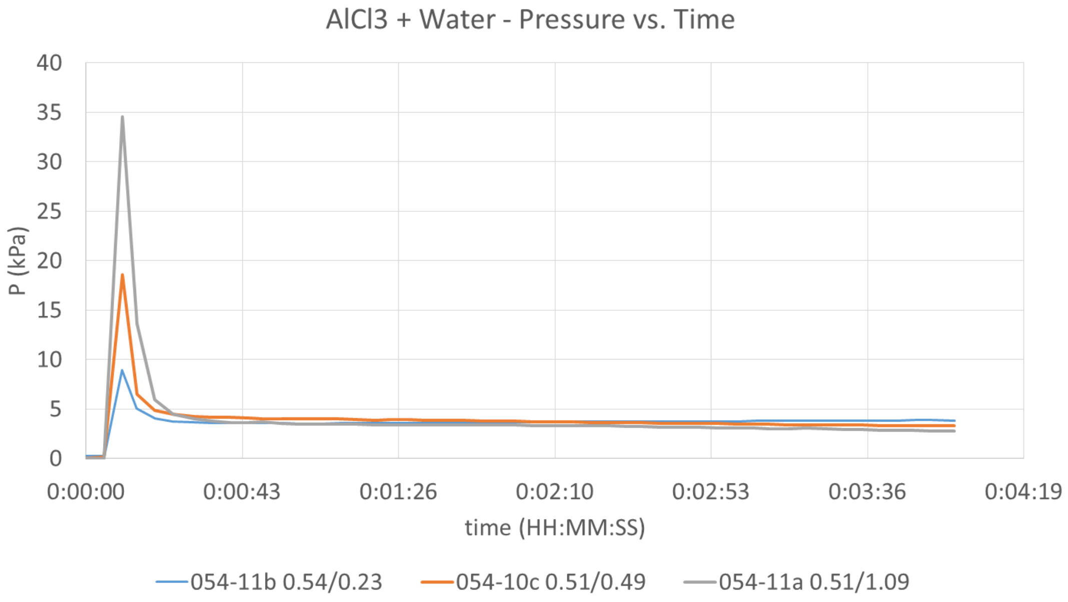

Figure 18. Temperature corrected pressure traces for the reaction of water and $AlCl_3$ (water added to $AlCl_3$). Traces or for 0.23 g water and 0.54 g $AlCl_3$ (3.1:1.0 water:$AlCl_3$ mole ratio). 0.49 g water and 0.51 g $AlCl_3$ (7.1:1.0 water:$AlCl_3$ mole ratio), and for 1.09 g water and 0.51 g $AlCl_3$ (16:1.0 water:$AlCl_3$ mole ratio).

In Figure 18 there is an immediate surge in pressure (gas production) for each reaction which, however, quickly subsides, leaving just the pressure due to water vapor (see Figure 19, and experiments with $AlCl_3$ added to water). Transient rates of (apparent) gas production go as high as 3,600 l/kg-min (34.6 kPa/5 sec. for 0.51 g $AlCl_3$ with 1.09 g water), but <u>net</u> rates of production after more than 1 minute are quite low; in fact, they are negligible.

