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CaO-BASED HIGH TEMPERATURE CO_2 SORBENTS – LITERATURE REVIEW

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The use of CaO-based adsorbents has a high potential to capture CO_2 from various systems due to its high reactivity with CO_2, high capacity, and low cost of naturally derived CaO. The application of CaO-based sorbents to remove carbon dioxide is based on a reversible reaction between CaO and CO_2. However, multiple carbonation/calcination cycles lead to a rapid reduction in the sorption capacity of natural CaO, and therefore efforts are made to reduce this disadvantage by doping, regenerating, or producing synthetic CaO with stable sorption properties. In this review, the synthesis methods used to obtain CaO-based sorbents were collected, and the latest research on improving their sorption properties was presented. The most commonly used models to describe the CO_2 sorption kinetics on CaO-based sorbents were also introduced. The methods of sorbent regeneration and their effectiveness were summarized. In the last part of this review, the current state of advancement of work on the larger scale, possible problems, and opportunities during scale-up of the calcium looping process were presented. Concluding (i) the presented methods of adsorbent synthesis allow for the production of doped CaO adsorbents on a laboratory scale, characterized by high CO_2 capture efficiency and good cyclic stability, (ii) the most commonly used in practice models describing CO_2 chemisorption are empirical models and the shrinking core model, (iii) the use of sorbent regeneration allows for a significant improvement in sorption capacity, (iv) the scale-up of both the production of new CaO adsorbents and the CO_2 capture technology with their use requires further development.

Keywords: carbon dioxide, Ca-based sorbents, synthesis methods, sorbent regeneration, Ca-looping

1. INTRODUCTION

Climate change has become one of the most popular topics for debate around the world due to the threat to sustainable development. The excessive emission and accumulation of greenhouse gases in the atmosphere, in particular CO_2 (Wood et al., 2014), is a recognized cause of global warming (Dong et al., 2017). Due to the rapid economic growth, the demand for energy is increasing, which is associated with the increase in the consumption of fossil fuels such as oil, coal, and natural gas (Zhang et al., 2020). Combustion of this type of fuel leads to the emission of large amounts of CO_2 to the atmosphere, which is a harmful phenomenon for the environment. Based on the average results of Earth System Models (ESMs), global warming in the 21st century is projected to be between 1.0 and 3.7 °C, depending on greenhouse gas emissions (Anderson

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et al., 2016). At the United Nations Climate Change Conference in Madrid in 2019, a plan to reduce CO_2 and other greenhouse gas emissions was agreed. It is estimated that CO_2 emissions should be reduced by at least 50% to limit the increase in global average temperature to 2 °C by 2050 (Pardakhti et al., 2019), and thus 73 countries are committed to net zero emissions by 2050. Therefore, currently the subject of many studies is the reduction of emissions, as well as the management of waste CO_2 (Wang et al., 2011).

The most popular methods to reuse waste CO_2 are Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU) technologies (Chang et al., 2017). CCS technologies include the separation of CO_2 from industrial sources, its compression, and transport to the deposition site. This solution enables safe geological or oceanic storage instead of carbon dioxide emissions to the atmosphere. Such technologies are mainly used in large point sources of CO_2 emissions such as power plants or cement plants (Leung et al., 2014). However, large-scale deployment of CCS technology is not so far widespread. This is due to both economic and technical barriers. The main obstacle is that CCS requires large financial outlays, and therefore it is unprofitable (Cuéllar-Franca and Azapagic, 2015). Moreover, in some countries, a CCS solution is an unrealistic option due to the limited geological possibilities of CO_2 storage, which significantly increases transport and injection costs (Khoo et al., 2011). CCU technologies are based on the capture of waste carbon dioxide and its further use as a substrate for the production of substances or products of economic value, such as plastics, fillers, concrete or chemical synthesis reagents (Barzagli et al., 2017; Chang et al., 2017; Zdeb et al., 2019). In this case, reuse of captured CO_2 may partially offset the overall cost of its capture (Bui et al., 2018). However, the purity and pressure requirements of the CO_2 gas stream are high in most CCU technologies. The exhaust gases emitted from industry and transportation necessitate advanced treatment and pressurization, which limits the development and reduces the applicability of CCU (Czaplicka and Konopacka-Łyskawa, 2020).

Three main CO_2 capture methods can be used in CCS and CCU technologies (Jansen et al., 2015). These are post-combustion, pre-combustion, and oxy-fuel combustion (Blomen et al., 2009). The selection of the appropriate capture technology depends on the composition of the exhaust gases produced by a given plant (Jansen et al., 2015). The post-combustion method relying on the removal of carbon dioxide from flue gases after combustion is the easiest technology to implement (Goto et al., 2013; Robles et al., 2018) and is usually used as a modification of existing installations. However, a low concentration of CO_2 negatively affects the capture efficiency (Leung et al., 2014). Thus, due to the low CO_2 content in the exhaust gas, e.g., 4% for natural gas combustion and 7–14% for coal combustion, obtaining a gas stream containing more than 95% CO_2 using this type of technology is an expensive process. Furthermore, such a solution significantly increases the cost of electricity consumption (Kanniche et al., 2010). Pre-combustion capture refers to the separation of CO_2 formed as an undesirable by-product of the indirect reaction of the conversion process. By contrast, oxy-fuel combustion consists of burning fuel with pure oxygen in order to produce exhaust gases with a high concentration of CO_2 and free of nitrogen and its compounds, such as NO and NO_2. A diagram showing the division of carbon dioxide capture technologies is presented in Figure 1.

The most popular and widely used method is CO_2 absorption using aqueous amine solutions (Pellegrini et al., 2010; Puxty et al., 2010). This technology is characterized by high efficiency (de Ávila et al., 2015), although it also has many disadvantages, such as corrosion of the equipment, inefficient regeneration of the absorbent, and significant energy losses (Blomen et al., 2009; Kuramochi et al., 2012; Luis, 2016). An alternative method is CO_2 capture by solid adsorbents, the advantages of which are high adsorption capacity, easy recovery and handling, high absorption efficiency under humid conditions, and material stability (Satyapal et al., 2001). Moreover, solid adsorbents can be used at temperatures much higher than liquid absorbents, even up to 700 °C (Wang et al., 2011). Figure 2 shows the types of CO_2 adsorbents and their adsorption capacity, depending on the adsorption temperature.

