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Hydrogen production using waste aluminium dross: from industrial waste to next-generation fuel

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Abstract. This article describes the production of hydrogen from white aluminium dross, an industrial waste generated in the aluminium smelter plants. Hydrogen is generated by metal-water reaction between aluminium and water in presence of alkalis like sodium hydroxide and potassium hydroxide. Aluminium dross is described as a heterogeneous material with its major constituents being metallic aluminium, alumina and other salt fluxes like NaCl and KCl. Utilizing the metallic aluminium content entrapped in the matrix of alumina for the metal-water reaction has been the driving force for the waste recycling and simultaneous hydrogen production. Bulk aluminium dross was crushed and downsized. The finer fraction of the powdered aluminium dross is used for the experiments. The effects of dross in the alkaline solution, temperature of the solution and the time of the reaction were studied to understand the generation of hydrogen. The alkaline solution breaks the protective layer of alumina and exposes the entrapped aluminium content to water, thereby commencing the hydrogen liberation.

Key words: aluminium dross, hydrogen, waste management, recycling.

INTRODUCTION

The development of the next-generation fuels is very crucial to match the demands of the world. Fuel consumption per capital has increased radically in the present day and it is projected to rise as the technological advancement takes place. The growth in industrial and transport sector simply necessitates the research in the field of fuel and energy.

In this scene of technological rush, hydrogen comes into the picture. Hydrogen is an important fuel and source of energy. Compared to the conventional fuels, the combustion of hydrogen gives rise to water vapour, whereas other fuels tend to release carbon dioxide and carbon monoxides. The gross calorific value of hydrogen is nearly 39.4 kWh kg^{-1} compared to gasoline (12.89 kWh kg^{-1}). The value of hydrogen increases readily as the conventional fuels are limited resources and the prices of these fuels are increasing with the passing day.

The production of hydrogen is usually carried out by coal gasification and water electrolysis. These methods are the conventional processes that have been optimized and studied thoroughly to improve the output of the hydrogen. These processes include the utilization of external fuels and energies to release the gas. Recently, the focus has shifted to developing newer and better methods to produce hydrogen. One of the processes is the exploitation of metal-water reaction.

It is well known that when metal comes in contact with water, the formation of metal oxide and hydroxide takes place. This is accompanied with the release of hydrogen gas. The rate of gas evolution varies with the metal and the metal-water reaction rate. When highly reactive metals are employed for the hydrogen evolution, the chances of explosion are greater and it becomes very unsafe. Using aluminium for the purpose of metal-water reaction has always attracted the researchers. The two main reasons for this are: 1. Aluminium-water reaction is aggressive enough to produce sufficient amount of hydrogen. Theoretically, nearly 1.2 L of hydrogen can be generated from 1 g of aluminium. Also, the reaction with aluminium is controllable. The chances of explosion are reduced as the reactivity of aluminium is far less than sodium and other reactive metals. 2. The abundance of aluminium is fairly higher than any other metal.

Using aluminium as a raw material for hydrogen generation has been studied (Uehara et al., 2002). When fresh surface of metallic aluminium comes in contact with water, the generation of hydrogen takes place rapidly. The production of fresh surface takes place when the metal is machined and chipped. Just as the layer of aluminium is produced, the reaction for hydrogen generation increases.

The researcher fraternity has conducted many experiments and a large variety of opinions are already developed regarding the production of hydrogen using aluminium. Directly applying aluminium to produce hydrogen is expensive. To solve this problem, aluminium dross can be successfully used to supply for the metallic aluminium essential for aluminium-water reaction. Aluminium dross is a by-product waste generated in the aluminium industries. During the melting and remelting of aluminium ingots, the formation of aluminium dross takes place when molten aluminium comes in contact with atmospheric oxygen. This semisolid oxide layer is removed during the taping of molten metal. When this skimmed product is allowed to cool to room temperature, it becomes very rigid. This resultant product is aluminium dross.

