Utilization of Aluminum Waste with Hydrogen and Heat Generation

O A Buryakovskaya\textsuperscript{1,2}, E A Meshkov\textsuperscript{1}, M S Vlaskin\textsuperscript{1}, E I Shkolnokov\textsuperscript{1} and A Z Zhuk\textsuperscript{1}

\textsuperscript{1}Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya str., 13, build. 2, 125412 Moscow, Russian Federation
\textsuperscript{2}National Research Nuclear University MEPhI, Kashirskoe shosse 31, 115409 Moscow, Russian Federation
E-mail (O. A. Buryakovskaya): osminojishe@yandex.ru

Abstract. A concept of energy generation via hydrogen and heat production from aluminum containing wastes is proposed. The hydrogen obtained by oxidation reaction between aluminum waste and aqueous solutions can be supplied to fuel cells and/or infrared heaters for electricity or heat generation in the region of waste recycling. The heat released during the reaction also can be effectively used. The proposed method of aluminum waste recycling may represent a promising and cost-effective solution in cases when waste transportation to recycling plants involves significant financial losses (e.g. remote areas). Experiments with mechanically dispersed aluminum cans demonstrated that the reaction rate in alkaline solution is high enough for practical use of the oxidation process. In the experiments aluminum oxidation proceeds without any additional aluminum activation.

1 Introduction

The total amount of waste (municipal and industrial) generated annually worldwide is about 4 billion tons \cite{1}. Municipal solid waste contributes about 2.0 billion tons and the rate of waste generation is constantly growing. Municipal solid waste contains several percents of non-ferrous metals \cite{2} and aluminum represented mostly by packaging waste accounts for about 60% of the non-ferrous metals \cite{3}. Another considerable source of aluminum waste is processing waste (generally scrap and chips). Aluminum waste also includes aluminum flakes, electrotechnical scrap, parts of vehicles, radiators, foil etc. In other words, a large amount of products made of aluminum is transformed into waste and the problem of its effective utilization becomes very actual.

Today the most widely used method of aluminum waste utilization is aluminum recycling from municipal or industrial waste with further production of secondary aluminum. Aluminum already achieves almost 60% recycling for all aluminum packaging and about 68% for beverage cans\cite{4}.

Main consumers of aluminum are transport industry, construction industry, packaging industry and mechanical engineering. To produce 1 kg of primary aluminum 4-5 kg of bauxite and 15-17 kWh of electricity is required.

To produce secondary aluminum from aluminum waste a number of technical procedures have to be carried out including collection, sorting and melting. Metal waste sorting is a labor-intensive multi-staged process. Toremove organic coatings and paints from aluminum cans surface, two techniques can be applied: heating to a specific temperature and long-term thermal treatment at this temperature or a short cyclical heating almost to the melting point of aluminum. Both methods are not environmentally friendly because they can lead to the formation of large quantities of environmentally
harmful substances, for example, dioxins discharged into the atmosphere. After sorting and organic impurities removing the aluminum is melted. Due to inhomogeneous chemical composition a significant amount of slag is formed during melting process. The weight of slag can reach 15% of the original metal weight. In some countries this slag is classified as hazardous waste [5].

Although the production of secondary aluminum reduces the consumption of primary aluminum the quality (chemical purity) and the cost of secondary aluminum in some cases don’t meet the requirements of primary aluminum consumers. Due to the growth of aluminum waste generation a problem of aluminum waste utilization enhances.

It is an interesting way of aluminum waste utilization by corroding it in water with hydrogen production in accordance with the following equation:

$$\text{Al} + 2\text{H}_2\text{O} = \text{AlOOH} + 3/2\text{H}_2$$

Thin passive layer of aluminum oxide produced on aluminum and aluminum alloy surfaces protects them against further oxidation and corrosion.

The methods of intensification of the reaction between aluminum and water and development of approaches to efficient conversion of chemical and thermal energy into useful thermal and electrical energy were studied in [6-8]. Chemical energy of aluminum can be converted into electricity with an efficiency of 40% as reported in [9, 10]. By-product of aluminum-fueled power plant – aluminum oxide can be used as separate market product in different areas including catalysts and sorbent production or construction material [11, 12].

