

Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE 19 FEB 2010		2. REPORT TYPE		3. DATES COVERED 00-00-2010 to 00-00-2010	
4. TITLE AND SUBTITLE Co-generation of acetylene and hydrogen for a carbide-based fuel system				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Undersea Warfare Center Division Newport, Code 8231,1176 Howell Street, Newport RI, 02,98105				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The co-generation of acetylene and hydrogen from the hydrolysis of calcium carbide and calcium hydride was investigated as part of a unique carbide-based fuel system intended for high-temperature fuel cells. To gain better control of this highly energetic reaction, glycerin was used to coat the reactant particles to form slurry prior to their reaction with water. This process was shown to moderate the rate of gas production, as well as to provide a means for preparing slurry that could be pumped into the reactor vessel. It was also observed that the presence of calcium hydroxide, a by-product of hydrolysis, lowered the solubility of acetylene resulting in a higher initial flow rate due to less acetylene being dissolved in solution. However, the buildup of calcium hydroxide with time inhibited the hydrolysis of both calcium carbide and calcium hydride causing the acetylene and hydrogen flow rates to decrease.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			



Co-generation of acetylene and hydrogen for a carbide-based fuel system

Louis G. Carreiro^{a,*}, A. Alan Burke^a, Lily Dubois^b

^a Naval Undersea Warfare Center Division Newport, Code 8231, 1176 Howell Street, Newport, RI 02841, USA

^b Stonehill College, Department of Chemistry, 320 Washington Street, Easton, MA 02357, USA

ARTICLE INFO

Article history:

Received 16 September 2009

Received in revised form 19 February 2010

Accepted 13 March 2010

Keywords:

Calcium carbide

Acetylene

SOFC

ABSTRACT

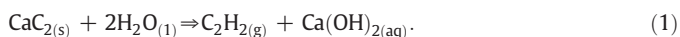
The co-generation of acetylene and hydrogen from the hydrolysis of calcium carbide and calcium hydride was investigated as part of a unique carbide-based fuel system intended for high-temperature fuel cells. To gain better control of this highly energetic reaction, glycerin was used to coat the reactant particles to form slurry prior to their reaction with water. This process was shown to moderate the rate of gas production, as well as to provide a means for preparing slurry that could be pumped into the reactor vessel. It was also observed that the presence of calcium hydroxide, a by-product of hydrolysis, lowered the solubility of acetylene resulting in a higher initial flow rate due to less acetylene being dissolved in solution. However, the buildup of calcium hydroxide with time inhibited the hydrolysis of both calcium carbide and calcium hydride causing the acetylene and hydrogen flow rates to decrease.

Published by Elsevier B.V.

1. Introduction

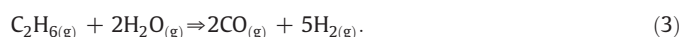
High-temperature fuel cells, such as Solid Oxide Fuel Cells (SOFCs), usually operate on syngas (a mixture of hydrogen, carbon monoxide and methane) that is derived from the fuel processing (catalytic reforming) of hydrocarbons. The SOFC electrochemically converts hydrocarbon reformat and air (oxygen) to water and carbon dioxide to produce electrical power. While liquid hydrocarbons have been the fuel of choice due to their high energy content and ease of storage, solid fuel sources are also being considered since they offer the distinct advantages of extended shelf-life and non-volatility. One source in particular is calcium carbide (CaC_2), which is manufactured by the high-temperature endothermic reaction of calcium oxide and carbon [1]. Calcium carbide is best known for its hydrolysis reaction to produce acetylene (C_2H_2) gas, a potential fuel for SOFCs.

The reaction of calcium carbide and water is highly exothermic, generating acetylene and the by-product calcium hydroxide ($\text{Ca}(\text{OH})_2$) according to Eq. (1).

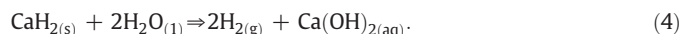


However, acetylene cannot be fed directly into the SOFC because it will pyrolyze [2] at the high operating temperatures of the fuel cell (700–1000 °C), depositing elemental carbon on the anode. To avoid this situation acetylene is processed in two steps: hydrogenation of acetylene to ethane (Eq. (2)) at 80–250 °C [3–5] followed by steam

reforming of ethane to syngas (Eq. (3)) at 400–800 °C [6,7]. This scheme allows acetylene to be converted to ethane and subsequently to syngas well below its pyrolysis temperature of 450 °C.