Zeolites, carbon, and MOFs, included in low-temperature adsorbents, adsorb CO_2 mainly through their physical interaction. While the adsorption with the use of alkali metal carbonates and amine-based ad-

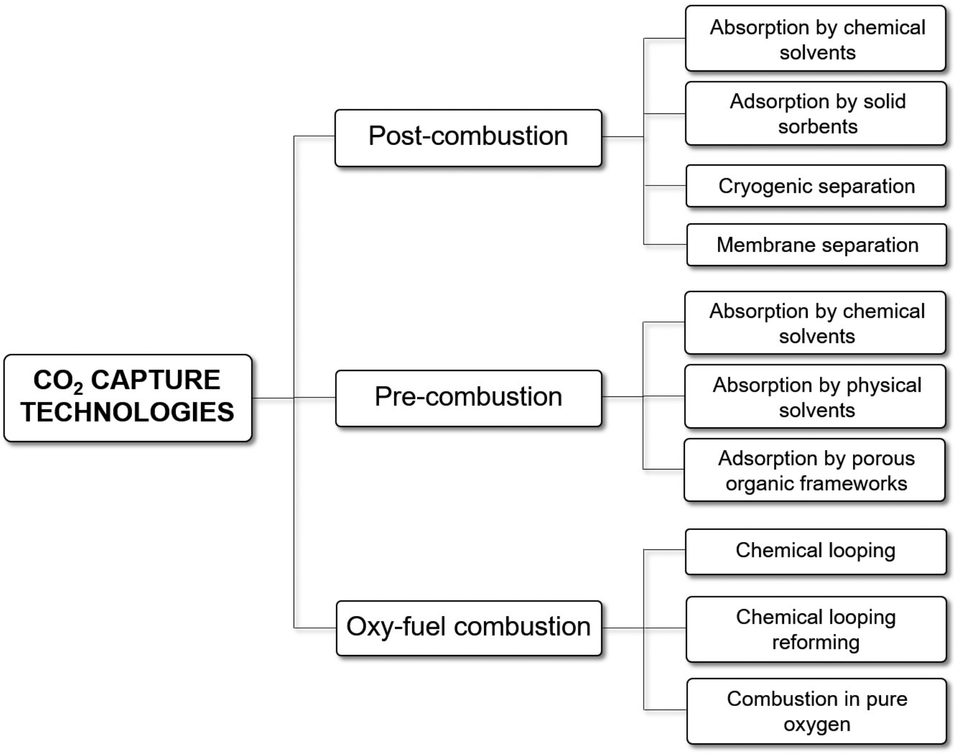

Fig. 1. CO_2 capture technologies

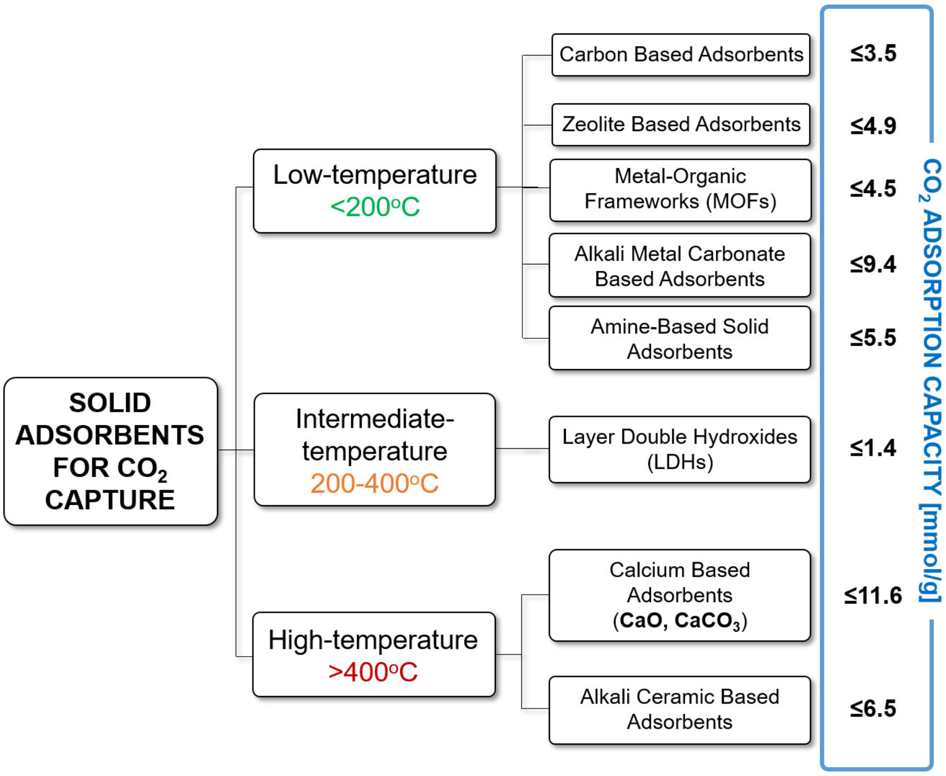

Fig. 2. Types of CO_2 adsorbents and their adsorption capacity used in low-, intermediate- and high-temperature adsorption

sorbents is based on a chemical bond with CO_2. Most of these types of adsorbents are characterized by proper CO_2 adsorption capacity. However, they have some disadvantages. Carbon-based adsorbents are cheap, readily available in large quantities, and easy to prepare, moreover, they exhibit high chemical and hydrothermal stability (Creamer and Gao, 2016; Lee and Park, 2013). However, the presence of other gases in the stream, such as hydrogen, nitrogen, or methane, reduces their selectivity for CO_2 (Wang et al., 2011). Zeolites and MOFs, despite their high adsorption capacity, relatively proper stability, and very high porosity and surface area, are characterized by high prices (Demessence et al., 2009; Harlick and Tezel, 2004; Leperi et al., 2019; Zabielska et al., 2018). In contrast, in the case of alkali metal carbonates and amine-based adsorbents, the main disadvantage is the low long-term stability (Khatri et al., 2006; Lee et al., 2006). In addition, the CO_2 adsorption temperature of amine-based materials is < 60 °C, which is lower than the actual flue gas temperature of about 90 °C. Therefore, an additional, energy-consuming exhaust gas cooling step is required. In the case of intermediate-temperature adsorbents, LDH materials have proper thermal stability, relatively fast CO_2 adsorption kinetics, and moderate regeneration temperature (Gao et al., 2013; Wang et al., 2012). However, the structure of the active sites for CO_2 adsorption and the structural evolution of such materials during CO_2 absorption and desorption are still not fully understood and require further studies (Wang et al., 2011).

The use of high-temperature adsorbents, including CaO, has a high potential to capture CO_2 from various systems (Sreenivasulu et al., 2015), both in pre-combustion and post-combustion capture (Perejón et al., 2016). Such materials are characterized by high reactivity with CO_2, high capacity, and low cost (Florin and Harris, 2009). High temperature adsorbents have a decisive advantage in removing CO_2 from shifted synthetic gas (Gao et al., 2020). Due to the high temperature of this stream, conventional adsorbents have a low CO_2 adsorption capacity in these conditions (Kanniche et al., 2010). Moreover, high-temperature adsorbents are definitely better in sorption enhanced water gas shift reactions for the production of hydrogen, because the temperature of the fuel gas stream from the sour water gas shift reaction in the pre-combustion scheme is equal to 250–500 °C, while the partial pressure of carbon dioxide is 15–30 bar (Hanif et al., 2015). In addition, high-temperature adsorbents provide higher efficiency of CO_2 capture in precombustion systems compared to low- and intermediate-temperature materials, because cooling of the gas stream before capturing CO_2 is not necessary.

