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ENFORCEMENT CONFIDENTIAL / PREPARED AT THE REQUEST OF COUNSEL IN ANTICIPATION OF LITIGATION / ATTORNEY-CLIENT PRIVILEDGED
DRAFT MEMORANDUM

SUBJECT: Comments on Westinghouse Research and Technology Operations Report entitled "Calorimetry and Offgas Generation from Hydrolysis of Magnesium Chloride," dated July 27, 2012
Western Zirconium, Inc., Ogden, Utah
NEIC Work Product: VP1004X01

FROM: Joe Lowry, Ph.D.
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THROUGH: David Parker
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TO: Charles Figur
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As requested, I have reviewed and prepared comments on the Westinghouse Research and Technology Operations (WRTO) report entitled "Calorimetry and Offgas Generation from Hydrolysis of Magnesium Chloride," dated July 27, 2012, which provided testing results and opinions concerning the identification of Resource Conservation and Recovery Act (RCRA) characteristics of zirconium production waste from Western Zirconium Inc., in Ogden, Utah. In the following, a summary of the major points is provided, which is followed by quoted WRTO statements with my detailed comments.

In summary, the major points are:

1) Heat release and temperature rise
   a. WRTO claims the maximum temperature from a mixture of the waste and water is 165 degrees Celsius (°C). *This is simply not true as there are published solubility data for magnesium chloride at temperatures greater than 165 °C.*
   b. WRTO states that the National Fire Protection Association's (NFPA) grading is based on measuring the heat of reaction of a 1:1 weight mixture of the substance

with water, expressed as calories per gram (cal/g) of the total mixture and the computed heat of reaction for anhydrous magnesium chloride tested in this way would be -90.5 cal/g, consistent with NFPA water reactivity hazard grading of one criterion of between -30 and -100 cal/g. *This is simply not true. The computation resulting in a value of -90.5 cal/g provided by WRTO is for the reaction of 1 gram waste and 0.438 grams of water and not a 1:1 weight mixture and, therefore, based on the amount of reactants (1.438 grams rather than 2 grams) the value reported should have been about -125 cal/g. In 1975, NFPA provided that sulfuric acid "reacts violently with water," yet the computed heat of mixing for a 1:1 weight mixture with sulfuric acid and water is only -71.5 cal/g. The quantitative criteria provided in NFPA 704 are only guidance.*

c. WRTO provides that mixing sulfuric acid and water is the formation of a hydrate, as is the reaction of the waste with water and both reactions give approximately the same temperature rise regardless of the order of mixing. *In 1975, NFPA provided that sulfuric acid "reacts violently with water." The United States Environmental Protection Agency (EPA) adopted much of the narrative of the reactivity characteristic from NFPA. Since the Western Zirconium waste reacts with water similarly to how sulfuric acid reacts with water, the waste also reacts violently with water and hence exhibits the reactivity characteristic.*

d. WRTO noted the NFPA water reactivity grading of 1 is defined as "May become unstable at elevated temperatures and pressures; may be mildly water reactive," while a grading of 2 is defined as "Unstable; may undergo violent decomposition, but will not detonate; may form explosive mixtures with water." *NFPA also provides a water reactivity grading of 1 has the following qualitative criteria "Materials that react vigorously with water, but not violently," while grading of 2 has the following qualitative criteria: "Materials that react violently with water, including the ability to boil water, or that evolve flammable or toxic gas at a sufficient rate to create hazards under emergency response conditions." The Western Zirconium waste reacts violently with water, including the ability to boil water and evolves flammable and toxic gas at a sufficient rate to create hazards.*

2) Hydrogen evolution

a. WRTO claims the lower explosive limit of hydrogen is not equal to 4 percent (%). *This is simply not true. As provided by EPA and Occupational Safety and Health Administration (OSHA) regulation, the RCRA reactivity characteristic background document, the National Institute for Occupational Safety and Health (NIOSH) and the NFPA, an explosion is a deflagration and, hence, the 4% explosion limit for hydrogen is appropriate.*

b. WRTO states that none of the three magnesium chloride grades taken individually or averaged exceed the United Nations N5 threshold of producing greater than one liter of hydrogen per kilogram per hour. *This is simply not true. WRTO does report measurements for the Grade B waste over one liter of hydrogen per kilogram per hour. The rate of release and perhaps the amount of hydrogen gas released may be a function of the temperature. The manner in which the N5 test was conducted by WRTO and NEIC underestimates the magnesium content of the waste. The N5 threshold is for protecting communities from a nearby accident such as Bhopal and, hence, is not sufficiently protective with regard to the RCRA*

reactivity characteristic.

c. WRTO claims the NEIC hydrogen measurements are for dry air. *This is simply not true. NEIC hydrogen measurements were corrected for altitude and temperature and are reported relative to the original sample volume of the headspace. Again, the rate and amount of hydrogen gas released may be a function of the temperature and the amount of steam formed. The N5 test does not measure the amount of elemental magnesium that reacts at high temperature or in the presence of steam.*

d. WRTO claims that hydrogen evolution from the mixing of water with the waste will create steam sufficient to reduce its explosivity. *Elemental magnesium reacts readily with steam to produce hydrogen and, therefore, more hydrogen may be produced in the presence of steam. Steam, like the addition of nitrogen or diluent gas, can cause an oxygen-deficient atmosphere. However, not much steam will be created when the waste is mixed with a large amount of water. Further, under confinement such as in a container, steam formed upon the addition of a small amount of water reacts quickly with excess magnesium chloride, not affording dilution of the oxygen content of the headspace. Under confinement such as in a container, the steam can condense, not affording dilution of the oxygen content of the headspace. NEIC has conducted experiments showing that the atmosphere above such mixtures will ignite.*

3) Hydrogen sulfide evolution

a. WRTO measured a trace of hydrogen sulfide as being evolved from the waste. *The reasons WRTO did not measure much hydrogen sulfide is an apparent misunderstanding of fundamental chemical principles involving Henry's Law and acid dissociation, and avoidance of sampling the reaction gas bolus of the Mason-Cooper testing.*

b. WRTO claims NEIC's use of electrochemical detection for hydrogen sulfide is novel. *This is simply not true. The Agency for Toxic Substances and Disease Registry (ATSDR) states: "Electrochemical sensors are the most commonly used sensors for toxic gases, including hydrogen sulfide, and are the best sensor for ambient toxic gas monitoring. These sensors are specific to a particular gas, are very accurate, do not get poisoned, and monitor at the ppm level." Nevertheless, NEIC has conducted experiments confirming that the signal for the electrochemical detector for the headspace air was due to hydrogen sulfide and made measurements with another commercially available monitor.*

c. WRTO states that a material balance calculation for one of the NEIC dumpster scenario tests shows that a test result of 236 parts per million by volume (ppmv) hydrogen sulfide is not credible. *Re-examination of the underlying records for the 236 ppmv measurement shows all quality control measures were acceptable. In fact, the absorbing solution for the 236 ppmv was analyzed neat and diluted in half. Both measurements are in agreement as to the concentration. The rate of release and amount of hydrogen sulfide released may be a function of temperature. The acid volatile sulfide determination made by NEIC does not measure total sulfide. The acid volatile sulfide was conducted at rather low temperature with 2 milliliters of 0.1 N hydrochloric acid and a 0.5-gram sample, while the dumpster scenario test used equal weight waste and water (200 grams*

and 200 milliliters [mL]) and, hence, achieved a temperature near 140 °C. Perhaps zirconium sulfide formation in the acid volatile sulfide test caused underestimation. Further, the WRTO mass balance calculation is for a static system with uniform mixing throughout the headspace. For such a system, the hydrogen sulfide concentration would increase and plateau. This did not happen. The actual system was dynamic due to the violent exothermic reaction of the waste with water, and the 236 ppmv measurement is for the hot reaction gas bolus, which is rapidly released from the waste. The hydrogen and hydrogen sulfide concentrations peaked immediately and decreased rapidly.

HEAT RELEASE AND TEMPERATURE RISE

WRTO statements on pages 2 and 36.

The maximum theoretical temperature that is possible from mixing $MgCl_2$ and water at atmospheric pressure is computed to be 165°C (the boiling point of a saturated 48.7% wt solution at that temperature), so that the temperature rise is self-limiting.

It should be noted at this point that the maximum temperature that can be generated by any $MgCl_2$-H_2O mixture at atmospheric pressure is the normal boiling point of the solution, which changes with $MgCl_2$ concentration. Addition of more heat will only boil the water but will not increase the liquid or vapor temperature. This limiting value is plotted as a function of solution concentration in Figure 19.(43) Also plotted is the solubility as a function of temperature (where the x-axis represents solubility, and the y-axis temperature). Since the solution can neither exceed its boiling point (at atmospheric pressure) nor its saturation concentration, the intersection of the two curves at 50.0% wt and 165°C represents both the most concentrated and highest temperature solution that can exist without pressurization.

Comment

This notion is negated by the solubility data given in Wagman et al.[1], where solubilities were determined for temperatures of 180 °C, 181.5 °C, and 186 °C. Further, extrapolation of the Wagman et al. boiling point data using a polynomial fit indicates that the predicted boiling point always exceeds the temperature that the saturation experiment was conducted. This is reasonable, as a solubility determination at 186 °C could not be made if the boiling point was less than 186 °C.