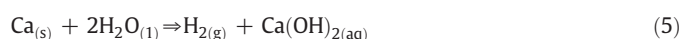


One method for supplying hydrogen to the hydrogenation step is the hydrolysis of calcium hydride (CaH_2) as shown in Eq. (4).



By combining Reactions (1) and (4), acetylene and hydrogen can be co-generated from a mixture of calcium carbide and calcium hydride. A 1:1 molar ratio of CaC_2 and CaH_2 provides exact stoichiometry for the hydrogenation of acetylene to ethane; however, excess hydrogen will likely be used in the carbide-based fuel system (CFS) to ensure adequate conversion of acetylene.

The reaction of calcium metal and water can also be used to generate hydrogen (Eq. (5)) with slower reaction rates, hence providing better control of hydrogen production. However, the trade-off is less hydrogen is produced per mole of calcium reactant.



A detailed description of the CFS in an Unmanned Undersea Vehicle (UUV) application is discussed elsewhere [8,9]. In brief, the CFS is designed to generate fuel for a SOFC and to also produce a carbon dioxide

* Corresponding author. Tel.: +1 401 832 5097; fax: +1 401 832 2908.
E-mail address: louis.carreiro@navy.mil (L.G. Carreiro).

sorbent in the form of calcium hydroxide solution. The sorbent removes carbon dioxide from the SOFC exhaust stream and converts it to calcium carbonate (CaCO_3). This paper will focus on methods for co-generating acetylene and hydrogen, as well as examine the effect of calcium hydroxide by-product on gas generation.

2. Experimental

2.1. Materials

Lump calcium carbide (Sigma-Aldrich, Technical Grade, ~80%) and calcium hydride granules (Sigma-Aldrich, Reagent Grade, 95%) were used to generate acetylene and hydrogen, respectively. Glycerin (Fisher, USP Grade) was used in the preparation of calcium carbide and calcium hydride slurry. Molecular sieve (Fisher, Type 4A, 8–12 mesh beads) was used to remove any moisture in the glycerin. 0.1 M solution was prepared from calcium hydroxide powder (Aldrich, ACS Reagent >95%) to examine its effect on gas generation.

2.2. Gas generation

Three methods for generating acetylene and/or hydrogen were employed: (1) pumping water into the reaction chamber containing reactant powders, (2) pumping water into the reaction chamber containing reactant powders coated in glycerin, and (3) pumping glycerin slurry of reactant powders into the reaction chamber containing water.

2.2.1. Reaction of calcium carbide and water

Calcium carbide as received from the manufacturer was in the form of stones ranging in size from 0.5 cm to over 2 cm and not suitable for use as an acetylene generator due to its lack of uniformity and surface area. Therefore, the stones were pulverized using a laboratory crusher (Scientific Model PE-150TC, ASC Scientific, USA) equipped with tungsten carbide jaw plates and the resulting particles sorted using a #12 mesh sieve with 1.7 mm opening (USA Standard Sieve Humboldt MFG Co., USA). The particles trapped in the sieve (1.8–5 mm) were used in this experiment.

Five grams of carbide powder was placed in the reaction chamber directly below a water delivery tube as shown in Fig. 1. The reaction chamber was an acrylic cylinder with an I.D. of 13 cm and total volume of approximately 2400 cm³. It was fitted with a removable top that had three ports: an inlet to allow water (or slurry) to enter, an outlet for gases to exit and an inlet for flushing the chamber with argon gas. A peristaltic pump (Masterflex L/S Pump Head 7518-10, Cole-Palmer Instrument Co., USA) supplied water at a rate of 0.34 mL/min to the chamber and a magnetic stirrer (Type 100 Stir Plate, Thermolyne, USA) was employed to aid in mixing the calcium carbide and water. A flow meter (Definer 220 low flow, BIOS, USA) was used to monitor the volumetric rate of gas generated. A gas chromatograph (Model GC17A, Shimadzu, USA) equipped with a Porapak N column (1/8-in × 3 m with 80/100 mesh adsorbent) and thermal conductivity detector (TCD) was

used to analyze the effluent gas composition from the reactor. In subsequent experiments, calcium carbide was mixed with 10 mL of glycerin before addition of water.

