

University of Southampton's, Research for Industry report – 06FCW/00247/C3 - dated 3 November 2006

1. Introduction and Scope

This report concerns an MAIB investigation into the explosion of the starboard boiler on board the LNG tanker 'Hilli' on 10 October 2003 during a chemical cleaning process. The report follows a discussion meeting at MAIB, Southampton on 29 September 2006 (F.C. Walsh, K. Dixon, W. Hart, N. Hughes) and focuses on the possibility of hydrogen evolution during chemical cleaning of the internal boiler surface by the sulfamic acid based cleaner. This report also provides background information on the acid chemical cleaning process, electrochemical corrosion and the importance of inhibitors.

2. The Acid Chemical Cleaning Process

Acid cleaning of surfaces containing scale and corrosion products is routinely practiced to maintain the heat exchange efficiency of boilers. The acid is required to chemically attack surface mineral scale and corrosion products, leading to their dissolution. While the scale is chemically complex, an example of the process may be shown via the dissolution of calcium carbonate scale to soluble calcium ions:



and the dissolution of an iron oxide to soluble ferrous (Fe^{2+}) or ferric (Fe^{3+}) ions:



Sulfamic acid is widely used for the chemical cleaning of boilers. This white solid ($\text{NH}_2\text{SO}_3\text{H}$) is readily soluble in water (60-100% wt concentrates are possible). The concentrate is typically diluted to a level of 2-10%wt before use and it is common for proprietary sulfamic acid cleaners to also contain additives such as surfactants to improve their wetting power and activity. It is also common practice to use a colorimetric pH indicator in the acid to provide a visual diagnosis of acid level. Sulfamic acid is a strong acid and readily dissociates into ions in a water based solution:



The resultant, high concentration of H^+ ions (protons) provides an effective reagent for scale removal in many cases.

In the absence of an effective type and concentration of corrosion inhibitor in the cleaning acid, significant corrosion of the internal boiler surfaces can occur during cleaning. Such corrosion is an electrochemical process which consists of anodic and cathodic reactions. A simplified treatment follows.

At anodic regions on the surface on a steel surface, the metal loses electrons, i.e., it is oxidised to ferrous ions:



In some cases ferric ions (Fe^{3+}) are also formed.

At cathodic sites, the most common reaction is hydrogen evolution due to acid attack:



The overall corrosion (redox) process is attack of the steel by acid resulting in dissolution of the steel surface into the acid:



At later stages in the cleaning process, the corrosion rate can be accelerated by the presence of a partial covering of the steel surface by scale, since uncovered parts of the surface will tend to be anodic in comparison to the scaled areas. The result is a high ratio of cathodic area to anodic area, which will tend to lead to localized corrosion at the unscaled sites.

3. The Importance of an Inhibitor

Addition of a suitable inhibitor to the acid cleaner, at a sufficiently high concentration, can greatly

reduce the rate of corrosion of the steel surfaces while allowing a high rate of scale removal. It is common to use proprietary inhibitors (which are typically mixtures of chemicals) dissolved in the acid. These materials act as catalytic poisons to reactions (4) and (5), i.e. they significantly lower the rate of corrosion by poisoning iron dissolution and hydrogen evolution. The inhibitor efficiency varies considerably with conditions (including acid temperature, type of steel, surface finish of the steel, acid concentration, inhibitor type and inhibitor level) but can be as high as 95 to 98+% for appropriate inhibitors. In other words, the corrosion rate is lowered to 5 to <2% of its value in uninhibited acid. Inhibitors act by strong adsorption and film formation on the steel surface.

4. The Explosion following Chemical Cleaning of the Starboard Boiler on the 'Hilli'

During chemical cleaning of a boiler, it is important to stop the process when the scale is substantially removed but before significant corrosion attack occurs on the underlying steel. It appears that a suitable inhibited acid cleaner (Unitor 'Descalex') was used at a reasonable temperature (a value in the range 45-60 °C is a common choice). It is understood that 'Descalex' contains approximately 95% sulfamic acid and approximately 5% of additives (the latter including the corrosion inhibitor). It is common practice to monitor the extent of the cleaning process by using (a) visual observation of the colour of the pH indicator in the acid (red to orange when the acid is largely consumed) together with a test sample of wire wool (which shows a low corrosion activity when acid has been largely consumed). It is, however, often difficult to see such a clear colour change in practice. Prior to the explosion incident, it is notable that the acid was reported to be grey in colour (which may indicate a combination of undissolved material and dissolved steel)

