Promiseing Chemisorption Cycles for CO₂ Isolation from Flue Gases

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Abstract

Prospective cyclic hydrocarbon combustion processes those differ by the type of chemisorbent are considered. In the carbonate cycle for CO₂ isolation from flue gases a high-temperature solid regenerable CO₂ chemisorbent is used. In the oxygen cycle, solid oxygen chemisorbent is used that is restored via contacting with fuel and oxidized when exposed to air. A common feature of such processes consists in solid-state reactions of binding and releasing the products or reactants at different stages of the process. Requirements for chemisorbents are determined concerning cyclic processes. Various factors affecting the efficiency of their use are considered, literature data concerning the efficiency of proposed CO₂ concentration cycles are presented.

Key words: flue gases, CO₂, chemisorbents, CaO, carbonate cycle, oxygen cycle, greenhouse effect, power engineering

INTRODUCTION

In recent years the amount of CO₂ emitted into the atmosphere resulting from the combustion of fossil fuels increases steadily (Fig. 1), which is accompanied by an increase in the concentration of CO₂ in the atmosphere [1–3].

![Graph showing annual CO₂ emissions and concentration in the atmosphere over years](image)

Fig. 1. Annual man-caused emissions of CO₂ into the atmosphere and changing the concentration of CO₂ in the atmosphere [1–3].

The power industry accounts for about 40% of all the CO₂ emissions [4]. The main part of electricity is generated at large power plants, which allows using large-capacity technologies for CO₂ isolation from flue gases, its concentration and further use.

In recent years different solutions of this problem are offered, including absorption, membrane, adsorption, cryogenic and other methods to extract CO₂ from flue gases [5, 6]. A separate place among these is taken by the methods wherein chemisorbents are used those allow CO₂ isolation at a high temperature. The greatest attention of researchers is attracted by two promising processes; those differ from each other by the type of chemisorbent and an approach to CO₂ concentration. In the first case, CO₂ is recovered by regenerated chemisorbent based on calcium oxide. Another technology is based on the oxidation of fuel by the chemisorbent of oxygen, where after the reduced chemisorbent is oxidized by atmospheric oxygen.

In this paper, basing on the characteristics of each process we formulate requirements for chemisorbents, advanced materials are determined and the possibility of their use is discussed.
CARBONATE CYCLE FOR CO₂ ISOLATION FROM FLUE GASES

In the English literature the carbonate cycle is termed as calcium looping cycle [7], which emphasizes the fundamental importance of using calcium oxide in this process. An important advantage of CaO consists in the fact that it can reversibly absorb carbon dioxide at high temperature values. Indeed, in order to obtain superheated steam, modern power plants require for high-potential heat sources with the temperature values higher than 600 °C [8]. There are several elements known to form carbonates at such temperature: alkali metals, calcium, strontium and barium. Carbonates of the first group elements exhibit the melting point lower than 900 °C and an extremely high corrosion activity in the molten state. Strontium and barium carbonates decompose at the temperature values above 1000 °C, but the compounds of these elements are of limited occurrence, and their use in a large-capacity process is connected with higher material costs. In contrast, calcium-containing limestone and dolomite species are generally available and cheap. Calcium oxide exhibits thermal stability to absorb carbon dioxide at an appreciable rate at the temperature values above 600 °C. The decomposition of calcium carbonate formed at CO₂ pressure of 1 atm occurs at 900 °C.

Other materials are also proposed in the literature such as lithium, sodium silicates and zirconates those did not received any special attention owing to a higher cost [9] and a lower rate of CO₂ sorption [10–13]. In what follows we consider only the carbonate cycle, where the working medium is presented by a chemisorbent based on calcium oxide.

