ST14 - Production of Hydrogen Using Waste Aluminium Dross: Secondary Source of Next Generation Fuel

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Abstract

The production of hydrogen is usually carried out by coal gasification and water electrolysis. 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. As the amount of metallic aluminium is significant in waste aluminium dross, the utilization of waste aluminium dross for generation of hydrogen would be an alternative to pure aluminium. Hydrogen production using aluminium dross as a raw material has been a research area around the world. During the last two decades, the elaboration of the hydrogen-based economy has made important progress an account of numerous research such as the hydrogen fuel cell and the hydrogen cars. The hydrogen is released as a gas and the oxygen combines with aluminium to form aluminum oxide compounds. Using aluminum from this source to produce hydrogen has two impacts, one over the environment by recycling this waste and the second on the production cost.

In the chemical leaching, mineral acid/base reacts with metallic aluminium present in waste dross and evolution of hydrogen (H_2) takes place. In present study we are optimizing the process parameters to generate hydrogen (H_2) gas and purification as next generation fuel. The next-generation fuels i.e. hydrogen 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. The gross calorific value of hydrogen is nearly 39.4 kWh/kg compared to gasoline (12.89 kWh/kg). 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. Taking the raw material as white waste 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 acidic/basic solution and the recycling of waste aluminium dross for value addition.

Keywords: Waste aluminium dross, Hydrogen, Chemical leaching.

1. Introduction

The development of next-generation fuels is very crucial to match the demands of the world and of India as well. Fuel consumption per capita has increased radically in the present day and it is projected to further increase as technological advancement takes place.

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

Hydrogen is known as one of the best clean energy carriers because of its minimal impact on the environment regarding greenhouse gas emissions such as carbon dioxide and other gases [1-3]. Hydrogen can be used directly in molecular form, (i.e., as a fuel for vehicles) or indirectly to generate electricity for other industrial applications [4-7]. A major advantage which it has over other fuels is that it does not cause pollution because its burning reaction results in only water. Hydrogen is also an almost ideal fuel gas in terms of reducing smog when it is burned. However, safe storage and generation at low cost are technical challenges that need to be considered. For these reasons, new ways are sought to produce hydrogen at low cost from other sources than are known [8-10]. The alkali metals (such as sodium, potassium, and lithium) and alkaline earth (calcium, strontium, aluminium, magnesium, etc.) are very active when they come in contact with water, and react spontaneously, generating hydrogen and heat. Based on this chemical property, the hydrolysis reaction of pure aluminium powder is commonly used for high-purity hydrogen generation [6, 11]. Although the use of pure aluminium in reaction with water to produce hydrogen is a viable method, it is expensive, if one considers the cost of producing pure aluminium and the use of an alkali metal hydroxide, also an expensive product.

To handle this problem, secondary aluminium dross can be used as an ingredient for aluminum water reaction in acidic medium. Aluminium dross is a process reject of aluminium metal production [12]. The main constituents of dross are Al metal and its oxides. However, due to the increasing awareness of environmental issues, the need for maximum economy and the importance of value addition/recycling/reuse, the problem of dross utilization is presently attracting more attention. Aluminium dross represents a residue from primary and secondary melting processes. Drosses are classified according to their metal content into white and black dross. White dross is of higher metal aluminium content and is produced from primary and secondary aluminium smelters and re-melt shops, whereas black dross has a lower metal content and is generated during aluminium recycling (secondary industry sector). White dross may contain from 15 to 80 % recoverable metallic aluminium and it comprises a fine powder from skimming the molten aluminium. Black dross typically contains a mixture of aluminium oxides and slag, with recoverable aluminium content ranging between 8 to 20 %. The non-metallic residues generated from dross smelting operations are often termed ‘salt cake’ and contain 3 to 5 % residual metallic aluminium [13].

A conservative estimate of around 3 million tonnes of white dross and more than 1 million tonnes of black dross is being produced every year and about 95 % of it is landfilled. It was also reported that some portion of the dross is reprocessed by primary and secondary aluminium industries to recover metallic aluminium [14]. As the composition of aluminium dross is found to vary significantly from batch to batch, more focus is required to find potential applications for this material. Through cost-effective recovery processes, aluminium metal can be recovered by means of physical and chemical routes, metallic aluminium could be recovered by smelting and the rest of the metallic aluminium could be extracted by chemical leaching in the form of various salt such as alum/poly aluminium chloride/salts as water aids. During the chemical leaching process, hydrogen gas is generated which can be separated and purified to use as a renewable fuel.

