Chapter- 6

Hydrogen generation

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6.1 Introduction

It has been found that with 1 g of pure aluminium nearly 1.2 L of hydrogen gas can be produced [140]. The use of water for the experiments is dictated by the fact that water is available in plenty and the amount of hydrogen per unit volume for water is quite high, as compared to other common liquids that can be used for hydrogen production. The ease of access is a major deciding factor for the economic production of the gas.

As described in the previous sections, aluminium-water reaction for hydrogen generation can be illustrated as under:
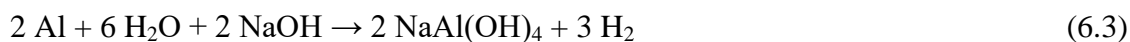
$$2\ Al + 6\ H_2O \rightarrow 2\ Al(OH)_3 + 3\ H_2 \tag{6.1}$$

This reaction releases heat which is employed to heat $Al(OH)_3$. It has been found that under alkaline conditions, the decomposition of aluminium hydroxide takes place, generating aluminium oxide hydroxide, as shown by eq. (6.2):

$$Al(OH)_3 \rightarrow AlOOH + H_2O \tag{6.2}$$

Aluminium oxide hydroxide is used as an input for the generation of cement clinkers and refractory materials.

The most important factor that reduces the contact of aluminium and water thereby hindering the hydrogen evolution is the presence of the protective layer of alumina (Al_2O_3) on the exterior of aluminium metal content. Due to this protective layer, the aluminium-water reaction may not even begin. Under alkaline operation conditions (in

presence of sodium hydroxide), the reactions can proceed as shown in eq. (6.3)-(6.4) [140]:

$$2\ Al + 6\ H_2O + 2\ NaOH \rightarrow 2\ NaAl(OH)_4 + 3\ H_2 \tag{6.3}$$

$$NaAl(OH)_4 \rightarrow NaOH + Al(OH)_3 \tag{6.4}$$

The evolution of hydrogen gas by recycling white aluminium dross is an alternative method with coupled benefits of industrial resource management and reduction in the environmental burden. The idea of using aluminium dross for the production of hydrogen has been very lucrative as using metallic aluminium for the production of hydrogen does not essentially contribute to the economy. The cost of aluminium used for the production of hydrogen added to the cost of the process itself becomes quite large, overshadowing the profit attained from the hydrogen production. To find an alternative source of aluminium, aluminium dross can be chosen as it contains fair amount of aluminium that can be utilized for the purpose.

It has been found that subjecting fine powdered aluminium dross to high energy ball milling for nearly 75 minutes helps to generation of hydrogen. This is due to the fact that the milling process increases the surface area exposed to the water, making it available for the reaction [76]. The major drawback of this process is the energy consumption for the sample preparation. Using the high energy ball mill for this method itself defines that the process is energy intensive. Although the results obtained are fruitful in laboratory scale, massive production of fine aluminium dross sample for hydrogen production using this method is not quite possible.

The utilization of aluminium dross for hydrogen production can be done under the alkaline conditions. Although the alkaline conditions have been studied for pure

aluminium-water reaction, similar studies are required for aluminium dross-water system. This method has been investigated in the present work.

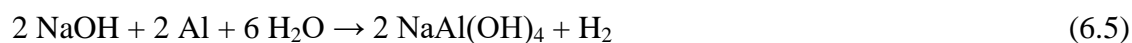*6.2 Generation of hydrogen gas from aluminium dross*

As described in the previous section, the evolution of hydrogen gas is due to the reaction of metallic aluminium entrapped in the white aluminium dross and water. This aluminium content lies within the alumina matrix. When the solution is turned alkaline, the reaction of aluminium and alumina with water take place. The protective layer of alumina is destroyed and a fresh metallic aluminium surface is exposed.

To understand how the reactions actually take place, a close examination of the raw material is necessary. As illustrated in the previous chapters, the dross is a heterogeneous industrial waste comprising of oxides of aluminium, silica and salt fluxes along with metallic aluminium. In the present sample of white aluminium dross, the amount of salts (in salt fluxes) was nearly 5 %. In the presence of water, these salts tend to be dissolved leaving behind insoluble dross. The salts render no effect in the leaching process of the dross under alkaline conditions. As these phases come in contact with water, only the dissolvable impurities interact with water, which are mostly salts present in minor quantities. No reaction takes place. This is due to the alumina layer mentioned above.

The alkaline solutions of sodium hydroxide and potassium hydroxide of various concentrations have been prepared to conduct the experiments, as mentioned in the Chapter 2. The temperature of the solutions was raised and white aluminium dross powder was added to the solution in the conical flask to commence the reactions. Just as the powder was introduced into the solution, the flask was sealed with the cork fitted with rubber pipe to collect the gas evolved.

The gas produced is collected in an inverted measuring cylinder and the readings of the cylinder have been noted in a period of 15 minutes. When the reading of the gas evolved reaches beyond its maxima, the cylinder was replaced and the readings were continued. The reactions were continued to a period of 90 minutes, as the rate of gas evolution reduced to around 1-2 mL/ minute.

