Decarbonization methods of electric energy production in a solid oxide fuel cell

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***Abstract* — The global decarbonization policy has led to the widespread development of solid oxide fuel cells (SOFCs). Fuel cells are electrochemical devices that convert the fuel oxidation chemical energy directly into electrical and thermal energy. However, during the fuel cell operation, carbon dioxide is released, which must be captured and utilized. CO_2 capture can be carried out by adsorption, absorption and membrane methods. A laboratory setup was created to determine the efficiency of carbon dioxide capture and tested some absorbents. According to the results of the experiments, the NaOH solution showed the highest sorption capacity. Based on the data obtained, a technological scheme and an installation for carbon dioxide capture and utilization have been developed. An alkaline solution of sodium hydroxide 6% was used as an absorbent. The absorbent is subsequently regenerated and reused. Solid waste in the form of a suspension (calcium carbonate solution) is dehydrated in a filter press and can then be used as a raw material for the construction industry.**

Keywords— solid oxide fuel cell (SOFC), carbon dioxide, carbon dioxide capture and utilization, thermal power plants, absorption

I. Introduction

The global growth in the consumption of organic energy carriers (natural gas, refined petroleum products, coal) is associated with a negative impact on the environment. Environmental problems associated with emissions of gases (carbon oxides, sulfur, nitrogen) have become global problems. The amount of greenhouse gases in the atmosphere has increased significantly since the Industrial Revolution, and the concentration of carbon dioxide has increased by 37%. The increased concentration of greenhouse gases in the atmosphere causes global warming. Without the introduction of a decarbonization policy, the amount of gas emissions by 2030 may increase to 25–90% compared to 2000 [1].

Today, industrialized countries are implementing modern technologies to minimize harmful gas emissions. These technologies include the use of low-carbon fuels (nuclear fuel, hydrogen, etc.), the use of renewable energy sources (wind power, solar energy, geothermal energy, low-grade heat, etc.), improving energy efficiency, as well as technologies for capturing and further carbon dioxide utilization [2].

The use of fuel cells is recognized as an important direction for the decarbonization policy and increasing energy production efficiency. Fuel cells are electrochemical devices that convert the fuel oxidation chemical energy directly into electrical and thermal energy. The reaction proceeds between hydrogen-containing fuel and oxygen (Figure 1). One of the products of a chemical reaction is carbon dioxide, which must be captured and utilized. Therefore, the development of methods and technologies for carbon dioxide capturing is very relevant nowadays.

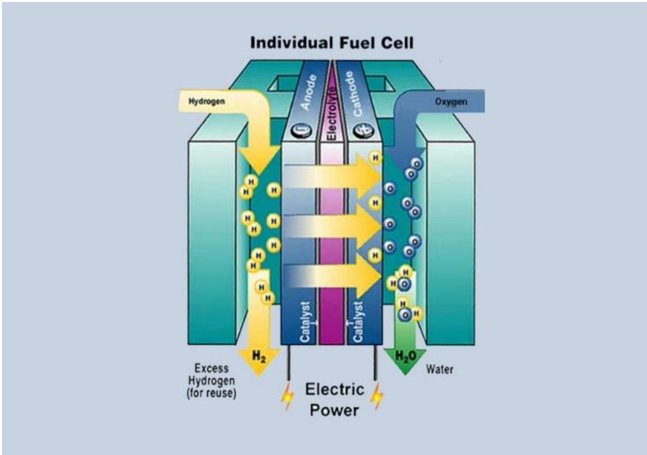

Fig. 1. – Solid oxide fuel cell (SOFC)

Carbon dioxide capture from flue gases of thermal power plants and petrochemical enterprises has been recognized as one of the most important areas for reducing greenhouse gas emissions into the atmosphere. To maintain the concentration of greenhouse gases at an acceptable level, a significant reduction in carbon dioxide emissions is required, due to its separation and further disposal. In developed countries, there are regional clusters that represent communities of industrial enterprises that are directly or indirectly related to each other. The activity of clusters is aimed at obtaining common benefits from the production of high-quality products at a lower price through the use of common resources. The cluster unites several industrial enterprises and power plants with a common infrastructure for carbon dioxide capture, transportation and disposal [2].

The first stage in the decarbonization policy is the development and implementation of an effective CO_2 capture technology. Carbon dioxide can be captured in several ways:

- the release of CO_2 in a chemical technological process, when the entire gas flow is directed to a common network;

- if there is a sufficient amount of oxygen in the gas mixture, according to stoichiometric coefficients, gas combustion is a possible way in organizing the process with heat removal from an external source. Boilers, thermal power plants, industrial kilns and cement plants can be used as external heat sources. In related industries, more rational use is possible;

- the use of modern capture technologies, which are based on the use of liquid, solid or other forms of absorbing materials that can selectively absorb carbon dioxide.