It is prudent to carefully and completely vent gas spaces in the boiler after cleaning operations. Indeed, it is good practice to remove the acid content, wash thoroughly and vent the boiler for a considerable time before an inspection. The use of hydrogen sensitive gas sensors is also important. Such sensors do not appear to have been used in the present case. In addition, inadequate ventilation may have occurred. For example, there may have been insufficient time allowed to vent gases from the boiler. The most likely method of venting the boiler during the cleaning operation was through the small, 20 mm internal diameter vent tube fitted to the top of the steam drum. It is possible that the arrangement of tubing on the vent did not allow for free escape of gas through the vent. Some venting may have occurred from release of entrained gases

from the acid-mixing tank, although it is not possible to estimate the degree of hydrogen escape from this source.

In section 2, the evolution of hydrogen by corrosive attack of an acid on steel surfaces in an inadequately inhibited cleaner was noted. It is important to consider two aspects:

- (a) the possible volume of hydrogen evolved and
- (b) whether such hydrogen evolution could constitute an explosive hydrogen-air mixture in the gas space above the acid in the boiler.

Appendix 2 provides an estimation of the volume of hydrogen evolved and the possible gas composition, following a number of simplified assumptions, which include:

- (i) the corrosion reaction is simplified to corrosion of iron by acid attack via hydrogen evolution,
- (ii) the gas space above the acid in the boiler is taken as 5 m^3 ,
- (iii) the area of the exposed internal surface of the boiler is taken as 700 m^2 ,
- (iv) the worse case condition of zero percent inhibition of the acid is considered; laboratory trials show a measured, mean corrosion rate of 23.6 to 27.5 microns in 6 hours and 45 minutes (which is the estimated time for contact between the acid cleaner and the boiler). This range of values was obtained under static flow conditions in a 5%wt sulfamic acid solution.
- (v) the worst case of zero ventilation is considered and
- (vi) hydrogen is treated as an ideal gas.

The calculations indicate that the gas space could contain sufficient hydrogen to constitute a flammable and explosive hydrogen-air mixture, which was ignited by the hot halogen lamp as a source during the inspection. The flammability limits of hydrogen in air gas mixtures are approximately 4% (LFL) and 74% by volume (UFL) under standard temperature and pressure (STP) conditions [1, 2]. It is also well known that flammable hydrogen in air mixtures have a high flame velocity (typically 3 metres per second) [1-3]. It is likely that the hot halogen lamp acted as a point of initiation for flame propagation. The possibility also exists of an electrical fault in the wiring or connections inside the halogen inspection lamp, which might have contributed to the ignition of the hydrogen-air mixture.

Conclusions

1. The most likely source of an explosive gas mixture in the boiler is hydrogen gas, which was generated by corrosion of the internal surfaces of the steel boiler in the acid cleaner.
2. Estimations show that modest corrosion of the boiler (to the extent of approximately 24 microns loss of thickness over the entire boiler area within 6 hours and 45 minutes) can result in sufficient hydrogen to cause an explosive hydrogen-air mixture in the boiler gas space above the cleaner.
3. The halogen inspection lamp used is likely to have acted as the source of ignition, which was followed by rapid flame propagation..
4. Inspection of the steel drum boiler via the access cover without first removing the acid cleaner from the boiler, followed by adequate water rinsing and careful ventilation, did not represent good practice.

References

1. H.K. Abdel-aal, M. Sadik, M. Bassyouni, M. Shalabi, "*A New Approach to Utilize Hydrogen as a Safe Fuel*", *International Journal of Hydrogen Energy* **30**, (2005), 1511-1514.
2. I.L. Drell, F.E. Belles, NACA Report 1383, "*Survey of Hydrogen Combustion Properties*", pp 1161-1199;
<http://naca.central.cranfield.ac.uk/PhP?NID=7206>; access date 26 Oct. 2006.
3. "*Hydrogen Properties*", *Hydrogen Fuel Cell Engines and Related Technologies*", Dec.2001;
http://www.eere.energy.gov/hydrogenandfuelcells/tech_validation/pdfs/fcm01r0.pdf; accessed 26 October 2006.