Apart from eq. (6.1), the following reactions take place that lead to the evolution of the hydrogen gas [140]:

$$2\ NaOH + 2\ Al + 6\ H_2O \rightarrow 2\ NaAl(OH)_4 + H_2 \tag{6.5}$$

$$NaAl(OH)_4 \rightarrow NaOH + Al(OH)_3 \tag{6.6}$$

$$2\ NaOH + Al_2O_3 + 3\ H_2O \rightarrow 2\ NaAl(OH)_4 \tag{6.7}$$

These reactions begin instantaneously when white aluminium dross comes in contact with the sodium hydroxide solution. As seen from the above reactions, the formation of sodium aluminate takes place. This aluminate generated is not stable and breaks into sodium hydroxide and aluminium hydroxide. The sodium hydroxide regenerated in the reaction is utilized again for the hydrogen evolution. It can also be consumed in producing sodium aluminate, if it reacts with alumina. This ensures the attack on the surface of alumina, thereby producing fresh layer of aluminium for hydrogen evolution.
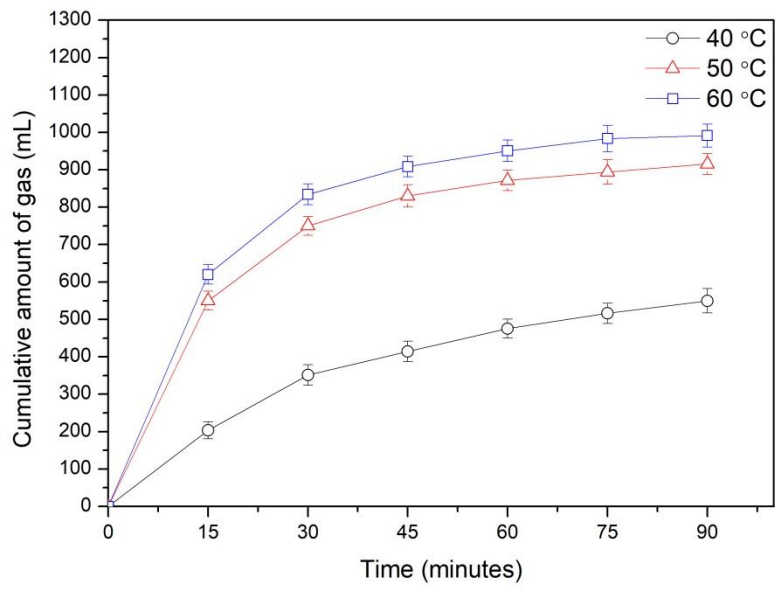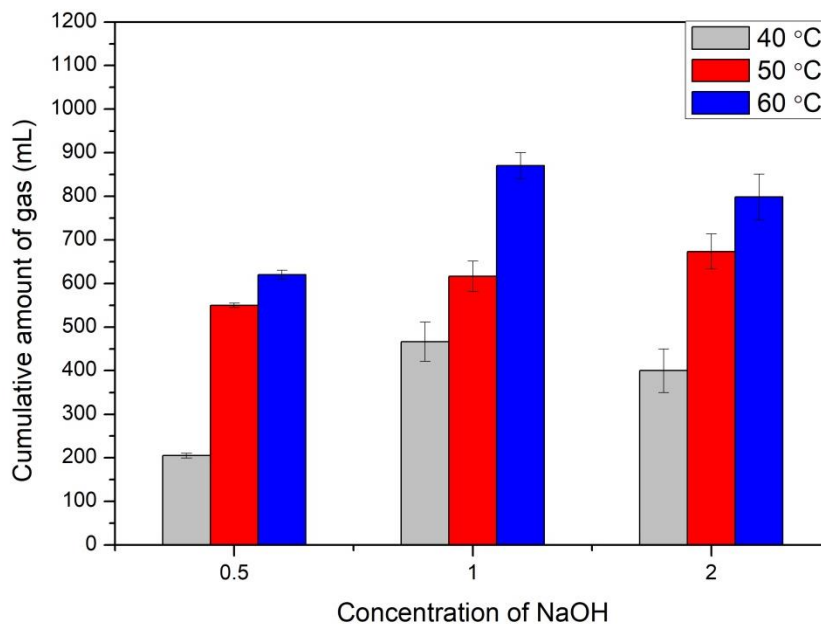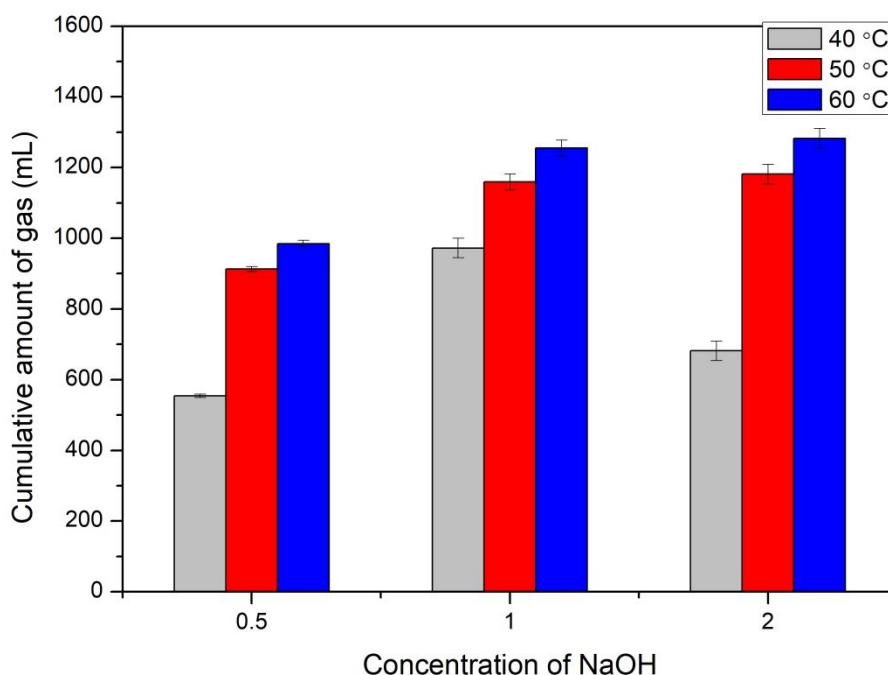
a. 0.5 M NaOH
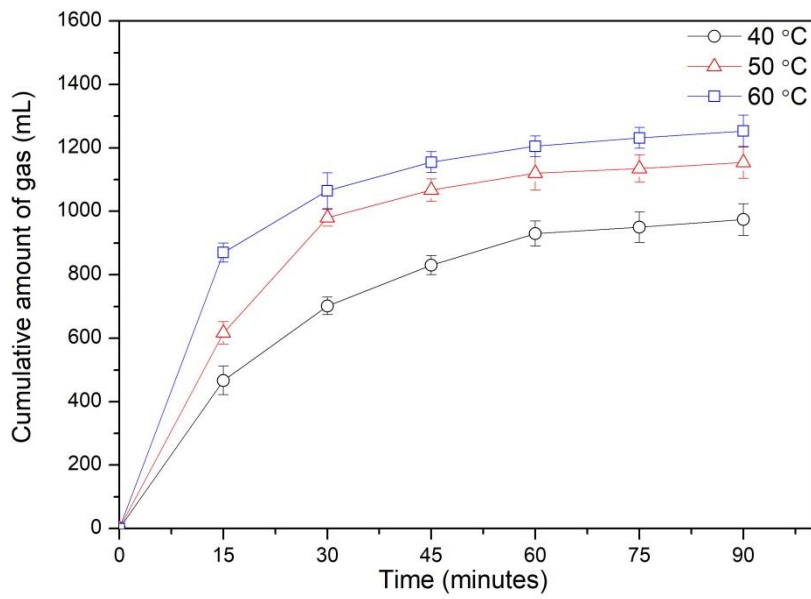
b. 1 M NaOH
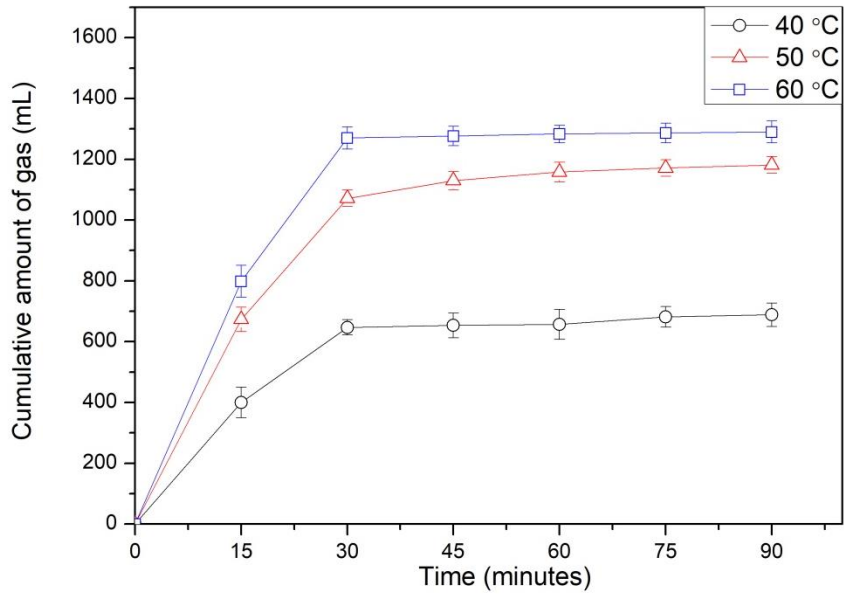
c. 2 M NaOH