The carbonate cycle for removing CO₂ from flue gases was first proposed in the late 1990s [14]. Its technical realization consists in moving the CaO sorbent between two fluidized bed reactors, in one of those there is CO₂ absorption occurring at a low temperature, whereas in the other there is calcium carbonate decomposition at a higher temperature. Supplying the necessary amount of heat is provided by fuel combustion in the flow of pure oxygen (Fig. 2). The use of the carbonate cycle allows reducing the amount of oxygen used in comparison with the method of IGCC (Integrated Gasification Combined Cycle), wherewith the oxidation of hydrocarbons requires for the stoichiometric amounts of pure oxygen. The authors of [15] considered the efficiency of the carbonate cycle assuming that the already existing air-based heat and electric power plants (HEPPs) would be complemented by oxygen-based HEPP. Both HEPPs, traditional HEPP and oxygen-based HEPP generate electrical energy, whereas CO₂ released by conventional (air) HEPP is captured by a chemisorbent and released in concentrated form, together with the flue gas of oxygen-based HEPP (see Fig. 2). According to the calculations by the authors of [15], the process would be economically sound in the case of approximately equal power of both plants.

The efficiency of the carbon dioxide removal process in the carbonate cycle is determined by the dynamic capacity of a chemisorbent, i.e., by the number of carbon dioxide, transferred by chemisorbent unit mass in the cycle of CO₂ absorption-regeneration. In order to determine the requirements for chemisorbent capacity we use the following assumptions:

1. The absorption of CO₂ from flue gases of an air-based HEPP is performed isothermally at 650 °C, which allows obtaining the residual CO₂ concentration of about 1 vol. % as well as isolating about 90 % of the total amount of CO₂.
2. The regeneration of the chemisorbent is performed when it is heated in an oxygen-based HEPP up to the temperature of 950 °C, which is 50 K higher than the equilibrium temperature of CaCO₃ decomposition at CO₂ pressure equal to 1 atm. Somewhat rise in temperature is necessary to increase the rate of regeneration.

3. Both stages were carried out at a pressure close to atmospheric value.

In the oxygen-based HEPP, the sorbent is heated to the temperature of its regeneration and the decomposition of calcium carbonate with the liberation of CO₂. As the first approximation we can assume that all the heat of fuel combustion is consumed for the regeneration of the chemisorbent, ignoring other sources of heat loss (e.g., heat consumption for heating fuel and oxygen up to the temperature of regeneration):

\[ Q_{\text{ox}} = Q_{\text{dec}} + Q_{\text{heat}} \quad (1) \]

Regenerated chemisorbent absorbs carbon dioxide formed in the air by burning fuel in air-based HEPP. The heat released during combustion in air-based HEPP and heat consumption for regeneration chemisorbent related by the equation

\[ \eta Q_{\text{air}} = (Q_{\text{dec}}/\Delta H_{\text{dec}}) \Delta H_{\text{comb}} \quad (2) \]

The coefficient \( \eta \approx 0.9 \) takes into account an incomplete removal of CO₂ from flue gases of air-based HEPP.

Heat balance eqs. (1), (2) are between each other by a relationship determining the efficiency of the carbonate cycle:

\[ \varepsilon = Q_{\text{air}}/(Q_{\text{air}} + Q_{\text{ox}}) \quad (3) \]

When \( \varepsilon < 1 \) only a small amount of pure oxygen is sufficient for carbon dioxide isolation from the flue gases of an air power station. For \( \varepsilon = 0 \) almost all the fuel can be burned in oxygen-based HEPP, and the carbonate cycle is inefficient. According to the calculations performed by the authors of [15], the implementation of the process is economically sound when \( \varepsilon \geq 0.5 \).

The values of sorbent regeneration heat and the heat of sorbent heating are connected with the chemisorbent dynamic capacity through the relationships

\[ Q_{\text{dec}} = \frac{A_{\text{syn}} m_{\text{th/s}}}{M_{\text{CO}_2}} \Delta H_{\text{dec}} \quad (4) \]

\[ Q_{\text{heat}} = \left[ \frac{m_{\text{th/s}}}{M_{\text{CO}_2}} C_{\text{CaO}} + \frac{A_{\text{syn}} m_{\text{th/s}}}{M_{\text{CaO}}}(C_{\text{CaCO}_3} - C_{\text{CaO}}) \right] \times (T_{\text{reg}} - T_{\text{th/s}}) \quad (5) \]