Some researchers consider carbon dioxide capture by absorption. The technology is based on the contact of gas with an absorbent, which is a mixture of an alkali metal salt or an alkali metal hydroxide, polyamine, alkonolamine. Among the alkanolamines used in industrial processes are monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA). Among the polyamines, special attention has been paid to piperazine. It has a large number of derivatives (N-(2-hydroxyethyl)-piperazine, N,N'-Bis-(2-hydroxyethyl)-piperazin, N-(2-aminoethyl)-piperazine) that have different properties and excellent efficiency [3,4].

Badal G.P. and the colleagues presented a step-by-step purification method using various amines. Thus, at the first stage, primary amine is used, as the most effective, at the second stage of purification (post-purification), a mixture of secondary and tertiary amines is used [5].

In the patent [6], carbon dioxide is captured using aqueous mixtures of alkanolamines, with the addition of alkali metal salts.

Some reserchers have proposed an adsorbent based on a mesoporous organometallic frame structure selected from the structures IRMOF3, MOF177, HKUST1 (MOF199), ZIF8, MIL100, MOF200, MOF210, MIL101 or MIL53. The selected base is treated with an aqueous zinc salt solution and heated to form a modifying additive in the zinc oxide form. As a result, the capacity of this adsorbent is approximately 2 times higher than the capacity of known adsorbents for CO_2 at atmospheric pressure [7-9, 14].

High-temperature sorbents based on calcium oxide and zirconium dioxide can be used to capture carbon dioxide. This type of sorbents is produced by mixing powdered materials of calcium carbonate (73-89% wt.) with baddeleyite concentrate (11-27% wt.). Subsequently, this mixture is grounded to nanoparticles in a bead mill in an aqueous medium using beads made of stabilized zirconia [10].

Nikolaev V.V. et al [11] proposed a method for gas mixture purification. The method consists in subsequent contact with the adsorbent and synthetic zeolite, followed by regeneration of saturated zeolite and adsorbent by countercurrent at raised temperature. Silica gel and zeolite were chosen as the adsorbent. The purified gas was in contact with silica gel and zeolite at their mass ratio of 1-10:1, respectively. The regeneration of the adsorbent should be carried out in the temperature range 180-220°C.

Belyaev V.D. et al [12] proposed a method based on a two-stage gas passage through a catalyst at a temperature not lower than 20 °C and a pressure not lower than 0.1 atm. Different catalysts were used at each stage. At the first stage, metal oxides were used. The oxides were deposited in a thin layer on the carrier surface (zeolites, oxides of aluminium, zirconium). It is also possible to use a graphite-like carbon material. At the second stage, noble metal catalysts were used, which made it possible to reduce the concentration of carbon oxides to 10 ppm. The disadvantage of this method is the low catalysts selectivity at the first stage of the process. In the presence of water vapor in the gas mixture, the activity of the catalyst decreases sharply. In this case, the process temperature exceeds 170°C. This method can be used to purify hydrogen-containing gas mixtures in a reactor with two-stage catalyst bed. In the first layer at a temperature of 160 °C there is a catalyst containing 5 wt.% $CuO\text{-}CeO_2/Al_2O_3$. In the second layer at a temperature of 110 °C there is a catalyst containing 1.0 wt.% $CoPt/A1_2O_3$.

Eliseev A.A. et al [14] have developed a membrane method for a gas mixture separation. Their installation makes it possible to intensify the transmembrane absorption process for the effective removal of undesirable components from natural and technological gas mixtures. The device described by the authors involves the passage of the gas mixture through a nanoporous membrane and their selective absorption by a liquid absorbent. The efficiency of extracting components is more than 99.993% for H_2S and more than 99.9% for CO_2.

The use of contactors is proposed in US patent No. 5753009 [13]. The contactor is a membrane device, where hollow fibers with a two-layer membrane material are used. The membrane consists of a porous and non-porous layer. The non-porous layer is used for selective purification.

After carbon dioxide is captured and concentrated, it can either be utilized or buried for a long time. A specially designed storage facility is required for underground storage. This method has proven to be a risk-free technical solution. Carbon dioxide can be used as a raw material for the chemical industry or as an enhanced oil recovery fluid. A promising way of CO_2 disposal is the transformation into valuable chemical products and materials. To date, it is possible to produce urea, salicylic acid, ethylene carbonate and methanol from CO_2 on an industrial scale (Figure 2) [2].

