Hydrogen Generation by Means of the Aluminum/Water Reaction

I. E. Smith*
Cranfield Institute of Technology Cranfield, Bedfordshire, England

An aluminum amalgam will react with water at ordinary temperatures with the formation of aluminum hydroxide and the liberation of free hydrogen. In the case of a block or sheet of the metal having an amalgamated surface, this reaction will continue until all the aluminum has been consumed. The reaction rate is observed to be temperature dependent, and this affords a simple means of regulating the output of hydrogen. If the supply of water and disposal of waste is discounted the reaction is shown to be superior, on a volumetric basis, to all other common means of producing hydrogen, and furthermore is competitive on a weight and cost basis with other chemical production methods. The inherent simplicity of such a scheme for hydrogen generation offers attractive advantages in terms of reliability.

Introduction

DEVELOPMENTS in the field of fuel cells have given rise to the need for a supply of hydrogen having a high degree of purity, particularly with respect to carbon monoxide. In some cases the need is met by the cryogenic storage as liquid hydrogen or as a compressed gas. In others a more complex generating system such as hydrocarbon reformation, ammonia cracking or metallic hydride decomposition fulfills the requirements more adequately. As a result, the chemical engineering problems associated with the generation of hydrogen are not infrequently greater than those of the fuel cell itself. In the general case the source of hydrogen should be lightweight, compact, simple, i.e., reliable, controllable and safe, and inevitably all these considerations apply when fuel cells are employed as an energy source in aerospace systems.

In other applications, however, these requirements may sometimes be relaxed. For example, in the case of a fixed land-based system, cost and safety considerations may outweigh size and weight, while for a seaborne application compactness and safety may be the principal criteria for the selection of the hydrogen generator.

It is the purpose of this article to study a possible system of hydrogen generation provided by the reaction between aluminum and water, and to discuss the potentialities of such a system on the basis of low volume, simplicity, safety and controllability. In the comparisons which will be made it has been tacitly assumed that unlimited quantities of water both as a reactant and a coolant are available, and that the disposal of contaminated water presents no problem nor incurs any penalty.

Aluminum-Water Reaction

Under normal conditions aluminum does not react with water owing to the formation of a protective layer of aluminum hydroxide. However, an amalgamated aluminum surface reacts vigorously with water as was first shown by Cohen and Ormond,[1] G. le Bon[2] and others, the products being aluminum hydroxide and hydrogen. This reaction may be represented by the equation

$$Al + 3\ H_2O \rightarrow Al(OH)_3 + 1\tfrac{1}{2}\ H_2 - 99.8\ \text{kcal}$$

The presence of mercury appears to prevent the adherence of aluminum hydroxide to the metal surface, at the same time permitting the diffusion of aluminum through the amalgam layer.

Aluminum may be amalgamated by contact of the metal with mercury in the presence of any agent which removes the protective oxide film. Tissier[3] produced an amalgam by employing a dilute solution of potassium hydroxide and Casamajor[4] by using a dilute acid to remove the oxide or hydroxide film. Baille and Fèry[5] claim to have isolated a compound $Hg_3\,Al_2$ in crystalline form, but the results of subsequent workers on the melting point of aluminum amalgams casts a certain amount of doubt on this claim.

Cohen and Hartley,[6] Wislicenus[7] and Kohn-Abrest et al.[8] found that an amalgam could be formed by the immersion of aluminum in a solution of mercuric chloride. They showed that the presence of amalgam could be detected down to concentrations less than 0.001% of $HgCl_2$ and also discovered that the process was inhibited by the presence of copper in the aluminum, but not by either iron or silicon which occur more frequently as impurities. This process has been suggested as a possible means of producing hydrogen from aluminum scrap in a paper by Schmidt,[9] although it postulates the provision of a continuous supply of mercuric chloride to the cell.

The original investigators[1,2] contented themselves with observing that amalgamated aluminum reacted with water, and did not attempt to measure the rate or elucidate the rate controlling mechanism. Furthermore, apart from commenting that the rate of reaction appeared to increase with the temperature, no quantitative assessment of the temperature dependence was made.