APPENDIX 1: UNITOR CHEMICALS 'DESCALEX' CLEANER SPECIFICATIONS

MATERIAL SAFETY DATA SHEET

1. PRODUCT AND COMPANY

TRADE NAME:	Descalex	APPROVED:	YES
CHEMICAL NAME:		RECEIPT NO:	
FORMULA:		ARTICLE NO:	651 571646 (25 kg)
SYNONYMS:		EC-NO:	
INDEX NO:		CAS NO:	
GROUP:		PR.NO:	
SUPPLIER:	Unitor Chemicals Kjemt Service as, A unitor Group Company P.Box. 49 N-3163 Borgheim Tlf: +47 33 35 15 00 Fax: +47 33 35 14 40		
TOXIC INFORMATION:	22 59 13 00	EMERGENCY PHONE:	
RESPONSIBLE:			
AUTHOR:	Leen de Visser (+31 6 538 63736)		
APPLICATION:	Cleaning agent		
MORE INFORMATION:	Product Part Number: 571646 (25 kg). Datasheet Number: 571646 2. 0. 0. Emergency Telephone: NCEC: +44 1865 407333 CHEMTREC (800) 424 9300 CMA +1 703 527 3887 Greece +30 1 7793777		

2. COMPOSITION

COMPOSITION	CAS-NO	EC-NO	% CONC.	CH	CF	CE	R-phrases	NOTE
Sulphamic acid	5329-14-6	226-218-8	60-100	Xi			36/38-52/53	
Non classified ingredients			1-10					

EXPLANATION:

CF/CH/CE=Classification fire-/health-/environment, Tx=Very Toxic, T=Toxic, C=Corrosive, Xn=Harmful, Xi=Irritating, IK=No classification required, E=Explosive, O=Oxidizing, Fx=Extremely flammable, F=Highly flammable, N=Danger for environment, M=Genotoxic, A=Sensitisation, K=Carcinogen, R=Causes birth defects.

COMPOSITION COMMENTS:

See chapter 16 for the complete wording of all R-phrases as stated in chapter 2.

3. HAZARDS IDENTIFICATION



MORE INFORMATION:

Health: Irritates eyes and skin

Environment: Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

4. FIRST AID MEASURES

GENERAL:

- In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible) (S45)

INHALATION:

- Inhalation is unlikely to occur
- Remove patient to fresh air
- When in doubt or symptoms persist, seek medical attention

SKIN CONTACT:

- Wash affected area with plenty of soap and water
- Contaminated clothing should be laundered before reuse
- Seek medical attention if irritation persists

EYE CONTACT:

- If substance has got into eyes, immediately wash out with plenty of water for at least 15 minutes
- Irrigate eyes thoroughly whilst lifting eyelids
- Obtain immediate medical attention

INGESTION:

- Do not induce vomiting
- Never give anything by mouth to an unconscious person
- Give water or milk to drink
- Obtain immediate medical attention

5. FIRE FIGHTING MEASURES

SUITABLE EXTINGUISH MEDIA:

In case of fire use extinguishing media appropriate to surrounding conditions.

FIRE AND EXPLOSION HAZARDS:

- Not flammable.
- Non-combustible solid.
- Smoke from fires is irritating.

SPECIAL FIREFIGHTING PROCEDURES:

- Prevent run off water from entering drains if possible.

6. ACCIDENTAL RELEASE MEASURES

PERSONAL PRECAUTIONS:

Wear protective clothing as per section 8.

ENVIRONMENTAL PRECAUTIONS:

Do not allow to enter public sewers and watercourses.

CLEANING MEASURES:

Sweep or shovel-up spillage and remove to a safe place.
Wash spill site with water and detergent.

7. HANDLING AND STORAGE

HANDLING:

Wear protective clothing as per section 8.
Avoid contact with skin and eyes (S24/25).
Eyewash bottles should be available.

STORAGE:

Keep only in the original container in a cool, well ventilated place (S3/9/49)
Keep in acid store

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

EXPOSURE CONTROL:

There are no recommended or established controls for this product.

EYE PROTECTION:

Wear suitable dustmask e.g. to BS 2091.