Figure 1 plots the solubility data and the boiling point data for magnesium chloride from Wagman et al. and a Microsoft Excel polynomial fit equation and line for the boiling point data.

[1] Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H, Halow, I., Bailey, S.M., Churney, K.L., and Nuttall, R.L. "The NBS Tables of Chemical Thermodynamic Properties," J. Chem. Ref. Data, Volume 11, Supplement Number 2, pp 2-260 – 2-261, 1982.

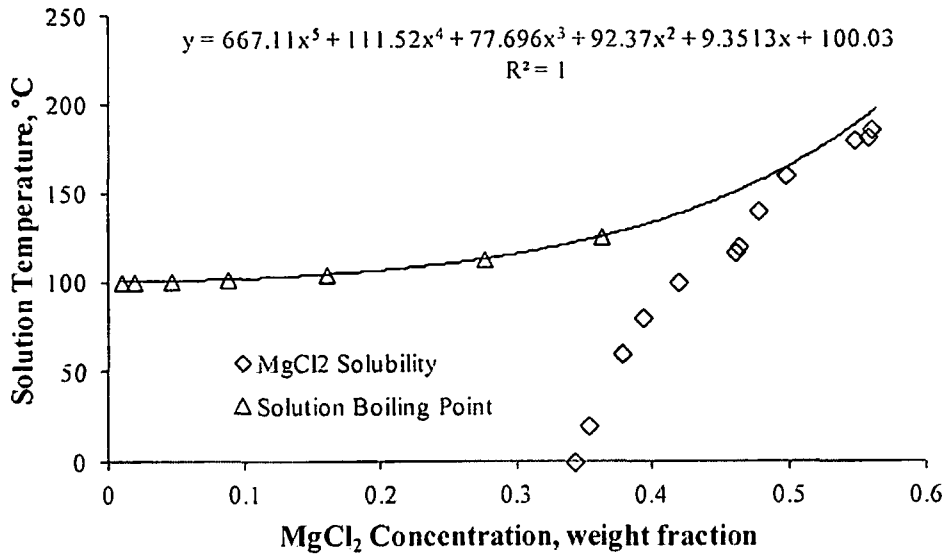

Figure 1 Aqueous Solubility of Magnesium Chloride with Temperature and Boiling Point of Magnesium Chloride Aqueous Solutions from Wagman et al.

The boiling point calculated from the polynomial fit is above the respective temperature of the saturation experiment for any given magnesium chloride solubility. It should be pointed out that calculated boiling points from extrapolation beyond the actual measured values can be associated with considerable uncertainty. Table 1 gives for various temperatures the solubility and the computed boiling point using the polynomial fit of the saturated solution.

Table 1 Calculated Boiling Point at Saturation Experiment Temperature.

Temperature of Saturation °C	$MgCl_2$ Solubility weight fraction	Polynominal Calculated Boiling Point °C
186	0.559	195
181.5	0.557	194
180	0.547	188
160	0.497	164
140	0.478	156

de Bakker[2] plotted considerably more measurements than provided in Wagman et al. and prepared the following figure (Figure 2).

[2] de Bakker, J.S.C., "The recovery of magnesium oxide and hydrogen chloride from magnesium chloride brines and molten salt hydrates." Ph.D. Dissertation, Department of Mining Engineering, Queen's University, Kingston, Ontario, Canada, p 34, 2011.

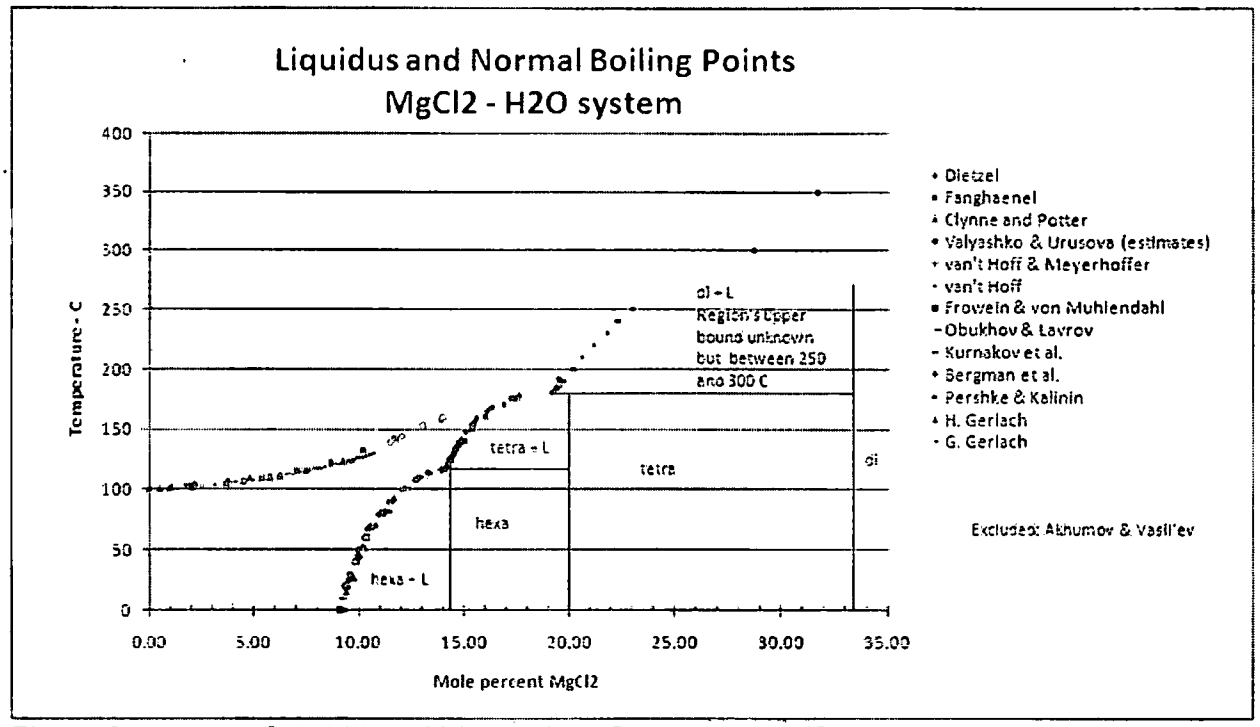

Figure 2 Aqueous Solubility of Magnesium Chloride with Temperature and Boiling Point of Magnesium Chloride Aqueous Solutions. Source: de Bakker, 2011.

This figure shows that liquid (L) exists above 250 °C, which would not be the case if the WRTO contention was true. The figure shows three solid phases including magnesium chloride hexahydrate (hexa), magnesium chloride tetrahydrate (tetra) and magnesium chloride dihydrate (di). de Bakker provides that, at about 117 °C, the hexahydrate melts incongruently forming the tetrahydrate and liquid. A similar phase transition appears in the figure for the tetrahydrate to dihydrate and liquid at about 181°C.

WRTO statement on page 17

Note that a National Fire Protection Association ("NFPA") water reactivity rating of 1 is defined as "May become unstable at elevated temperatures and pressures; may be mildly water reactive;" while a rating of 2 is defined as "Unstable; may undergo violent decomposition, but will not detonate; may form explosive mixtures with water."

Comment

According to the 2012 edition of NFPA 704[3], a water reactivity grading of 1 has the following qualitative criteria: "Materials that react vigorously with water, but not violently". A grading of 2 has the following qualitative criteria: "Materials that react violently with water, including the ability to boil water, or that evolve flammable or toxic gas at a sufficient rate to create hazards under emergency response conditions." The Western Zirconium waste reacts violently with water, including the ability to boil water, and evolves flammable and toxic gas at a

[3] NFPA® 704 *Standard System for the Identification of the Hazards of Materials for Emergency Response – 2012 Edition*. p. 704-19, NFPA, 1 Batterymarch Park, Quincy M. Available online (last accessed August 29, 2012) at http://www.nfpa.org/onlinepreview/online_preview_agreement.asp?id=70412.

sufficient rate to create hazards.

In 1980, in the rulemaking background document for the hazardous waste characteristic of reactivity, EPA provided the following regarding the narrative provided in the regulations: "The prose definition chosen is a paraphrase of the top three of the reactive classes of the National Fire Protection Association (NFPA) reactivity classification system. The other two classes in the NFPA classification system are not included since these would include materials which are inert under normal handling conditions."[4] This seems to provide that materials with NFPA reactivity grading of 2 or more were intended by EPA to be regulated as reactivity characteristic hazardous waste. However, tabulation of the hazardous waste listed (Table 2) because of the reactivity characteristic includes zinc phosphide, which has a NFPA grading of 1.

Table 2 Listed Hazardous Waste because of the Reactivity Characteristic

EPA Hazardous Waste No.	Substance	NFPA Reactivity Grading
U006	acetyl chloride	2
P006	aluminum phosphide	2
U133	hydrazine	3
U223	toluene diisocyanate	2
U189	phosphorus sulfide	2
P122	zinc phosphide	1

Hence, regardless of statements in the background document, materials with NFPA reactivity grading of 1 or more are regulated by EPA as hazardous waste that exhibit the characteristic of reactivity.

WRTO statement on page 17

The NFPA rating is based on measuring the heat of reaction of a 1:1 weight mixture of the substance with water, expressed as cal/g of total mixture. From the thermodynamics in Reference 4, the computed heat of reaction for anhydrous $MgCl_2$ tested in this way(13) would be -0.38 kJ/g (-90.5 cal/g), consistent with NFPA Water Reactivity Hazard Degree 1 criterion of between -30 and -100 cal/g.