A simple experiment was therefore carried out which demonstrated that hydrogen output from the reaction of about 0.25 l/m^2 sec (N.T.P.) at a temperature of 100°C was possible. As this corresponds to an electrical power of 2.66 kw/m^2, if the hydrogen is consumed in a perfectly efficient fuel cell, the process appeared sufficiently attractive to warrant further investigation.

Experimental Investigation

A parallel section of commercial glass pipe with end covers retained by the bolts was employed as a reactor, with appropriate connections for water supply, waste withdrawal and gas outlet. A flow diagram of the apparatus is indicated in Fig. 1.

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* Reader in Applied Thermodynamics, School of Mechanical Engineering. Member AIAA.

Aluminum plates measuring 20.3 × 7.6 × 0.15 cm were first amalgamated and then stacked vertically in the reactor with nonmetallic separators inserted along their edges. The separators extended to within 3 cm of the bottom of the plates in order to allow free ingress of water to replace that removed by the air-lifting action of the liberated hydrogen. The number of plates varied between 7 and 14, according to the output required, and the assembly was contained by means of elastic bands, in order to compensate for the varying thickness of the pile as the aluminum was consumed.

In operation the vessel was filled with cold water until the plates were submerged and then allowed to stand vented until the desired operating temperature was reached. Although initially hydrogen bubbles could be observed issuing from the interstices between the plates, the precipitate of hydroxide which formed quickly obscured the view. For the particular reactor dimensions employed the warm up period occupied between 30 and 60 min, depending on the number of plates in the pile, following which the inlet water flow rate was adjusted to maintain a constant temperature. The ullage space enabled the removal of the excess water and hydroxide to be carried out batchwise, and no attempt was made to control the level automatically. The pressure within the vessel was maintained constant by means of a spring-loaded relief valve in the gas line having a variable setting, and the hydrogen was passed through a cooling coil prior to metering in a standard wet gas meter.

The following variables were investigated: 1) temperature, 2) pressure, 3) plate spacing, 4) plate orientation, and 5) solution pH and electrolyte concentration.

Effect of Temperature

For this investigation assemblies consisting of 7, 12 and 14 parallel plates were employed with an average plate spacing of 1.5 mm. At the low temperatures control was effected by manually regulating the supply of fresh water, but above 100°C, when the reaction became very rapid, control was achieved by allowing the solution to boil under a constant pressure.

The results of these experiments are shown in Fig. 2 where the logarithm of the reaction rate is plotted against the reciprocal of absolute temperature. The temperatures embraced a range of from 10 to 134°C.

The results are well correlated by a straight line corresponding to the expression:

$$R = 6.6 \times 10^5 \cdot e^{-11{,}100/RT}$$

where R is in 1/m²sec of hydrogen at N.T.P. It will be observed that a hundred-fold change in the rate may be realized by altering the temperature from 10°C to 100°C.

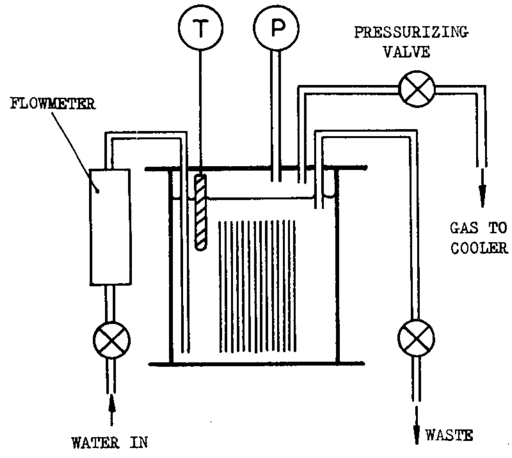


Fig. 1 Flow diagram of reactor.

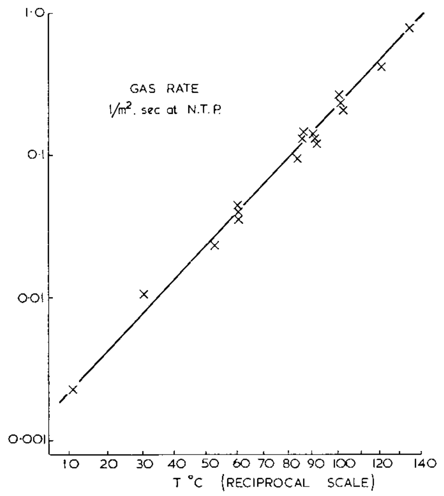


Fig. 2 Reaction rate vs temperature.

