Experience in Creation and Exploitation of Energetic and Energy-Technological Plants Based on Hydrothermal Oxidation of Aluminum

A V Grigorenko*, E I Shkolnikov, A Z Zhuk and M S Vlaskin

Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
E-mail: presley1@mail.ru

Abstract. Present paper is devoted to the description of our recent experience in the creation and exploitation of energetic and energy-technological plants based on hydrothermal oxidation of aluminum. Two plants based on reactor for hydrothermal oxidation of aluminum were created for today. These are experimental co-generation power plant and energy-technological plant with hydrogen production rate of 10 and 100 nm³/hour respectively. The principle of operation of the reactor for hydrothermal oxidation as well as the plants based on such reactor is discovered in present paper.

1. Introduction
Aluminum is considered as a prospective material for hydrogen or/and energy generation due to its high efficiency (1.24 l of H₂ or 31 kJ per 1 g of Al), availability, environmental safety of the reaction products, safety storage and transportation, and relatively low price. Aluminum reacts with water producing hydrogen and hydroxides or oxides of Al according to the following reactions (1)–(3):

\[
\text{Al} + 3\text{H}_2\text{O} \rightarrow 0.5\text{Al}_2\text{O}_3 + 3\text{H}_2 + 427.98 \text{ kJ/mole},
\]

\[
\text{Al} + 2\text{H}_2\text{O} \rightarrow 0.5\text{Al}_2\text{O}_3 + \text{H}_2 + 415.24 \text{ kJ/mole},
\]

\[
\text{Al} + 1.5\text{H}_2\text{O} \rightarrow 0.5\text{Al}_2\text{O}_3 + 1.5\text{H}_2 + 407.7
\]

The reaction enthalpies in (1)–(3) correspond to standard conditions P = 1 atm, T = 298 K. Reaction heat and structure of products depend on thermodynamic conditions. Channel (1) prevails at temperature under 200°C, (2) prevails in the field of 200-400 °C and further temperature increase leads to Al₂O₃ formation (channel (3))[1].

Aluminum oxidation in water or aqueous solutions has been under intensive study for the last decades [2-3]. An interest in this process was called due to the high chemical activity of aluminum. The use of pure water as an oxidant in its reaction with aluminum makes it possible to synthesize high pure hydrogen, a large amount of high-temperature steam, and a variety of aluminum hydroxides. Main problem in this field is to start the reaction of aluminum oxidation because it is inhibited by an oxide film on the surface of aluminum. A number of methods of aluminum activation have been already proposed. These methods include preparation of highly reactive aluminum powders alloyed with various galliums [4], milling with salts [5-6], oxidation in alkaline aqueous solutions [7] etc. There are many proposed methods applying additional chemicals designated for fast and complete aluminum oxidation in aqueous media.
Recently a method of aluminum micron powder oxidation in high-temperature steam [8] was developed. It allows applying pure (without alkali and any other chemical activators) water as oxidant. Kinetics of aluminum micron powders oxidation in high-temperature boiling water was studied in [9] where it was established that commercial aluminum powders with average particle sizes from 4 to 70 μm are intensively oxidized by water steam under about 300°C and 10 MPa.

Hydrothermal oxidation of aluminum is the process that produces not only hydrogen and/or energy but also a variety of alumina-based materials [10-13]. Economic of this process should be based on all products of the process. The process of aluminum oxidation in water can be used directly for hydrogen and heat production in energy applications, while the solid products of aluminum oxidation can be sent to aluminum recycling or obtaining the marketable aluminas. These aluminas may be used in a wide spectrum of non-metallurgical applications including ceramics, adsorbents, catalysts, etc.

Present work gives the description of our recent experience in the creation and exploitation of energetic and energy-technological plants based on hydrothermal oxidation of aluminum. Description includes two plants based on reactor for hydrothermal oxidation of aluminum: experimental cogeneration power plant and energy-technological plant with hydrogen production rate of 10 and 100 nm³/hour respectively.

2. Reactor for hydrothermal oxidation of aluminum

Schematic view of the reactor for hydrothermal oxidation of aluminum is shown on Fig. 1. Fig. 1 illustrates the supplying of reagents into the reactor and the products withdrawing. Aqueous suspension of aluminum powder is supplied from top through nozzle using a dosing pump. The outlet of gaseous products is in the upper part of the reactor and the bottom has the outlet for the solid and liquid products.