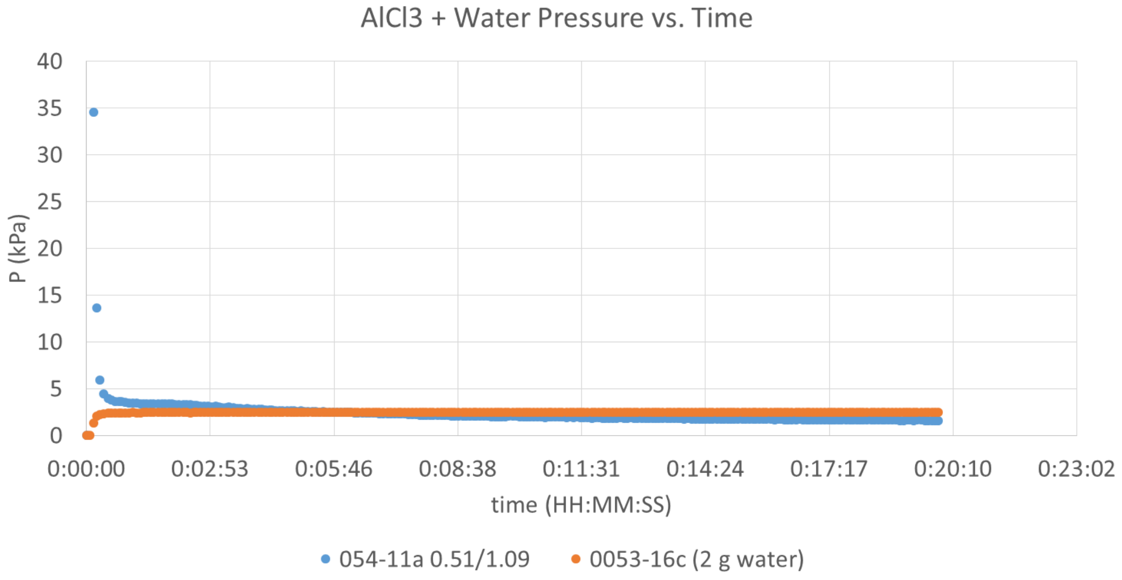

Figure 19. Temperature corrected pressure trace for the reaction of 1.09 g water and 0.51 g $AlCl_3$ (16:1.0 water:$AlCl_3$ mole ratio) compared to a “blank” using 2 g of water only. The pressure remaining at the end of the reaction between water and $AlCl_3$ is due simply to water vapor, as demonstrated by the ‘blank’ data.

Figure 19 compares one of the experiments to a ‘blank’ run with just water, demonstrating that the residual pressure is from the water, not any net production of gas. Experiments with $AlCl_3$ added to water also show this. This is true even for the run with 0.23 g water and 0.54 g $AlCl_3$; in this reaction the ratio of water to $AlCl_3$ is just 3.2:1.0 so, in principle, most of the water might have reacted.

Figure 20 shows one of two experiments where the $AlCl_3$ was added to water. Essentially the same behavior is observed here.

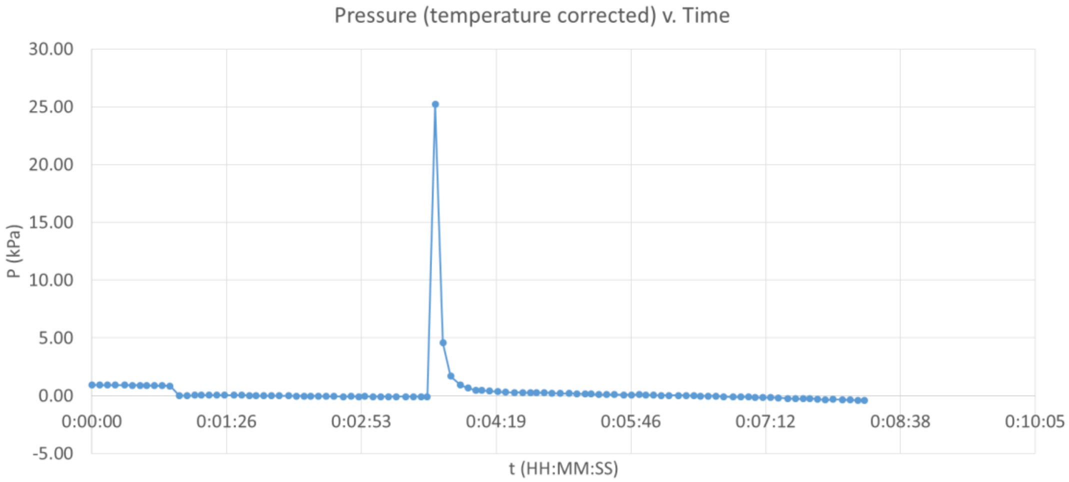

Figure 20. Temperature corrected pressure trace for the reaction of 1.05 g water and 0.41 g $AlCl_3$ (19:1.0 water:$AlCl_3$ mole ratio), with the $AlCl_3$ added to the water. Compare this to the run in Figure 17 and 18 with 1.09 g water added and 0.51 g $AlCl_3$ (16:1.0 water:$AlCl_3$ mole ratio). In this case a pressure spike of ~ 25 kPa was observed, in the Figure 18/19 result, a pressure spike of 30-35 kPa was observed. A similar result obtains when 0.22 g $AlCl_3$ is added all at once to 1.09 g water (8 kPa surge).