2.2.2. Reaction of calcium hydride and water

As received calcium hydride granules were sifted through a #35 sieve with 0.5 mm opening and the trapped particles (0.6–2 mm in size) were reacted with water, both in the dry state and as glycerin-coated, in a manner similar to that described for calcium carbide. Five grams of the powder that passed through the sieve (<0.5 mm) was mixed with 10 mL of glycerin to form slurry and then pumped at a rate of 0.6 mL/min into 300 mL of water. For the pumped slurry experiments, the gas generator in Fig. 1 was modified so that the reaction chamber contained water and the reservoir held slurry.

2.2.3. Reaction of calcium hydride/calcium carbide slurry and water or 0.1 M $\text{Ca}(\text{OH})_2$

Mixed slurry of calcium carbide (3.81 g)/calcium hydride (2.5 g), designed to produce hydrogen and acetylene in a 2 to 1 ratio, was prepared from 500-micron powders dispersed in 12 mL of glycerin. In one experiment the slurry was pumped at a rate of 1 mL/min into 300 mL of water and in another into 300 mL of 0.1 M calcium hydroxide solution.

3. Results and discussion

3.1. Materials issues

Calcium carbide and calcium hydride are extremely reactive with water and care must be exercised to ensure they are kept dry. Extended exposure of small particles of these materials to air can result in the formation of calcium hydroxide and/or calcium carbonate on their surface, which decreases their reactivity. Furthermore, since glycerin is hygroscopic and readily absorbs moisture from air, it should be dried using a desiccant, such as molecular sieve, prior to slurry preparation. Once slurry is prepared it must be stored under moisture-free conditions.

Slurry consistency and reactivity are influenced by both particle size and glycerin content. Decreasing the particle size of calcium carbide and calcium hydride favors fast reaction rates, while increasing the amount of glycerin suppresses the reaction rate and also lowers the energy density of the slurry. Particle size of less than 0.5 mm is required to produce homogeneous slurry that can be pumped. Slurry containing larger particles (>2 mm) suffers from settling of reactants with time creating inhomogeneous regions, and hence does not produce uniform gas generation when pumped into water.

3.2. Reaction of calcium carbide and water

Fig. 2 is a plot of acetylene flow vs. time for the addition of water to carbide at a rate of 0.34 mL/min. It clearly displays erratic acetylene

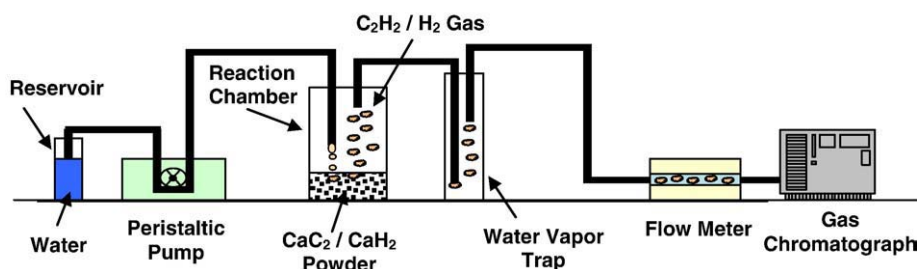


Fig. 1. Schematic of laboratory scale gas generator. Water is pumped into the reaction chamber containing calcium carbide and/or calcium hydride to produce acetylene and/or hydrogen.

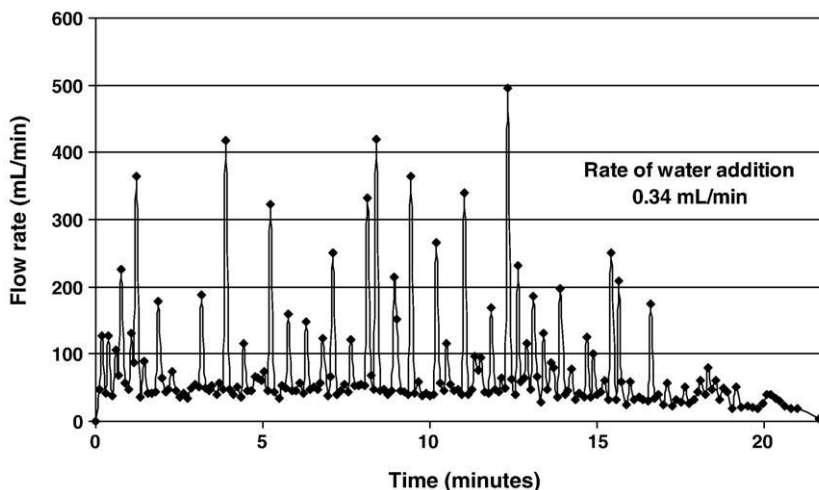


Fig. 2. Plot of acetylene flow vs. time for the carbide reaction at a constant water addition rate of 0.34 mL/min. The graph displays an erratic acetylene generation with a rate fluctuating between 40 and 500 mL/min.