In general, the reaction appeared to be perfectly smooth and controllable within the limitations of the equipment, and the rate of erosion, which is discussed in more detail later, was remarkably constant. If the water was drained from the vessel, a rapid reaction occurred with the film of water remaining on the plates leading to a rapid increase in their temperature. The fluffy deposit of aluminum hydroxide which remained when the water evaporated was greyish in color suggesting that the elevation of temperature had resulted in the removal of mercury from the metal surface. This was confirmed by the fact that a few such cycles left the aluminum plate inert.

It was also noticed that at temperatures above 100°C the suspension of hydroxide precipitate appeared slightly grey instead of white, indicating loss of mercury from the aluminum plates. At no time was this severe enough to cause any apparent reduction in the reaction rate, nor the eventual complete solution of the aluminum plates. This mercury loss might, however, have achieved significant proportions had still higher temperatures been investigated, and this possibility must be born in mind in extrapolating Fig. 2.

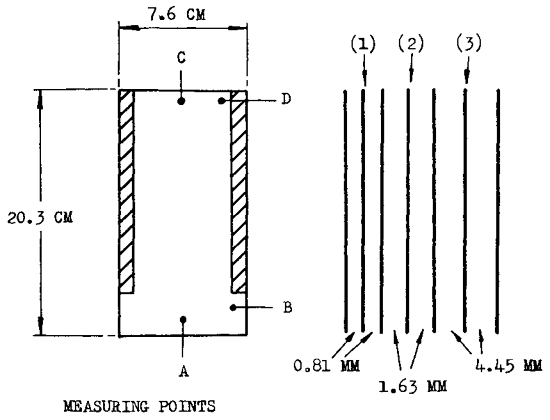
Freshly amalgamated plates appeared to react less rapidly than those which had been reacting for some time, and an inspection of the used plates showed that surface etching had taken place. No attempt was made to investigate the degree of increase of surface area and the figures for the rate of gas evolution are based on the projected area of the plate.

Effect of Pressure

While the effect of pressure would not be expected to influence the reaction rate per se, the flow rate of solution over the plates would be governed by the air-lift effect of the rising hydrogen bubbles. Thus the pressure might affect the overall reaction rate by virtue of the reduction in the volumetric rate of gas evolution. In order to determine whether or not this was so the pressure was varied between 1 and 3 atm absolute at an operating temperature of 90°C. No variation in the rate of gas evolution was observed, indicating that solution flow rate within this range was not a controlling influence on the reaction.

Effect of Plate Spacing

From these observations it appeared reasonable to suppose that the plate spacing could be reduced below 3 mm without impairing the output. For this series of tests the temperature was maintained at 90°C, and the reaction rate was determined by removing the plates at known time intervals and measuring their thickness. In order to minimize the rapid



RATE OF CHANGE IN PLATE THICKNESS (MM/MIN x 10^3)

PLATE NO.	SPACING (MM)	POSITION A	B	C	D
1	0.81	4.2	4.2	5.0	5.0
2	1.63	4.2	4.3	4.7	5.0
3	4.45	4.7	4.2	4.2	4.3

Fig. 3 Erosion rate variation with position and plate spacing.

oxidation which occurs when amalgamated aluminum is exposed to air the plates were removed and quickly transferred to a bath of cold water while the measurements were being made.

The principal results are shown in Table 1 where the erosion rate is listed (corresponding to one half of the actual change in plate thickness). Essentially, the table demonstrates an independence of reaction rate with respect to plate spacing down to 0.13 mm for plates 20 cm high, since the observed variation in rate erosion could be encompassed by an uncertainty in temperature of 1°C.

Measurements of the plates were taken at four locations as shown in Fig. 3 in order to determine whether the erosion occurred uniformly. The results, which are shown in the adjoining table, indicate an almost complete uniformity of erosion across the surface of the plate, and at no time during the series of experiments was there any indication of appreciable nonuniformity.