In India, there is no organized sector in aluminium dross handling except metal recovery. Dross residue after metal recovery are disposed to landfill. The residue contains undesired elements such as nitride, fluoride, carbide and others which are likely to result in leaching of toxic metal ions into ground water causing serious pollution problems and threat to the ecosystem. It is a big challenge for researchers to develop a process for complete utilization of waste aluminium dross. In the present research work, we studied a process technology for clean and green hydrogen generation by exploiting waste grade aluminium dross. The hydro-metallurgical process was adopted to leach out all the free metal using HCl under controlled reaction condition. This process yields a value-added product such as PAC (Polyaluminium chloride), high alumina residue and H_2 gas which was detected by water displacement method as well as hydrogen detector at lab scale. Extensive research work is under progress to generate and quantify the hydrogen generation using waste dross.

2. Materials and Methods

The aluminium dross used in this study was collected from local industry. The dross sample was prepared by crushing and grinding using ball mill machine for around 30 minutes. The powder (fine size dross) is treated as low grade aluminium dross as it contains lower metal content and is considered uneconomical for recovery of metal by conventional metallurgical processes for the present study. Dross with particle size under 100 mesh was used in the experiment. A sample before and after grinding is shown in Figure 1.

Figure 1. Aluminium dross sample lumps (left) and fine dross (right).

2.1 Chemicals and Reagents

Hydrochloric acid (HCl, AR grade) and distilled water were used for the acid leaching of dross. All AR grade reagent were used for wet chemical analysis. For trace metal analysis standard solution (VWR) 1000 mg/L were used to prepare multi-element aqueous solution for calibration in ICP-OES. All laboratory glassware's were of Class A grade.

2.2 Instrumentation

Trace metal analysis were performed using Optical emission spectrometry (ICP-OES iCap 7400 Duo Thermo Scientific). X-ray diffraction study was performed using XRD (Panalytical X-Pert Pro) to study the different phases present in the sample.

2.3 Leaching Reactor

A flat-bottomed borosilicate glass reactor (1 liter) with PTFE agitator fitted with heating mantle was used to handle the acidic reactants. Stirrer with variable speed from 0 to 150 RPM was used for mixing of solid and acid. The reaction was initiated by introducing 160 ml of 3N HCl solution through the side vessel neck. Around 100 g of Al dross was poured in the flask from side neck. The agitator was continuously stirring at 100 rpm at the time of addition. The temperature of the process was maintained at 90 $^{\circ}$C and it was measured by a specially designed thermometer. After dross introduction the flask was corked to minimize any further gaseous loss. In order to remove all water vapor from the produced gas, it was passed through a condenser. The scrubbed gas was then collected in a separate tank that already had water solution to contain all the gases. The water displacement method was used to calculate the H_2 volume. The cork-through-neck tube ensures that hydrogen gas is directed through water into a 2000 ml burette that has been turned upside down. The water in the burette has been displaced by the hydrogen gas emitted, and the burette's fluctuating water level was recorded as a function of time. The difference between the initial and final water levels in the burette has indicated the rate of hydrogen production from the reaction, and the rate of change of the water level gives an indicator of the rate of hydrogen generation from the reaction. The experimental setup used to study the leaching efficiencies of aluminium dross and hydrogen production is shown in Figure 2.

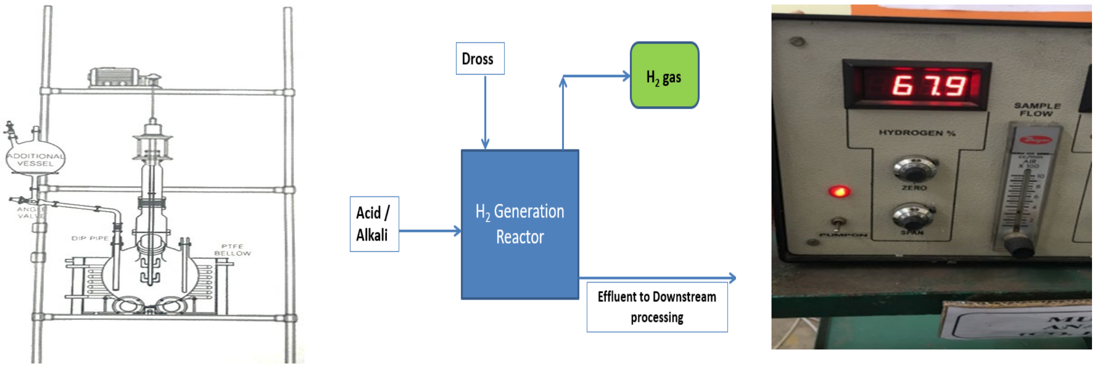

Figure 2. Laboratory experiment set up for acid leaching (left), schematic representation of the steps taken for hydrogen production (center), hydrogen detector (right).