Substituting (1), (2), (4), (5) to eq. (3), we obtain the efficiency of the carbonate cycle depending on the dynamic capacity of the chemisorbent:

\[ \varepsilon = \frac{1}{1 + \eta \frac{\Delta H_{\text{dec}}}{\Delta H_{\text{comb}}}(1 + \frac{Q_{\text{heat}}}{Q_{\text{dec}}})} = \frac{1}{1 + \eta \frac{\Delta H_{\text{dec}}}{\Delta H_{\text{comb}}} + \frac{\eta(A_{\text{syn}} - 1)}{A_{\text{syn}}}(C_{\text{CaO}} + C_{\text{CaCO}_3})(T_{\text{reg}} - T_{\text{th/s}})} \quad (6) \]

As expected, the maximum efficiency of the carbonate cycle is achieved at equal values of CO₂ absorption sorbent regeneration temperature, since in this case there is no heat consumption observed in the thermal power plant for heating the oxygen chemisorbent. The efficiency of the carbonate cycle appeared higher for fuels with a higher combustion heat \( \Delta H_{\text{comb}} \).

Figure 3 demonstrates the relationships calculated for \( \varepsilon \) value inherent in carbon and methane. It is seen that in both cases, the efficiency increases with the dynamic capacity of chemisorbent and reaches a maximum value amounting to 0.79 and 0.65 for methane and carbon, respectively, with stoichiometric CaO capacity with respect to carbon dioxide in 78.5 mass %.

In the course of multicycle CaO operation, the dynamic capacity is to a considerable extent lower than the stoichiometric value. Taking into account the efficiency of modern HEPPs, the introduction of the carbonate cycle would require for consuming the chemisorbent...
amounting to several dozen thousand tons, so the source of CaO must be a cheap naturally occurring material. The authors of [16–26] studied the possibility of obtaining chemisorbents from natural minerals. It is demonstrated that calcites of different origin after a few dozen of CO₂ adsorption–regeneration cycles, the dynamic capacity tends to a limiting value equal to about 7 mass % [27]. A higher value of the stationary dynamic capacity could be obtained for synthetic CaO [28–31], but this dramatically increases the cost of the chemisorbent. A more detailed analysis of chemisorbents based on CaO and the problems of their use is presented in reviews [23–34], wherein possible ways are also indicated to increase the dynamic capacity: preliminary calcination, hydration, etc. On the other hand, the introduction of additional stages would inevitably complicate the technical implementation of the carbonate cycle and increase the cost of its use.

The efficiency of modern air-based HEPP with respect to electrical energy is about 40 %, and that for oxygen thermal power plants amounts to 28 % [35]. Additional losses inherent in oxygen-based HEPP consist of the costs of CO₂ compression (about 5 %) and that of air separation (about 7 %). Since the physical volume of the carbon dioxide under compression could not change, the use of the carbonate cycle would reduce the consumption of oxygen and, consequently, would reduce the loss of mechanical energy for air separation. Assuming that the dynamic capacity of a chemisorbent achievable under the current state of the art amounts to about 7 mass %, the efficiency of the carbonate cycle is about 0.7 for natural gas and 0.5 for coal (see Fig. 3). Therefore, the oxygen consumption can be reduced by 70 and 50 %, respectively. Thus, the use of the carbonate cycle could increase the efficiency of a gas up to 33 %, and that of a coal power plant up to 31.5 %.

Using the carbonate cycle is focused primarily on coal-fired power plants whose CO₂ emission per unit of produced energy is almost two times higher than that for a gas power station. At the same time, even with the use of carbonate cycle the efficiency of prospective coal-fired power plants with CO₂ isolation from flue gases is to a considerable extent lower compared to the existing analogs.