SKIN PROTECTION:

Wear suitable protective clothing, including eye/face protection and gloves (plastic or rubber are recommended).

9. PHYSICAL AND CHEMICAL PROPERTIES

FORM:	Crystals	ODOUR:	Characteristic odour
COLOUR:	Orange.	SOLUBILITY:	
MELTING/FREEZING POINT:	205 °C at 760 mm /Hg	BOILING POINT:	not applicable
DENSITY:	1200 kg/m ³	FLASH POINT:	
EXPLOSION LIMITS LEL-UEL %:		PH (CONCENTRATE.):	
SOLUBILITY IN WATER:	~ 200 g/l	MOL MASS:	
VAPOUR PRESSURE:	not known	VISCOSITY:	
SATURATION CONC.:		AUTO IGNITION TEMP:	
DECOMPOSITION TEMP.:		SMELL LIMIT:	
PH (SOLUTION):	pH 1 at 10 % concentration	REL. VAPOUR DENSITY (AIR=1):	

MORE INFORMATION:

Non-combustible solid

10. STABILITY AND REACTIVITY

STABILITY:

This article is considered stable under normal conditions.

REACTIVITY:

Avoid overheating.
Incompatible with alkalis (strong bases).

HAZARDOUS DECOMPOSITION PRODUCTS:

Contact with nitrite (e.g. Dieselguard NB, Rocor NB Liquid) liberates toxic gas.

11. TOXICOLOGICAL INFORMATION

GENERAL:

Repeated or prolonged exposure may cause irritation to eyes and skin.

INHALATION:

May cause severe irritation.
May cause shortness of breath.

SKIN CONTACT

May cause irritation.

EYE CONTACT:

Causes severe irritation.

INGESTION:

The ingestion of significant quantities may cause burning sensation.

MUTAGENICITY:

No evidence of carcinogenic effects.

CANCER:

Carcinogenic properties are not known.

ORAL TOXICITY:

LD50 (oral,rat) 3160 mg/kg

12. ECOLOGICAL INFORMATION

MOBILITY:

Completely soluble in water.

BIODEGRADABILITY:

Most components in this product are not readily biodegradable.

ACCUMULATION:

Bioaccumulation of the components in this product is insignificant.

ECOTOXICITY:

Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment (R52/53).

OTHER EFFECTS:

No environmental problems are expected when the product is used / handled correctly.
In its intended use, the product will not be released into the environment.

13. DISPOSAL

DECONTAMINATION/DISPOSAL:

Classification

- EU Waste class: 06.01

- This material and/or its container must be disposed of as hazardous waste

Disposal considerations

- Do not discharge into drains or the environment, dispose to an authorised waste collection point

- Disposal should be in accordance with local, state or national legislation.

14. TRANSPORT INFORMATION

ADR(Road)			
UN NO:	2967	CLASS:	8
LABEL:		DANG. GOODS:	
PACKING GROUP:		HAZ. ID NO:	80
RID(Railway)			
UN NO:	2967	CLASS:	
HAZ. ID NO:		DANG. GOODS:	
PACKING GROUP:			
IMDG(SEA)			
UN NO:	2967	CLASS:	8
LABEL:	8	DANG. GOODS:	
EMS:	F-A, S-B	PACKING GROUP:	III
MARINE POLL:	-	SUB.RISK:	-
IATA(Airplane)			
UN NO:	2967	CLASS:	8
LABEL:	8	DANG. GOODS:	
SUB.RISK:		PACKING GROUP:	III

PROPER SHIPPING NAME:

Sulphamic acid, mixture

MORE INFORMATION:

Tremcard: 80GC2-III

15. REGULATORY INFORMATION



R-PHRASES:

R36/38 Irritates eyes and skin.

R52/53 Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

S-PHRASES:

S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S28 After contact with skin, wash immediately with plenty of water.

S37/39 Wear suitable protective gloves and eye/face protection.

S61 Avoid release to the environment. Refer to special instructions/Safety data sheets.