Comment

The water reactivity identification criteria of Annex F of NFPA 704, "is not a part of the requirements of this NFPA document but is included for informational purposes only."[5]

As provided in footnote 13 on page 17, the WRTO-computed heat of reaction is not for a 1:1 weight mixture of the substance with water. The heat of reaction was calculated for the reaction of 1 gram of anhydrous magnesium chloride and 0.438 gram of water. The heat of reaction was then divided by the sum of 1 gram of magnesium chloride and 1 gram of water to obtain a value of -90.5 cal/g. The WRTO calculation is nonsensical. On one hand, WRTO

[4] EPA, Background Document Resource Conservation and Recovery Act, Subtitle C – Identification and Listing of Hazardous Waste, §261.23 – Characteristic of Reactivity, May 2, 1980, p 11.

[5] NFPA® 704 *Standard System for the Identification of the Hazards of Materials for Emergency Response – 2012 Edition.* p. 704-18, NFPA, 1 Batterymarch Park, Quincy M. Available online (last accessed August 29, 2012) at http://www.nfpa.org/onlinepreview/online_preview_agreement.asp?id=70412.

calculates the heat of reaction of 1 gram of magnesium chloride with 0.438 gram of water, while on the other hand, WRTO divides the heat of reaction by the sum of 1 gram of magnesium chloride and 1 gram of water.

Footnote 13 on page 17 correctly provides that 1 gram of anhydrous magnesium chloride is 0.0105 mole and 1 gram of water is 0.0559 mole and the mole ratio of water to magnesium chloride is 5.29 (actually 5.285). However, the products of the reaction used by WRTO of 0.0046 mole of magnesium chloride tetrahydrate and 0.0059 mole of magnesium chloride monohydrate is a ratio of 2.31 mole of water per magnesium chloride, which means only 0.438 gram of water was reacted. For this reaction, the heat of mixing is -124 cal/g rather than -90.5 cal/g. Table 3 shows the correct calculation for the WRTO reaction.

Table 3 Calculation for the Heat of Mixing for WRTO Reaction of 1 gram Anhydrous Magnesium Chloride with 0.438 grams of Water forming Monohydrate and Tetrahydrate using Heat of Formations from Wagman et al.

$MgCl_{2(s)} + 2.31\ H_2O_{(l)} \rightarrow 0.562\ MgCl_2 \cdot H_2O_{(s)} + 0.438\ MgCl_2 \cdot 4H_2O_{(s)}$

					ΔH_f			ΔH_{mix}
		g/mole	g	mole	kJ/mol	kJ	calorie	cal/gram
Reactant	$MgCl_{2(s)}$	95.2104	1	0.010503	-641.905	-6.74196		
Reactant	$H_2O_{(l)}$	18.01528	0.438	0.024313	-285.83	-6.9493		
Product	$MgCl_2 \cdot 4H_2O$	167.2715		0.0046	-1898.99	-8.73535		
Product	$MgCl_2 \cdot H_2O$	113.2257		0.0059	-966.63	-5.70312		
				$\Delta H_{rxn} = \sum$Products - $\sum$Reactants =		-0.74721	-178.588	-124.192

Magnesium chloride tetrahydrate ($MgCl_2 \cdot 4H_2O$) and magnesium chloride monohydrate ($MgCl_2 \cdot H_2O$) were not detected by NEIC using X-ray diffraction for the reaction product of ATI titanium production waste with water. Only magnesium chloride hexahydrate was detected. Magnesium tetrahydrate was detected as a minor component for some of the original samples of waste from ATI. The WRTO calculation, however, assumes no magnesium chloride hexahydrate is formed, which is contrary to the existing evidence and WRTO's own statement on page 45: "This behavior is consistent with WRTO observations, where large quantities of undissolved solids remained behind, probably $MgCl_2 \cdot 6H_2O$ that consumed water at the reaction surface by hydration rather than solution." On one hand, WRTO concludes that magnesium chloride hexahydrate is formed by the reaction with water, while on the other hand, WRTO's calculation of the reaction does not form magnesium chloride hexahydrate but rather magnesium chloride monohydrate and magnesium chloride tetrahydrate.

It is impossible for a combination of magnesium chloride tetrahydrate and magnesium monohydrate to give a molecular ratio of 5.285 water molecules per magnesium chloride molecule. Such a combination must give something less than 4 water molecules per magnesium chloride molecule. However, a combination of magnesium chloride hexahydrate and magnesium chloride tetrahydrate could give 5.285 water molecules per magnesium chloride molecule. The mole fraction mass balance equation is as follows, where x is the mole fraction of magnesium chloride hexahydrate.

$$5.285 = 6x + 4(1-x) = 2x + 4$$
$$2x = 1.285$$
$$x = 0.6425$$

Applying the WRTO calculation to these products of the reaction gives -1.386 kilojoules (kJ) or -165.68 cal/g for the reaction, which is about 1.8 times the heat of the WRTO calculated value and well over -100 cal/g, as shown in Table 4.

Table 4 Calculation for the Heat of Mixing for the Reaction of 1 gram Anhydrous Magnesium Chloride with 1 gram of Water forming Tetrahydrate and Hexahydrate using Heat of Formations from Wagman et al.

$MgCl_{2(s)} + 5.285\ H_2O_{(l)} \rightarrow 0.645\ MgCl_2 \cdot 6H_2O_{(s)} + 0.355\ MgCl_2 \cdot 4H_2O_{(s)}$

					ΔH_f			ΔH_{mix}
		g/mole	g	mole	kJ/mol	kJ	calorie	cal/gram
Reactant	$MgCl_{2(s)}$	95.2104	1	0.010503	-641.905	-6.74196		
Reactant	$H_2O_{(l)}$	18.01528	1	0.055508	-285.83	-15.866		
Product	$MgCl_2 \cdot 6H_2O$	203.3021		0.006748	-2499.02	-16.8639		
Product	$MgCl_2 \cdot 4H_2O$	167.2715		0.003755	-1898.99	-7.13041		
				$\Delta H_{rxn} = \sum$Products - $\sum$Reactants =		-1.38639	-331.354	-165.677

WRTO statement on page 25 footnote 25

Of all the compounds shown in Figure 7, the only one where the reaction with water is formation of a hydrate plus heat of mixing is H_2SO_4 (all others are hydrolysis reactions). Since sulfuric acid actually does provide essentially the same temperature rise irrespective of order of mixing, it was hypothesized that $MgCl_2$ might as well. The actual value of ΔT is also very similar for $MgCl_2$ and H_2SO_4.

Comment

Figure 7 shows that sulfuric acid gives a temperature rise very close to that of the Western Zirconium waste. In 1975, the NFPA reactivity grading for sulfuric acid was two (2) with a water reactivity symbol of ~~W~~. The following was also provided: "Not flammable but highly reactive and capable of igniting finely divided combustible materials on contact. Reacts violently with water and organic materials with the evolution of heat. Extremely hazardous in contact with many materials, particularly carbides, chlorates, fulminates, nitrates, picrates, powdered metals and other combustible materials. Attacks many metals, releasing hydrogen."[6] EPA regulations at 40 Code of Federal Regulations (CFR) §261.23 provide the following for the characteristic of reactivity: "(a) A solid waste exhibits the characteristic of reactivity if a representative sample of the waste has any of the following properties:" and (2) "It reacts violently with water." Therefore, samples of waste, such as the Western Zirconium waste, reacting similarly to sulfuric acid with water would have the reactivity characteristic.

Applying the WRTO heat of mixing calculation for the reaction of 1 gram of sulfuric acid and 1 gram of water and using the heat of formations from WRTO's reference, (Wagman et al.) gives -71.6 cal/g as the heat of mixing. This indicates the NFPA description of reacts violently with water for sulfuric acid does not rely on a heat of mixing of greater than -100 cal/g.

HYDROGEN EVOLUTION

WRTO statement on page 3

[6] NFPA®, Hazardous Chemicals Data 1975, NFPA No. 49, pp 49-275 – 49-276, National Fire Protection Association, Boston, MA, 1975.

The lower explosive limit ("LEL") of hydrogen is not equal to 4%; this belief is a widely circulated misconception, with the misunderstanding extended to NFPA guidelines but refuted by organizations including the Underwriters Laboratories and several National Laboratories. The actual LEL value is greater than 18% in dry air, whereas the 4% number represents the lower flammability limit ("LFL") in dry air.

Comment

An Idaho National Engineering and Environmental Laboratory publication provides that the hydrogen lower "deflagration explosion" limit and hence the flammability limit is 4.1%, while the hydrogen lower detonation explosion limit is 18.3%.[7] In 1980, EPA provided in the rulemaking background document for the hazardous waste characteristic of reactivity, the following regarding the narrative provided in the regulations: "Additionally, these categories overlap not only with each other, but also with the other characteristics. For example, the difference between flammability (conflagration) and explosiveness (deflagration) is only one of degree...."[8] The statement indicates that a deflagration explosion was the concern for the hazardous waste characteristic of reactivity for the rulemaking. Further, the background document states that much of the reactivity narrative was taken from the National Fire Protection Agency, which had also been adopted by the Navy, the Chemical Manufacturers Association, and States of California and Oklahoma.