The following strategies are proposed to obtain high values of the adsorbent sorption capacity and high stability allowing for effective removal of CO_2 in multiple carbonization/calcination cycles (Sun et al., 2018): (i) introduction of various CaO precursors, (ii) improvement of synthesis methods, (iii) incorporating CaO particles into inert materials characterized by high Tamman temperature, (iv) surface modification of CaO and (v) the use of special calcination conditions that allow for effective regeneration of the adsorbent.

In this review, the synthesis methods used to obtain CaO-based sorbents were collected, and the latest research on improving their sorption properties was presented. The models used to describe CO_2 sorption on CaO-based sorbents and the methods of their regeneration were also summarized. In the last part of the review, the current state of advancement of work on scale-up is presented.

2. PRINCIPLES OF CO_2 REMOVAL USING CaO-BASED ADSORBENTS

CO_2 removal with the use of CaO-containing sorbents occurs by the mechanism of chemisorption. The reversible reaction describing the adsorption/desorption of CO_2 using CaO as a sorbent is given by Eq. (1).

$$\mathrm{CaO(s)} + \mathrm{CO_2}(g) \leftrightarrow \mathrm{CaCO_3}(s), \quad \Delta H^\circ = -178\ \mathrm{kJ/mol} \tag{1}$$

The direction of the reaction depends on the temperature and partial pressure of CO_2. The Ellingham diagram is often used to predict the temperature of the conversion of $CaCO_3$ to CaO (André and Abanades, 2017; Zhang et al., 2017). On its basis, it is possible to determine whether CaO carbonation or $CaCO_3$ calcination will occur. Gibbs free energy change for the reaction (1) vs. temperature as well as the line showing the change in the Gibbs energy when the partial pressure of carbon dioxide is varied from the standard state is shown in this diagram (Fig. 3). Temperature of carbonation and calcination reaction (1) increases with the increase of the CO_2 concentration in the environment.

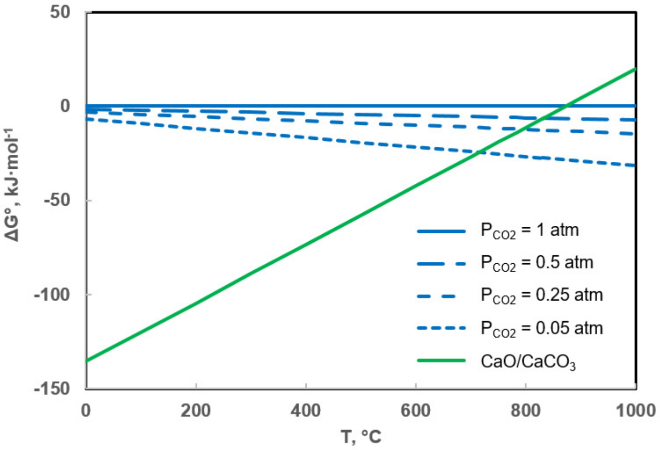

Fig. 3. The Ellingham diagram for the carbonation/calcination of $CaO/CaCO_3$

The temperature value predicted from the Ellingham diagram is usually slightly lower than that determined experimentally (André and Abanades, 2017). The experimental relationship between carbon dioxide pressure $P_{CO2(atm)}$, and temperature T, for reaction (1) was determined by Baker (1962) (Eq. (2)).

$$\log P_{\mathrm{CO2(atm)}} = 7.079 - \frac{8308}{T} \tag{2}$$

It should be emphasized that this equation was determined for pressures in the range of CO_2 pressures of 1–30 atm and for temperatures in the range 90–1200 °C, therefore it limits its applicability.

3. SYNTHESIS METHODS OF CaO-BASED SORBENTS

Synthesis of novel sorbents characterized by high carbon dioxide capture efficiencies and good cyclic stability is an approach in the development of CO_2 adsorption techniques. Classic CaO production methods are based on the calcination of natural or synthetic calcium carbonate. Currently, many recently proposed routes for the synthesis of calcium oxide make use of the thermal decomposition of calcium organic salts into calcium oxide. The methods for producing CaO-based adsorbents collected in this chapter can be applied to the synthesis of both pure and doped calcium oxide. However, it should be noted that the amounts of adsorbents produced by the presented methods were relatively small and were used to adsorb CO_2 on a laboratory scale. Therefore, future works on the development of new sorbent production technologies require an assessment of the possibility of their synthesis on a large-scale. In addition, for the proposed production methods, a techno-economic analysis should be performed, taking into account the costs of raw materials, energy, and waste management as well as the costs for the regeneration of used adsorbents. A cost analysis and a comprehensive life cycle assessment can be the basis for valuation of the competitiveness of a new adsorbent compared to natural limestone.

3.1. Dry (DM) and wet mixing (WM)

Physical dry mixing consists in grinding the CaO solids together with the additives, e.g., MgO, and then calcination of the resulting mixture to obtain the appropriate adsorbent (Li et al., 2009; Phromprasit et al., 2016).

In the wet physical mixing method, adsorbents are obtained by mixing calcium oxide with additives in the presence of water (Phromprasit et al., 2016) or an organic solvent (Li et al., 2009). The admixtures can be added in the form of metal oxides (Li et al., 2009) or as water-soluble salts (Phromprasit et al., 2016). The resulting mixture consisting of fine ground particles is then dried and calcined.

The doped calcium carbonate particles can also be obtained by the wet impregnation method (Sun et al., 2012). For this purpose, a salt solution of the additive is prepared and primary calcium carbonate particles are admixed thereto. The slurry is stirred for the specified time, then filtered, dried, and calcined. Calcium carbonate particles obtained by this method contain a relatively small amount of admixture compared to other proposed methods.

Doped CaO particles can be produced by mixing aqueous solutions containing calcium organic salt (gluconate, acetate, lactate, citrate, acetic, formic, oxalic) (Hu et al., 2016; Liu et al., 2010; Pecharaumporn et al., 2019; Radfarnia and Iliuta, 2013; Ridha et al., 2013) and salt or hydroxide or oxide of the doping component. In the variation of this method, the calcium and magnesium nitrates are dissolved in an aqueous solution of isopropanol (Park and Yi, 2012). After mixing the solutions, the solvent is evaporated from the mixture obtained and the dried residue is calcined.

The method of physical mixing combined with extrusion and spheronifization has recently been used to obtain calcium hydroxide granules containing bamboo powder (Xu et al., 2018). A paste made of powdered ingredients with the addition of water was extruded to form cylinders, which were then used to produce spherical particles using a spheronizer.