Schematic process flow chart for value added products to achieve zero waste concept for Al dross is presented in Figure 3.

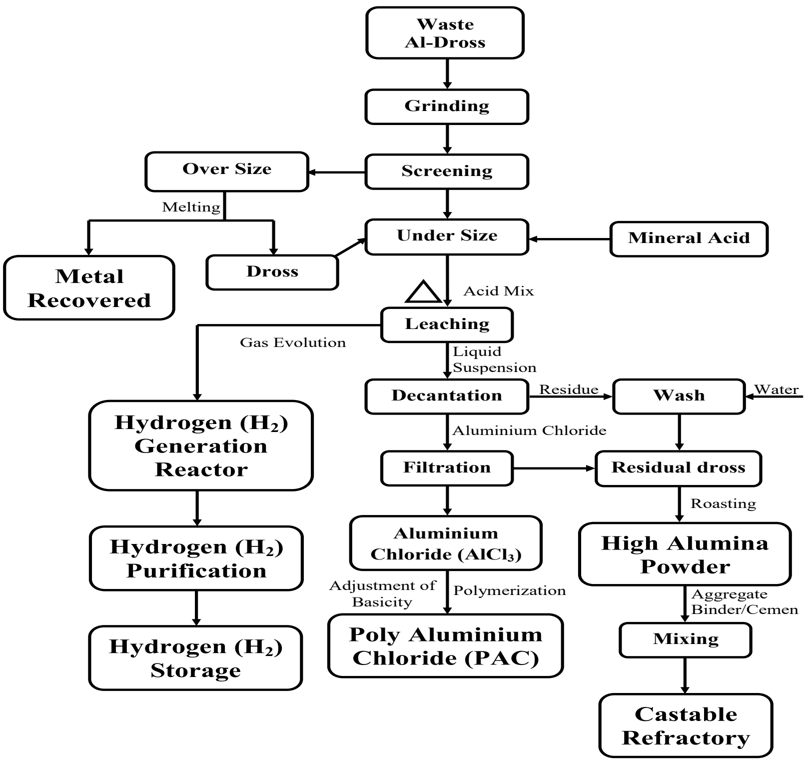

Figure. 3 Schematic illustrating the complete utilization for waste dross and hydrogen generation.

3. Results and Discussion

3.1 Characterization of Aluminium Dross

After screening, dross sample was taken for chemical analysis and leaching tests. 5 g of dross was mixed with HCl and kept on a hot plate for 1 hour. After cooling, the solution was filtered and analyzed for metallic aluminium and other constituents. The characterization of the dross of the major elements was performed using conventional wet analysis procedures, while ICP-OES for the trace elements and complete analytical data are presented in Table. 1

Table 1. Typical Chemical Analysis of Aluminium Dross.

Sr No.	Constituents	% Concentration
1.	Al (Metal)	15.15
2.	Ca	0.25
3.	Fe	0.24
4.	Mg	0.50
5.	Mn	0.021
6.	Ti	0.0051
7	Na	0.35
8	Si	0.51
9	Total Fluoride	1.15
10	Nitride	4.39

3.2 XRD Analysis

A qualitative analysis was performed using the powder XRD method to analyze the different Al phases present in the dross. XRD analysis of dross was carried out for before and after leaching samples to evaluate the metallic Al extraction, and it is presented in Figure 4. In the diffractogram 2 top (before leaching), the XRD pattern reveals a sharp peak at (2θ- 38.5), which attributes to the presence of aluminium metal in the dross.

In the diffractogram 2 bottom (after leaching), the disappearance of the peak at d-spacing 2.338 (2 theta 38.5) shows that there is total recovery of metallic aluminium from waste grade dross. This also indicates that the complete chemical leaching process adapted is efficient to recover total metal content from the dross.