The preceding results suggest that $AlCl_3$ produces HCl transiently in contact with water, with the HCl rapidly (within seconds) reabsorbed into the solution. As an alternative, it’s difficult to rule out a transient hot-spot from the exothermic reaction that momentarily expands gas within the apparatus (by as much as 155 ml), before it rapidly re-equilibrates in temperature with the bulk of the apparatus. The project team is inclined the former position, however: on storage, without rigorous exclusion of humidity, $AlCl_3$ samples develop slight pressure, and on exposure to humid air a transient ‘fog’ forms around spilled $AlCl_3$.

Table 5. Results for $AlCl_3$ reaction with water.

$AlCl_3$	Water	water/$AlCl_3$		Transient gas (5 sec)	Transient rate (5 sec)	ml/kPa	Rate ($AlCl_3$)	Rate (water)
g	g	mol/mol	ml/kPa	ml	kPa/day		(l/kg-hr)	(l/kg-hr)
0.5354	0.2274	3.14	4.62	40	150,000	4.62	54,000	127,000
0.5123	0.4881	7.05	4.27	79	319,000	4.27	111,000	116,000
0.5112	1.0869	15.8	4.44	154	598,000	4.44	216,000	102,000
0.4142	1.0497	18.7	4.62	117	437,000	4.62	203,000	80,000
0.2164	1.0907	37.3	4.27	33	133,000	4.27	109,000	22,000

Table 5 summarizes the results from all the experiments with $AlCl_3$. When water is added to $AlCl_3$, the amount of transient gas produced clearly tracks the amount of water added; likewise, the rate (based on transient gas) is more constant when computed per kg of water, than per kg $AlCl_3$. When $AlCl_3$ is added to water, at comparable conditions, comparable results are obtained. For $AlCl_3$ added to water, with larger amounts of water present, transient gas production begins to fall.

The key findings from this experiment, for the purposes of HM-14, appears to be

- $AlCl_3$ demonstrates yet another type of behavior, transiently producing gas, which is rapidly reabsorbed, even at lower amounts of water relative to $AlCl_3$ at least within the confines of the test apparatus.
- As with DMDCS, as the amount of water reaches high enough levels, production of gas is suppressed. Unlike DMDCS, where (for lower amounts of water) the gas production rate tracked DMDCS, in this case it tracks (for lower amounts of water) the amount of water used.

Para-toluenesulfonyl chloride

Para-toluenesulfonyl chloride (tosyl chloride) is a well-known organic synthesis reagent that is a solid sulfonyl chloride. In solution, it converts alcohols to toluene sulfonate esters with the release of HCl.

$$CH_3C_6H_4SO_2Cl + ROH \rightarrow CH_3C_6H_4SO_2OR + HCl$$

On this basis, it might be expected to react with water. However, in several experiments, beginning with one where 0.12 g water was added to 0.51 g tosyl chloride, including one where 0.50 g water was added to 0.53 g tosyl chloride, and two where ~ 2 g of tosyl chloride were added to ~ 2 g of water, no detectable reaction was observed at room temperature over nearly an hour (> 50 minutes).

Magnesium Powder + Salt Water

One experimental parameter the project has been tasked with examining is the impact of salt water on test results. Bearing in mind that different materials will react differently with salt water, some experiments were conducted on the reactivity of Mg powder (-200 mesh) toward salt water.