3.2. Precipitation (P) and co-precipitation (CP)

In this method, calcium carbonate is usually first precipitated, which is then decomposed into calcium oxide. Precipitation is carried out in the liquid-liquid or gas-liquid system. In the liquid-liquid method, two solutions are prepared, one containing a soluble calcium salt and the other being a carbonate solution. After these solutions are mixed, a precipitation reaction occurs and the particles obtained are separated on a filter using centrifugation. They are then dried and calcined (Chang et al., 2011; Li et al., 2009; Lu et al., 2009). If doped adsorbent particles are produced, then a soluble salt of the second component is also added to the first calcium ion-containing solution in the precipitation reaction. However, in the gas-liquid method, calcium carbonate is obtained during the carbonation of calcium hydroxide suspension with CO_2 gas (Florin et al., 2010). Then, as in the liquid-liquid method, the obtained particles are filtered, dried, and calcined. To obtain doped calcium carbonate particles, a suitable soluble salt is added to the $Ca(OH)_2$ slurry prior to carbonation.

The co-precipitation method can also be carried out under hydrothermal conditions to produce doped calcium hydroxide, which is then filtered, dried, and calcined (Wang et al., 2016).

Hollow Ca_2SiO_4-stabilized CaO nanoparticles can be synthesised by two-step precipitation in water-ethanolic solution. $Ca(OH)_2$ nanoparticles are obtained in the first step, and then they are added to the reaction mixture containing organic SiO_2 precursors and surfactant. The precipitate obtained in this reaction is calcined after washing and drying, and the product is hollow CaO/Ca_2SiO_4 particles (Huang et al., 2021).

3.3. Re-crystallization (RC)

Recrystallization is another method proposed to obtain CaO adsorbents, both pure and doped (Broda et al., 2014). To obtain pure CaO, calcium acetate powder is added to the organic solvent (methanol, ethanol, 1-pentanol, pentane, hexane, toluene) and heated to boiling. The particles are recrystallized in the boiling mixture for a specified time (e.g. 1 hour) under total reflux conditions. In the case of a doped adsorbent, a mixture of calcium acetate and magnesium acetate is subjected to recrystallization in the assumed proportions. Then, the obtained particles are washed with acetone, filtered, and calcined.

3.4. Sol-gel (SG) and sol-gel combustion (SGC) method

In this method, firstly a gel containing calcium ions is created. The gel may be based on hydroxides, e.g., magnesium, aluminium (Broda et al., 2012), chelate forming compounds, e.g., citric acid (Chen et al., 2016a, 2016b; Luo et al., 2013), surfactants, e.g., CTAB (Akgsornpeak et al., 2014), a mixture of citric acid and surfactant Pluronic P123 (Radfarnia and Sayari, 2015), a mixture of citric acid and charcoal (Gao et al., 2020). Organic substances like citric acid or urea are also added to the aqueous solution of calcium nitrate and nitrate of other ions, which are additives stabilizing the adsorbent (Nawar et al., 2020), and then they act as a substance that facilitates the combustion of nitrogen salts in sol-gel combustion synthesis (Antzara et al., 2014; Granados-Pichardo et al., 2020). The obtained gel is dried and then calcinated. To enhance CO_2 adsorption, the synthesized CaO powders can be treated by high-energy ball milling (Granados-Pichardo et al., 2020).

3.5. Flame-spray pyrolysis (FSP)

Flame-spray pyrolysis (FSP) is a method by which precursor droplets are produced, then converted into solid nanoparticles in a flame. This technique allows to obtain particles characterized by high purity and a large specific surface. The particles produced by FSP may contain new metastable phases which are not formed by wet methods. In addition, the advantage of this method is the ability to control the chemical composition of the obtained products, which is of great importance in the case of doping (Lu et al., 2009).

A solution of the calcium precursor (e.g. Ca-naphthenate) and dopants is prepared with an organic solvent (e.g., xylene) and is fed to the nozzle along with a stream of gas (O_2) to form droplets. The droplet size is controlled by the liquid flow rate. The resulting spray is mixed with methane and oxygen and burned. The synthesised particles are removed from the combustion zone, e.g., by means of a vacuum pump.

3.6. Capillary impregnation/dry impregnation (CI)

CaO on a nanosilica support is produced by the capillary impregnation method in two steps (Sanchez-Jimenez et al., 2014). The first step is to produce calcium silicate particles. For this purpose, the calcium nitrate solution is drowned into the pores of the nanosilica powder and the soaked silica obtained is first heated to a temperature of 650 °C, then the calcium nitrate decomposes, and then the powder is calcined at a temperature higher than 900 °C. In the second step, the impregnation of calcium silicate with calcium nitrate is repeated several times to obtain an active CaO layer.

3.7. Template-assisted synthesis (TAS)

Hard-templating synthesis uses a solid organic support to create the desired form of adsorbent particles. The template can be, e.g., absorbent cotton (Chi et al., 2019), a carbonaceous crosslinked nanosphere obtained by hydrothermal carbonization of glucose (Bian et al., 2021) which is added to a pre-prepared aqueous solution of calcium precursor and additives, if used for synthesis. Then, after drying, the obtained precipitate is subjected to successive pyrolysis and combustion combined with calcination, where the template is removed.

An oil-in-water emulsion can also be used as a sacrificial template for the production of hierarchical, porous adsorbent particles. In the method proposed by Kurlov et al. (2020a), the emulsion was produced via a microfluidic technique in a microcapillary reactor. The obtained emulsion with the required concentration of the oil phase was then mixed with a freshly prepared suspension of calcium carbonate nanoparticles in an aqueous solution with the composition of the aqueous phase of the emulsion. Then, after removing the excess water phase by settling, the preparation was dried and calcined. The last step was to cover the obtained CaO particles with monomolecular Al_2O_3 using the atomic layer deposition technique.

Another approach is to generate an in-situ template. The carbon gel template can be prepared by mixing a solution of resorcinol and formaldehyde and the aqueous solution of calcium and aluminium precursors (Broda et al., 2012). The formed gel contains carbonaceous spheres covered by an amorphous Ca-Al-based film. Next step is a pyrolysis of the gel in N_2 and formation of a crystalline film of calcium carbonate polymorphs. The last step is the calcination in air to remove the carbon gel template via calcination in air and hollow Al_2O_3/CaO micro-spheres with a nano-structured shell are obtained. Another way to create an in-situ template is the hydrothermal synthesis of particles composed of calcium carbonate and magnesium carbonate combined with the preparation of a matrix from xylose proposed by Naeem et al. (Naeem et al., 2018). This method uses urea as a precursor to carbonate ions and glycine, which causes calcium and magnesium ions to be homogeneously distributed in the produced particles. Xylose under hydrothermal conditions produces highly dispersed carbonaceous spheres which are used as template for calcium and magnesium carbonate particles. After the particles obtained are separated and washed, they are calcined.