There are mainly three types of aluminium dross: white dross, black dross and salt cakes. White dross is the dross generated during the primary processing of aluminium at primary aluminium smelter units. This type of dross has higher metallic aluminium content, hence the white colour. Black dross is produced in the secondary aluminium smelter units. It has relatively lower amount of metallic aluminium with greater percentage of aluminium oxide and salt fluxes. Salt cakes are generated after aluminium is extracted from white dross. These cakes essentially have higher amount of salts in it, with lower amount of oxides and metallic aluminium (Meshram & Singh, 2018).

As the amount of metallic aluminium is greater in white aluminium dross, the utilization of white aluminium dross for generation of hydrogen is a good alternative to pure aluminium. The major challenge associated with the utilization of aluminium dross is its lower tendency of reaction. It is well known that aluminium has a thin layer of alumina over it, which acts as a protective shield. This layer simply hinders all contact with the metallic content within the oxide layer. This oxide protection is removed when the water is turned alkaline or acidic. Since aluminium and alumina react with acids and alkalis, the protective layer gets damaged and metallic aluminium therein gets exposed for further reactions (Meshram & Singh, 2017).

Hydrogen production using aluminium dross as a raw material has been studied by researchers around the world (David & Kopac, 2012). The fine powder of aluminium dross has been subjected to high energy ball milling to reduce the particle size to a range of few micrometres. Due to the great drop in the size of the particles, the specific surface area of the particles increases rapidly. This leads to greater exposure of surface to water and greater tendency of hydrogen evolution. It must be noted here that the water used for the reaction was tap water and no use of alkaline solution was carried out. The virtue of small particle size and larger specific surface area leads to the hydrogen evolution. The major disadvantage of this process is the use of high energy ball milling. This is a highly energy intensive process and the amount of sample prepared for the experiment is very less. The commercial applications of this process are quite not possible due to the economic reasons.

The use of alkaline solutions for aluminium-water reactions has not been thoroughly studied. Taking the raw material as white aluminium dross, the generation of hydrogen is a great opportunity to explore and establish another method to efficiently produce hydrogen. The present research deals with the generation of hydrogen using alkaline solutions and the recycling of white aluminium dross.

MATERIALS AND METHODS

As received aluminium dross is crushed and downsized to achieve fine powders. Since metallic content of white aluminium dross is quite high compared to black dross, the coarser fraction of the downsized dross is separated. The coarser fraction of white aluminium dross has a greater amount of aluminium in it because the metal drops tend to accumulate and agglomerate in the molten state. The finer fraction has a greater amount of oxide matrix that binds the metallic aluminium in it. Due to the greater specific area of finer fraction, it is used in the aluminium-water reaction.

The temperature of the water is increased using a hot plate with magnetic stirrer. Separately, aluminium dross fine powder is crushed with sodium hydroxide and potassium hydroxide pellets to make a homogeneous mixture using mortar and pestle. The weight of aluminium dross in the mixture is increased, keeping the amount of alkali constant. The objective is to study the variation in the amount of gas generated with change in amount of dross fed for the reaction and change in temperature.

The aluminium-water reaction takes place in a 100 mL conical flask. When aluminium dross-alkali mixture is added to the distilled water at the reaction temperature, a sudden surge of gas is observed. Care is to be taken that the evolution of gas doesn’t take place before the mixture is added to water. The generation of hydrogen is possible even before that as the atmospheric water vapour can interfere severely, due to the hygroscopic nature of alkalis. It is important to make sure that just as the mixture comes in contact with water, the conical flask is sealed with a rubber cork fitted with a pipe. This arrangement will help in the transfer of the gas generated in the conical flask. This gas is collected and measured in an inverted measuring cylinder filled with water placed in a water bath.