REFERENCES:

Revised in compliance with national regulations for health, fire and environment labelling. (The Working Environment Act, Pollution Control Act, Act relating to Prevention of Fire, Explosion and Accidents involving Hazardous Substances and the Fire Services) Norwegian Databases: List of Dangerous Substances, The Observation List, List of Priority Substances. Authorities: Norwegian Labour Inspection Authority, Directorate for Civil Protection and Emergency Planning, Norwegian Petroleum Directorate, Petroleum Safety Authority Norway. Transport legislation: The Carriage of Dangerous Goods and Use of Transportable Pressure Equipment (ADR/RID), The International Maritime Dangerous Goods (IMDG), International Air Transport Association Dangerous Goods (IATA) EU-directives : 67/548/EEC, 1999/45/EC, 2001/58/EC, 2004/73/EF (29. ATP) with later amendments.

16. OTHER INFORMATION

Replace date:: 23.12.2003

MORE INFORMATION:

R-sentences as given in chap. 2:

R36/38: Irritating to eyes and skin.

R52/53: Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

The information provided about the product on this Safety Data Sheet has been compiled from knowledge of the individual constituents.

The data given here is based on current knowledge and experience. This Safety Data Sheet describes the product in terms of safety requirements and does not signify any warranty with regard to the product's properties.

The data given here only applies when product used for proper application(s). The product is not sold as suitable for other applications usage in such may cause risks not mentioned in this sheet. Do not use for other application(s) without seeking advice from manufacturer.

This Safety Data Sheet is provided in compliance with The Dangerous Substances Directive (67/548/EEC).

This Safety Data Sheet is provided in compliance with The Dangerous Preparations Directive (88/379/EEC).

This Safety Data Sheet is provided in compliance with The Safety Data Sheets Directive (2001/58EC).

HMS Logiconsult has no legal responsibility for mistakes or faulty information which is given from the producer. The producer given in chapter 1 is responsible for this MSDS and is legally responsible for the content. Approved and revised in compliance to 29. ATP.

HMS Logiconsult AS

Leif Weldings vei 14

3208 Sandefjord Norway

Phone: +47 33 42 34 50 Fax : +47 33 42 34 59

www.hmslogiconsult.com

Signature: E.N.E

Revisioncomments:

Replaces datasheet from 23.12.2003

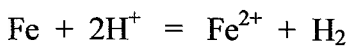
Revised 24.07.2006: No changes.

APPENDIX 2:

CALCULATIONS TO ESTIMATE THE VOLUME OF HYDROGEN EVOLVED

At a 5%wt concentration of uninhibited sulfamic acid in distilled water at 58°C, the mean measured corrosion rate of mild steel (prepared by 600 grade silicon carbide paper) corresponds to a penetration (thickness loss) of 17.5 microns in 5 hours immersion (under static conditions). This corresponds to a thickness loss of 23.6 microns in a contact time of 6 hours and 45 minutes.

It can be assumed that metal dissolution can be simplified to a 2 electron removal from iron together with hydrogen evolution:



This reaction is equivalent to the dissolution of 1 mol (or 55.9 g) of iron to generate 22.4 litres of hydrogen gas under standard conditions (assuming the gas behaves ideally).

If the exposed area of the wetted internal surface of the boiler is taken as $A = 700 \text{ m}^2$ and the volume of metal corroding (V) is the product of thickness loss (x) and area is:

$$V = A \cdot x$$

$$V = (700 \text{ m}^2)(23,6 \times 10^{-6} \text{ m})$$

$$V = 0.01652 \text{ m}^3$$

Taking the density of iron as $\rho = 7860 \text{ kg m}^{-3}$, the mass of metal lost due to corrosion (w) is:

$$w = \rho \cdot V$$

$$w = (7860 \text{ kg m}^{-3})(0.01652 \text{ m}^3)$$

$$w = 129.8 \text{ kg}$$

This can be converted into an amount of metal (n , units mol) on division by the molar mass (M):

$$n = \frac{w}{M}$$

$$n_{\text{Fe}} = \frac{129.8 \text{ kg}}{0.0588 \text{ kg mol}^{-1}}$$

$$n_{\text{Fe}} = 2208 \text{ mol}$$

This amount of metal is equivalent to 2208 mol hydrogen. Assuming ideal gas behaviour, the volume occupied by the gas at a temperature of 58°C (331 K) will be:

$$V_{H_2} = \frac{(22.4 \times 10^{-3} \text{ m}^3)(2208 \text{ mol})(331 \text{ K})}{(298 \text{ K})}$$
$$V_{H_2} = 54.9 \text{ m}^3$$

If the mean inhibitor efficiency is 95%, then the hydrogen volume becomes 2.7 m³. Some loss of hydrogen is expected by ventilation and via opening of the inspection door.