**FUEL COMBUSTION WITH THE USE OF OXYGEN CYCLE**

The main problem of traditional methods for CO₂ concentration from flue gases consists in the necessary of releasing CO₂ from the mixture with the other components of air. Oxygen cycle provides an initial solution, where air and fuel are not in contact with each other, except for the dilution of flue gases with nitrogen. At the first stage the atmospheric oxygen reacts with the reduced form of chemisorbent (oxidation). At the second stage the oxidized chemisorbent is reduced directly by gaseous fuels or by the gasification products condensed fuels [36, 37]. In the case of complete fuel oxidation the products of the second stage are presented by carbon dioxide and water (Fig. 4).

In fact, the oxygen cycle represents a RedOx cycle with spatially separated oxidation and reduction stages. The driving force behind these reactions is presented by the affinity between the reduced form of chemisorbent and oxygen and the affinity between the oxidized form of chemisorbent and the reducing agent. Despite a huge number of compounds capable of RedOx transformations, only some of those could be used in the oxygen cycle of fuel combustion. Here are the basic requirements for oxygen chemisorbent listed:

1. The thermodynamics of oxidation and reduction reactions should be favourable to the reactions occurring in the course of contacting
with air and fuel within the temperature range 600–1200 °C.

2. A high rate of oxygen absorption and oxidation of the fuel.

3. Easy separation of the gaseous products and reactants, i.e., the sorbent should be solid under the process conditions.

4. A number of operational properties, including resistance with respect to abrasion in the fluidized bed, the stability of the dynamic capacity, resistance to water vapour and carbon dioxide.

5. Low cost.


Among these items of crucial importance are thermodynamic requirements, since they to a considerable extent determine also the kinetic parameters of the corresponding processes. The valid range of reaction affinity values could be determined via performing a thermodynamic consideration of the oxygen cycle for the case of hydrogen or CO oxidation:

\[ \text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O} \]  \hspace{1cm} (7)

\[ \text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2 \]  \hspace{1cm} (8)

The choice of hydrogen and CO for the estimations is non-random. The direct oxidation of solid fuels by chemisorbents is impossible, therefore, the oxygen cycle requires for gasifying solid fuels. For gaseous and liquid fuels, the oxidation would also be accompanied by the reactions of steam and carbon dioxide conversion and, consequently, by the formation of hydrogen and CO as intermediate reactants.

At 1100 K and standard pressure values for the reagents, the Gibbs energy values for reactions (7) and (8) are very close to each other being equal to \( \Delta G_{\text{RedOx}}^0 = 187 \text{kJ/mol} \). In the oxygen cycle, the oxidation process is divided into two half-reactions involving chemisorbent \( \text{M}_x\text{O}_y \):

\[ \text{M}_x\text{O}_y + \text{S} \xrightarrow{K_{\text{Red}}} \text{M}_x\text{O}_y + \text{SO} \quad K_{\text{Red}} = \frac{P_{\text{SO}}}{P_S} \]

\[ \text{M}_x\text{O}_y + 0.5\text{O}_2 \xrightarrow{K_{\text{Ox}}} \text{M}_x\text{O}_{y+1} \quad K_{\text{Ox}} = \frac{1}{\sqrt{P_{\text{O}_2}}} \]

For estimation, we could assume that the values of the standard Gibbs energy of both phases for an optimal chemisorbent should be roughly equal, in order to provide a high rate of oxidation and reduction reactions:

\[ \Delta G_{\text{Ox}}^0 = \Delta G_{\text{Red}}^0 = 1/2\Delta G_{\text{RedOx}}^0 \]

Consequently, the optimal affinity between the reduced form of chemisorbent and oxygen as well as that between the oxidized form of the sorbent and hydrogen or CO must amount approximately 90–100 kJ/mol. Choosing an oxygen chemisorption agent one should note that in the course of the oxidation reaction the molar volume of the chemisorbent increases, and this can lead to the formation of a gas-tight cover consisting of an oxidized product and to blocking the complete conversion in the reaction. In the course of reducing this problem is not observed, thus preferable are materials with a somewhat higher affinity at the stage of oxidation.