EPA[9] regulations reference NFPA and define an explosion as a 1 pound per square inch (psi) increase. OSHA regulations[10] specify the flammable limit is the explosion limit and define an explosion as a 7% pressure increase or 1 psi increase starting at one atmosphere. NFPA defines an explosion as "The bursting or rupture of an enclosure or a container due to the development of internal pressure from deflagration," define deflagration as "Propagation of a combustion zone at a velocity that is less than the speed of sound in the unreacted medium," and define detonation as "Propagation of a combustion zone at a velocity that is greater than the speed of sound in the unreacted medium."[11] A recent study by NIOSH comparing various testing devices verified the 4% explosion limit for hydrogen and provided discussion of the explosion criterion.[12] As well, a National Academy of Science publication[13] referencing an EPA

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[7] Cadwallader, L.C.; Herring, J.S. *Safety Issues with Hydrogen as a Vehicle Fuel*, INEEL/EXT-99-00522, Idaho National Engineering and Environmental Laboratory, Lockheed Martin Idaho Technologies Company, Idaho Falls, Idaho, p.13, 21-26, 1999.

[8] EPA, Background Document Resource Conservation and Recovery Act, Subtitle C – Identification and Listing of Hazardous Waste, §261.23 – Characteristic of Reactivity, May 2, 1980, p 11-12.

[9] 40 CFR 68.22(a)(i) "Explosion. An overpressure of 1 psi." "Lower flammability limit. A lower flammability limit as provided in NFPA documents or other generally recognized sources." p. 167, July 1, 2011 edition.

[10] 29 CFR 1915.11(b) "*Lower explosive limit* (LEL) means the minimum concentration of vapor in air below which propagation of a flame does not occur in the presence of an ignition source." "*Upper explosive limit* (UEL) means the maximum concentration of flammable vapor in air above which propagation of flame does not occur on contact with a source of ignition." p 36, July 1, 2010 edition.

[11] NFPA® 69 Standard on Explosion Prevention Systems – 2008 Edition. p. 69-7, NFPA, 1 Batterymarch Park, Quincy MA. Available online (last accessed August 30, 2012) at http://www.nfpa.org/onlinepreview/online_preview_agreement.asp?id=70412.

[12] "In the 20-L chamber, the 7% pressure-rise criterion was satisfied at 6% H2 in air. With a meter-long upward flame propagation criterion in vertical flammability tubes, the LFL was found to be 4%. The much shorter 30 cm tubes used in the EN 1839 (T) method gave an LFL of 3.6%" Zlochower, I.A.; Green, G.M. "The limiting oxygen concentration and flammability limits of gases and gas mixtures," *Journal of Loss Prevention in the Process Industries*, 22(4), 499-505, 2009.

publication[14] states that 4.1% is the explosive limit.

WRTO references a presentation given by Harry Jones of Underwriters Laboratories at a Hydrogen Safety Sensor Workshop in Washington, DC, hosted by the Las Alamos National Laboratory and the Lawrence Livermore National Laboratory in April 2007. In NEIC's personal communication with Harry Jones, he said the difference between conflagration, deflagration, and detonation was not his expertise. His concern was that persons preparing specifications for devices and equipment for use in a hazardous environment be aware of the hazards presented by hydrogen.

WRTO statement on page 4

The NEIC data also measured the maximum hydrogen by gas chromatography, which requires that the sample be dry before injection; the 10.8% figure reported was therefore on a dry-gas basis. Energy balance calculations indicate that whatever H_2 is produced will be highly diluted with steam by as much as an estimated 250:1, making the actual hydrogen concentrations from a "real-world" situation much lower than those reported by NEIC.

Comment

This contention is simply not true. The NEIC hydrogen measurements were corrected for altitude and temperature and are not reported on a dry-gas basis. All measurements were corrected to the initial sample volume drawn from the headspace. The "real-world" values are reported. Water condensed in the injection loop was evaporated by backflushing between injections.

Considerable steam was created for the Mason and Cooper testing for the addition of 10 grams of water to 10-gram and 20-gram subsamples and in the dumpster scenario testing, where an equal weight water and sample was used. However, this was not the case for the 1-gram and 2-gram subsamples for the Mason and Cooper testing or for the N5 testing. For the N5 testing, hydrogen concentrations of the gas evolved ranged from 36 to 66%. The remaining gas was the air in the sample and dissolved in water. These mixtures were well above the lower explosive limit and contained little water vapor because the temperature was near ambient at the gas-water interface.

Janès et al.[15] recently studied the effects of some experimental design parameters for the N5 test using elemental magnesium to generate hydrogen and concluded that mass-to-water ratio, temperature, etc., can play a significant role in the testing results. WRTO and NEIC conducted the N5 testing such that the temperature achieved was moderate, generally around 30 °C to 40 °C, while the NEIC dumpster scenario testing and Mason-Cooper testing were conducted at temperatures as high 140 °C. Janès et al. show that the rate of release and amount

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[13] "Hydrogen is an explosive gas. The U.S. Environmental Protection Agency (EPA 1988) recommends evacuation of personnel when the concentration of an explosive gas reaches 10% of the lower explosive limit. Ten percent of the lower explosive limit, or 4,100 ppm, of hydrogen is less than the hydrogen concentration required to reduce oxygen in submarine air to the 1-h or 24-h EEGL or the 90-day CEGL." *Emergency and Continuous Exposure Guidance Levels for Selected Submarine Contaminants*: Volume 2. p 153, Washington, DC: The National Academies Press, 2008.

[14] EPA. Air Surveillance for Hazardous Materials. Environmental Response Team, Office of Emergency and Remedial Response , U.S. Environmental Protection Agency, Washington, D.C. 1988.

[15] Janès, A.; Marlair, G.; Chaineaux, C.J.; Towards the improvement of UN N.5 test method for the characterization of substances which in contact with water emit flammable gases. Journal of Loss Prevention in the Process Industries 25, 524-534, 2012.

of hydrogen generated from the reaction of the waste with water is a function of temperature. According to Janès et al. work, less than 1 % of the total elemental magnesium reacts during the N5 testing.

WRTO statement on page 5

To produce an explosive mixture with 0.90 L H_2 from 1 kg of Grade C material (data from Figure 30), using the more conservative potential detonation limits (14 to 70%) from Reference 65, would require the entire hydrogen generation from a kilogram of salt to be mixed with a very limited volume X of dry air:

$$0.14 \leq (0.90)/(X + 0.90) \leq 0.70$$

or $0.4 \leq X \leq 5.5$ liters. While theoretically possible, accidental occurrence of this configuration seems highly unlikely, especially since the hydrogen being evolved will also be mixed and diluted with a large amount of steam which reduces its explosivity.

Comment

As mentioned previously for NEIC's N5 testing, the hydrogen concentrations of the gas evolved ranged from 36 to 66%. This concentration range brackets the concentration expected from the waste's bulk density of about 0.9 gram per cubic centimeter and the crystal density of anhydrous magnesium chloride of 2.32 grams per cubic centimeter. This means that any volume of the waste is composed of approximately 38.8% magnesium chloride and 61.2% air. One kilogram of waste would occupy a volume of about 1.11 liters, which would contain about 0.68 liter of air. The generation of 0.9 liter hydrogen mixed with 0.68 liter air would give a hydrogen concentration of 57%. Thus, the waste as generated contains the air when mixed with water that could generate an explosive atmosphere. Hence, handling the waste in a confined space or container with no headspace may not arrest the hazard presented by the waste's ability to generate hydrogen.

Certainly, any generation of hydrogen from a waste has a concentration gradient if it is dispersed and not all concentrations would pose a hazard. For such dispersal, the hydrogen concentration would be greatest near the waste reactions and less at distance. Nevertheless, some type of confinement is usually necessary for an explosion to occur. Wastes are handled indoors and in containers such as drums and totes and in tanks, and some are disposed of in dumpsters and rolloffs. All such confinement has the potential to result in a hydrogen and air mixture falling in the WRTO's range. The current storage of the Grade A waste in a silo at Western Zirconium is another situation that has the potential to result in explosive atmosphere if nitrogen were not used to exclude air and water.

Mixing sodium chloride with water will not generate an explosive atmosphere, regardless of the weight mixture with water or the mixture's headspace ratio or the level of confinement. This is, however, not the case for the zirconium production waste. Special procedures must be used to ensure the zirconium production waste does not get wet at certain ratios, is not stored with certain waste to air ratios or is stored under nitrogen, is not stored in plastic with a melting point of less than 250 °C or 350 °C, and does not get confined so that its reactivity characteristics are not demonstrated.

Using a 14 to 70% detonation explosive range is not conservative with regard safety. The more conservative approach would be to use the 4 to 84% deflagration explosive range for this calculation. Further, WRTO also measured 1.4 liters of hydrogen per kilogram, which, if used in

the calculation, would be more conservative than the 0.9 liter of gas per kilogram. WRTO's estimate of the elemental magnesium content of the waste based on insoluble magnesium was three times more than the elemental magnesium content reacted for the N5 testing. Hence, the use of 4.2 liters of hydrogen per kilogram of waste in the calculation would be more conservative with regard to safety considerations.

NEIC recently conducted experiments showing the headspace ignitions above mixtures of waste and water, with the waste representing 15 weight percent and 84 weight percent of the mixture. The ignitions for mixtures of 15 weight percent waste where the reaction was allowed to proceed overnight are shown in **Video 1.**

By allowing the reaction to occur overnight, the steam that was formed condensed, leaving a hazardous atmosphere.