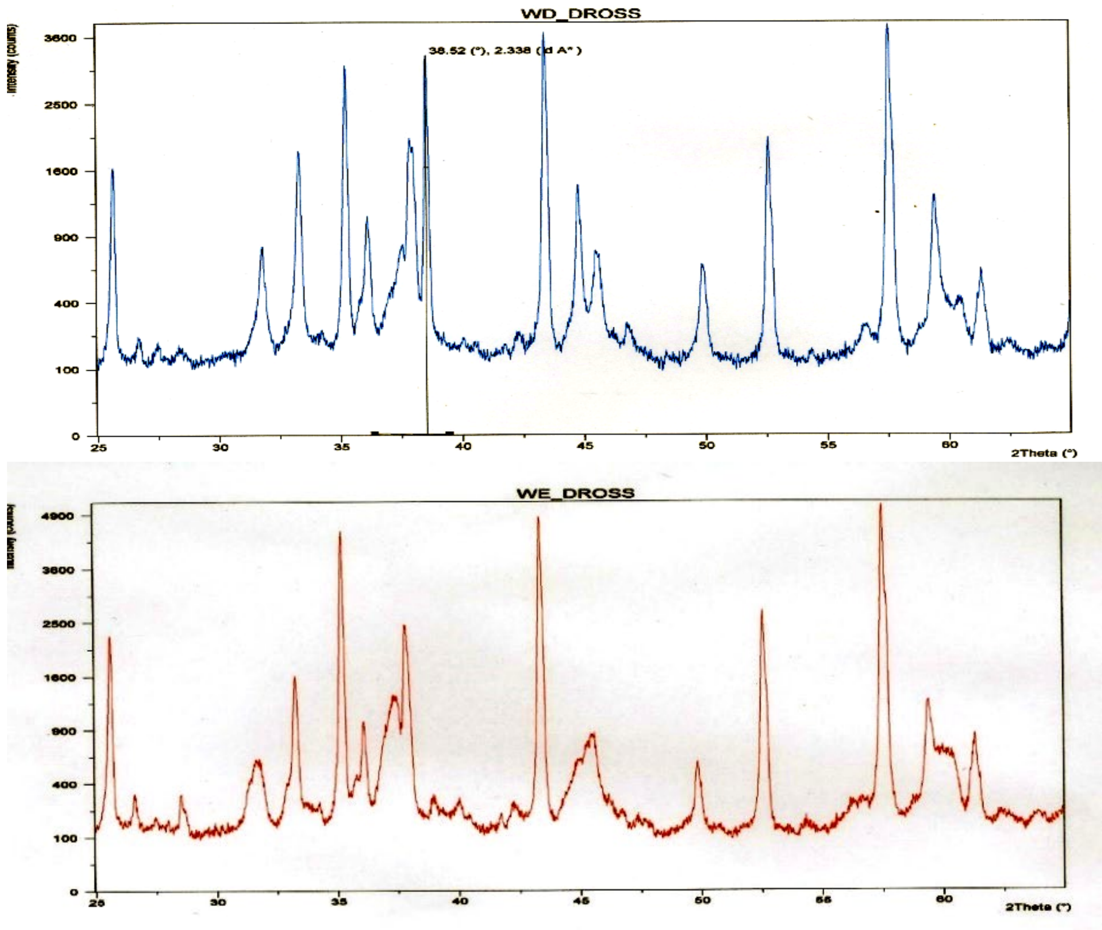

Figure 4. XRD analysis of waste dross before chemical leaching (top), XRD analysis of residual dross after metal recovery (bottom).

3.3 Leaching of Waste Aluminium Dross

Acid leaching is a crucial stage in the utilization of aluminium dross. To get a good recovery of aluminium from aluminium dross, one needs to understand the complex behavior of the leaching process. The main factors that affect the leaching process includes temperature, time and acid concentrations. Different leaching experiments were performed by varying temperature and reaction time by keeping other variables constant. Leaching efficiency of aluminium dross is depicted in table 2.

Table 2. Different leaching experiments of Al dross.