The aim of this study is to investigate oxidation of aluminum-containing waste in different forms in alkali aqueous solutions for hydrogen generation and analyze the structure of solid oxidation products.

2 Materials and Procedures

In this research waste aluminum cans mechanically dispersed into small pieces and aluminum wire in the form of cylinders with the length of 3 mm and diameter of 2 mm were used. Specific surface of aluminum cans was approximately 75.6 cm$^2$/g. In the experiments with alkali aqueous solutions preparation of waste aluminum cans included mechanical dispersion only without removing varnish and paint. Only about 5% of the aluminum can reaction surface was free of varnish and paint. Aluminum content in aluminum wire was 99.5 wt.%. Specific surface area of aluminum cylinders was approximately 11 cm$^2$/g. Experiments on oxidation of aluminum in forms of can particles and cylinders were carried out to establish the influence of paint and varnish (on the surface of waste aluminum cans) on oxidation process.

The experimental plant included a 500 cm$^3$ reactor made of Simax glass with a thermostatic jacket which input and output were connected to the thermostat Huber CC-308. Reactor was located on a magnetic stirrer intended for adjustment rotation speed of the stirring bar at the bottom of the reactor. During the experiments the temperature of reaction medium was measured by a resistance thermometer with the accuracy of 0.01 °C. The scheme of experimental plant is shown in [13].

Hydrogen produced within the reactor from aluminum oxidation passed through a gas bubbler filled with distilled water for cooling down to room temperature. Then hydrogen was supplied into a collecting flask filled with water and the hydrogen pushed water out from the flask. The volume of water pushed out from the flask was equal to the volume of gas collected within the flask. Water replaced by hydrogen was collected in another flask placed on the Sartorius balance with the accuracy of 0.01 g. The balance was connected with a computer and transferred the mass data every 0.5 sec.

3 Results and Discussion

The results of the experiments on oxidation of waste aluminum cans and aluminum wire are presented in Table 1. Fig. 1 shows hydrogen generation curves for two experiments. As it can be seen in Fig. 4, regardless of the fact that the mass of aluminum can pieces was twice more than that of aluminum wire pieces, the peak of hydrogen generation rate for aluminum wire is sharper and shorter than that of waste aluminum cans. For aluminum wire the maximum value of hydrogen generation rate was 61.5 cm$^3$/min per 1 g or 5.6 cm$^3$/min per 1 cm$^2$ of the initial reaction surface area; this value was achieved after 100 sec of the experiment, the induction period was 30 sec. For waste aluminum cans the
maximum value of hydrogen generation rate was 27.1 cm³/min per 1 g or 0.4 cm³/min per 1 cm² of the initial interaction surface area; this value was achieved after 640 sec of the experiment, the induction time was 40 sec. Experimental results show that waste aluminum can pieces react slower than the pieces of aluminum wire with a close value of specific surface area. The induction time for waste aluminum cans was longer than that for the aluminum wire due to the inhibiting effect of the paint. The specific surface area of the aluminum can pieces may reach its maximum value after total coating removal. The experiment with waste aluminum cans was stopped after about 5 hours when no hydrogen gas bubbling was observed. The conversion degree for aluminum cans was 73%.

Figure 1. Hydrogen production rate vs time: a) kinetic curves and b) initial sections of the kinetic curves for aluminum can pieces oxidation in KOH aqueous solution (1) and aluminum wire pieces in NaOH aqueous solution (2)

Table 1. Initial parameters and results of experiments on oxidation of waste aluminum cans and aluminum wire.

| Parameter                                      | Waste aluminum cans | Aluminum wire |
|------------------------------------------------|---------------------|---------------|
| Alkali                                         | KOH                 | KOH           |
| Initial pH of aqueous solution                 | 13.0                | 13.0          |
| Temperature, °C                                | 90                  | 90            |
| Stirring speed, rpm                            | 300                 | 300           |
| The volume of alkali solution, cm³             | 300                 | 340           |
| The mass of alkali, g                          | 1.7                 | 1.7           |
| The mass of aluminum, g                        | 1.07                | 0.52          |
| Experiment duration, h                         | 4.72                | 1.33          |
| Aluminum conversion degree in the sample       | 73                  | 94            |
| (without correction for the weight of the paint),% wt. |                     |               |

The solid oxidation product produced from aluminum cans was filtered, washed with distilled water, dried in a vacuum oven and then it was calcinated in air at a temperature of 1200 °C in order to obtain alumina.