The ignitions for mixtures of 15 weight percent waste where the reaction was allowed to proceed two hours are shown in **Video 2**.

By allowing the reaction to occur for two hours, the steam that was formed condensed, leaving a hazardous atmosphere.

The ignitions for mixtures of 15 weight percent waste where the reaction was allowed to proceed for about 30 minutes are shown in **Video 3**. These videos show an initial ignition and then re-ignition of the headspace for two reactions. WRTO claims the majority of hydrogen was generated within 30 minutes and, hence, the use of this duration. Because some cooling did occur, a little steam condensed. Nevertheless, the atmosphere was hazardous.

The ignition for a mixture of 84 weight percent waste where the reaction was allowed to proceed for 30 minutes is shown in **Video 4.**

Considerable steam initially formed for this reaction but quickly reacted with excess anhydrous magnesium chloride and elemental magnesium, leaving a hazardous atmosphere.

Steam formation is a hazard itself; besides the heat which could cause scalding and violent rupture of a closed container, air displacement occurs which might result in an oxygen-deficient atmosphere.

WRTO statement on page 53

The flammability map shown in Figure 31 indicates slightly broader ranges, namely 4 to 78% mole (volume) for flammability, and 14 to 70% for potential detonation.

Comment

Figure 31 of the WRTO report was taken from Sherman et al.[16] Sherman et al. provides that the figure shows the flammability limits taken from Marshall.[17] This figure, as it appears in Sherman et al., does not appear in Marshall. Figures similar to the following Figure 3 are contained in Marshall.

[16] M. P. Sherman, M. Berman, and R. F. Beyer, "Experimental Investigations of Pressure and Blockage Effects on Combustion Limits in H2Air Steam Mixtures," SAND-91-0252, Sandia National Laboratory, Albuquerque NM, 1993, p. 35.

[17] Marshall, B.W, "Hydrogen:Air:Steam Flammability Limits and Combustion Characteristics in the FTS Vessel." NUREG/CR-3468. SAND84-0383, Sandia National Laboratory, Albuquerque NM, 1986, p. 20.

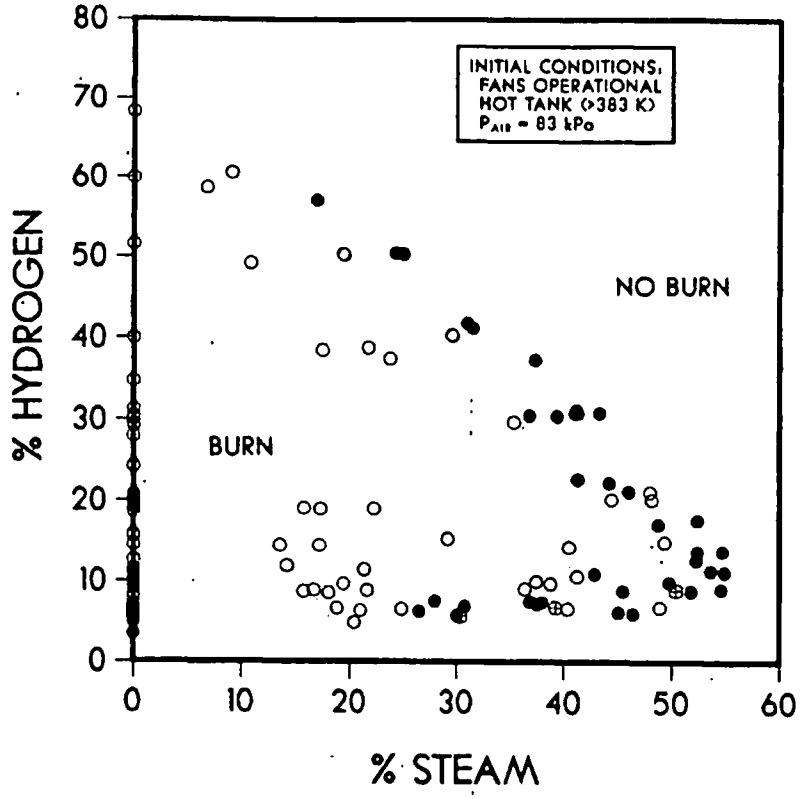

Figure 3 Hydrogen:Air:Steam Flammability Data Presented as Figure 8 in Marshal.

WRTO statement on page 57

The question of whether Mg or Zr is responsible for generation of H_2 is clarified by the following argument. Magnesium reacts to form solid MgO per Reaction (7), and MgO will in turn react with water to form magnesium hydroxide according to:

$$MgO + H_2O \rightarrow Mg(OH)_2 \quad (11)$$

The $Mg(OH)_2$ is essentially insoluble in water (solubility S° = 0.009 g/L at 18°C).(71) Therefore, any MgO or $Mg(OH)_2$ formed from reaction of magnesium metal would both report to the insoluble materials, so that the Mg content of the insolubles represents all of the elemental Mg present in the initial salt sample.

Comment

de Bakker provides a review of the studies of the formation of a magnesium oxychloride complex that increases the solubility of magnesium oxide. de Bakker conducted experiments and concludes the amount of magnesium oxide dissolved and speed with which it did so was strongly dependent on the magnesium chloride concentration. Table 5 presents the solubility of magnesium oxide with increasing dissolved magnesium chloride.

Table 5 Maximum transient concentrations of dissolved MgO in MgCl2 solutions. Data of Chassvent.

Wt % MgCl2	0 (pure water)	10%	20%	25%	30%
g MgO per 1000 g water	0.0086	1	14	27	43

The stability of the complex is transient and its breakdown can be very slow. Therefore, the reliability of an elemental magnesium content determination based on measuring the magnesium that did not dissolve depends on whether the experimental design favored the aqua complex formation.

HYDROGEN SULFIDE EVOLUTION

WRTO statement on page 28

Corrections were also made for the solubility of H_2 in water; Henry's Law constants for both hydrogen and hydrogen sulfide are shown in Figure 11 and Figure 12, where K is the ratio of the partial pressure of the gas in the vapor space (torr) divided by the mole fraction of the gas dissolved in the liquid phase.

Comment

The units for the Henry's law constant for the y-axis of the figures are incorrect. The power should be positive rather than negative. For example, the figures give Henry's law constants at 25 °C of about 5.4×10^{-7} torr/mole-fraction for hydrogen and about 4.2×10^{-5} torr/mole-fraction for hydrogen sulfide. These values give the partial pressure of hydrogen as smaller than the partial pressure of hydrogen sulfide, which is not reasonable. The values should be 5.4×10^{7} torr/mole-fraction for hydrogen and about 4.2×10^{5} torr/mole-fraction for hydrogen sulfide.

The National Institute of Standards and Technology (NIST) gives Henry's law constants at 25 °C of 0.00078 molal/bar for hydrogen and 0.10 molal/bar for hydrogen sulfide.[18] Inverting these values gives 1282 bar/molal for hydrogen and 10 bar/molal for hydrogen sulfide. A bar is 750 torr, and conversion gives 961,615 torr/molal for hydrogen and 7,500 torr/molal for hydrogen sulfide. One molal equals 0.0177 mole-fraction, and conversion gives 54,300,000 torr/mole-fraction for hydrogen and 424,000 torr/mole-fraction for hydrogen sulfide.

WRTO statement on page 28

Analysis of test runs shows that with 650 mL of water in a 1 L flask, the fractions of H_2 and H_2S dissolved in the liquid phase are only 3.3% and 4.0% respectively at 30°C liquid temperature. The Henry's Law correction is therefore minor in both cases.

Comment

The partitioning calculation is incorrect. Having 3.3% of the hydrogen and 4.0% of the hydrogen sulfide remain in the liquid would mean the Henry's law constants of two substances would have to be almost the same. However, this is not the case. The Henry's law constants

[18] Sander, R., "Henry's Law Constants" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, March 2003, National Institute of Standards and Technology, Gaithersburg MD, 20899. Available online: http://webbook.nist.gov.

differ by more than a factor of 100.

The partition calculated for hydrogen sulfide is incorrect. The effective Henry's law constant for hydrogen sulfide is pH dependent. Solving for the partitioning at a temperature of 30 °C with 0.65 liter (L) of aqueous liquid at pH at 10 and a 0.35 L headspace gives only 0.025% of the sulfide partitioning to the headspace.