3.8. Mechanochemical reduction (MR)

In this method, the adsorbent is produced by the reaction of CO_2 reduction from methane with CaH_2 and MgH_2. The reaction occurs when solid calcium and magnesium hydrides are mixed in the presence of CO_2 gas. Apart from methane, CaO and MgO are the main reaction products. In addition, the samples also contain small amounts of amorphous carbon and carbonates (Ping et al., 2020).

3.9. Decomposition of Ca-organic precursors (DCP)

Decomposition of Ca-organic precursor (DCP) is a method that requires the production of calcium and magnesium salts of adamantanecarboxylic acid (a polycyclic organic compound). Synthesis takes place under hydrothermal conditions in a mixture containing water, $Ca(OH)_2$, $Mg(OH)_2$ and adamantecarboxylic acid. Then the precursor obtained is decomposed at 700 °C under nitrogen atmosphere. The resulting adsorbent contains CaO and MgO, and disordered graphitic carbon supports generated *in situ* in the product.

4. CO_2 ADSORPTION PROPERTIES OF CaO-BASED ADSORBENTS

Effectiveness of adsorbents of sorbents is most often characterized by the following parameters:

- CO_2 adsorption capacity in the n-th cycle ($C_{\text{cap},n}$):

$$C_{\text{cap},n} = \frac{m_{\text{CO2},n}}{m_{ad}} \tag{3}$$

where $m_{\text{CO2},n}$ is the CO_2 taken up mass by the adsorbent in the n-th cycle, m_{ad} is the mass of calcined adsorbent,

- carbonation conversion in the n-th cycle (X_n):

$$X_n = \frac{n_{\mathrm{CO2},n}}{n_{\mathrm{CaO}}} \tag{4}$$

where $n_{\mathrm{CO2},n}$ is the moles of CO_2 adsorbed in the n-th cycle, and n_{CaO} is the number of moles of CaO in the adsorbent.

The sorption properties of CaO-based adsorbents are influenced by the following factors: the preparation method, the type and amount of the additional component, the type of precursor used in the production, carbonation and calcination conditions (i.e. temperature, CO_2 concentration, pressure), number of carbonation/calcination cycles.

Many studies have shown that the method of preparation significantly affects the characteristics of the adsorbent obtained, including particle size, specific surface area, pore volume, and size of nanocrystallites from which the sorbent particles are made. Recently, Pecharaumporn et al. (2019) investigated the effect of the type of Ca precursor and the surfactant additive (CTAB) on the sorption properties of $Ca_{12}Al_{14}O_{33}$/CaO. In these tests, the adsorbent obtained from calcium citrate showed a greater ability to adsorb CO_2 than calcium nitrate, and the presence of CTAB resulted in an increase in the surface and porosity of the adsorbent. Gao et al. (2020) has obtained an adsorbent using the sol-gel combustion method with the addition of charcoal and citric acid. Comparison of the properties of adsorbents with the same components, but synthesised by physical dry mixing and wet impregnation method, showed that the SGC adsorbent was characterized by higher sorption capacity and better stability than with DM and WM methods. The authors explain the observed differences are the results of the prevention of the growth and agglomeration of CaO particles and the porous structure of parent charcoal, which has been significantly smaller in the case of the product obtained by the SGC method.

Many studies on the preparation of CaO sorbents indicate that the addition of an inert carrier, which is characterized by a high Tamman temperature, improves the stability of the sorbent, allowing to maintain a relatively high sorption capacity even after a large number of adsorption/desorption cycles. Hu et al. (2016) tested 12 different additives and found that Y- and Al – based supports exhibited much superior cyclic performance that the other tested additives. CaO-based sorbents doped with Mn, Mg, La, Yb, and Nb also had good effectiveness in cyclic adsorption capacity. The worst results were obtained for sorbets containing Ti, Ce, Zr, Si and Pr. According to these studies, the melting point of the inert support and the surface area of the prepared sorbents were the key parameters influencing the sorption properties.

In the study described by Hu et al. (2015), it was shown that the presence of neodymium oxide supported in the CaO:Nd_2O_3 ratio equal to 30:70 caused significant enhances in the conversion of the sorbent and cyclic durability. Moreover, the influence of the CaO precursor type was demonstrated, and the sorbent produced using calcium DL-lactate pentahydrate precursor exhibited the best performance.

It has also been shown that the addition of alkali metal carbonates (Li, K) to CaO-based sorbent also reduced the aging of the sorbent during carbonation/calcination cycles (Huang et al., 2017). It was presumed that the effect of $(Li\text{–}K)_2CO_3$ was to prevent the formation of a rigid $CaCO_3$ layer on the surface of the CaO particles and to facilitate the access of CO_2 to unreacted CaO (Huang et al., 2017). On the other hand, the presence of Na_2CO_3 in the CaO-based sorbent particles had an unfavourable effect, as the addition of this compound decreased the effectiveness of CO_2 removal (Kurlov et al., 2020b).

Another strategy aimed at improving the sorption properties of CaO-based sorbents was devised by Kurylov et al. (2020a). They synthesised calcium carbonate particles coated with Al_2O_3, and as a result of calcination, $Ca_3Al_2O_6$ layer was formed. The results of CO_2 adsorption on the prepared adsorbent particles depended on the thickness of the produced $Ca_3Al_2O_6$ layer. After ten carbonation/calcination cycles, the highest sorption capacity was obtained for particles in which the Ca:Al ratio was 5:3, which corresponded to the Al_2O_3 film thickness of 2.7 nm.

To improve the adsorption characteristics, it is also proposed to use several admixtures that have a synergistic effect on the properties of the CaO-based adsorbent. For example, a sorbent containing an admixture of cerium and manganese in the form of CeO_2 and $CaMnO_4$ in the proportion of Ca:Ce:Mn = 15:0.5:0.5 had a higher sorption capacity than the adsorbents obtained with the addition of only one of these components (Guo et al., 2018). (Zr–Ce) – additive CaO sorbents were also found to be promising candidates for practical applications (Guo et al., 2017). The adsorbent containing components in proportion Ca:Zr:Ce = 30:0.5:0.5 was characterized by the highest sorption capacity and the best stability up to 35 carbonation/calcination cycles. However, the use of C-supported mixed oxide MgO/CaO also resulted in significantly better sorption capacity compared to the adsorbent containing only CaO (Nityashree et al., 2020). Moreover, these adsorbents were characterized by a smaller decrease in sorption capacity during their repeated use. Additionally, the adsorbent with a relatively small addition of Mg and Al, when the Ca:Mg:Al ratio in the adsorbent was 97: 2.5: 0.5, showed high sorption capacity and high relative sorption stability after 30 carbonation/calcination cycles (Wu et al., 2020).

Pellet adsorbent particles are proposed for the larger scale adsorption process using CaO-based adsorbent. More recently, Zhang et al. (2018) presented research on the adsorption properties of pellets containing CaO and metal oxides as inert support and additionally cellulose modifying the pore structure of sorbent pellets. Adding cellulose was found to be effective for promoting the CO_2 sorption capacity of sorbents, which was mainly ascribed to the enlarged specific surface area and pore volume during cellulose burning.