According to XRD analysis the solid product produced from waste aluminum cans contains Al(OH)₃ in two crystallographic forms (gibbsite and bayerite). Gibbsite and bayerite contribute 86 % and 14 % to the aluminum hydroxide volume respectively. Non-oxidized aluminum, as well as α- and γ-Al₂O₃ (< 5%) were also registered in the product. The sample contained inconsequential amounts of potassium aluminate that may indicate low stability of this compound under the experimental conditions.
Surface morphology of solid products was studied using scanning electron microscopy (SEM). Fig. 2 shows microphotographs of the oxidation product obtained after the calcination at 1200 °C. As it can be seen the oxidation product obtained from waste aluminum cans represents a cluster of local buildup crystals, the size of a single crystal varies from several microns to several scores of microns. After heat treatment the crystal volume became highly porous with a typical pore size of 100 nm.

**Figure 2** – The texture of the solid oxidation products produced from aluminum cans

4. Conclusion
An alternative method for aluminum-containing waste utilization was investigated and compared with the conventional method of melting.

The solid oxidation products from aluminum cans were analyzed and the results proved formation of porous materials with complex structure.

The concept of using the method of aluminum-containing waste utilization in the remote areas was proposed.

5. Acknowledgment
The study was supported through a grant of the Russian Science Foundation (project No. 14-50-00124).

6. References
[1] 2012 Globalization & waste management. Phase 1: Concepts and facts: ISWA
[2] 2014 Municipal Solid Waste Generation, Recycling, and Disposal in the United States. Tables and Figures for 2012. U.S. Environmental Protection Agency. Office of Resource Conservation and Recovery
[3] Biganzoli L, Ilyas A, Praagh M v, Persson K M and Grosso M 2013 Aluminium recovery vs. hydrogen production as resource recovery options for fine MSWI bottom ash fraction Waste Management33 1174-81
[4] Bloxsome N September 15, 2014 Commitment to sustainable packaging in Europe Aluminum International Today
[5] Nappi C 2013 The global aluminium industry 40 years from 1972 *London: International Aluminium Institute*

[6] Larichev M N, Laricheva O O, Shaitura N S and Shkolnikov E I 2012 Possibilities of practical usage of dispersed aluminium oxidation by liquid water *Thermal Engineering* 59 1000–9

[7] Dudoladov A O, Buryakovskaya O A, Vlaskin M S, Shkolnikov E I and Zhuk A Z 2015 Generation of hydrogen by aluminium oxidation in aqueous solutions at low temperatures *International Journal of Hydrogen Energy* 41

[8] Vlaskin M S, Shkolnikov E I, Lisitsyn A V and Bersh A V 2010 Thermodynamic calculation of the parameters of a reactor for oxidizing aluminum in wet saturated steam *Thermal Engineering* 57 794-801

[9] Franzoni F, et. al. 2011 Operating maps of a combined hydrogen production and power generation system based on aluminium combustion with water *Intern. J. Hydrogen Energy*. 36 2803–16

[10] Franzoni F, et. al. 2010 Combined hydrogen production and power generation from aluminum combustion with water: analysis of the concept *Intern. J.Hydrogen Energy* 35 1548–59

[11] Shkolnikov E I, Shaitura N S and Vlaskin M S 2013 Structural properties of boehmite produced by hydrothermal oxidation of aluminum *The Journal of Supercritical Fluids* 73 10-7

[12] Lisitsyn A V, Dombrovsky L A, Mendeleyev V Y, Grigorenko A V, Vlaskin M S and Zhuk A Z 2016 Near-infrared optical properties of a porous alumina ceramics produced by hydrothermal oxidation of aluminium *Infrared Physics & Technology* 77 162-70

[13] Ambaryan G N, Vlaskin M S, Dudoladov A O, Meshkov E A, Zhuk A Z and Shkolnikov E I 2016 Hydrogen generation by oxidation of coarse aluminum in low content alkali aqueous solution under intensive mixing *International Journal of Hydrogen Energy* 41 17216-24