$M_{sulfide}$: moles of total sulfide in the system (headspace + aqueous phase)
M_{air}: moles of hydrogen sulfide in the headspace
$M_{aqeuous}$: moles of total sulfide in the aqueous phase
C_{air}: concentration of hydrogen sulfide in the headspace
$C_{aqueous}$: concentration of total sulfide in aqueous phase
V_{air}: headspace volume
$V_{aqueous}$: aqueous phase volume
K_h = Henry's law constant = 0.10 M/bar
$d(\ln(K_h))/d(1/T) = K_h$ change with temperature
$*K_h$ = effective Henry's law constant
$pK_a = 7.02$[19], negative the logarithm of the acid dissociation constant

Mass balance
$M_{sulfide} = C_{aqueous}V_{aqueous} + C_{air}V_{air}$

Henry's law
$K_h(T) = (K°_h)(\exp(d(\ln(K_h))/d(1/T)\ ((1/T) - 1/(298.15\ K))$
$K_h(T) = (0.10\ M/bar)(\exp((2100)\ ((1/T) - 1/(298.15\ K)))(1.01325\ bar/atm)$
$T = 30°C = 303.2°K$
$K_h = 0.0902\ M/atm$
$K_h* = (K_h)(1+10^{(pH - pKa)}) = (0.0902)(1+10^{(10-7.02)}) = 86.242\ M/atm$

Solving for the dimensionless Henry's law constant
$m = C_{air}/C_{aqueous} = 1/(K_hRT) = 0.000466$
$C_{aqueous} = C_{air}/m$
$C_{air} = mC_{aqueous}$

Substitution for $C_{aqueous}$ in the mass balance
$M_{sulfide} = (C_{air}/m)V_{aqueous} + C_{air}V_{air}$

Rearrangement and solving for M_{air}
$C_{air} = (M_{sulfide}) / [(V_{aqueous}/m) + V_{air}]$
$C_{air} = (M_{sulfide}) / [(0.65\ L/0.000466) + 0.35\ L]$
$C_{air} = (M_{sulfide}) / 1395\ L = 0.000717\ M_{sulfide} / L$
$M_{air} = (0.000717\ M_{sulfide} / L)(0.35\ L) = 0.00025\ M_{sulfide}$

Substitution for C_{air}

[19] Motekaitis, R.J. "NIST Critically Selected Stability Constants of Metal Complexes," Standard Reference Database 46; Version 4.0; Eds. A.E. Martell and R.M. Smith, November 1997. National Institute of Science and Technology, Gaithersburg MD, 20899.

$M_{sulfide} = C_{aqueous}V_{aqueous} + mC_{aqueous}\ V_{air}$

Rearrangement and solving for $M_{aqueous}$
$M_{sulfide} = (C_{aqueous})(V_{aqueous} + mV_{air})$
$C_{aqueous} = M_{sulfide} / (0.65\ L + (0.000466)(0.35\ L))$
$C_{aqueous} = M_{sulfide} / (0.65016\ L) = 1.53808\ M_{sulfide} / L$
$M_{aqueous} = (1.53808\ M_{sulfide} / L)(0.65\ L) = 0.99975\ M_{sulfide}$

WRTO statement on page 5

Careful analysis of the offgas from mixing WZ $MgCl_2$ with water showed traces of hydrogen sulfide above the 0.1 ppm lower detection limit ("LDL") of the Dräger®-style tube colorimetric analysis. The Grade A-1 and Grade C materials, constituting greater than 99% of all the $MgCl_2$ produced by Western Zirconium, produced no greater than 0.60 ppm H_2S (as measured in the headspace above a reacting water-salt mixture).

Comment

WRTO's analysis was not careful, as WRTO apparently misunderstand fundamental chemical principles involving Henry's law and acid dissociation.

NEIC conducted experiments similar to WRTO's testing involving 10 grams and 650 mL of water in a 1-liter glass flask. Instead of Drager tubes, NEIC used a Jerome 631X hydrogen sulfide analyzer. The pH of these solutions were greater than 9 based on pH paper, and a pH of 9.3 was calculated using EPA's computer program for aqueous chemistry, MINTEQA2[20], and measured potentiometrically for this ratio for one of the samples. Contrary to WRTO's contention, little hydrogen sulfide will partition to the headspace at pH 9.3. After headspace measurements similar to WRTO's were made, the test solution was acidified to about pH 2 and headspace hydrogen sulfide measurements were made. Table 6 shows the results of this testing corrected for barometric pressure (0.822 atmosphere).

[20] Allison, J.D., D.S. Brown, and K.J. Novo-Gradac (1991) MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual. United States Environmental Protection Agency, Office of Research and Development, Washington, DC, EPA/600/3-91/021, 106p. [MTQ3.11].

Table 6 Headspace Hydrogen Sulfide Concentrations with and without Acidification to pH 2 for the NEIC Zirconium Production Waste Samples.

NEIC Tag Number	Sample Mass g	Water Volume mL	H_2S Headspace No Acid ppmv	2 N HCl Volume mL	H_2S Headspace With Acid ppmv
NE30178	10	650	0.043	5	8.6
NE30178	10	650	0.000	3	1.6
NE30178	10	650	0.002	3	2.7
NE30178	10	650	0.170	3	30
NE30179	10	650	0.000	3	0.157
NE30179	10	650	0.000	3	0.99
NE30179	10	650	0.000	3	5.0
NE30179	10	650	0.067	3	0.011
NE30179	10	650	0.043	3	9.1
NE30180	10	650	0.024	3	3.4
NE30180	10	650	0.030	3	4.4
NE30180	10	650	0.019	3	5.1
NE30180	10	650	0.017	3	4.3

As the results in Table 6 show, considerable hydrogen sulfide was generated in the system once the pH was lowered. The RCRA hazardous waste characteristic of reactivity for sulfide-bearing waste is concerned with release of hydrogen sulfide between pH 2 and pH 12.5. Even at pH 2, the majority of the hydrogen sulfide is in the water for a system with 650 mL of water and 430 mL of air. The water acts as a sink. The maximum temperature for the system was about 25 °C for the tests. At higher temperatures, such as for Mason-Cooper testing and dumpster scenario testing where equal weight sample and water were used and temperatures up to 140° C were measured, considerably more hydrogen sulfide would partition to air.

The headspace hydrogen sulfide measurements with acid are generally much higher than for those without acid. This behavior is predicted by common chemical equilibria principles as provided below. The high heterogeneity of the waste with relative standard errors as high as 62% were observed for the test data for sample NE30178, with headspace hydrogen sulfide ranging from 1.6 ppmv to 30 ppmv. This heterogeneity was also observed in the acid volatile sulfide results reported previously. The smell of hydrogen sulfide was evident upon opening the samples, which had been stored for about 9 months, while transferring the test solutions from the flasks to the waste containers and while cleaning the flasks.

For some headspace tests, the hydrogen sulfide concentration would decrease over time after the addition of the acid. This behavior is illustrated in Figure 4.

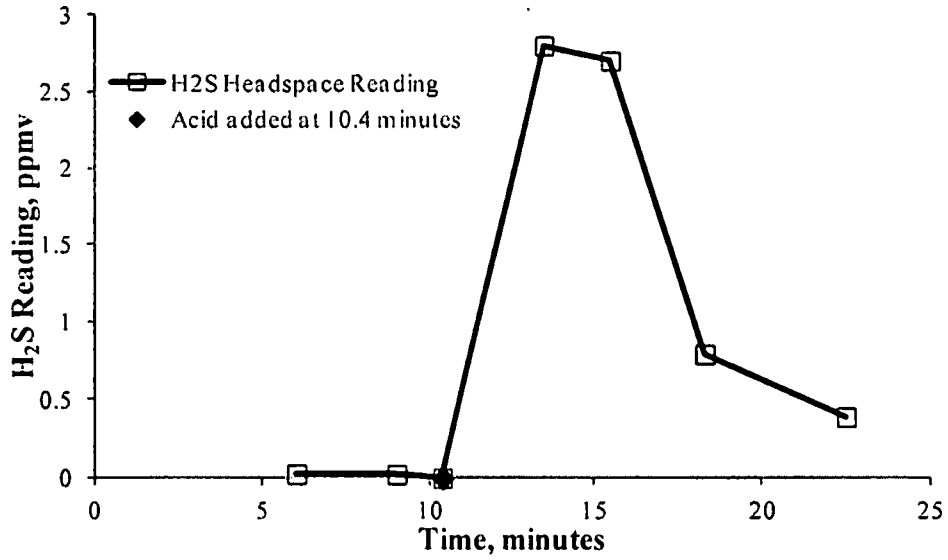

Figure 4 Hydrogen sulfide headspace concentration time profile for 10 grams of NE30180 and 650 mL water.

The addition of acid may cause the dissolution of some zirconium oxide, which leads to the precipitation of zirconium sulfide and, hence, the lowering of the hydrogen sulfide headspace concentration. Since the acid volatile sulfide test was conducted similarly under acidic conditions, this chemistry may have led to underestimation of the sulfide content of the samples. The acid volatile sulfide was determined by combining 0.5 gram of sample and 2 mL of 0.1 N hydrochloric acid. To further investigate the behavior, 5 grams of sample were combined with 20 mL of 0.1 N hydrochloric, the solutions were filtered through a 0.45-micron filter, and the filtrates were diluted and analyzed for zirconium by inductively coupled argon plasma optical emission spectroscopy. The hydrochloric acid dissolved considerable zirconium, which is consistent with the sulfide precipitation mechanism.

Presumably, the pH of greater than 9 is attributed to magnesium hydroxide formation from the hydrolysis of elemental magnesium by the following reactions.

$$Mg^{\circ} + H_2O \rightarrow MgO_{(solid)} + H_{2(gas)}$$
$$MgO_{(solid)} + H_2O \rightarrow Mg(OH)_{2(solid)}$$
$$Mg(OH)_{2(solid)} \rightleftarrows Mg^{2+} + 2OH^-$$

Magnesium hydroxide ($Mg(OH)_2$) has the mineral name of brucite. MINTEQA2 gives a pH of 10.37 for a saturated solution of brucite at 25 °C, 10.54 at 20 °C, 9.92 at 40 °C and 9.00 at 75°C. In the presence of 0.162 molal magnesium chloride (10 grams per 650 mL water), MINTEQA2 gives a pH of 9.095 at 25 °C and 9.254 at 20 °C for a saturated solution of brucite, which reflects the co-ion effect of the magnesium ion from the magnesium chloride and proton production from the hydrolysis of ionic magnesium. For sample NE30179, WRTO reports that it contains 22% insoluble solids. Therefore, in the presence of 0.126 molal magnesium chloride (7.8 grams per 650 mL of water), MINTEQA2 gives a pH of 9.145 at 25 °C and 9.304 at 20 °C for a saturated solution of brucite. A solution of 1 gram of sample NE30179 in 65 mL of reagent grade had a pH of 9.33 at 20.5 °C, as measured using glass membrane electrode potentiometry.