The thermodynamic requirements and other requirements are satisfied by group IV \( d \)-elements (metals and oxides): Mn, Fe, Co, Ni, Cu. Below are presented the standard Gibbs energy values at 1100 K and the stoichiometric capacity level with respect to oxygen for the oxidation reactions of these elements:

\[ \text{Fe} \xrightarrow{-201 \text{kJ/mol}} \text{FeO} \xrightarrow{-169 \text{kJ/mol}} \text{Fe}_3\text{O}_4 \]

\[ \text{Co} \xrightarrow{-157 \text{kJ/mol}} \text{CoO} \xrightarrow{-18 \text{kJ/mol}} \text{Co}_3\text{O}_4 \]

\[ \text{Ni} \xrightarrow{-141 \text{kJ/mol}} \text{NiO} \]

\[ \text{Cu} \xrightarrow{-88 \text{kJ/mol}} \text{Cu}_2\text{O} \xrightarrow{-28 \text{kJ/mol}} \text{CuO} \]

\[ \text{Mn} \xrightarrow{-304 \text{kJ/mol}} \text{MnO} \xrightarrow{-54 \text{kJ/mol}} \text{Mn}_3\text{O}_4 \]

\[ \xrightarrow{-12 \text{kJ/mol}} \text{Mn}_2\text{O}_3 \]

The best thermodynamic parameters in the oxidation reaction are exhibited by Cu, Fe\(_3\)O\(_4\), and MnO. The greatest stoichiometric capacity is demonstrated by Co, Ni and Cu. The advantages of Fe\(_3\)O\(_4\) may also include its low cost in comparison with other chemisorbents.

When operating in pure form, the dynamic capacity of oxygen chemisorbents rapidly decreases due to sintering and the decreasing the reaction surface area [38]. To maintain a high reaction surface area one uses heat-resistant carriers based on \( \alpha \)-\( \text{Al}_2\text{O}_3 \), TiO\(_2\), MgO, ZrO\(_2\), calcium and magnesium aluminate [39–58]. Some of the carriers can form a mixed oxide phase with chemisorbent [36]. In the case of weak interaction between the carrier and a chemisorbent the interaction is reversible, al-
though resulting in a significant decrease in the dynamic capacity. When applied onto SiO₂ most chemisorbents form silicates stable under the conditions of oxygen cycle [56].

Currently, there are several publications about testing the oxygen cycle in a pilot plant with the thermal power of several tens of kilowatts. Several types of oxygen chemisorbents were tested, including naturally occurring material ilmenite and synthetic chemisorbent Ni/Al₂O₃ [59, 60]. The best results concerning the conversion level of fuel were achieved with the synthetic material. CO and hydrogen were oxidized completely, whereas the level of deep oxidation of methane was about 90–95 % within the temperature range of 800–950 °C. Both for the fuel reactor, and for the air reactor researchers failed to reach a complete conversion level of nickel: in the first case about 20 % of chemisorbent was in the form of NiO, whereas in the second case this value amounted to about 10 %. Thus, the dynamic capacity of the chemisorbent under operation conditions was equal to only 10 % of the stoichiometric capacity level.

With increasing the fraction of NiO in the fuel reactor we observed a decrease in the conversion level of methane. To all appearance, the rate of methane oxidation should be higher in the case that chemisorbent has the surface of metallic nickel available for the reaction wherein the decomposition of methane to form hydrogen could occur. Further, hydrogen rapidly reacts with NiO, whereas water appeared among the reaction products initiates the reaction of steam methane reforming on the surface of metallic nickel. Thus, the process is of autocatalytic nature.

Our calculations demonstrate that the use of the oxygen cycle for CO₂ isolation from flue gases can increase the fuel consumption level to a considerable extent. For a coal thermal power plant, the amount of CO₂ produced increases from 750 g/(kW·h) to 950 g/(kW·h) [61]. Thus, the fuel consumption exhibits a more than 20 % increase. There is a paradoxical situation, when all the attempts to reduce CO₂ emission result in its accelerated production. A similar situation is observed for other methods of purifying the flue gases, such as membrane purification or absorption by solutions. To all appearance, the problem of man-caused CO₂ emissions of into the atmosphere cannot be achieved via the implementation of technologies for CO₂ isolation from flue gases.