The amount of gas collected is measured in a fixed period of time (15 minutes) and simultaneously the rate of gas evolution is determined. When the rate of gas evolution drops down to less than 5 mL minute^{-1}, the reaction is stopped and the final reading is measured. The final liquor obtained is filtered and the solution is separated from the residual solid. In all of the experiments, the weight of the dross has been varied from

1 to 3 g, while the weight of the alkali (NaOH and KOH) was kept constant at 1 g. This led to the variation of the weight ratios employed for the experiments.

Fig. 1 shows the schematic representation of the experimental procedure to efficiently produce hydrogen. The characterization of the dross has been done using the X-ray diffraction facility. Rigaku Tabletop Miniflex 600, Dtex Ultra with copper target has been used for this characterization. The XRD pattern has been illustrated in the Fig. 1,b.

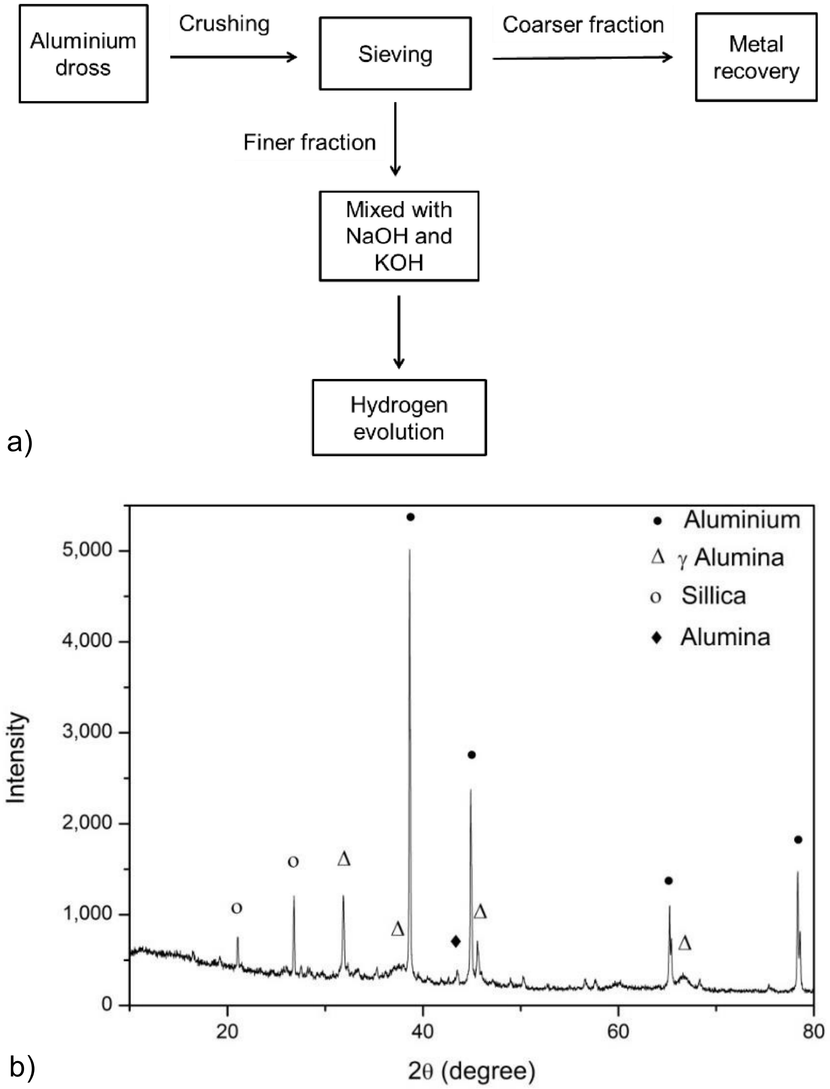

Figure 1. a) Schematic diagram illustrating the procedure for hydrogen gas evolution using aluminium dross is shown; b) X–ray diffraction pattern for powdered aluminium dross.

RESULTS AND DISCUSSION

The evolution of hydrogen gas is shown in Fig. 2 and Fig. 3. It can be seen from the graphs that the overall rate of gas evolution was initially high and then it became very less, thereby resulting in the stability of the overall gas production. The same trend is observed in both the alkalis used for the metal-water reaction.