For the Mason-Cooper testing and the dumpster scenario testing, equal weight sample

and water were used. For these tests, hydrogen and hydrogen sulfide evolved immediately. The pH of the mixture of equal weight sample and water after reaction was about 4 to 5 using pH indicator paper. This low pH indicates that considerable acid was formed. Because of high ionic strength, the U.S. Geological Survey (USGS) computer program PHREEQC[21] with its Pitzer database was used instead of MINTEQA2 to calculate a pH of 4.5 at 25 °C for a 3 molal magnesium chloride solution. PHREEQC provides that the acid (proton) is from the hydrolysis of the magnesium ion forming a monovalent hydroxyl complex.

$$Mg^{2+} + H_2O \rightleftarrows MgOH^+ + H^+, \log K = 2.6$$ [22]

Table 7 presents the results corrected for barometric pressure (0.822 atmosphere) for the second set of experiments with the Jerome analyzer using the 1-liter flask with 10 or 20 grams of sample followed by an equal weight of reagent water (10 mL or 20 mL) as done for the Mason-Cooper testing.

Table 7 Headspace Hydrogen Sulfide Concentrations for Equal Weight Waste and Water.

NEIC Tag Number	Sample Mass g	Water Volume mL	H_2S Headspace No Acid Added ppmv
NE30179	10	10	2.6
NE30180	20	20	13
NE30180	10	10	6.2
NE30180	10	10	4.6
NE30180	10	10	2.8
NE30180	10	10	1.1
NE30180	10	10	5.1

The headspace temperature returned near ambient after about 30 minutes when measurements commenced. The average concentration for the 10-gram aliquot tests was 3.7 ppmv and 4.0 ppmv for sample NE30180. The headspace volume for testing results reported in Table 7 was about 1060 mL. The volume of the test tubes used for the Mason-Cooper testing was about 134 mL. For the headspace hydrogen sulfide measurements, the Mason-Cooper testing used 10 grams of zirconium production waste and 10 mL of water. The headspace volume would have been about 113 mL. Therefore, if the reaction gas bolus were diluted into a headspace volume of 113 mL, then concentrations of approximately 10 times those reported in Table 7 would be measured. Concentrations from 5.3 ppmv to 102 ppmv were measured for the

[21] Parkhurst, D.L., and Appelo, C.A.J. (1999). User's guide to PHREEQC (version 2)—a computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations. 99-4259, U.S. Geological SurveyWater-Resources Investigations Report. U.S. Geological Survey, Reston, VA.

[22] Motekaitis, R.J. "NIST Critically Selected Stability Constants of Metal Complexes," Standard Reference Database 46; Version 4.0; Eds. A.E. Martell and R.M. Smith, November 1997. National Institute of Science and Technology, Gaithersburg MD, 20899.

Mason-Cooper testing. The overall average for the Mason-Cooper testing was 38 ppmv, while an average of 33 ppmv was obtained for sample NE30180. Hence, the results reported in Table 7 are consistent with the results for the Mason-Cooper testing.

WRTO statement on page 5

In addition, NEIC reports that "a few samples" exhibited the characteristic rotten-egg smell of H_2S; whereas, their reported concentrations in all cases exceeded the olfactory threshold (0.07 ppm) by four orders of magnitude.

Comment

For NEIC's Mason-Cooper testing, after the reaction of the sample with water in the open test tube setting for at least 30 minutes in a fume hood, for a few tests the smell of rotten eggs was evident while the test tube was cleaned out. The test tubes were not cleaned in a fume hood, and a systematic procedure was not followed, with regard to how long after the reaction the test tubes were cleaned. This observation is not inconsistent with the NEIC hydrogen sulfide measurements, as the release of hydrogen sulfide is very rapid and would be expected to be vented to the fume hood.

Upon opening the containers, some 9 months after sample collection, the smell of hydrogen sulfide was still evident in the headspace. NEIC conducted additional testing with regard to hydrogen sulfide evolution, and the smell of hydrogen sulfide was present for test solutions for all three wastes.

WRTO statements on pages 5 and 45

Further, in closed-container "dumpster" mixing tests, NEIC reported concentrations as high as 236 ppm H_2S. However, a material balance around this "dumpster" test shows that the reported gas concentration must be at least an order of magnitude too high based on NEIC's own analysis of the total sulfide in the sample

This value is not credible. Reference 2, Table 11, reports that the total acid-volatile sulfide in the same Class C sample was only 0.41 ppmw, so the headspace gas analysis is too high by a least an order of magnitude, even assuming 100% reaction of all sulfide-containing species during the 30 second needed to reach the reported 236 ppm peak.

Comment

Review of the underlying records for the 236 ppmv measurement shows all quality control measures were acceptable. In fact, the absorbing solution for the 236 ppmv was analyzed neat and diluted in half. Both measurements are in agreement as to the concentration. Further, this peak hydrogen sulfide concentration coincides with the peak headspace temperature, as shown in Figure 9 of the NEIC report, and with the peak hydrogen measurement and is consistent with other hydrogen sulfide measurements made for the same temporal profile (see Figure 5 below) and for the other dumpster scenario testing conducted for sample NE30180 where the peak concentration was 123 ppmv.

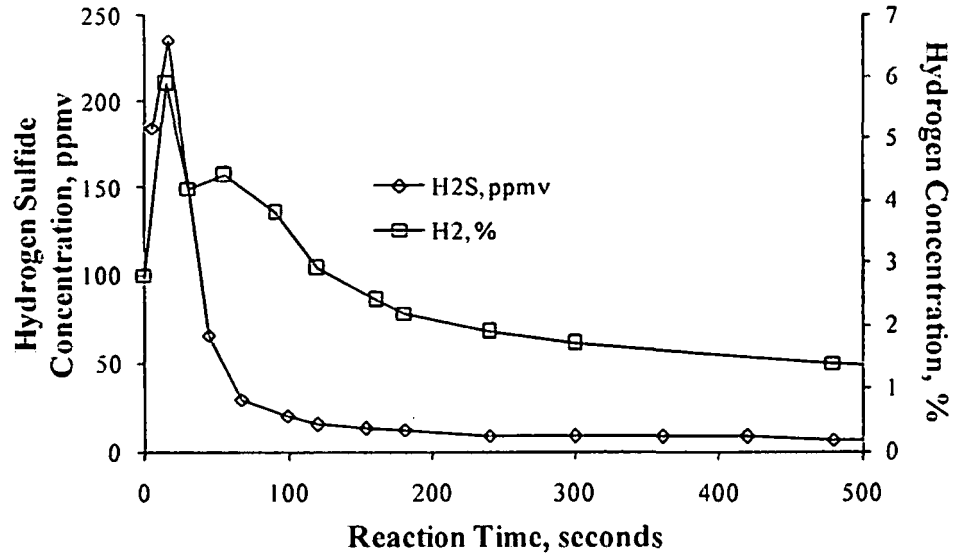

Figure 5 Headspace Hydrogen Sulfide and Hydrogen Concentrations for 200 grams of NE30180 and 200 grams of Water.

WRTO assumes that acid volatile sulfide is total sulfide. This is not the case. Acid volatile sulfide does not measure total sulfide. The acid volatile sulfide test used 0.5 gram of sample and 2 milliliters of 0.1 molar hydrochloric acid to evolve hydrogen sulfide in a Conway diffusion cell. Recently, NEIC determined that considerable zirconium is dissolved in such mixtures. This, together with another set of measurements, indicates that zirconium sulfide precipitates. Further, NEIC acid volatile sulfide measurements were associated with high variability. Measurements for the Grade A material ranged from 0.04 to 2.2 milligrams per kilogram (mg/kg), while the range for all samples was 0.04 to 5.2 mg/kg. Until recently, it was thought the variability was attributable to the sulfide content of the waste at the small test aliquot size. However, the results of the recent experiments indicate that the variability of the zirconium content may affect the measured acid volatile sulfide.

Further, the WRTO mass balance calculation is for a static system with uniform mixing throughout the headspace. For such a system, the hydrogen sulfide concentration would increase and plateau. This did not happen. The actual system was dynamic due to the violent exothermic reaction of the waste with water, and the 236 ppmv measurement is for the hot reaction gas bolus which is rapidly released from the waste. As shown Figure 5, the hydrogen sulfide concentration peaked immediately and decreased rapidly.