**CONCLUSION**

The advantage of chemisorption cycles consists in the possibility of isolation and concentration of CO₂ at the temperature values above 600 °C. The carbonate cycle could be used in order to extract CO₂ from the flue gases of existing thermal power plants via modifying the latter. The efficiency of the carbonate cycle is determined by the dynamic capacity of CaO based chemisorbents with respect to CO₂. To use the carbonate cycle at coal thermal power plants one need to find the ways of processing and use of chemisorbent made of natural materials with an increased capacity comparing to the current level (7 mass %).

The oxygen cycle can be realized only at newly constructed power stations. The oxygen cycle involves synthetic oxygen chemisorbents based on Ni, Cu, Mn, Co, Fe or their oxides deposited onto inert carriers. Experiments at the pilot plant have demonstrated the potentiality of using the oxygen cycle for combusting gaseous fuels and have indicated a number of problems (in particular, necessity for increasing the dynamic capacity of chemisorbents and the level of methane conversion into the products of deep oxidation).

**LIST OF SYMBOLS**

- \( A_{\text{dyn}} \) – the dynamic capacity of chemisorbent with respect to CO₂;
- \( A_{\text{max}} \) – CaO stoichiometric capacity with respect to carbon dioxide, 0.785 g CO₂/g CaO;
- \( C_{\text{CaCO}_3} \) – the heat capacity of CaCO₃, 83.47 J/(mol·K);
- \( C_{\text{CaO}} \) – the heat capacity of CaO, 42.12 J/(mol·K);
- \( \Delta G_{\text{Red}}^{\circ} \) – Gibbs energy for the reduction oxygen by chemisorbent;
- \( \Delta G_{\text{fuel}}^{\circ} \) – Gibbs energy for fuel oxidation;
- \( \Delta G_{\text{O}_2}^{\circ} \) – Gibbs energy for chemisorbent oxidation by oxygen;
\[ \Delta H_{\text{dec}} \] — molar heat of \( \text{CaCO}_3 \) decomposition, 178 kJ/mol;
\[ \Delta H_{\text{comb}} \] — molar heat of combustion (393.5 kJ/mol for C and 802.6 kJ/mol for \( \text{CH}_4 \));
\[ K_{\text{Red}} \] — the equilibrium constant for the reduction of oxygen chemisorbent;
\[ K_{\text{Ox}} \] — the equilibrium constant of the oxidation of oxygen chemisorbent;
\[ m_{\text{ch/s}} \] — the mass of \( \text{CO}_2 \) chemisorbent;
\[ M_{\text{CaO}} \] — molar mass of \( \text{CaO} \), 56.08 g/mol;
\[ M_{\text{CO}_2} \] — molar mass of \( \text{CO}_2 \), 44.01 g/mol;
\[ P_{\text{O}_2} \] — the partial pressure of oxygen;
\[ P_{\text{S}} \] — the partial pressure of the fuel;
\[ P_{\text{SO}} \] — partial pressure of the oxidized form of fuel;
\[ Q_{\text{air}} \] — heat released during the combustion of fuel in air-based HEPP;
\[ Q_{\text{dec}} \] — heat spent for the decomposition of calcium carbonate in oxygen-based HEPP;
\[ Q_{\text{ox}} \] — heat released during the combustion of fuel in oxygen-based HEPP;
\[ Q_{\text{heat}} \] — heat spent for heating of a chemisorbent in oxygen-based HEPP;
\[ T_{\text{reg}} \] — the temperature of the regeneration reactor in the carbonate cycle;
\[ T_{\text{sorb}} \] — the temperature of the \( \text{CO}_2 \) absorption reactor in the carbonate cycle;
\[ \varepsilon \] — the efficiency of carbonate cycle;
\[ \eta \] — the level of \( \text{CO}_2 \) removal from flue gases at air-based HEPP.

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