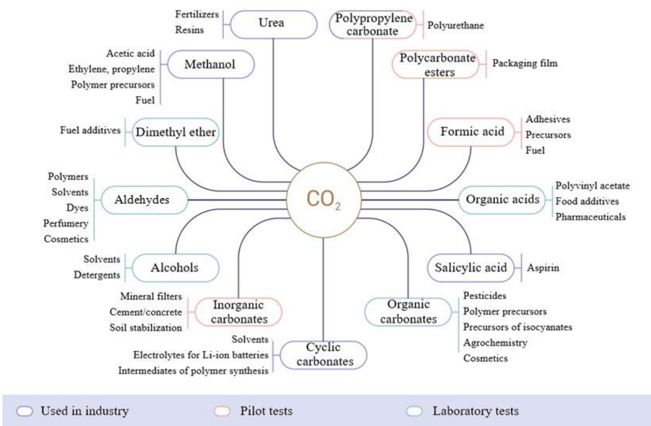

Fig.2. CO_2 processing products

The relevance of this work is that the conducted laboratory experiments made it possible to determine the sorbents that have the highest efficiency. Based on these experiments, a technological installation was proposed with the possibility of regenerating the absorbent and reusing it in the installation.

II. MATERIALS AND METHODS

A laboratory installation (Figure 3) was created for conducting experiments. The main advantages of the installation are the simplicity of design and the ability to quickly replace the sorption material.

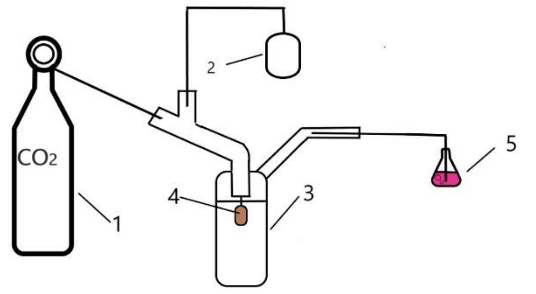

Fig.3. Scheme of laboratory installation of CO_2 absorption. 1 – CO_2 tank, 2 – a compressor, 3 – an absorber,4 – an air stone, 5 – a conical flask with an alkaline solution.

A CO_2 tank 1 with a gas reducer was used as a source of carbon dioxide. With the help of a gas reducer, a gas flow rate of 0.05 l/min was set. Carbon dioxide was supplied together with air supply in a ratio of 1:5, respectively (air consumption – 0.25 l/min). The air was supplied using an air compressor 2.

A mixture of gases is fed into the absorber 3 through a tube, an air stone 4 is installed at the end of the tube to break the gas bubbles into smaller ones. In this case, the contact of the gas phase and the absorbent is maximal.

Purging with a gas mixture was carried out for 4 minutes. The consumption of carbon dioxide and air was 0.02 l and 0.25 l, respectively.

From the absorber, after the absorption process, the gas is fed into the flask 5 with an alkaline solution of sodium hydroxide. The concentration of the sodium hydroxide solution was 0.01 N (Figure 4). CO_2, which is not captured by the absorbent, reacts with sodium hydroxide to form carbonates and bicarbonates. The sodium hydroxide solution is tinted with the indicator phenolphthalein, which in an alkaline medium has a pink color. In the case of weak CO_2 absorption, the gas passes into the conical flask and reacts with the sodium hydroxide solution. As a result, the solution changes color from pink to colorless. This indication helps to determine the effectiveness of the CO_2 capture process.

Carbon dioxide absorption results were obtained using titrimetric analysis, determination of free and total alkalinity. Titration was carried out according to GOST 31957-2012 "Methods for determining the alkalinity and mass concentration of carbonates and hydrocarbonates" [15]. This method allows us to determine the mass concentrations of carbonates and bicarbonates. A 0.1 N HCl solution was used as a titrant. Titration was performed using phenolphthalein and methyl orange indicators.

The purpose of the experiments was to identify "working" absorbers that effectively capture carbon dioxide. During laboratory experiments, the following absorbents were used: running water, 10% sodium hydroxide solution, 10% aqueous ammonia solution, 1% chelamine, calcium hydroxide solution, 6% calcium hydroxide solution, 25% sodium carbonate solution, 6% quicklime solution, 6% calcium chloride solution, 6% pre-treatment sludge solution. The choice of these absorbents is justified by their availability and low cost.