If the gas void space above the acid is 5 m³, then the percentage by volume of hydrogen in the air-based mixture will be:

$$\% \text{vol Hydrogen} = \frac{2.7 \text{ m}^3}{5 \text{ m}^3}$$
$$\% \text{vol Hydrogen} = 55\%$$

This value is within the flammability limits for hydrogen-air mixtures (approximately 4-75% vol hydrogen).

Further laboratory trials on duplicate mild steel samples (abrasively cleaned by 400 grade silicon carbide paper, showed slightly higher corrosion rates of 4.1 microns per hour. This corresponds to a thickness loss of 27.5 microns in 6 hours and 45 minutes. These values correspond to the generation of 3.1 m³ hydrogen gas.

In accordance with reactions (4) and (5), the uninhibited acid became noticeably green in colour due to the buildup of ferrous ions and copious hydrogen evolution took place from the surface of the mild steel samples.

APPENDIX 3:

CONCISE CURRICULUM VITAE OF PROF FRANK C. WALSH

EurIng Professor **Frank C. Walsh**, *BSc, MSc, PhD,*
CSci, CEng, FIMMM, CChem, MInstP, FRSC, FICorr, FIMF

Current Positions: *Professor in Electrochemical Engineering; Deputy Head of School; Director, Centre for Energy Studies, Senior Consultant for the Research Institute for Industry, School of Engineering Sciences, University of Southampton.*

Non-Executive Director, Poeton Industries Ltd, Gloucester,

Contact - Work: Tel: +44 (0)2380 598752

E-mail: F.C.Walsh@soton.ac.uk

Contact – Home: Tel: +44 (0)1489 581310

Email: electro@chemeng.fsnet.co.uk

Previous experience: *Head of Department of Chemical Engineering and Professor in Electrochemical Engineering, University of Bath.*

Business Development Director, Science Faculty, Head of School, Reader in Electrochemistry, Senior Lecturer in Physical Chemistry, Chair of SCI Electrochemical Technology Group, Industrial Chemical Engineer and Corrosion Consultant.

Qualifications: BSc (Applied Chemistry, *Portsmouth*), MSc (Materials Protection, *Loughborough*), PhD (Electrochemical Engineering, *Loughborough*), CSci, CChem, FRSC, MInstP, FIMF, FICorr, CEng, FIMMM, NACE International Certificated NACE Corrosion Specialist, EurIng, CertEd. Member of the Electrochemical Society and International Society of Electrochemistry. Member of the Institute for Learning and Teaching.

Publications: Research output spans the areas of corrosion engineering, energy conversion, coating technology, electrochemical monitoring and sensors, surface finishing and electrochemical process engineering. Output includes: 4 text books, 30 short course papers, >200 conference papers, >200 research papers and >50 educational papers.

Achievements: Awarded the Westinghouse Prize (*best paper on metallic coatings*) of the Institute of Metal Finishing (1999) and the Breyer Medal of the Royal Australian Chemical Institute (2000) for international contributions to electrochemical science, engineering and education.

Membership of: the editorial board for five international journals, the Education and Publications Committees of the Institute of Metal Finishing and the Executive Committee of the Institute of Corrosion; past Chair of the Electrochemical Technology Group of the SCI and member of the RSC Electrochemistry Group.

In collaboration with industry, over 45 industrial electrochemical processes have been developed or improved, primarily in the areas of energy conversion, environmental treatment, corrosion control and materials recycling. Consultancy services have been provided to a wide range of industries, ranging from SMEs to large corporate organisations. Troubleshooting assignments in surface finishing, corrosion, fuel cells and electrochemical reactor design have involved research and production problems in SMEs through to policy advice to large international corporates.