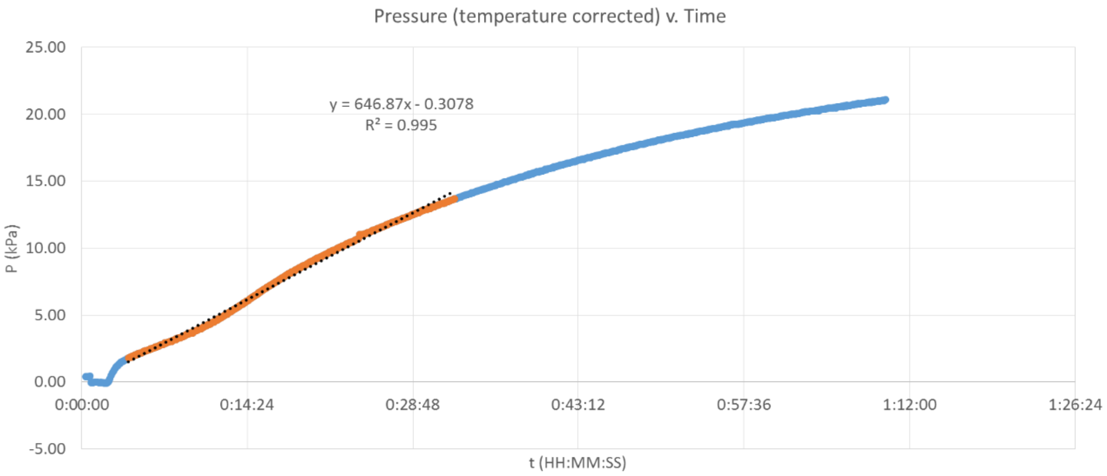

Figure 21. Addition of 0.2.01g -200 mesh Mg powder to 8.19 g 3.5 % salt water. The rate shown corresponds to 64 l/kg-hr. Compare to Figure 6 and 7.

Figure 21 (in comparison to Figures 6 and 7) shows that the presence of salt in the water does change the reaction (in this case) slightly. There appears to still be a brief initial surge in hydrogen production, but otherwise the reaction behaves more like the reaction of SBH with water; the rate is mainly fairly steady, and slowly falls off with time. Note that the reactions observed with salt-water are also somewhat faster than with water (See Table 6)

Table 6. -200 Mg powder results.

ESM-SMT -200 Mesh Mg Powder	Initial (l/kg-hr)	Mid-term (l/kg-hr)
Run 1 (1.2 g Mg/5.0 g water)	104	23.8
Run 2 (1.9 g Mg/8.2 g water)	101	26.4
Run 3 (2.1 g Mg/8.0 g water)	96	16.4
Run 4 (2.0 g Mg/8.0 g water)	123	19.7
		Sustained Initial (l/kg-hr)
Run 5 (0.48 g Mg/8.3 g salt water)		79
Run 6 (2.0 g Mg/8.2 g salt water)		64

The key findings from this experiment, for the purposes of HM-14, appears to be

- Salt water can affect both the nature, and the rate of reaction between WRS and water.
- In the case of Mg, it appears to increase the rate, and enable reaction to continue longer than with distilled water.

5. CONCLUSIONS

While this work remains in progress, and any conclusions are tentative, the following conclusions appear to be emerging from this work.