d. Gas evolution at15 minutes

e. Gas evolution at 90 minutes

Figure 6.1: Hydrogen evolution at fixed NaOH concentration: 5.a. 0.5 M NaOH, 5.b. 1 M NaOH, 5.c. 2 M NaOH, 5.d Gas evolution at 15 minutes, 5.e Gas evolution at 90 minutes

From the figure 6.1, it can be seen that three plots of gas evolution are illustrated for three concentrations of sodium hydroxide solutions. As mentioned earlier, the amount of the solution taken for every reaction is 50 mL. Calculating for the fixed volume of the aqueous alkaline solution, it can be found that 25, 50 and 100 milli moles are available for the reactions in 0.5, 1 and 2 M solutions. The first plot is for 0.5 M NaOH solutions.

With the rise in the reaction temperature, the cumulative amount of gas liberated also increases. The total amount of gas evolved after a period of 90 minutes is around 530 mL for 40 °C, whereas it reaches around 900 mL for 50 °C and nearly 1000 mL for 60

°C. The trend of the gas evolution is almost similar for all the three reaction temperatures. The rate of gas evolution is very large at the commencement of the reaction and gradually the rate decreases with time.

From the table 6.1, it is observed that the rate of gas evolution is highest for 60 °C is at around 42 mL/minute and it gradually decreases to 1-2 mL/minute. This drop in the rate of gas evolution is visible from the 60 minute period, as the rate reduces to around 4 mL/minute. The lower temperatures (50 °C and 60 °C) have even lesser initial rate of gas evolution (14 mL/minute and 37 mL/minute, respectively).

The second plot (figure 6.1.b) is shown for 1 M NaOH aqueous solutions. Although the trend for gas evolution is similar to the previous plot, the overall amount of gas evolved is higher in this case. For 40 °C, around 970 mL gas is generated. The volume of gas liberated increases with temperature; at 50 °C and 60 °C, nearly 1150 mL and 1250 mL gas was produced, respectively.

The initial surge of hydrogen gas evolution was nearly 58 mL/minute at 60 °C for 1 M NaOH solution, as seen from table 6.1. Just like the rates for 0.5 M NaOH solutions, the rates dropped to less than 1-2 mL/minute by the end of 90-minute period. The rate of gas evolution was around 32 mL/minute for 40 °C and 42 mL/minute for 50 °C.

The third plot (figure 6.1.c) is for 2 M NaOH solution. The increase in the volume of gas generation is observed in this case as well, but the gas evolution was constant after 30 minute period for 2 M NaOH solutions. As seen from the plot, not much change in the volume of gas evolution is observed after 30 minutes. At 40 °C, the total volume of gas is around 700 mL and as the temperature increase to 50 °C and 60 °C, the total volumes of gas are approximately 1200 mL and 1300 mL. As the molarity of the

solution and the reaction temperature are increased, the rate of gas evolution and the cumulative amount of gas also increase.

Compared to the rate of gas evolution for 1 M NaOH solutions, the initial rate for 2 M solutions was lesser for 60 °C (around 54 mL/minute), but as the time passed by, the rate remained higher (nearly 43 mL/minute and 16 mL/minute for 30 and 45 minute periods). This led to the overall increase in the volume of gas evolution. After a period of 60 minutes, the rate reduced to less than 1-2 mL/minute, as seen from table 6.1.
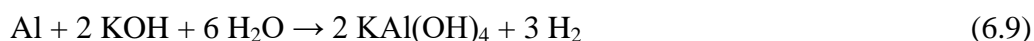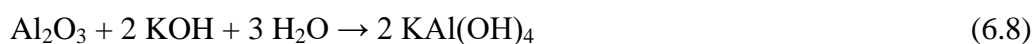
Figure 6.1.d and e describe the gas evolution with respect to the molarity of sodium hydroxide solution. As mentioned earlier, the lower concentration solutions have lower amount of NaOH available for the reactions. With increase in the concentration, the amount of gas produced also increases. The temperature rise also leads to the increase in the gas evolved.

With the passage of time, the reaction involved for the evolution of hydrogen tends to cease. The other reactions, like the formation of oxides and hydroxides take place. This results in the reduction of the rate of gas evolution. Also, the amount of aluminium in the aluminium dross available for the reaction also tends to get exhausted after a period of 60 minutes.

Table 6.1: Rate of gas evolution for different temperatures at different time periods for fixed concentration of NaOH solution

Concentration of NaOH	Time period (minutes)	Rate of gas evolution for given temperatures (mL/ min.)		
		40 °C	50 °C	60 °C
0.5 M	15	13.58	36.67	41.33
	30	11.72	25	27.81
	45	7.02	9.33	9.61
	60	4.12	4.06	3.88
	75	3.39	2.13	2.5
	90	2.48	1.47	1.36
1 M	15	31.11	41.11	58
	30	23.39	32.67	35.5
	45	12.11	15	9.5
	60	7.61	4.67	4.67
	75	4	2.27	2.56
	90	1.47	1.13	1.61
2 M	15	26.67	44.89	53.22
	30	21.56	35.72	42.33
	45	8.44	15.22	15.94
	60	1.06	2.88	0.44
	75	0.94	1.39	0.33
	90	0.33	0.79	0.22

The major reactions taking place in the case of potassium hydroxide aqueous solution are shown as under:

$$Al_2O_3 + 2\ KOH + 3\ H_2O \rightarrow 2\ KAl(OH)_4 \quad\quad (6.8)$$

$$Al + 2\ KOH + 6\ H_2O \rightarrow 2\ KAl(OH)_4 + 3\ H_2 \quad\quad (6.9)$$

As similar to the aqueous solutions of NaOH, the reactions of aluminium dross with KOH involve the formation of potassium aluminate. As described above, when metallic aluminium comes in contact with the KOH solution, the hydrogen evolution is observed, along with aluminate formation. However, this is not possible when the

protective layer of alumina reacts with KOH solution. In that case, the formation of potassium aluminate takes place. No hydrogen is evolved. There is one difference between the reactions of white aluminium dross with NaOH and KOH. The dissociation of sodium aluminate to sodium hydroxide and aluminium hydroxide is possible. This leads to the regeneration of NaOH. This helps in reutilization of sodium hydroxide for further reactions.