Reactor represents the elongated cylinder. Reactor is heat-insulated and ohmic heater is used. Initial reagents (aluminum and water) enter into the reactor with the help of high-pressure pump. Aluminum enters into the reactor in the form of aluminum-water mixture, which is preliminary prepared in mixing tank. Reaction products are removed from the reactor into the oxidation products receiving tank. Experimental plant is equipped by cutoff valves, thermocouples installed on reactor external surface and pressure detectors. Experimental plant is managed from remote operating room by means of computer-based control system. Indications of all sensors are written on hard disk drive of the computer.

Reactor for hydrothermal oxidation of aluminum is supplied by aluminum micron powder (with average particle size of about 100 μm) as primary fuel and water as primary oxidant.

![Figure 1. Schematic view of the reactor of hydrothermal oxidation of aluminum](Image)
3. Experimental co-generation power plant with 10 nm³/hour hydrogen production

Energy-effective and multi-purpose technology of hydrothermal aluminum oxidation was firstly realized in experimental co-generation power plant CGPP-10 intended, first of all, for autonomous energy supply. The view of this plant is shown in Fig.2. For the first time the power plant utilized aluminum as a fuel. CGPP-10 worked in non-stop autonomous regime without of external grid. It produced hydrogen, electrical and thermal energy, as well as nanostructured aluminum hydroxide. Technical characteristics of experimental co-generation power plant CGPP-10 are shown in Table 1. Useful power of CGPP-10 is about 10 kW, electrical efficiency and total efficiency regarding to combustion heat of aluminum are 14 % and 72 % respectively. Plant consists from reactor block, cooler, hydrogen tanks, 16 kW fuel cell battery, inverter and control system. Power plant can produce both electrical energy and hydrogen with 10 nm³/hour hydrogen production rate. It is important that hydrogen is produced at already high pressure without additional devices and energy inputs on its compression due to high pressure in chemical reactor. Electrical energy produced by fuel cell in direct current is converted into three-phase current and supplied to power plant auxiliary thus allowing its autonomous working.

4. Energy-technological plant with 100 nm³/hour hydrogen production

The technology of hydrothermal aluminum oxidation with the production of marketable products (AlOOH and H₂), electrical and thermal energy was realized in experimental energy-technological plant ETP-100, which produces marketable products: nanocrystalline aluminum hydroxide, hydrogen, as well as electrical and thermal energy. Nanostructured aluminum hydroxide, which is produced by plant in industrial scale, is market product. The view of energy-technological plant ETP-100 is shown in Fig. 3. It is consisted from two blocks. The first is designated for the preparation aluminum-water suspension and the second is designated for hydrothermal oxidation of aluminum and product accumulation. Main technical characteristics of energy-technological plant ETP-100 are shown in Table 2.

Recently, the opportunity to produce high purity aluminum oxide (with the purity of more than 99.997%) from AlOOH obtained in ETP-100 has been demonstrated. The process of aluminum oxide purification was based on high temperature vacuum treatment [11-12]. The physics of this process is based on the diffusion of impurities to the surface of the crystal (surface segregation) and their subsequent evaporation at high temperatures (about 1800°C)[14].
Figure 2. The view of experimental co-generation power plant CGPP-10 for autonomous energy supply

Table 1. Technical characteristics of experimental co-generation power plant CGPP-10

| Parameter                                           | Value |
|-----------------------------------------------------|-------|
| Aluminum consumption rate, kg/hour                  | 9.4   |
| Aluminum hydroxide (boehmite) production rate, kg/hour | 19    |
| Thermal power, kW                                    | 40    |
| Hydrogen production, nm³/hour                        | 10    |
| Auxiliary, kW                                        | 4     |
| Electrical power, kW                                 | 10.6  |
| Electrical efficiency, %                             | 14    |
| Total efficiency, %                                  | 72    |
Figure 3. The view of energy-technological plant ETP-100

Table 2. Technical characteristics of energy-technological plant ETP-100

| Parameter                                      | Value  |
|------------------------------------------------|--------|
| Aluminum consumption rate, kg/hour            | 101    |
| Water consumption rate at the input to         | 484    |
| the water-preparatory device, kg/hour          |        |
| Average reactor temperature, °C               | 324    |
| Average reactor pressure, MPa                 | 150    |
| Auxiliary, kW                                 | 28     |
| Hydrogen production, nm³/hour                 | 110    |
| Thermal power, kW                             | 260    |
| Aluminum hydroxide (boehmite) production rate | 203    |
| kg/hour                                       |        |