- The apparatus and general approach described here is suitable for assessing the reaction with water of both water reactive substances (that produce flammable gasses) and water reactive materials that (that produce toxic gasses). Monitoring pressure in a closed, gas-tight (important!), heavy-wall, glass vessel − with appropriate precautions − is a generally applicable and versatile way to deal with a wide range of reaction rates and types evolved gasses, in a simple and straight-forward way. Calibration the pressure response by addition of known volumes of gasses is simple and eliminates a number of otherwise problematic issues (materials compatibility, solubility of gasses in fluids, ability of small changes to displace a syringe piston, etc.). Overall, the apparatus used here comprises:
  - A heavy-wall glass vessel, with primarily o-ring seal fittings.
  - A pressure transducer and electronic data acquisition system (or mechanical pressure gauge and timer for manual data acquisition).
  - A compression fit GC septum for liquids addition and/or a flexible polyethylene tube & bulb for solids addition.
  - A stirring mechanism.
- The apparatus used in this work has observed rates of gas that ranged from ~ 2 ml/hour (10 kPa/day @ 4.5 ml/kPa; result not reported here; 60 kPa/day is clearly shown in Figure 7) to nearly 20 liters/hour (based on >100,000 kPa/day at 4.5 ml/kPa, single point, 5-second interval, measurements; see Table 5). Combined with the ability to work with from 0.1 to 10 grams of test materials, a dynamic range in rate measurement (per kg test substance) with the apparatus of at least 10,000:1 (observable gas rates) and potentially 1,000,000:1 (observable gas rates combined with ability to vary reagent charges) is accessible.
- Within that range, for multiple replicates of well-behaved materials (e.g. sodium borohydride), repeatability in the range of 5 % relative standard deviation is possible.
- It appears that there will NOT be a simple, ‘one-size-fits-all’ procedure which can be applied by rote. In some cases, adding water to a WRM/WRS yields the clearest results; in others, adding the WRM/WRS to water is more appropriate. Also, in some cases the rate observed is not highly dependent on the ratio of water to WRM/WRS; in other cases

it is. In other words, in some cases a rate expressed as l/kg_{WRM}-hr generally represents the reactivity of a material. In other cases, there is not a single value that represents the reactivity of the material. Also, because of the possible absorption of gas, or even WRM, in excess water, unless the gas produced is definitely not soluble in water, the total amount of water used will need to be limited. Finally, there are significant qualitative variations among the different types of WRM/WRS. Guidance from UN experts on how to approach this problem will be needed, and is solicited.

- Regardless of the exact procedure needed to arrive at representative metric, the *general* procedure needed is emerging:
  - Begin with an assessment, based on chemical knowledge and experience with the WRM/WRS in question, of the amount of gas likely to be produced.
  - Use that knowledge to set up some range-finding experiments.
  - As part of the range-finding experiments evaluate the optimal order of addition (WRM/WRS to water, or vice-versa), and establish the extent to which having excess water present may affect the result (for more on this, see discussions below).
  - After establishing the reactivity in trial runs, conduct several replicate runs under conditions that yield a readily measureable evolution of gas over a reasonable period of time.
- Looking at the specific materials tested to date,
  - In reactions with water, Mg powders show a rate of reaction that varies somewhat with time. Observed rates for one specific type of Mg powder ranged from slightly under 20 l/kg-hr to over 100 l/kg-hr (for a short, initial surge). Rates for other types of powder (coarser mesh, not reported here) are lower. Reactions with salt water were generally faster, and sustained rates of 65-80 l/kg-hr were observed.
  - Sodium borohydride reacts smoothly and controllably with water; in this work, initial (highest) rates observed were 105-117 l/kg-hr (mean = 111, std. dev. = 6 l/kg-hr).
  - The liquid WRM dimethyldichloro silane was an example where it appeared to be more useful to add water to the WRM for the measurement. So long as the water was sufficiently limited, the observed rate was fairly independent of the ratio of water to WRM, and it ranged from 522-615 l/kg-hr (4 measurements), ignoring one outlier, as well as lower results at higher water/WRM ratios.
  - Acetyl chloride was highly reactive. As for Mg, it is nevertheless difficult to assign a specific rate to it. Short-term rates from 50-550 l/kg-min were observed.
  - Aluminum chloride showed particularly unique behavior. Transient rates of over 3000 l/kg-min were observed, but in a closed vessel, within a few minutes, all gas was reabsorbed, even with relatively limited water (42 % w/w or 3:1 on a mole ratio).

  - Para-toluenesulfonic acid chloride shows no detectable evolution of gas.

Overall, the project team has made remarkable progress; arriving at a workable approach and apparatus that can accommodate a wide range of materials. However, the wide range of materials is itself creating some challenges: with reactivity patterns varying widely from one material to the next, it is challenging to arrive at a single procedure, and a single metric, that can be applied to universally to arbitrary unknown materials by rote.

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