Observing the figure 6.2, it can be seen that at lower concentrations of KOH solution, the amount of gas generated is very less. This is due to lower amount of KOH present in the fixed volume of the solution. 25 milli moles of KOH are present in 50 mL of the solution. At lower reaction temperature of 40 °C, the reaction barely starts at the beginning; at the end of 90 minutes, the cumulative amount of gas evolved was a meagre value of 190 mL. As the temperature of the reaction is increased, the reaction rate increased and consequently the overall amount also increased. For 50 °C and 60 °C, the cumulative amounts of gas evolved were nearly 575 mL and 720 mL after a period of 90 minutes.

The maximum rate of gas evolution was highest for 60 °C, at 32 mL/minute. It reduced to around 1-2 mL after 60 minutes. This was just around 15 mL/minute for 50 °C and around 1-2 mL for 40 °C. The rate of gas evolution dropped to 1-2 mL for 50 °C after 75 minutes. The details about the gas evolution rates are provided in Table 6.2.
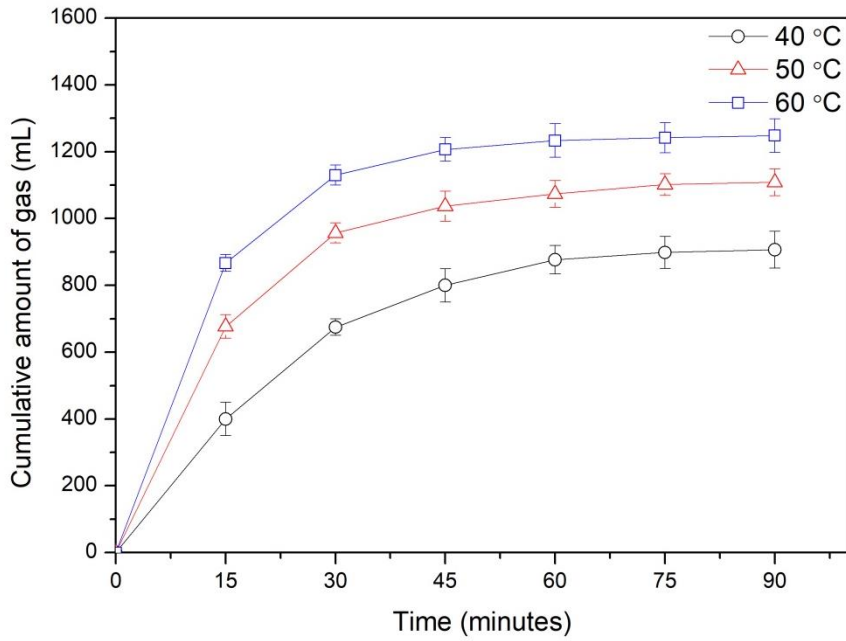
Comparing the cumulative volume of gas liberated for KOH solution for 0.5 M concentrations with that of NaOH solutions, it is seen that the volume is lower for KOH solutions. At lower temperature of 40 °C, the reaction for H_2 production does not progress as in the case for NaOH.
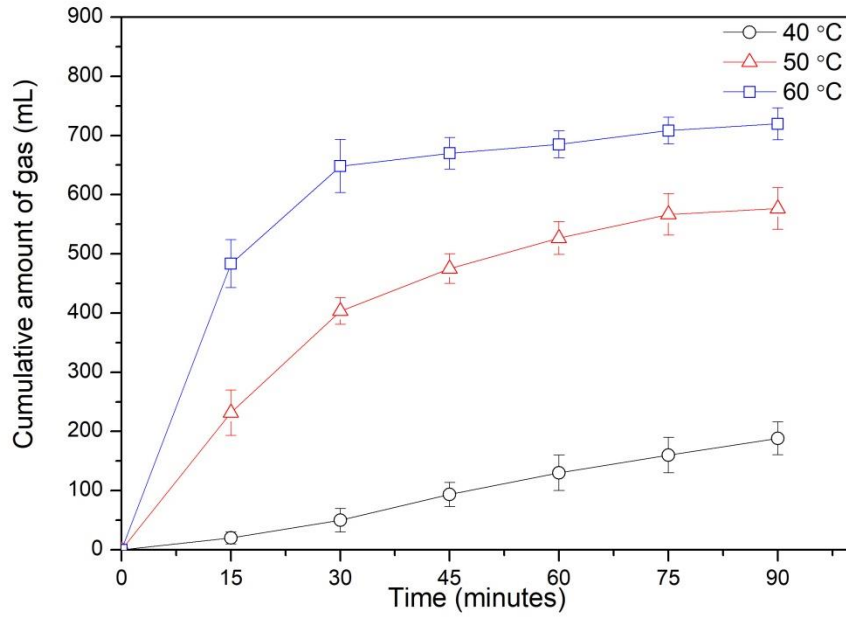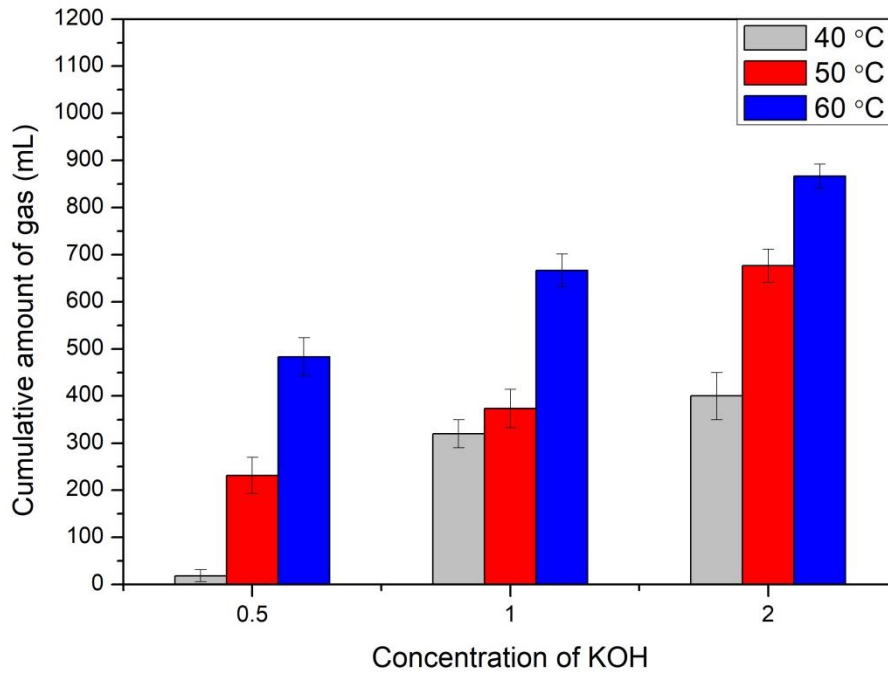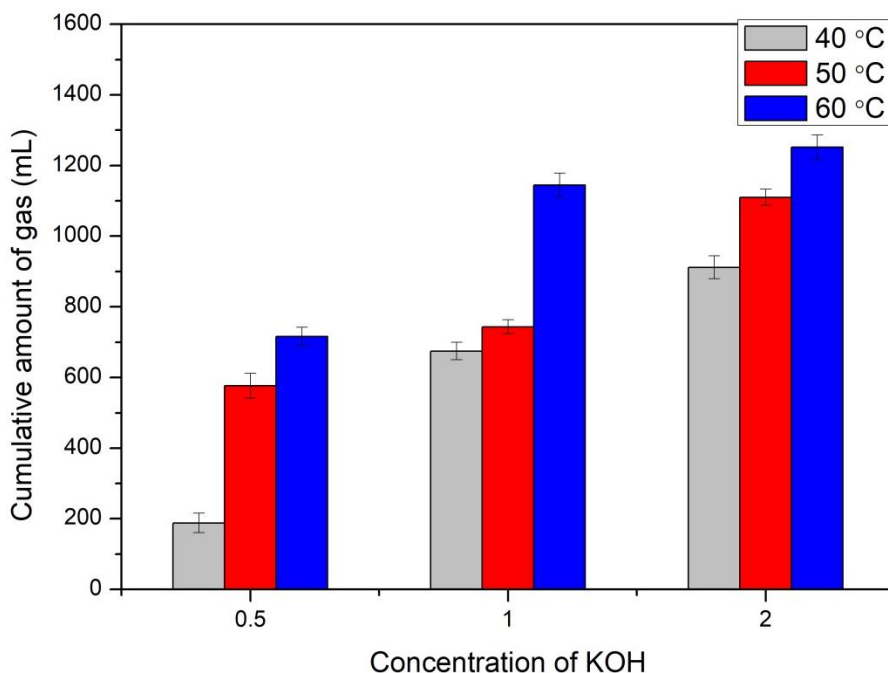
a. 0.5 M KOH
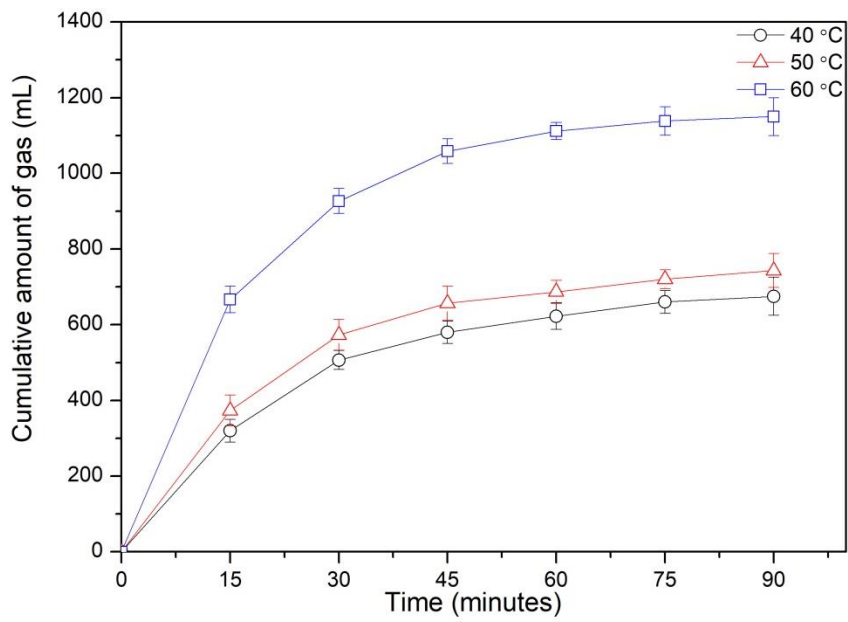
b. 1 M KOH

c. 2 M KOH

d. Gas evolution after 15 minutes

e. Gas evolution after 90 minutes

Figure 6.2: Hydrogen evolution at fixed KOH concentration: a. 0.5 M KOH, b. 1 M KOH, c. 2 M KOH, d. Gas evolution at 15 minutes, e Gas evolution at 90 minutes