Table 1 presents the selected adsorbents characterized by high values of CO_2 adsorption capacity and/or carbonation conversion after n-th carbonation/calcination cycles.

Table 1. Summary of selected CaO-based adsorbent properties

Adsorbent	Synthesis method	Carbonation	Calcination	n	$C_{\text{cap},n}$	X_n	Ref.
CaO/C	TAS	$T = 650$ °C $x_{CO2} = 0.15$	$T = 920$ °C $x_{CO2} = 0.7$	20	0.45	0.54	(Bian et al., 2021)
CaO/C	SGC	$T = 600$ °C $x_{CO2} = 0.5$	$T = 650$ °C $x_{CO2} = 0.5$	15	0.66	0.84	(Gao et al., 2020)
$(Li–K)_2CO_3/CaO$	WM	$T = 600$ °C $x_{CO2} = 1$	$T = 700$ °C $x_{CO2} = 0$	23	0.28	0.35	(Huang et al., 2017)
$CeO_2/CaMnO_4/CaO$	SGC	$T = 600$ °C $x_{CO2} = 0.5$	$T = 700$ °C $x_{CO2} = 0$	40	0.61	0.90	(Guo et al., 2018)
$Ce_2Zr_2O_7/CaO$	SGC	$T = 600$ °C $x_{CO2} = 0.5$	$T = 700$ °C $x_{CO2} = 0$	35	0.65	0.90	(Guo et al., 2017)
La_2O_3/CaO	SGM	$T = 650$ °C $x_{CO2} = 0.5$	$T = 850$ °C $x_{CO2} = 0$	20	0.50	0.94	(Nawar et al., 2020)
Nd_2O_3/CaO	WM	$T = 650$ °C $x_{CO2} = 0.15$	$T = 800$ °C $x_{CO2} = 0$	100	0.23	0.92	(Hu et al., 2015)
$Ca_3Al_2O_6/CaO$	TAS	$T = 650$ °C $x_{CO2} = 0.2$	$T = 900$ °C $x_{CO2} = 0.54$	10	0.41	0.81	(Kurlov et al., 2020a)
MgO/CaO/C (1:4)	MR	$T = 650$ °C $x_{CO2} = 1$	$T = 800$ °C $x_{CO2} = 0$	30	0.31	0.37	(Ping et al., 2020)
MgO/CaO/C	DCP	$T = 650$ °C $x_{CO2} = 0.14$	$T = 800$ °C $x_{CO2} = 0$	100	0.34	0.63	(Nityashree et al., 2020)
Ca_2SiO_4/CaO	CP	$T = 850$ °C $x_{CO2} = 0.15$	$T = 850$ °C $x_{CO2} = 0.5$	20	0.57	0.82	(Huang et al., 2021)

5. KINETICS OF CaO CARBONATION

The course of the gas-solid reaction (Eq. (1) can be divided into two stages (Di Giuliano et al., 2020). The first of them, kinetically controlled, is a fast step, the course of which depends on the heterogeneous surface chemical reaction between CaO and CO_2 (García-Labiano et al., 2002). Nucleation sites for calcium carbonate are then present on the surface of CaO exposed to carbon dioxide gas. The second stage occurs as the CaO conversion increases and is slower due to the $CaCO_3$ layer formed on the surface completely covering the calcium oxide. Thus, in order for CO_2 to contact CaO directly, it must exceed a certain diffusion resistance. Accordingly, this step is diffusion-controlled (Abanades and Alvarez, 2003; Dou et al., 2016; Li et al., 2014; Shokrollahi Yancheshmeh et al., 2016). Due to limitations, the reaction does not result in complete CaO conversion, and there are works in the literature that achieved a final conversion of up to 70–90% (Bhatja and Perlmutter, 1983; Gupta and Fan, 2002). There are several methods of modeling the course of the CO_2 chemisorption on CaO in the literature. These are empirical apparent models (Lee, 2004), random pore models (Grasa et al., 2009), shrinking core (unreacted core) models (Johnsen et al., 2006), ion reaction mechanism model (Wu and Lan, 2012), grain models (Liu et al., 2012; Yu et al., 2012), or the model of the theory of reaction rate equations (Li et al., 2012), also taking into account periodic external perturbations (Bizon and Tabiś, 2016).

5.1. Apparent kinetic model

The simplest model for noncatalytic gas-solid reactions is the apparent kinetic model. Lee (2004) proposed a model equation for CaO carbonation based on literature-reported data, which is presented by Eq. (5).

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k\left(1 - \frac{X}{X_u}\right)^2 \tag{5}$$

where $(\mathrm{d}X/\mathrm{d}t)$ is the rate of CaO carbonation, t is the time, k is a kinetic constant, X_u is a maximum (ultimate) CaO conversion, and X is the actual CaO conversion, which is described by Eq. (6).

$$X = \frac{kbt}{(b+t)} \tag{6}$$

where b is the constant equivalent to the time taken to reach half the ultimate CaO conversion. Both constants, k and b, were determined as a function of temperature for the two stages, under the control of a chemical reaction and under the control of diffusion. The main advantage of the proposed model, from the practical point of view, is the simplicity of the equation, and its application enables accurate prediction of the course of CaO carbonation at process temperatures higher than 700 °C (Lee, 2004). On the other hand, Li and Cai (2007) indicate that the rate of carbonation is influenced by the CO_2 concentration and the total pressure. The greater the proportion of CO_2, the higher the rate of carbonation reaction. As the total pressure increases, the CO_2 concentration increases proportionally, and the diffusion coefficient changes inversely. Therefore, a semi-empirical equation describing the rate of CaO carbonation is proposed as shown in Eq. (7).

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k\left(1 - \frac{X}{X_u}\right)^{2/3}\left(C_{\mathrm{CO2}} - C_{\mathrm{CO2},e}\right)^{(P/P_o)^{0.083}} \tag{7}$$

where $(C_{\mathrm{CO2}} - C_{\mathrm{CO2},e})$ is the average difference in the CO_2 concentration, P is a total pressure, and P_o is an atmospheric pressure.

5.2. Shrinking core model

The most classical and most frequently used model is the shrinking (unreacted) core model (SCM), the principle of which is shown schematically in Figure 4 (Ishida and Wen, 1968). According to this model, after the reaction, the solid phase consists of an unreacted core covered by a reacted layer. A chemical reaction occurs at the zone boundary, and as a result the outer reacted layer becomes wider as the reaction progresses (Di Giuliano et al., 2020). The rate-limiting factor for the reaction is the diffusion of the reactants and products through the reacted area (Szekely and Evans, 1971b).