5. Conclusion

Our recent experience in the creation and exploitation of energetic and energy-technological plants based on hydrothermal oxidation of aluminum has been described. Two plants based on reactor for hydrothermal oxidation of aluminum were created for today. These plants are the first aluminum-fueled power plants based on hydrothermal oxidation of aluminum. These are experimental cogeneration power plant and energy-technological plant with hydrogen production rate of 10 and 100 nm³/hour respectively. The principle of operation of the reactor for hydrothermal oxidation as well as the plants based on such reactor is discovered in this work. It is believed that power plants based on hydrothermal oxidation of aluminum can share the niches in transport and non-centralized energy in near future. It is supposed that such power plants are appropriate for eco-density regions, e.g. for megapoles. They can be successfully applied as emergency, on-peak power and standby plants. Such plants can be used in a number of military applications. For example, aluminum-water propulsion is favourable for submarine or ship energy supply, because in this case the craft takes on its board only fuel (aluminum), while oxidizer (water) is supplied from the outside. So, aluminum as a fuel might be used in a number of special energy applications.

Today the profit from the plants based on hydrothermal oxidation of aluminum can be reached by using them as energy-technological plants for co-production of energy and marketable products – high-purity hydrogen and high-purity aluminum oxides (or nanostructured oxides and hydroxides).
6. Acknowledgements
The study was supported through a grant of the Russian Science Foundation (project No. 14-50-00124).

7. References
[1] Vlaskin M S, Shkol’nikov 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
[2] Shkolnikov E I, Zhuk A Z and Vlaskin M S 2011 Aluminum as energy carrier: Feasibility analysis and current technologies overview Renewable and Sustainable Energy Reviews 15 4611- 23
[3] Vlaskin M S, Dudoladov A O, Buryakovskaya O A and Ambaryan G N 2018 Modelling of aluminium-fuelled power plant with steam-hydrogen enthalpy utilization International Journal of Hydrogen Energy
[4] Dudoladov A O, Buryakovskaya O A, Vlaskin M S, Zhuk A Z and Shkolnikov E I 2016 Generation of hydrogen by aluminium oxidation in aqueous solutions at low temperatures International Journal of Hydrogen Energy 41 2230-7
[5] Alinejad B and Mahmoodi K 2009 A novel method for generating hydrogen by hydrolysis of highly activated aluminum nanoparticles in pure water International Journal of Hydrogen Energy 34 7934- 8
[6] Czech E and Troczynski T 2010 Hydrogen generation through massive corrosion of deformed aluminum in water International Journal of Hydrogen Energy 35 1029- 37
[7] 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
[8] Bersh A V, Lisitsyn A V, Sorokovikov A I, Vlaskin M S, Mazalov Y A and Shkol’nikov E I 2010 Study of the processes of steam-hydrogen mixture generation in a reactor for hydrothermal aluminum oxidation for power units High Temperature 48 866- 73
[9] Vlaskin M S, Shkolnikov E I and Bersh A V 2011 Oxidation kinetics of micron-sized aluminum powder in high-temperature boiling water International Journal of Hydrogen Energy 36 6484-95
[10] 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
[11] Vlaskin M S, Grigorenko A V, Zhuk A Z, Lisitsyn A V, Sheindlin A E and Shkol’nikov E I 2016 Synthesis of high-purity α-Al2O3 from boehmite obtained by hydrothermal oxidation of aluminum High Temperature 54 322- 9
[12] Zhuk A Z, Vlaskin M S, Grigorenko A V, Kislenko S A and Shkolnikov E I 2016 Synthesis of high-purity α-Al2O3 from boehmite by high temperature vacuum treatment Journal of Ceramic Processing Research 17 910-8
[13] 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 aluminum Infrared Physics & Technology 77 162- 70
[14] Kislenko S A, Vlaskin M S and Zhuk A Z 2016 Diffusion of cation impurities by vacancy mechanism in α-Al2O3: Effect of cation size and valence Solid State Ionics 293 1-6