gas generation with the rate fluctuating between 40 and 500 mL/min. This behavior can be attributed to the spontaneous reaction of a water droplet with a carbide particle. The reaction quickly produces a large amount of acetylene and then subsides until more water is added. Since the CFS cannot tolerate large fluctuations in gas flow, this method for producing acetylene is unacceptable. The CFS requires uniform acetylene (and hydrogen) generation to produce syngas, the fuel for the SOFC.

In an attempt to slow the reaction and produce uniform gas flow, the carbide particles were coated in glycerin to form slurry prior to reaction with water. Since glycerin is soluble in water, it dissolves away allowing water to make contact and react with the carbide to produce acetylene gas in a controlled fashion. It should be noted that while glycerin coats the particles, it does not react with them.

Fig. 3 gives a curve divided into four sections (A–D) for acetylene generation vs. time for the calcium carbide slurry at constant water addition of 0.34 mL/min. In contrast to Fig. 2, this plot shows that the reaction took place over a longer period of time and with no spiking of the acetylene flow rate. The acetylene flow climbed rapidly to 38 mL/min within the first few minutes then declined to 20 mL/min, where it remained steady for about 25 min before gradually tapering off.

The high initial rate of acetylene generation (A) can be attributed to rapid dissolution of the glycerin coating followed by reaction of the carbide particles with water. However, as the reaction proceeds, calcium hydroxide by-product builds and surrounds the particles, thus impeding further reaction and causing a decline in gas production (B). As more water is added to the system the hydroxide is removed (dissolved away) and the reaction proceeds in a steady fashion (C) until all the calcium carbide is gradually consumed (D).

Integration of the curve in Fig. 3 indicated that a total volume of 1.36 L of acetylene was produced from the reaction of 5 g of calcium carbide and water over a 90 minute period. The theoretical yield of acetylene for this reaction is 1.75 L, which gives a conversion efficiency of approximately 78%. Inadequate mixing of reactants and the buildup of calcium hydroxide in solution, which would not be the case in the actual CFS, contributed to less than expected acetylene production.

3.3. Reaction of calcium hydride and water

Initial experiments were carried out using uncoated calcium hydride powder. Addition of water to the hydride powder resulted

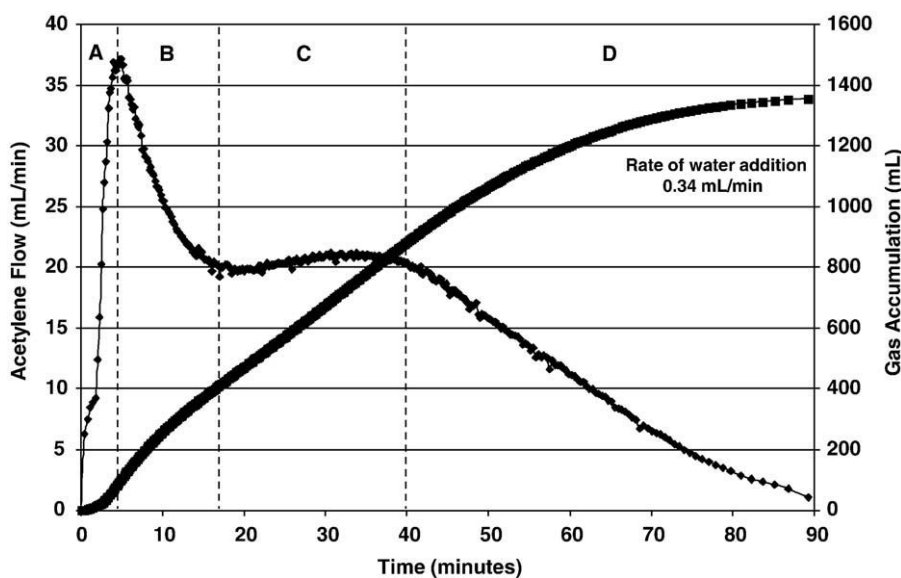


Fig. 3. Plot of acetylene flow and gas accumulation vs. time for the carbide reaction at a constant water addition rate of 0.34 mL/min. The graph displays smooth acetylene generation for the glycerin-coated calcium carbide. Integration of the flow rate yields a total volume of approximately 1.36 L.