External examiner duties have included undergraduate courses in chemistry at Brighton University and PhD examinations in chemical/mechanical engineering, chemistry and materials at the Universities of: Newcastle-upon-Tyne, Manchester, Imperial College, Nottingham, Liverpool, Limerick, Southampton and Sydney

Expertise: Electrochemical engineering, corrosion engineering and materials protection, electrochemical reactor design and process engineering, fuel cell materials and reactors, redox flow cell design and performance, nanomaterials for fuel cells and batteries, development of electrode materials, flow effects, electrode materials, porous electrodes and electrode coatings.

Hydrogen Safety - Extracts from the United States Schatz Energy Research Center's website

HYDROGEN SAFETY

Introduction

The principal hazard presented by hydrogen is the uncontrolled combustion of accidentally released hydrogen. In order for hydrogen to combust, an oxidizer and a source of ignition must be present. Hydrogen is combustible over a wide range of concentrations in air, and various common physical processes (open flames, hot surfaces, friction, electrical spark, static discharge) can serve as sources of ignition. Therefore, one of the most important ways to ensure the safe use of hydrogen is to make sure that there is adequate ventilation to prohibit the creation of a flammable gaseous mixture. In addition, eliminating ignition sources is an important safety measure. These types of safety measures are best implemented through sound engineering design and proper operation and maintenance practices.

Physical Properties of Hydrogen

	Hydrogen
Autoignition temperature	520° C
Heat of combustion (lower heating value)	120 MJ/kg
Lower flammable limit (in air)	4% by volume
Upper flammable limit (in air)	75% by volume
Stoichiometric mixture (in air)	29.5% by volume
Density (20C, 100kPa)	0.61 cm ² /s
Viscosity (20C, 100kPa)	8.814 μPa-s
Flame temperature (in air)	2045° C
Minimum ignition energy (in air)	0.017 mJ

Properties of Gaseous Hydrogen

Some important characteristics of hydrogen include: its high propensity to leak, its high dispersion characteristics, the difficulty of hydrogen gas and flame detection, its flammability and ignition characteristics and combustion characteristics,

Hydrogen Gas and Flame Detection

Hydrogen is a colorless, odorless, and tasteless gas. Its presence cannot be detected by human senses. In addition, the unique characteristics of a hydrogen fire make it difficult to perceive with the human senses. In contrast to other hydrocarbon fuels, which radiate most of their energy as visible light and heat, a hydrogen flame radiates significantly less heat and virtually no visible light. Instead, significant energy from a hydrogen flame is radiated in the ultraviolet region. As a result, hydrogen burns with a pale blue, almost invisible flame that is almost visually imperceptible in artificial light or daylight. Equally important, human physical perception of the heat from a hydrogen fire does not occur until direct contact with the combustion gases.

Flammability and Ignition

Hydrogen has a wide range of flammability in air (4% to 75% by volume). Weak ignition sources, such as an electrostatic spark, are often sufficient to ignite a combustible hydrogen-air mixture. However, a weak electrostatic spark from the human body releases about 10 mJ, which is enough energy to ignite methane, propane, gasoline, and other fuels as well.

Combustion Characteristics

Hydrogen-oxidizer mixtures can combust either as a fire at a fixed point, a deflagration, or a detonation. Depending on the rate of release of hydrogen from the source, fires can produce outputs ranging from that of a small candle to a high-pressure jet. At a fixed point hydrogen gas can burn as a jet flame, with combustion taking place along the edges of the jet where it mixes with sufficient air. In a stationary mixture in the open with no confinement a flammable hydrogen mixture will undergo slow deflagration. Deflagration refers to a flame that relies on heat- and mass-transfer mechanisms to combust and move into areas of unburned fuel.

If the flame speed is accelerated, perhaps due to extreme initial turbulence or turbulence induced by obstacles or confinement, the result is an explosion. In the extreme case the flame speed becomes supersonic and results in detonation. Once initiated, detonation is self-sustaining (no further turbulence or confinement is required) as long as the combusting mixture is within the detonatable range. A detonation explosion is capable of causing much greater physical damage due to the significantly higher pressure that is generated (as great as 20 times the initial stoichiometric pressure versus about 8 times the initial pressure for a deflagration).

The lower radiation from a hydrogen flame makes the flame itself hotter than a hydrocarbon flame, and objects engulfed by a hydrogen flame tend to heat faster. However, the lower radiation of heat from the flame means that less heat is transferred to objects or people outside the flame.