Fig. 4. Laboratory installation of CO_2 capture

Chelamine is a reagent based on amines and polyamines, most often used to adjust the boilers water-chemical regime. The composition of chelamine varies slightly and the presence of polycarboxylates is possible, as well as the presence of volatile amines such as ammonia. It was decided to test this reagent in order to compare the results with the invention, in which monoethanolamine and diethanolamine were tested.

Pre-treatment sludge is a natural stable mixture of elements, the content of which depends on the chemical composition of the raw water supplied to the water treatment plants. More than 80% of the sludge is calcium carbonate, the remaining 20% is divided between sulfates, silicate hydroxides. The sludge has a high mechanical strength and this is evidenced by the homogeneous granulometric composition of the crushed sample. Sludge is an inert material and belongs to substances of the 5th hazard class [4, 16-18]. Sludge can be used to remove carbon dioxide from flue gases. There is a technology of sludge preparation, namely the preparation of granular sludge with binding to liquid sodium glass in a volume ratio of 2:1, respectively [18-22].

The experimental part is based on the determination of free and total alkalinity, as well as calculations of hydrate, carbonate and bicarbonate alkalinity. The calculation was carried out according to the HCl solution consumption (titrant) at a concentration of 0.1 N. Total alkalinity was determined by the volumetric method by titrating the sample to pH=4.3 in the presence of methyl orange indicator. Free alkalinity was determined by titrating the sample to pH=8.3 in the presence of the phenolphthalein indicator.

After conducting laboratory experiments, the data obtained were processed. The amount of absorbed carbon dioxide was determined.

Carbon dioxide reacts with a solution of sodium hydroxide according to the formula:

$$\left(\frac{A_c}{2}+A_b\right)*V_{pr},\quad mmol \tag{1}$$

The calculation requires data on carbonate and bicarbonate alkalinity. The sample volume Vpr was 0.1 l.

In order to determine the amount of carbon dioxide captured by the absorbent, it is necessary to subtract the amount of gas that has reacted with the sodium hydroxide solution from the amount of carbon dioxide (0.89 mmol).

III. RESULTS AND DISCUSSION

The results of the determination of free and total alkalinity, as well as calculations of hydrate, carbonate and bicarbonate alkalinity are shown in Table I.

When calculating the amount of absorbed CO_2, the difference between the passed gas flow containing CO_2 and the amount of CO_2 passed into the conical flask with a 0.1 N sodium hydroxide solution was determined. The amount of CO_2 passed through the absorber in 4 minutes is 0.02 l. Then we convert this value into mmol, taking into account the molar volume of the gas mixture (22.4 l/mol) and we find out that 0.89 mmol of CO_2 passed through the installation.

TABLE I. RESULTS OF A LABORATORY EXPERIMENT ON CARBON DIOXIDE ABSORPTION

Sorbent	T, °C	Ions in water samples	Alkalinity, mg eq/l			Amount of absorbed CO_2, mmol
			Hyd-rate	Carbo-nate	Bicarbo-nate	
Water	25	HCO_3^-	-	-	8.9	0
10% NaOH solution	25	OH^-, CO_3^{2-}	8.9	-	-	0.89
10% ammonia solution	25	OH^-, CO_3^{2-}	9.9	-	-	0.89
Helamine 1%	25	CO_3^{2-}, HCO_3^-	-	3.6	5.3	0.18
$Ca(OH)_2$ solution	25	HCO_3^-	-	-	8.9	0
6% $Ca(OH)_2$ solution	25	HCO_3^-	-	-	8.9	0
6% $Ca(OH)_2$ solution	95	CO_3^{2-}, HCO_3^-	-	5	3.9	0.25
25% Na_2CO_3 solution	25	HCO_3^-	-	-	8.9	0
25% Na_2CO_3 solution	95	HCO_3^-	-	-	8.9	0
6% CaO solution	25	CO_3^{2-}, HCO_3^-	-	7.6	1.3	0.38
6% CaO solution	95	CO_3^{2-}, HCO_3^-	-	5.6	3.3	0.28
6% $CaCl_2$ solution	25	CO_3^{2-}, HCO_3^-	-	2.2	6.7	0.11
6% pre-treatment sludge	25	HCO_3^-	-		8.9	0

According to the results of experiments, the best efficiency of CO_2 capture was shown by solutions of sodium hydroxide 6% and quicklime 6%. The results of the experiment with ammonia are invalidated because ammonia is volatile.