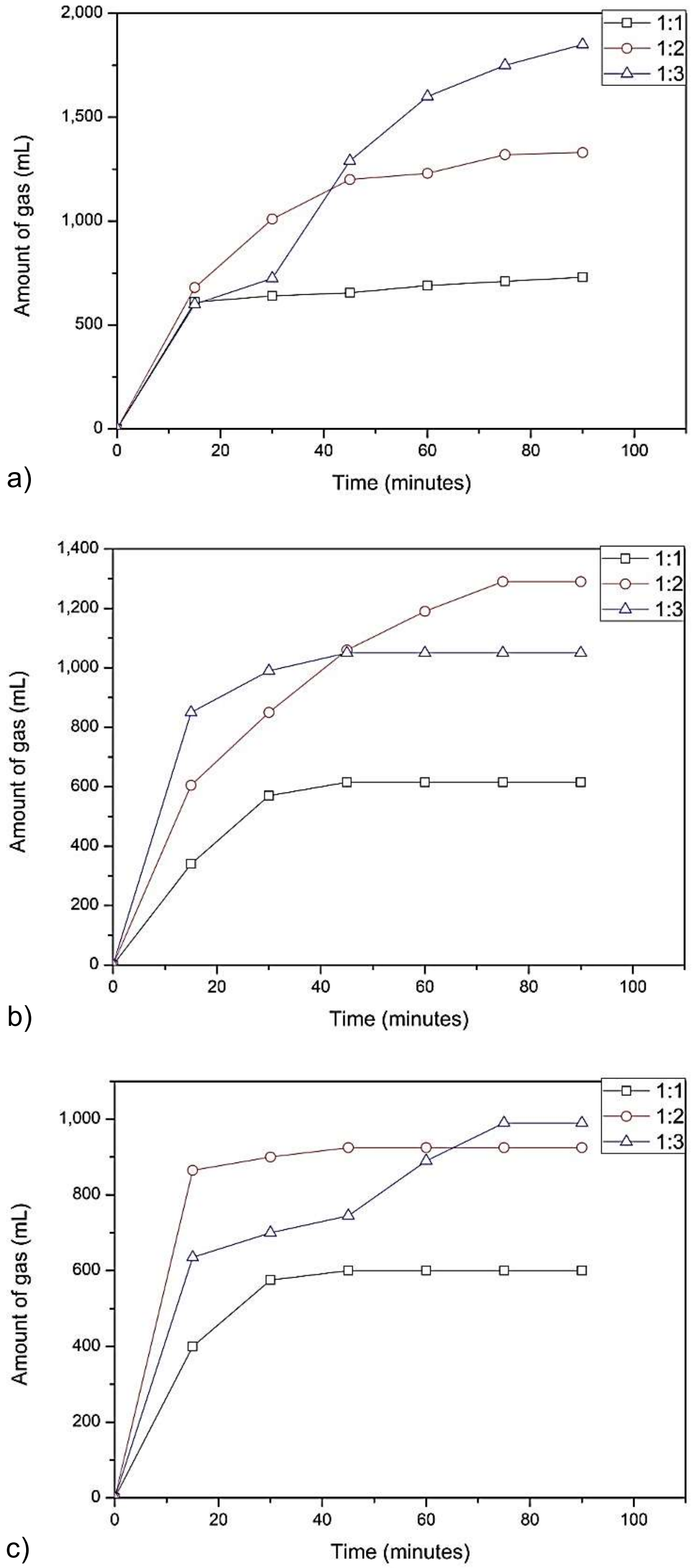

Figure 2. Gas evolution with the variation of temperature and weight ratios of NaOH:Dross is shown: a) reaction temperature is 40 °C; b) 50 °C and c) 60 °C.