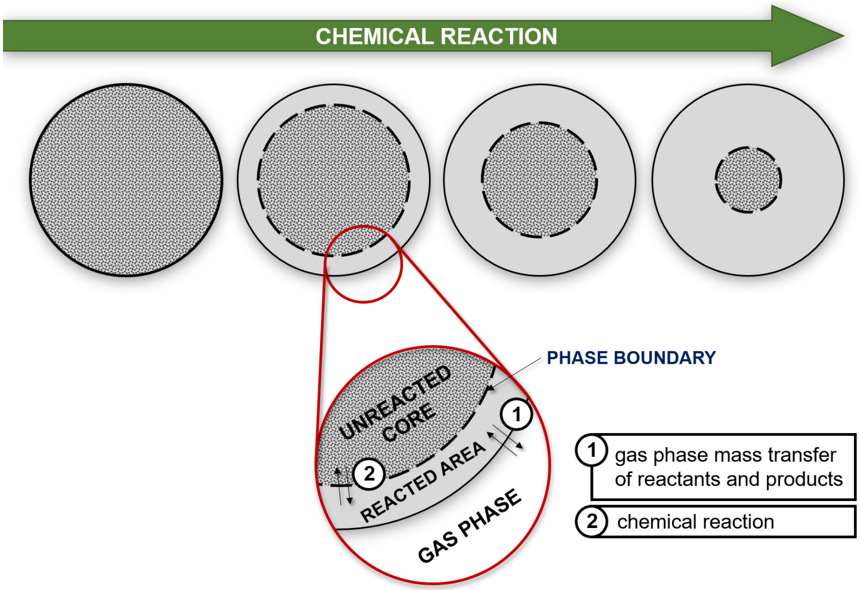

Fig. 4. Scheme of shrinking core model

SCM model is very convenient for the interpretation of experimental results. It describes the overall rate of the reaction taking into account its driving force and the three main limiting steps, namely, mass transfer in the gas phase, diffusion of compounds through the reacted region, and a chemical reaction at the phase boundary. Using this model, it is therefore possible to predict or estimate the gas phase mass transfer coefficient and the pore diffusion rate (Szekely and Evans, 1971b). However, this approach has two major drawbacks. First, the existence of a sharp interface between the reacted region and the unreacted core has not been substantiated by experimental evidence. There are many studies in which the authors argue that the two regions are separated by the so-called transition zone in which there are both completely and only partially reacted grains (Weisz and Goodwin, 1963). Moreover, in the unreacted core model, structural properties such as grain size and porosity are implicitly included in the reaction rate constant. Consequently, each reaction kinetic measurement is material specific. Therefore, it is not possible to determine the unique parameters of the reaction taking place, as well as to determine the influence of structural properties on the overall reaction rate. The shrink core model can be described by Equation (8 for the chemical reaction controlled stage and Equation (9 for diffusion controlled stage (Lee, 2004). These equations apply to spherical particles.

$$\frac{t}{\tau} = 1 - (1 - X)^{1/3} \tag{8}$$

$$\frac{t}{\tau} = 1 - 3(1 - X)^{2/3} + 2(1 - X) \tag{9}$$

where τ is the time required to completely convert an unreacted CaO particle into a product, t is the time, and X is the conversion of CaO.

5.3. Random pore models

The random pore model (RPM) is based on the relationship between the actual volume of the porous material and the ideal volume in the absence of intersection of the pores. In addition, it also takes into account additional factors such as diffusion and mass transport effects, including product layer build-up (Bhatja and Perlmutter, 1983; Nouri and Ale Ebrahim, 2016). The RPM model includes the structural parameters of the particle based on its geometry and the pore structure (Grasa et al., 2009). It is indicated that the CaO carbonation reaction in the kinetic region proceeds by filling small pores. While in the case of the diffusion regime, the reaction occurs in larger pores which have a much smaller specific surface (Fedunik-Hofman et al., 2019). The equations describing the rate of CaO carbonation reaction based on this model are shown in Equation (10 for the chemical reaction controlled stage, and in Eq. (11) in the case of diffusion controlled regime.

$$k't = \frac{1}{\Psi}\left[\sqrt{1-\Psi(1-X)}-1\right] \tag{10}$$

$$k''\sqrt{t} = \frac{1}{\Psi}\left[\sqrt{1-\Psi(1-X)}-1\right] \tag{11}$$

where k' and k'' are rate constants, X is the actual CaO conversion, and Ψ is the structural parameter depending on the porosity (ε_o) and initial specific surface area of the adsorbent (S_o), and the initial total length of the pore system per unit volume (L_o) (Eq. (12)).

$$\Psi = \frac{4\pi L_o\left(1-\varepsilon_o\right)}{S_o^2} \tag{12}$$

The RPM model is effective in predicting the course of CaO carbonation. However, its main drawback and limitation is its complexity and the need to know the structural parameters of the adsorbent. Furthermore, there are many modifications to this model in the literature, which consist both in the expansion by including parameters such as the size of the adsorbent particles, the process temperature, or the partial pressure of CO_2, and in the simplification of the model equations (Salaudeen et al., 2018).

5.4. Grain models

The grain model (GM) is based on the assumption that the material is in the form of non-porous solid spherical CaO grains that are randomly located in the particle and in the gas phase (Szekely and Evans, 1971a). During carbonation, a calcium carbonate (product) layer is formed on the outer surface of each CaO grain. Consequently, along with the course of the reaction, there is a gradual increase in the initial radius of the grains (changing grain model, CGM). In this model, the convective heat transfer at the particle surface as a function of heat conduction in the particles, the grain size distribution, and the effect of grain overlap are taken into account (Fedunik-Hofman et al., 2019; Zhou et al., 2013). The reaction rate according to GM model can be described by Eq. (13).

$$kt = \left[1-(1-X)^{1/3}\right] \tag{13}$$

The microstructure of the adsorbent plays a key role in the reaction of CaO with CO_2, as well as influencing the diffusion of CO_2 over the adsorbent (Ping et al., 2020).

5.5. Summary

The models proposed for the description of CaO carbonation are derived from the kinetics of the gas-liquid reaction. The most commonly used approaches to describing experimental results are empirical models and the shrinking core model. However, they do not take into account the characteristics of the solid particles, i.e. porosity and pore size distribution, which have a large influence on the rate of the CaO carbonation process. On the other hand, the random pore model and the grain models include the characteristics of the particles, but ignore the change in the shape and structure of the pores during the process. Thus, previously known and used models describing the kinetics of CaO carbonation are still being developed and improved. One of the proposed modifications is considering the evolution of the pore size during the reaction of CaO and CO_2 in RPM (Sun et al., 2008). On the other hand, Jiang et al. (2016) have taken into account the transition regime in the description of the kinetics. The additional step describes the course of the reaction between the chemical reaction-controlled regime and the diffusion-controlled regime.