To determine the experimental error, a certified solution was used as a control sample. The absolute error is P=0.95.

Based on experimental laboratory studies, a technological scheme for capturing and utilizing carbon dioxide was developed. The technological scheme was developed using a 6% sodium hydroxide solution, which showed the best efficiency.

The unique feature of this carbon dioxide capture scheme is that it allows the regeneration of used absorbents and forms a closed cycle. The main difference of this scheme is that CO_2 is captured by the absorbent, the absorbent is regenerated and returned to the cycle.

When developing the technological scheme, the following goals were pursued:

- simple design and ease of maintenance;
- economic efficiency of the process;
- closed technological cycle;
- environmental friendliness.

The technological scheme includes an absorber, a contact container, a filter press, tanks for preparing solutions of sodium hydroxide and lime milk (Figure 5).

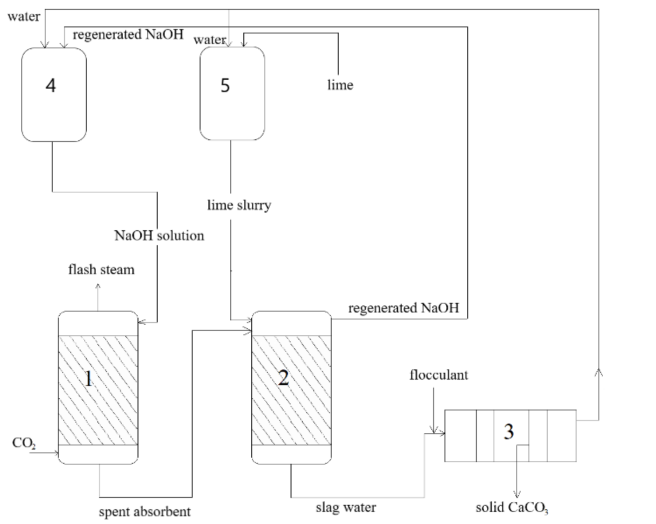

Fig.5. Technological installation for carbon dioxide capture and utilization. 1 – absorber, 2 – contact container, 3 – filter press, 4 – tank for sodium hydroxide solution preparation; 5 – tank for lime milk solution preparation.

Carbon dioxide enters the absorber 1, where it interacts with a 6% sodium hydroxide solution, which enters through a distribution device on top of the apparatus. The distribution device is necessary for crushing into small drops, since in this case the contact between the gas and liquid phases proceeds more completely.

Carbon dioxide reacts with sodium hydroxide and an intermediate product (sodium bicarbonate) is formed, which is further converted to sodium carbonate.

The spent absorbent for regeneration enters the contact container 2, where it is mixed with the lime milk solution. After regeneration process a sodium hydroxide solution and $CaCO_3$ are formed and removed from the bottom of the apparatus in the form of sludge water. Sludge water enters the filter press 3, where the it is dehydrated.

A polyacrylamide-based flocculant is dosed into the sludge water before the filter press 3 to improve the separation of the solid phase from the aqueous medium and reduce the time of sludge dehydration. The remaining dehydrated sludge can be used in the construction industry.

The regenerated sodium hydroxide solution after the contact container 2 is mixed with the water after sludge dewatering and re-enters the absorber 1. Thus, the cycle is closed. This technology captures and recycles carbon dioxide.

IV. Conclusion

A literature review of absorbents used to capture CO_2 was carried out. There are absorbers that can be effective in capturing carbon dioxide, but there are a number of restrictions related to sanctions and pricing policy. Therefore, the absorbents that are available at almost every thermal power plant were reviewed and tested. An installation for carrying out the absorption process and determining the effectiveness of the selected absorbents was created. Carbon dioxide absorption efficiency were defined using titrimetric analysis, determination of free and total alkalinity. According to experimental data, it was found that solutions of sodium hydroxide 6% and quicklime 6% have the greatest efficiency. Based on the data obtained, a technological scheme for carbon dioxide capture and utilization was developed. This scheme includes an absorber, a contact container, a filter press, tanks for preparing solutions of sodium hydroxide and lime milk. The peculiarity of the developed scheme is that it allows us to regenerate and reuse the absorbent. This scheme provides the formation of a closed technological process of CO_2 capture. CO_2 is absorbed by a solution of sodium hydroxide. The spent absorbent is regenerated with lime milk solution and recycled. As a result of the regeneration reaction, sludge waste is formed, which is dehydrated on the filter press and utilized. The developed technology allows capturing and utilizing carbon dioxide in accordance with the energy decarbonization policy.

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