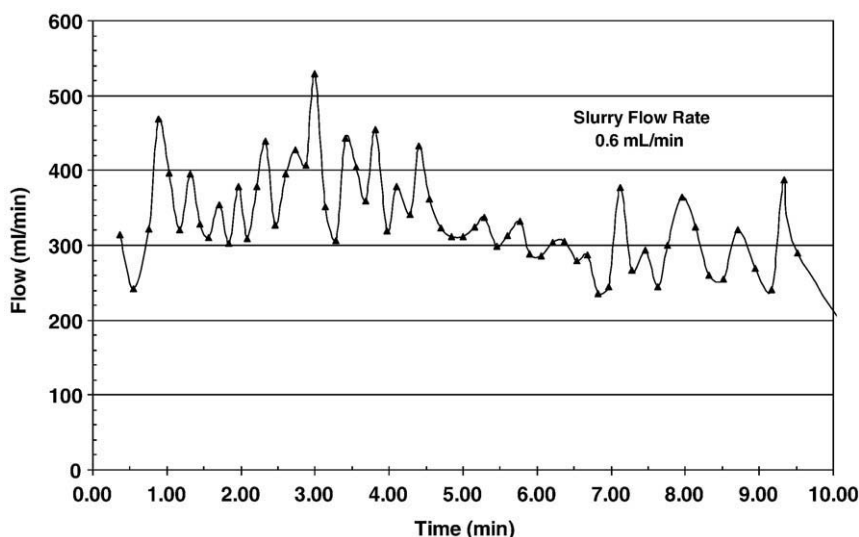


Fig. 4. Plot of hydrogen flow vs. time for the addition of calcium hydride slurry to water at a rate of 0.6 mL/min.

in a highly exothermic, uncontrollable reaction, which was considerably more energetic than calcium carbide and water. To moderate the reaction, glycerin slurry of the hydride was prepared, but unlike the procedure for the acetylene generation experiments whose results are given in Figs. 2 and 3, the slurry was pumped into water instead of water into the slurry. Fig. 4 shows the result from adding calcium hydride slurry to water to produce hydrogen gas at approximately 330 mL/min. In the CFS, slurry addition to water offers better thermal management since evaporation of water provides a means of moderating reactor temperature while providing steam for fuel processing.

3.4. Reaction of calcium carbide/calcium hydride slurry in water and 0.1 M $\text{Ca}(\text{OH})_2$

Fig. 5 shows results for the co-generation of hydrogen and acetylene from pumping calcium hydride/calcium carbide slurry into either water or 0.1 M calcium hydroxide solution. For the slurry in water, the flow rate ranged from 100 to 300 mL/min with an average composition of approximately 3:1 ($\text{H}_2/\text{C}_2\text{H}_2$) as determined from gas chromatography. This is an ideal ratio for acetylene hydrogenation since it is 50% greater than stoichiometric (2:1) and

should ensure complete conversion of acetylene to ethane in a hydrogenation reactor.

For the slurry pumped into 0.1 M calcium hydroxide solution, the acetylene/hydrogen flow started at about 450 mL/min then steadily declined to 100 mL/min. This behavior can be attributed to (1) the lower solubility of acetylene in calcium hydroxide solution compared with water [10], resulting in a higher initial flow rate due to less acetylene being dissolved in solution; and (2) the buildup of calcium hydroxide, which inhibits the reaction of calcium carbide (and calcium hydride) with water causing the acetylene (and hydrogen) flow rate to decrease with time. However, the self-contained CFS is designed to maintain the hydroxide concentration at a steady state by removing calcium hydroxide from solution via its reaction with carbon dioxide (from the fuel cell exhaust) to form calcium carbonate precipitate. Hence, the calcium hydroxide in solution is kept to a minimum, allowing acetylene/hydrogen generation to proceed uninhibited.