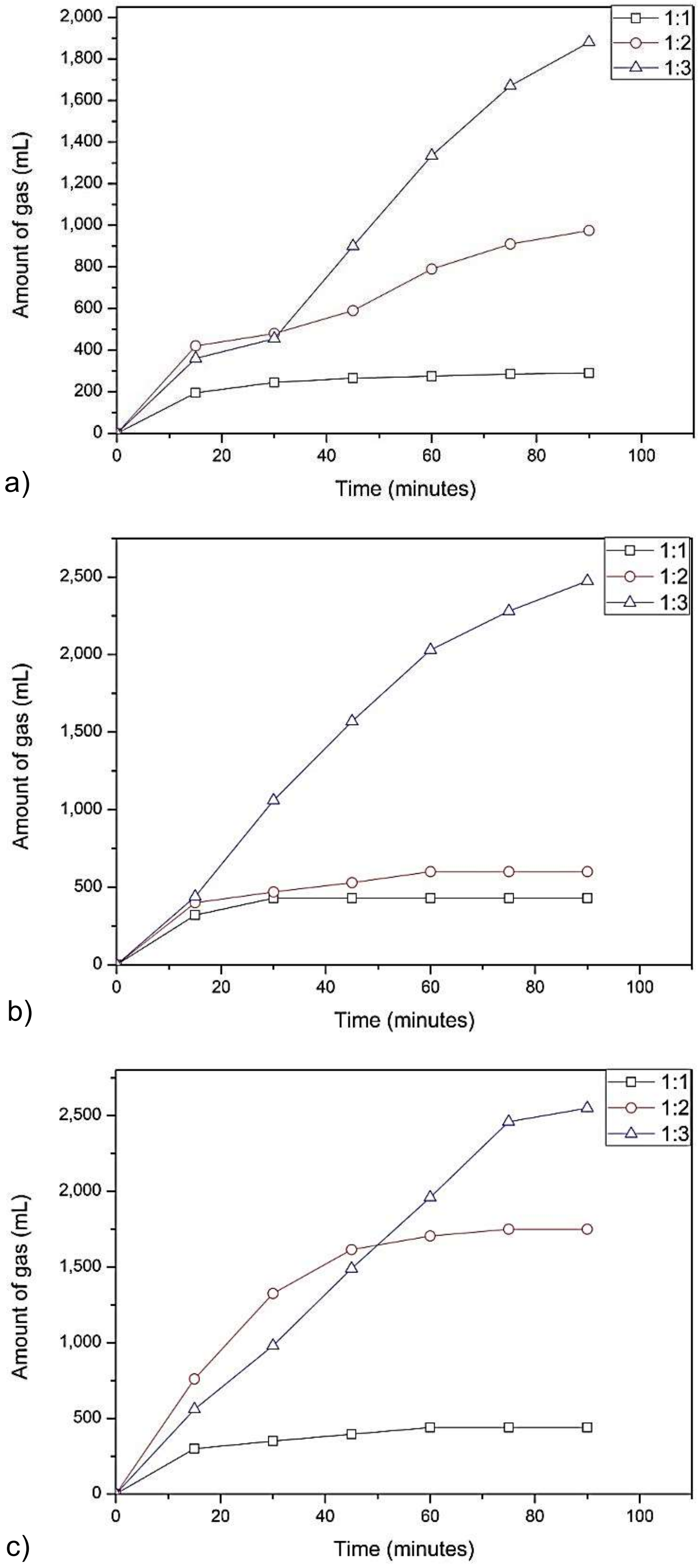

Figure 3. Gas evolution with the variation of temperature and weight ratios of KOH:Dross is shown: a) reaction temperature is 40 °C, b) 50 °C and c) 60 °C.

From the X-ray diffraction pattern analysis of the aluminium dross fines, it has been found that the major phases present in it are aluminium, alumina Al_2O_3, silica SiO_2 and γ alumina. With the presence of these phases, the heterogeneity of the raw material is clearly vivid. When aluminium dross is subjected to metal-water reaction under the presence of alkalis, the chances of reactions other than hydrogen production can take place. It is likely that these reactions interfere in the overall gas outcome.