As illustrated in figure 6.2, the cumulative volume of hydrogen gas evolved for 1 M KOH solutions at 40 °C is 675 mL after 90 minutes. Similarly for 50 °C and 60 °C, the cumulative volumes of gas are 735 mL and 1145 mL. The trends of gas evolution are similar to the NaOH solutions and the gas evolved in both cases is also comparable. The amount of KOH available in these solutions is 50 milli moles in 50 mL solution.

The rate of gas evolution was highest at 60 °C with nearly 45 mL/minute in the beginning. At 50 °C and 40 °C, the rates were around 25 mL/minute and 22 mL/minute. After a period of 60 minute, the rates for 40°C and 50 °C dropped to around 3-4 mL/minute, but for 60 °C it was still around 6-7 mL/minute. It reduced to a value of 1-2 mL/minute after 90 minutes.

Following the graph plot of figure 6.2, it is observed that with the rise in the molarity of the KOH solution, the rate of gas evolution and the cumulative volume of gas also rise. This is clearly due to the lower amount of KOH available in the fixed volume of the solution.

At lower temperature of 40 °C, the cumulative amount of gas evolution is around 910 mL after 90 minutes. This value is clearly higher, when compared to the volumes of gas evolved at lower concentrations at the same temperature. Similarly for 50 °C, the cumulative volume of the gas evolved is 1110 mL, while for 60 °C, it is nearly 1250 mL. The rate of the gas evolution is highest for 60 °C in the beginning, with around 58 mL/minute. For 40 °C and 50 °C, the initial surge of the gas evolution had rates of 27 mL/minute and 46 mL/minute. With the passage of time, the gas evolution rate reduced and after a period of 90 minutes, it reduced to around 1-2 mL/minute. This is similar for all the cases studied above.

A quick glance at the three plots for the three concentrations of KOH solutions shows that higher the concentration of the solution, higher is the volume of gas evolution. With higher reaction temperature, the gas evolution and the rate of gas evolution also increases.

A comparison is provided in figure 6.2 for gas evolution volumes at a period of 15 minutes and 90 minutes for various concentrations and temperatures. The bar charts assist in understanding the trends of gas evolution in a better way.

With the proceeding of the reactions, the metallic aluminium available for the reaction present in the charged feed reduces and this results in the reduction of the rate of gas evolution. Finally, an overall reduction in the gas evolution rate is seen after 60 minutes. The alkali in the solution is consumed in the leaching of the dross and other reactions tend to take place. At higher concentrations of the alkali solutions, the reaction of silica also takes place:

$$SiO_2 + 2\,NaOH \rightarrow Na_2SiO_3 + H_2O \tag{6.10}$$

The purity of the gas evolved has been determined by Gas Chromatography. The gas is found to be 96 % hydrogen and rest nitrogen. The gas samples have been collected when sufficient amount of gas had evolved and completely filled the pipe connecting the conical flask and the measuring cylinder. The gas syringe was used to collect the samples from the other end of the pipe and quickly injected into the gas chromatograph.

Table 6.2 Rate of gas evolution for different temperatures at different time periods for fixed concentration of KOH solution

Concentration of KOH	Time period (minutes)	Rate of gas evolution for given temperatures (mL/ min.)		
		40 °C	50 °C	60 °C
0.5 M	15	1.33	15.44	32.22
	30	1.67	13.44	21.61
	45	2.44	8.11	6.22
	60	2.67	4.11	1.22
	75	2.22	3.06	1.28
	90	1.94	1.67	1.16
1 M	15	21.33	24.89	44.44
	30	16.89	19.11	30.89
	45	8.67	9.44	13.06
	60	3.87	3.78	6.17
	75	2.67	2.11	2.67
	90	1.74	1.89	1.28
2 M	15	26.67	45.11	57.78
	30	22.5	31.89	37.67
	45	13.33	12	11.33
	60	6.72	3.89	3.44
	75	3.28	2.17	1.17
	90	1	1.17	0.5