This observation leads to the conclusion that a reactor could be designed having a cross section substantially that of the aluminum fuel, since the plate spacing (and the return passage for the circulating liquid) may be as low as 0.13 mm per plate. However, for other reasons such as temperature control, it may be desirable in a practical reactor to allow for a volume of water greater than this minimum.

Table 1 Plate spacing and erosion rate temperature = 90° C

Plate spacing mm	Erosion rate mm/min × 10^3
4.45	2.42
1.63	2.47
0.81	2.62
0.51	2.88
0.25	2.71
0.13	2.42

In order further to verify the independence of the rate of reaction on induced liquid circulation, comparative tests were carried out with a plate suspended vertically and horizontally in the solution. The results are shown in Fig. 4, from which it can be seen that the erosion rate appears to be quite independent of the attitude of the plate. The gradual increase in the erosion rate over the first 50 minutes of operation corresponds to the period of initial etching of the surface, and a comparison of the change in slope suggests that the etched surface is of the order of five times as reactive as an unetched surface. Finally, it was noted that a test in which a plate was rotated at a peripheral velocity of 1 msec gave an erosion rate identical with that for a stationary plate.

These observations suggest that the transport of fresh water to the reacting surface occurs as a result of hydrogen bubbles forming and then leaving the surface in an analogous manner to that which occurs in nucleate boiling. The rate of evolution of gas may thus be virtually independent of the mass circulation of the water, although this must not be taken to imply that an over-all circulation is unnecessary. Considerations of temperature control as well as the removal of hydroxide will require a finite, although possibly small, circulation.

It is tempting to speculate that the maximum rate of hydrogen evolution possible may correspond to the "crisis" which occurs in nucleate boiling, and if this speculation is true, the maximum will be in the region of 10^3l/m^{2}sec for horizontal plates facing upwards, a far higher rate than was ever observed in the present tests.

In reality, the maximum rate of evolution may be limited by other factors such as the rate of diffusion of aluminum through mercury or, even more realistically, the loss of the mercury in association with the hydroxide that has already been mentioned.

Substitution of N/100 NaOH for water gave rise to no increase in the erosion rate at 90°C. On the other hand, it was found that a solution of N/100 HCl approximately doubled the rate of erosion. So far as neutral electrolytes were concerned there was no observable change in the rate of erosion in the presence of sodium chloride at concentrations of 2N.

Hydrogen Purity

A sample of the gas was analyzed for impurities with a Perkin-Elmer gas chromatograph. It was found that the hydrogen contained approximately 20 ppm of oxygen and 80 ppm nitrogen, clearly corresponding to the liberation of dissolved air from the water. No other impurities were found down to an estimated detection limit of 1 ppm.

Performance Comparisons

Since the generation of hydrogen is of interest in fields other than that of fuel cell systems, outputs have been expressed in liters of hydrogen at N.T.P. In the context of the fuel cell it may be noted that 1 l/sec corresponds to an electrical output of 10.6 kw and 1 l corresponds to 2.94×10^{-3} kwh if the cell is perfectly efficient. Table 2 compares the performance of this and other sources of hydrogen on a basis of volume, mass and approximate cost. No account has been taken of any auxiliary equipment such as storage vessels or conversion plant, except that in the case of compressed hydrogen the figure for weight has been taken from a review of the subject by Singman and Fortziati[10] which includes that of a cylinder of $^1/_2$ l capacity. The use of larger cylinders would certainly improve on this figure, although it is unlikely that this source will ever become competitive on a weight basis with the other systems.

Table 2 Source volume, mass and cost comparison

Source	Hydrogen production liters of gas per liter	per kg	per dollar (approx.)
Aluminum	3,360	1,245	3,000
Lithium hydride	2,310	2,820	30
Calcium hydride	1,810	1,065	200
Hydrocarbon reformation	1,250	1,600	20,000
Ammonia cracking	1,615	1,976	15,000
Liquid hydrogen	789	11,100	16,000
Compressed hydrogen (100 atm)	110	84[a]	...

[a] Includes cylinder weight.