Some of the reactions that contribute to the gas evolution are as under (Meshram et al., 2019):

$$2Al + 2NaOH + 6\,H_2O \rightarrow 2NaAl(OH)_4 + 3H_2 \tag{1}$$

$$NaAl(OH)_4 \rightarrow Al(OH)_3 + NaOH \tag{2}$$

$$2NaOH + Al_2O_3 + 3H_2O \rightarrow 2NaAl(OH)_4 \tag{3}$$

It can be seen that when metallic aluminium reacts with sodium hydroxide and water, sodium aluminate forms with the evolution of hydrogen. However, when the same reactions take place with alumina, the hydrogen evolution is not observed. Also, it is observed that sodium aluminate decomposes into aluminium hydroxide and sodium hydroxide. Similar reactions take place in case of potassium hydroxide as well. The aluminate formed in this case, however, is relatively more stable than its sodium counterpart. Potassium aluminate does not dissociate into aluminium hydroxide and potassium hydroxide (Birnin-Yauri & Aliyu, 2014).

$$Al_2O_3 + 2KOH + 3H_2O \rightarrow 2KAl(OH)_4 \tag{4}$$

$$2Al + 2KOH + 6H_2O \rightarrow 2KAl(OH)_4 + 3H_2 \tag{5}$$

From Fig. 2, it is observed that the gas evolution is faster at the beginning. If the gas evolved at the beginning is not properly measured, or there are experimental errors during the trails, there is a fair chance that the overall amount of gas measured will have severe discrepancies. Just as the solid mixture of the dross and alkali comes in contact with the hot distilled water, the evolution of hydrogen takes place rapidly. It is this rate of gas evolution that needs to be measured properly.

At lower temperature (40 °C), the hydrogen evolution reaction is relatively slower. Also with lower amount of dross available for the reaction, the overall amount of gas generated is less, compared to higher ratios of dross and alkali. The trend is quite the same at higher temperatures (50 °C and 60 °C). Weight ratios 1:2 and 1:3 show greater evolution of hydrogen gas. This is merely due to the higher amount of aluminium available for the metal-water reaction. The temperature variation and the amount of aluminium in the system direct the gas generation.

Fig. 3 illustrates the gas evolution with potassium hydroxide mixture. It can be seen that the gas evolution has the similar trend as that of sodium hydroxide mixture. 1:1 weight ratio has least amount of gas evolution and rate of gas generation. 1:2 and 1:3 weight ratios perform better. The overall amount of gas increases with increase in the reaction temperature.

Comparing Fig. 2 with Fig. 3, it can be clearly observed that though the rate of gas evolution is initially less with potassium hydroxide mixtures, the amount of gas evolution is quite high at the climax of the reactions for a fixed period of time. While on the other hand, the initial surge of hydrogen is very large for sodium hydroxide. The reaction rate reduces after nearly 30 minutes and thus the overall amount of gas produced becomes less. These trends in variation are mainly due to the side reactions taking place in the system.

CONCLUSIONS

This research presents a method of effectively producing hydrogen using aluminium-water reactions. Aluminium dross fine powder has been used for this purpose. With this method, hydrogen generation is coupled with industrial waste utilization. The waste metallic content sealed within the dross is utilized by the metal-water reaction. Employing alkalis (NaOH and KOH) for the reaction leads to great rise in the gas evolution.

It has been found that the potassium hydroxide solid mixture performs well with higher reaction temperatures, whereas the rate of gas evolution is very high for sodium hydroxide mixtures. The increase in the amount of dross in the mixture increases the overall amount of hydrogen produced, as the amount of aluminium available for the reaction increases.

Therefore, this research illustrates an alternative process to produce hydrogen with aluminium dross recycling. A complete circle is observed when industrial waste is linked with next-generation fuel.

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