4. Conclusions

The controlled co-generation of acetylene and hydrogen was demonstrated via the hydrolysis reaction of a mixture of calcium

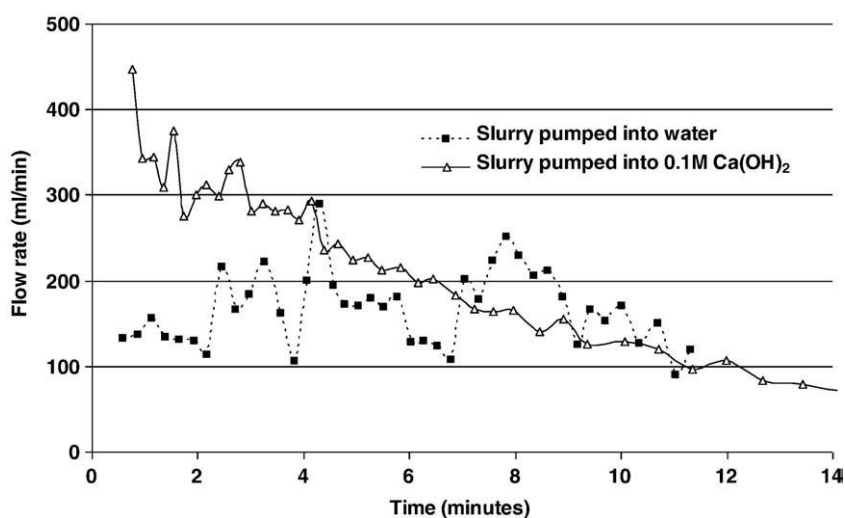


Fig. 5. Plots of combined hydrogen and acetylene flow vs. time from the reactions of calcium hydride/calcium carbide slurry in water and in 0.1 M calcium hydroxide.

carbide and calcium hydride. Glycerin was used to coat the reactant particles (to form slurry) in order to moderate the rate of this highly exothermic reaction.

It was shown that the use of slurry is an efficient way to deliver solid reactants to the reaction chamber of the CFS. By pumping slurry into water, the heat generated by the reaction is absorbed by the water offering better thermal management of the system. It was also shown that the presence of calcium hydroxide by-product in the reactant solution decreased the solubility of acetylene in the solution, as well as inhibited the reaction of calcium carbide and calcium hydride with water.

SOFc technology does not yet exist that can utilize direct acetylene utilization. In order to convert acetylene to a viable fuel stream, it must first be hydrogenated to ethane and then reformed to a hydrogen/methane-rich reformat in a two-step reactor process, which was demonstrated in earlier studies [9,11]. Calcium carbide and calcium hydride offer high energy storage as well as an entirely self-contained power system with no exhaust streams, attributes favorable for undersea vehicle applications.

Acknowledgements

We acknowledge the Independent Laboratory Initiative Research program at the Naval Undersea Warfare Center Division Newport in support of this work.

References

- [1] W.B. Sanford, *J. Chem. Educ.* 10 (7) (1933) 420.
- [2] H. Chiang, Y. Ho, K. Lin, C. Leu, *J. Alloys and Compounds* 434–435 (2007) 846–849.
- [3] A. Farkas, L. Farkas, *J. Am. Chem. Soc.* 61 (12) (1939) 3396–3401.
- [4] N.S. Schbib, M.A. Garcia, C.E. Gigola, A.F. Errazu, *Ind. Eng. Chem. Res.* 35 (5) (1996) 1496–1505.
- [5] A. Borodziński, A. Cybulski, *App. Catalysis A: Gen.* 198 (2000) 51–66.
- [6] N.A. Darwish, N. Hilal, G. Versteeg, B. Heesink, *Fuel* 83 (2004) 409–417.
- [7] J.R. Rostrup-Nielsen, *J. of Catalysis* 31 (2) (1973) 173–199.
- [8] U.S. Patent # 7,635,531, "Zero-effluent (self-contained) fuel cell system for solid oxide fuel cell-powered unmanned underwater vehicles".
- [9] A.A. Burke, L.G. Carreiro, E.S. Greene, *J. Power, Sources* 176 (2008) 299–305.
- [10] U.S. Patent # 6,294,148, "Process for high recovery of acetylene and lime from the reaction of calcium carbide with water".
- [11] A.A. Burke, L.G. Carreiro, R.C. Urian, *J. Fuel Cell Sci and Tech.* 7 (3) (2010) 034502.