With regard to mass balance, the 236 ppmv hydrogen sulfide measurement at 16 seconds after the water addition is a sampling of the initial bolus of reaction gases and vapors and is quite credible. The volume of each sample collected for the determination of hydrogen sulfide was 5 milliliters. For the 5 milliliters to contain 236 ppmv, there would have to be 0.00118 milliliter of hydrogen sulfide.[23] The average acid volatile sulfide for the sample (NE30180) was about 0.41 mg/kg. The test used 0.2 kg, which means at least 0.082 mg or 2.56 micromoles of sulfide was present before the addition of water. This mass would equal a volume of hydrogen sulfide of 0.0756 milliliter, 0.0943 milliliter, and 0.104 milliliter at 22 °C, 95 °C and 133 °C,

[23] (236 ppmv)(5 mL)/(1E6 ppmv) = 0.00118 mL.

respectively.[24] Hence, the 236 ppmv for the 5-milliliter sample volume represents only 1.1 to 1.5% of the hydrogen sulfide volume that could be generated by the sample based on the 0.41 mg/kg acid volatile sulfide value.

For the same test, there were 19 5-milliliter samples with an average hydrogen sulfide concentration of 34.5 ppmv. The total volume of sample would have been 95 milliliters. For 95 milliliters of sample at a concentration of 36 ppmv, the volume of hydrogen sulfide would be 0.00328 milliliters. This volume represents only 3.1 to 4.3 % of the volume of hydrogen sulfide that could be generated by the sample based on the 0.41 mg/kg sulfide value.

WRTO Statement on page 39

This test was replicated at WRTO using Class C $MgCl_2$ (10 mL H_2O added to 10 g salt, sampling after 60 seconds), with results as shown in Figure 21 and Figure 22.

Comments

For its Mason-Cooper testing, WRTO waited 60 seconds after the reaction commenced before sampling, which avoided sampling the hydrogen sulfide reaction gas bolus. As shown in the above Figure 5, the hydrogen sulfide and hydrogen are generated immediately for an equal weight waste and water mixture. WRTO did not sample the reaction gas bolus and, hence, avoided sampling the hydrogen sulfide. Figure 6 shows the temporal profile for Mason-Cooper testing conducted for 10 grams of sample NE30178 and 10 mL of water in September 2012.

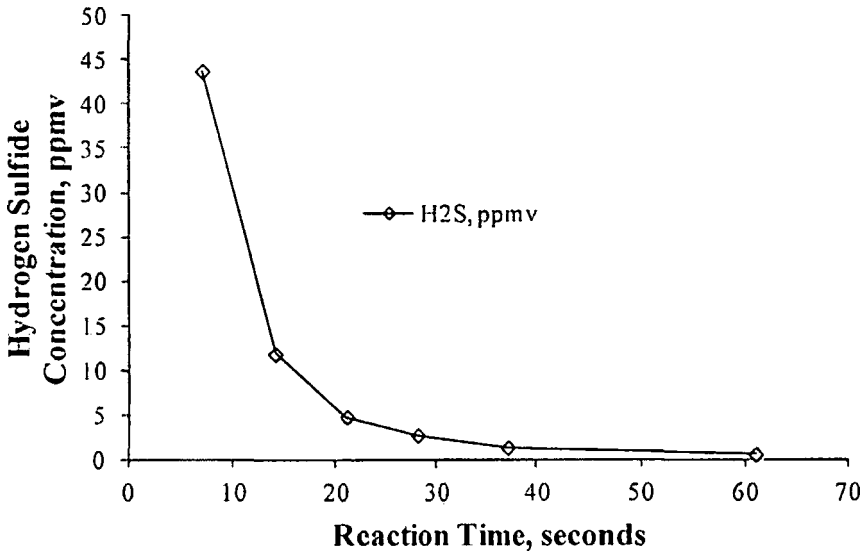

Figure 6 Mason-Cooper Headspace Hydrogen Sulfide Concentrations for 10 grams of NE30178 and 10 grams of Water.

As shown in the profile, the reaction gas bolus containing the hydrogen sulfide is rapidly vented from the open test tube to the fume hood exhaust.

[24] (0.41 mg/kg)(0.2 kg) = 0.082 mg;
(0.082 mg)(1000 μg/mg) / (32.066 g/mole) = 2.56 μmole
(2.56E-6 mole)(0.082057 L-atm/mol-°K)(273.15 + 133°K)(1000 mL/L) / (0.82 atm) = 0.104 mL

WRTO statement on page 44

Complete reaction is not credible, either. Sulfide cannot react until it contacts water, so the production of H_2S should track the rate of reaction of $MgCl_2$, which cannot even approach 100% under the given test conditions. NEIC states that "undissolved solids were always observed at the end of the [Mason-Cooper] determination for the 10 and 20 gram test portions." This behavior is consistent with WRTO observations, where large quantities of undissolved solids remained behind, probably $MgCl_2 \cdot 6H_2O$ that consumed water at the reaction surface by hydration rather than solution. A Mason-Cooper run with 10 g of $MgCl_2$ would contain the same ratio of water to salt as the Dumpster-Scenario run discussed above, so that substantial undissolved solids would certainly be present in the latter test as well. By reference to Figure 19 above, the solubility at a maximum temperature of 133.1°C is 47.6%wt, so the water addition is not even sufficient to completely dissolve the $MgCl_2$.

Comments

On one hand, WRTO argues that magnesium chloride hexahydrate is left after reacting an equal weight of waste and water, while on the other hand, WRTO argues that not all the anhydrous magnesium chloride contacted water and, therefore, not all the sulfide could react. NEIC testing indicates that no anhydrous magnesium chloride remains. NEIC testing with X-ray diffraction indicates that magnesium chloride hexahydrate largely remains. The undissolved solid does not look like the anhydrous magnesium chloride. The remaining solid often forms one hard piece, not pliable crystalline sheets like the waste material. Unlike the waste material, the remaining solid often takes the form of the bottom of the vessel. For magnesium chloride hexahydrate or other hydrates to form, the anhydrous magnesium chloride had to contact water.

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Given the simplicity and reliability of Dräger-style tube analysis for low-concentration gases and the widespread use of the method for environmental monitoring, it is not known why the NEIC laboratory chose to use the much more complex Milosavljević flow-injection/gas-diffusion method.

Therefore, because of the complexity of the method as described in the original paper, and lack of information about exactly how NEIC may have adapted the original procedure, it is not possible for Westinghouse to be more specific about possible reasons or flaws in the NEIC method that might explain why the reported NEIC H_2S results appear to be so high.

Comments

As explained above, the reasons WRTO did not measure much hydrogen sulfide is an apparent misunderstanding of fundamental chemical principles involving Henry's Law and acid dissociation, and avoidance of sampling the reaction gas bolus of the Mason-Cooper testing. The analytical methodology employed by NEIC was appropriate with regard to selectivity and sensitivity and in consideration of sample volume and the kinetics of the reactions.

For hydrogen sulfide, NEIC used a flow injection analyzer that employed a gas diffusion membrane and an amperometric electrochemical detector. The gas diffusion membrane offers selectivity for gases over other dissolved species; the electrochemical detector based on silver amperometry offers selectivity in its reaction chemistry; and the applied working potential of the potentiostat offers selectivity with regard to reduction/oxidation potentials of the reactions. The

Dräger-like tube chemistry is a darkening of the column premised on the precipitation of lead sulfide.

The Agency for Toxic Substances and Disease Registry (ATSDR) states: "Electrochemical sensors are the most commonly used sensors for toxic gases, including hydrogen sulfide, and are the best sensor for ambient toxic gas monitoring. These sensors are specific to a particular gas, are very accurate, do not get poisoned, and monitor at the ppm level."[25] Nevertheless, NEIC has conducted experiments confirming the signal for the electrochemical detector for the headspace air was due to hydrogen sulfide and, as discussed above, made measurements with another commercial available monitor.

As shown in Figure 6, some of the Mason-Cooper testing was repeated at NEIC. After the headspace samples were analyzed for sulfide content, the acidification reagent was replaced with an acidification reagent containing bismuth nitrate. In the flow injection analyzer, the caustic hydrogen sulfide trapping solutions are acidified to convert the hydrosulfide ion to hydrogen sulfide, and the hydrogen sulfide gas diffuses through the membrane, is absorbed into a caustic flow, and is reacted at the electrochemical detector, creating current that is measured. By adding bismuth nitrate, the hydrosulfide ion will be precipitated as bismuth sulfide, rather than converting to hydrogen sulfide. For the analysis of the Mason-Cooper headspace samples in the presence of bismuth nitrate, no peaks were detected. This demonstrates that the signals used to quantify hydrogen sulfide were due to hydrogen sulfide and not some interference.

WRTO used Gastec 4LL and 4LT hydrogen sulfide tubes. Manufacturer specifications provide a temperature operating range of 0 to 40 °C. For the Mason-Cooper testing and the dumpster scenario testing, the temperatures above the reactions were well above 40 °C and, hence, the tubes would be inappropriate. The manufacturer's literature for these tubes provides that one sampler pull takes 60 seconds with a volume of 0.1 liter per pull. The test tubes used by NEIC for the Mason-Cooper testing had a total volume of 0.134 liter, and the reaction gas bolus formed immediately and exhausted to the fume hood rapidly. NEIC collected a series of three 0.005-liter samples with syringes within 20 seconds and, hence, provides a temporal profile for the Mason-Cooper testing. Similarly, temporal profiles were obtained for the dumpster scenario testing. The fast reaction of the waste in these tests makes the Gastec tube sampler inappropriate.

[25] ATSDR, Toxicological Profile for Hydrogen Sulfide, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, p 186, 2006.