After heating the residual solid at 900 °C for 4 hours, the resultant product is alumina. The initial phases present were aluminium, alumina and hydroxides of aluminium. The product obtained is white and the characterization is provided in Fig. 6.3 and 6.4.
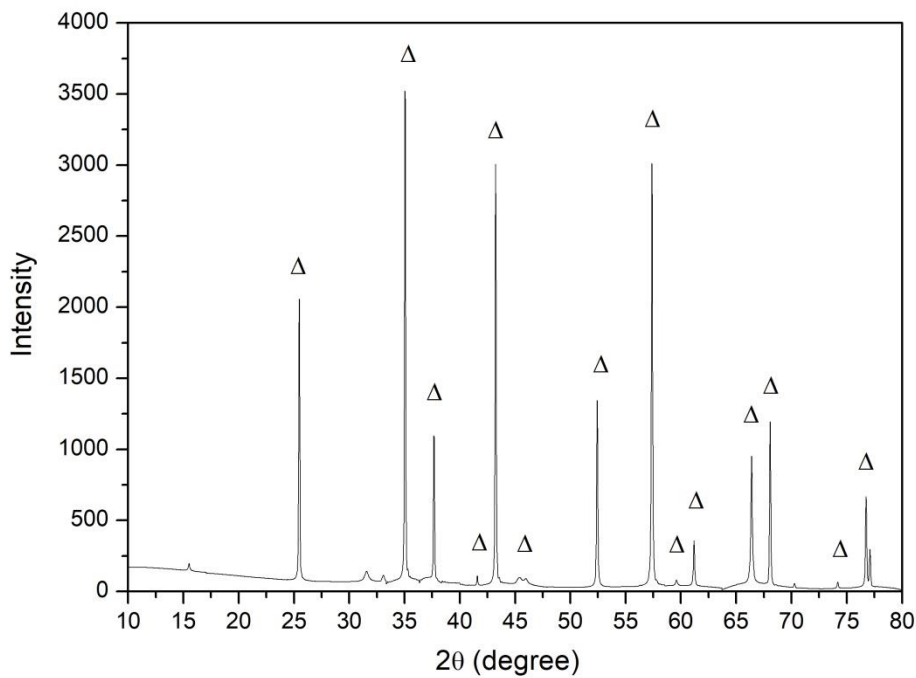
Figure 6.3: X – ray diffraction pattern for alumina produced from residual solid obtained after hydrogen generation

As seen from the XRD pattern, the 2θ range for the characterization was 10°-80°. The important peaks observed for the alumina phase are at 35.2°, 43.4°, 57.5° and 25.2°. These are accompanied with other peaks at 37.8°, 52.4°, 66.5°, 68.1° and 76.6°. The crystal system of this alumina is Hexagonal and lattice is Rhomb-centred.
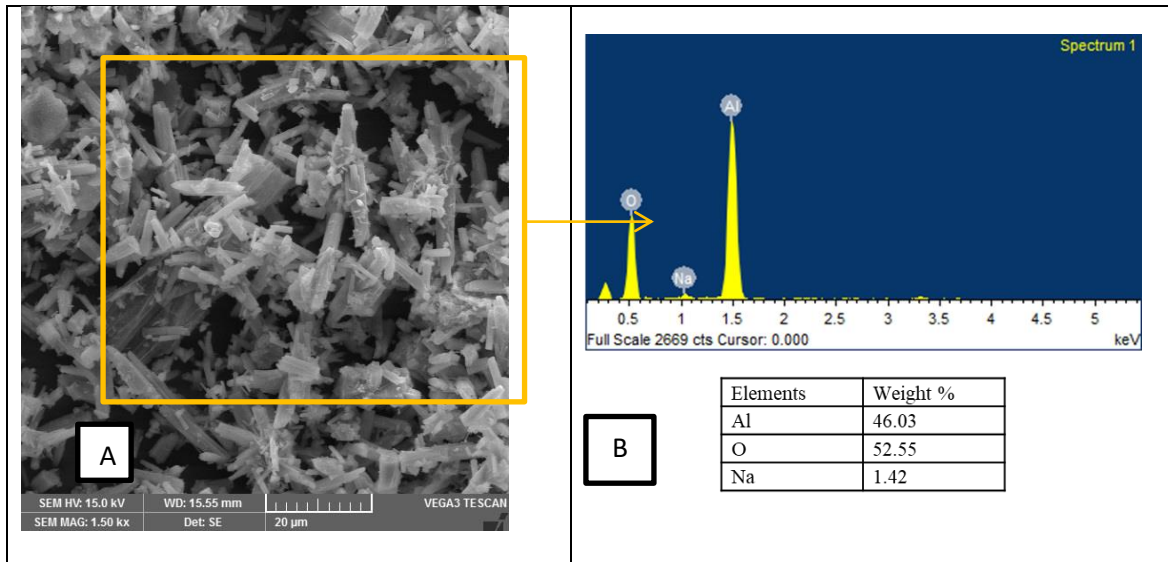
Figure 6.4: SEM – EDS report for alumina produced from residual solid

6.3 Conclusions

Although the present research work shows the possibility of hydrogen production from aluminium dross fines, a lot more can be done to make this process applicable for economic benefit and up scaling. The gas generated needs to be utilized simultaneously in various applications, for instance in experiments where hydrogen gas is essential. Also, the gas generation system can be improved to simultaneously store the hydrogen produced, so that it can be used afterwards as well. The hydrogen generator compatible for aluminium dross can also be developed.

It is already well known that hydrogen is the next-generation source of energy. The amount of heat released by the combustion of hydrogen is a simple deciding factor for its dominance in the emerging sources of energy. The combustion of hydrogen leaves behind nothing but water vapour and it is far less polluting than any other fuel available. Developing better ways of producing hydrogen is the way ahead to ensure better

resource utilization. Added with the benefit of industrial waste utilization, hydrogen production using aluminium dross as a source of aluminium is a good alternative.