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Comparative reactivity of industrial metal powders with water for hydrogen production

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ABSTRACT

The in-situ production of hydrogen from a metal-water reaction resolves some of the main obstacles related to the use of hydrogen as an alternative fuel, namely storage and safety. In this study, experiments are conducted in a batch reactor with sixteen different commercially-available industrial metal powders, with water temperatures ranging from 80 to 200 °C. The hydrogen production rate, total yield, and reaction completeness are determined for each metal-powder fuel and reaction temperature. Aluminum powder produces the largest amount of hydrogen per unit mass throughout the temperature range, followed by the magnesium powder. Manganese powder, which produces the largest amount of hydrogen per unit volume at high temperatures, exhibits a sharp increase in yield between 120 and 150 °C, suggesting the existence of a critical energetic threshold. The aluminum and magnesium powders exhibit high reaction rates, and together with the manganese powder, appear to be the most attractive candidates to serve as fuels for in-situ hydrogen production.

Introduction

The quest for a clean, carbon-free energy source to replace fossil fuels has been the focal point of many scientists and environmental organizations over the past couple of decades. One of the proposed solutions, widely discussed and investigated, is the use of hydrogen as an alternative to fossil fuels. Combustion of hydrogen, or its consumption in a fuel cell, produces zero carbon emissions and hydrogen can be readily manufactured using clean energy sources through water electrolysis. There are, however, two major obstacles that have so far limited the widespread implementation of hydrogen-based energy systems [1–4]: (a) *storage* – due to its extremely low density, the storage of gaseous hydrogen requires large high-pressure tanks; even in its liquid form, the density of hydrogen is only 0.071 kg/m^3, much lower than that of gasoline, and bulky well-insulated Dewar-type storage tanks are required to prevent the rapid boil-off of cryogenic hydrogen due to its low boiling point (−252.9 °C), and (b) *safety* – when premixed with air, hydrogen is explosive and has one of the widest flame and detonation propagation concentration ranges among common combustible gases [4,5]. Therefore, hydrogen poses a considerable safety risk during traffic accidents if stored onboard vehicles, or in the case of leaks from fuel stations in urban areas. Similar safety problems have limited the implementation of hydrogen storage in the form of chemical compounds such as metal hydrides [6,7], which are unstable, or ammonia [8], which is poisonous.

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Some novel alternative methods for hydrogen storage, such as carbon nanotube matrices [9], have not proven effective even in the small-scale laboratory environment and are far from practical use.

Water, of course, is a safe, abundant and accessible source of hydrogen, and in fact water contains 50% more hydrogen per unit volume than liquefied hydrogen. Releasing hydrogen from water *in situ*, at the point of utilization, can be achieved by reacting it with a metallic element. A number of environmentally-stable and widely-used metals such as aluminum, magnesium and silicon readily react with water, releasing not only hydrogen but also a large amount of heat. Many metals possess a volumetric energy density greater than that of gasoline if both the hydrogen and heat released during the metal-water reaction are utilized for energy conversion. In these systems, the metal powders effectively serve as secondary energy carriers, storing primary electrical or heat energy in a chemical fuel that can be converted to hydrogen and heat when needed [10–13]. Metal powders as fuels are safe to store and transport, and are expected to exhibit an indefinitely-long shelf life if protected from moisture in hermetically-sealed containers. Besides hydrogen and thermal energy, the only products of metal-water reactions are metal oxides/hydroxides, which in most cases are chemically inert and easy to collect and store. Metal oxides/hydroxides can be reprocessed back to pure metals using existing metal smelters [14–16] or novel technologies that utilize clean primary energy sources such as solar, wind or hydroelectric power [10,11,17]. Metal-powder fuels do not have the storage and safety problems endemic to hydrogen, and represent an energy commodity which can be stored and traded, in a similar manner to solid, liquid and gaseous hydrocarbons.

In the past, a number of attempts have been made to harness metal-water reactions for hydrogen generation [18–56], although few have suggested using the heat produced from the metal-water reaction. Many studies have been published regarding aluminum-water reactions [18–41], but most were performed at atmospheric pressure conditions and were therefore limited in terms of reaction temperature and hence, reactivity [19–40]. Conducting the aluminum-water reaction at elevated temperatures serves to increase the hydrogen production rate and total yield, as demonstrated in a study by Yavor et al. [18], and also enables the heat produced during the reaction to be used to drive a heat engine or thermoelectric generator with higher thermal efficiency. Other techniques to increase the metal-water reaction rate include: utilizing nano-sized powders [33,34], which are expensive, contain lower metal content due to the relative thickness of the oxide shell, and may have associated health and safety concerns; or adding reactive catalysts such as salts or metal alloys [20–32], which introduce corrosive materials to the compound, as well as lower the potential total yield and increase the costs. Using commercially-available micron-sized powders eliminates the above mentioned drawbacks, and allows the use of less expensive, pre-existing industrial powders.

Although most prior research work on metal-water reactions has used aluminum powder, some studies have also considered the use of magnesium [42–47], zinc [48–50] and boron [47,51,52] powders. Most of the previous studies have focused on the reaction of metals with water vapor rather than liquid water, or have utilized rate-enhancing additives such as metal alloys and salts. It is worthwhile to investigate the reactivity of water with other metals, because other practical considerations, such as the cost of the powders, the energy cycle economics, or the environmental impact of the metal-oxide recycling stage, may be as important as the overall thermodynamics of the process. For example, the current standard for aluminum smelting via the Hall-Heroult process [57] is accompanied by a relatively large amount of CO_2 emitted due to the reaction of oxygen, released from the aluminum oxide electrolysis, with carbon-based cathodes. Regarding the availability of metal powders, large amounts of silicon, iron and ferromanganese powders are available at minimal cost, since they are produced as byproducts of the electronics and powder metallurgy industries, and these have received little study.

A systematic comparison of the reactivity of water with different metal powders is not available in the literature to date. In the present work, an extensive survey of the reactivity of distilled water with sixteen commercially-available metal powders at different temperatures is performed, and parameters such as the hydrogen production rate, yield and reaction completeness are determined. The choice of the most important metric (e.g., hydrogen production rate vs. overall yield vs. energy density) will, in general, depend on the application and will govern the optimum choice of metal. The present study represents a first step in quantifying the relative reactivity and reaction yield of different metal powders with water as a function of temperature, although the conclusions are necessarily influenced by the properties (e.g., average particle diameter and distribution, particle morphology, specific surface area, etc.) of the particular powders studied. Further studies are required to determine, for a given metal, the relative influence of each of the particle properties on the reactivity parameters.

Thermodynamics

For a given oxidation state, the theoretical amount of hydrogen produced from the metal-water reaction has no bearing whether the reaction product is metal oxide or hydroxide, as demonstrated in Eqs. (1) and (2):

$$xM + yH_2O \rightarrow M_xO_y + yH_2 \tag{1}$$

$$xM + 2yH_2O \rightarrow xM(OH)_{2y/x} + yH_2 \tag{2}$$

Thus, the maximum theoretical hydrogen yield that can be produced from each metal powder is presented in Fig. 1(A), both per unit mass and per unit volume, with the metals arranged by increasing metal molecular mass.

The theoretical hydrogen yield from the metal-water reaction for various metals, shown in Fig. 1(A), provides a comparison of the different metals as potential candidates for hydrogen production. However, this will only serve as an initial guideline, since the maximum yield may not be reached, and it is possible that metals with a lower potential yield will produce larger amounts of hydrogen. In addition, the energy released from the metal-water cycle, composed of both