Experiment No	Wt. of dross (kg)	Volume of HCl (L)	Volume of Water (L)	Temperature (°C)	Reaction Time (min)	% Al
1	0.1 kg	0.045	0.115	80	60	11.6
2	0.1 kg	0.045	0.115	90	60	13.9
3	0.1 kg	0.045	0.115	90	90	15.1

The metal readily reacts with the acid, but in aluminium dross, oxides subsided in dross constitute an extended continuous network in which aluminium metal has been entrapped. Therefore, it requires temperature and more acid for digestion. From the above data, it was found that the digestion time, temperature and acid concentration affect the reaction efficiency: As reaction time increases, aluminium extraction efficiency increases. Based on the above experimental studies, the parameters (of experiment no. 3) were fixed for the further experiments to evaluate hydrogen generation from the aluminium dross.

When aluminium dross is subjected to metal acid reaction under the presence water, the chances of reactions other than hydrogen production can take place. It is likely that these reactions interfere in the overall gas outcome. The possible reaction are as follows;

$$2Al + 3H_2O = Al_2O_3 + 3H_2 \quad (1)$$

$$2AlN + 3H_2O = Al_2O_3 + 2NH_3 \quad (2)$$

$$Al_4C_3 + 6H_2O = 2Al_2O_3 + 3CH_4 \quad (3)$$

3.4 Hydrogen Generation Using Aluminium Dross Leaching

The aluminium dross and acid reaction was carried out in closed reactor to avoid any further loss in gas. When dross was added in acid, a sudden surge of gas observed. Hydrogen can be produced even at room temperature, but since Al is trapped inside the alumina cavities in dross, heating is necessary to release all of the Al metal.
The amount of gas measured for a fixed period of time (16 minutes) and simultaneously the rate of gas evolution was determined. The reaction was stopped and the final reading was taken when the rate of gas evolution decreased.

Table 3. Hydrogen Volume released from reaction of Al dross with HCl.

Time (min)	2	4	6	8	10	12	14	16
H_2 released (L)	0.300	0.609	0.892	0.921	1.038	1.093	1.112	1.065

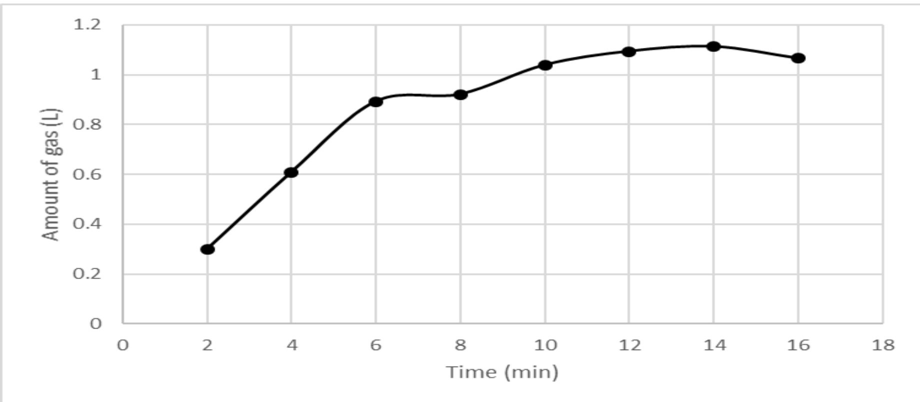

Figure 5. Hydrogen evolution with time.

Figure 5 illustrates how hydrogen gas evolved. The figure demonstrates how the overall rate of gas evolution was initially high and later significantly decreased, culminating in the stability of the total amount of gas produced.

Over a million tonnes of aluminium dross are generated annually by the aluminium industry worldwide. Each sort of dross has distinct physical and chemical characteristics, and the waste value is determined by the level of impurities contained and the cost required for metal recovery. According to table 1, which details the chemical composition of aluminium dross, 1 kg of dross comprises 0.15 kg of aluminium, which can react with HCl to generate hydrogen gas, aluminium chloride, or other Al compounds. Theoretically, 1 g of aluminium can produce near about 1.2 L of hydrogen; the aluminium dross used in this study has a metallic aluminium content around 15 percent.

4. Conclusions

- The research presents a process of effectively producing hydrogen using aluminium dross by acid reactions.
- Process shows that Al dross powder has a high hydrogen yield and hydrolysis rate, and that as the amount of dross in the mixture grows, more hydrogen will be created overall as more aluminium is made available for the reaction.
- The research illustrates an alternative process to produce hydrogen with waste aluminium dross as an alternative resource.
- The developed process is an alternative to conventional method and could be explored for commercial production of hydrogen. The work will enable generator of dross in recycling and management of waste.
- The process would definitely help dross processor for the complete utilization and value addition to achieve zero waste concept.

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