An assumption of 100% efficiency for the hydrocarbon reformation and ammonia cracking process has been made, whereas in practice it will be lower than this. In addition, no allowance has been made for the mass or volume of water consumed by these systems, whether for chemical or cooling purposes, since at the outset it was stated that the method was primarily under consideration for situations having an unrestricted supply of water.

The table clearly illustrates the superiority of the aluminum/water process over all others on a volumetric basis, and that on a weight basis, apart from lithium hydride, all the chemical systems with a long term storability have rather similar specific fuel consumptions. The table of costs is perhaps less satisfactory, and is based on current commercial prices of the fuel only. The generation of hydrogen by the reformation process, for example, appears inexpensive on account of the fact that the conversion and purification plant costs have not been included. It does, however, highlight the high cost of lithium hydride as a storable system, and also the low cost of liquid hydrogen if long term storability is not an essential requirement.

System Considerations

The utilization of the aluminum/water reaction in a practical hydrogen could be realized in a system employing the simplest continuous flow type of plant and equipment. A reactor vessel would contain a number of separated aluminum plates having a surface/volume ratio according to the duration and demand for which the hydrogen supply was required. The plates, amalgamated either prior to loading, or subsequently by flooding with a solution of mercuric chloride, would be fed with a water supply at a controlled rate in order to maintain the temperature and hence the supply of hydrogen constant. The waste product, aluminum hydroxide, would be withdrawn as an aqueous suspension at a similar rate once the reactor was filled and had reached its operating temperature. Although the time of response to a demand for an increase in the rate of gas supply will depend principally on the thermal capacity of the reactor as a whole and will not be unduly rapid, temporary acidification of the water following a demand for an increase in output would materially reduce the period. The response time for a reduction in output will depend on how rapidly the reactor can be cooled by fresh water circulation.

Although, as has been noted, a variation in the output of two orders can be achieved by a change of operating temperature of 10–100°C, a total shut-down can be achieved only by complete withdrawal of the water supply. Following this, even in an inert atmosphere such as nitrogen, the residual moisture on the plates was found to cause a rapid terminal reaction leading to overheating accompanied by the loss of mercury from the plates. However, by displacing the water with a miscible inert liquid such as acetone or an alcohol this problem could be avoided.

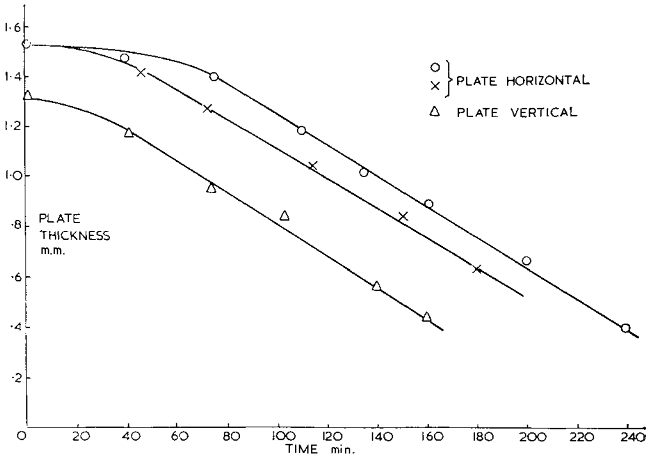


Fig. 4 Plate thickness variation with time.

It will be recognized that the disposal of a waste product contaminated by mercury could present problems. It was noted that for the tests carried out above 100°C, when a loss of mercury from the surface took place to some extent, the waste contained only elemental mercury, and this could to a large extent be extracted by circulating the effluent over copper gauzes. At temperatures below 100°C the loss of mercury from the amalgamated surface appeared negligible. This aspect might, however, require further investigation if large scale use of the process was contemplated.

Conclusions

The foregoing is not intended to form a comprehensive review of hydrogen generation systems for this has already been provided by Schmidt[9] and Singman and Fortziati.[10] Its purpose has been to draw attention to the viability of the aluminum/water reaction in situations where large quantities of water are available. That the process outperforms other systems on a volumetric basis and has also the merit of simplicity of construction and control suggests that further investigations on a pilot scale may be warranted.

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