6. REGENERATION OF SPENT CaO-BASED SORBENTS

During the carbonation/calcination cycle, the structure of the adsorbent changes, reducing the sorption capacity of CaO. Particle sintering during calcination and the consequent reduction in the porosity associated with the pore fraction below 200 nm are the main reasons for the decrease in the effectiveness of CaO-based sorbents (Blamey et al., 2010). Therefore, methods of sorbent regeneration are being developed, which allow the restoration of sorption properties and thus the extension of sorbent use, which is of great practical importance. Currently, the following solutions are proposed to improve the structure of spent adsorbent particles: hydration with water or steam, repelletization of used adsorbent particles, recarbonization and ball milling.

Hydration with water or steam is a useful method for reactivation of spent CaO-based sorbents based on the chemical reaction described by Eq. (14).

$$\mathrm{CaO} + \mathrm{H_2O} \leftrightarrow \mathrm{Ca(OH)_2}, \quad \Delta H^\circ = -109\ \mathrm{kJ/mol} \tag{14}$$

The molar volumes of CaO and $Ca(OH)_2$ are 16.9 and 33.1 cm^3/mol (Blamey et al., 2010), respectively, therefore the volume of the regenerated CaO particles increases, which results in their cracking. Consequently, the porous structure of the adsorbent is renewed both by creating larger pores, which are more difficult to block during calcination, and by providing access to deeper layers of sorbent particles.

In repelletization, water or steam is also used for the spent sorbent and granules are formed at the same time. This procedure allows the porosity to be improved, and the mechanical action makes some unreacted CaO available to adsorbed CO_2 (Manovic et al., 2012; Sun et al., 2018). The effectiveness of CaO reactivation with this method is additionally improved by doping the cement with the sorbent.

Recarbonization is an additional post-carbonation step in which unconverted CaO is exposed to a highly concentrated CO_2 stream at higher temperature (Grasa et al., 2014; Valverde et al., 2014). The conditions used in the recarbonator are conducive to increasing the degree of CaO conversion. The subsequent calcination step causes the decomposition of $CaCO_3$, and the release of CO_2 from the deeper layers of the sorbent particles changes its structure as a result of the formation of cracks increasing the porosity. The increased efficiency of recarbonization can be obtained by adding a small amount of water vapor (Grasa et al., 2014). Additionally, a model of the evolution of CaO-based sorbent properties in carbonation/recarbonization/calcination cycles was proposed (Bazaikin et al., 2016). The developed model predicting the changing of sorbent specific surface area and pore size was based on sintering physics, CO_2 capture kinetics, and CaO morphology.

Another approach, based on the mechanical grinding of the spent sorbent particles, has recently been proposed (Su et al., 2019; Yoon et al., 2021). Particles with reduced CO_2 removal efficiency were ground using a ball mill, and reducing size of the aggregated or sintered particles affected the increase in sorption capacity. Additionally, significant recovery of sorbent activity was achieved by milling of spent sorbent with ice and dry ice (Su et al., 2019).

Selected research examples on the reactivation of CaO-based sorbents are presented in Table 2.

Table 2. Effectiveness of selected methods used for the regeneration of spent CaO-based adsorbent

Adsorbent	Regeneration method	Regeneration conditions	Effect	Ref.
MgO/CaO (1:3)	Hydration	Water, 25 °C + drying and calcination	Stable capabilities for CO_2 capture up to 40 cycles, final capacity: 0.390 g CO_2/g CaO (*140%)	(Sun et al., 2020)
MgO/CaO (1:3)	Simultaneous hydration /impregnation	NaCl solution, 25 °C + drying and calcination	Stable capabilities for CO_2 capture up to 40 cycles, final capacity: 0.414 g CO_2/g CaO (*149%)	(Sun et al., 2020)
CaO	Hydration	Superheated steam added: a) during calcination; b) during carbonation; c) in both stages	After 4 cycles CO_2 capacity higher than for spent sorbents; final capacity a) 0.066 g CO_2/g CaO (*122%); b) 0.094 g CO_2/g CaO (*174%); c) 0.078 g CO_2/g CaO (*144%)	(Coppola et al., 2017)
CaO+10% cement	Repelletization	Addition of water spray; 20–30 min in a batch mechanical pelletizer	After 30 cycles CO_2 capacity higher than for spent sorbents; final capacity: 0.015 g CO_2/g sorbent (*136%)	(Manovic et al., 2012)
MgO/CaO (dolomite)	Ball milling	Addition of ice and dry ice	After 10 cycles CO_2 capacity higher than for spent sorbents; final capacity: 0.718 CO_2/g sorbent (*250%)	(Su et al., 2019)

*Percent of CO_2 capacity compared to non-regenerated sorbent

In addition to the previously mentioned methods of sorbent regeneration, acidification is also used. In this process, the spent calcium carbonate particles are dissolved in organic acids (e.g., acetic, lactic, propionic, malic, citric), then dried and calcined (Wang et al., 2019). This approach is thus a de facto re-production of CaO particles by wet mixing. The limitation of this method is the possibility of using the sorbent originally produced by this method and it is impossible to recreate the adsorbent particles with a complex structure obtained by other synthetic methods.

7. SCALE-UP OF CO_2 ADSORPTION PROCESS USING CaO-BASED SORBENT

New industrial processes are of serious interest for both scientific researchers and industry representatives, especially in regard to the reduction of carbon dioxide emissions. Currently, significant progress has been made in the field of obtaining new adsorbents with good sorption properties. However, most of the CO_2 removal research is done on a laboratory scale. Most often, these studies are carried out using thermogravimetric analysis (TGA) where typically samples of less than 1 gram are used. On the other hand, relatively few studies are conducted on a larger scale.

To obtain a high target capacity of the final full-scale installation, characterised by reliability, pilot-scale experiments are necessary. At pilot plant scales, it is also more convenient for engineers to obtain proper process conditions such as temperature, pressure, and required flowrate of substrates, or products (Kremer et al., 2013).

Carbon capture technologies using CaO-based sorbents in which a reversible chemical reaction occurs according to Eq. (1 are called calcium looping (CaL) processes. CaL is being conducted in two main process devices: a carbonator and a calciner. A carbonator is the device in which CO_2-contaminated flue gas enters and undergoes carbonation reaction with a sorbent at high temperature, usually in the range of 630–800 °C (Chang et al., 2013). As a result, calcium carbonate is formed and purified gas outlets a device. However, in the calciner, carbon dioxide retained in $CaCO_3$ is released and a sorbent from fresh limestone can be prepared. The calciner operating temperature is higher and most often in the range of 850–950 °C.

In Figure 5, an exemplary scheme of CaL installation is presented. The above-mentioned carbonator and calciner devices are supplied with a number of other process devices such as: blowing fans, heat exchangers (for preheating synthetic CO_2 as well as cooling down of gases), pollution control devices (cyclones, bag house), burner etc. Each pilot plant is also equipped with the necessary valves and control system devices (flowmeters, manometers, and gas analyzers). Storage tanks are necessary in the system for storing both fresh limestone and waste or ash.

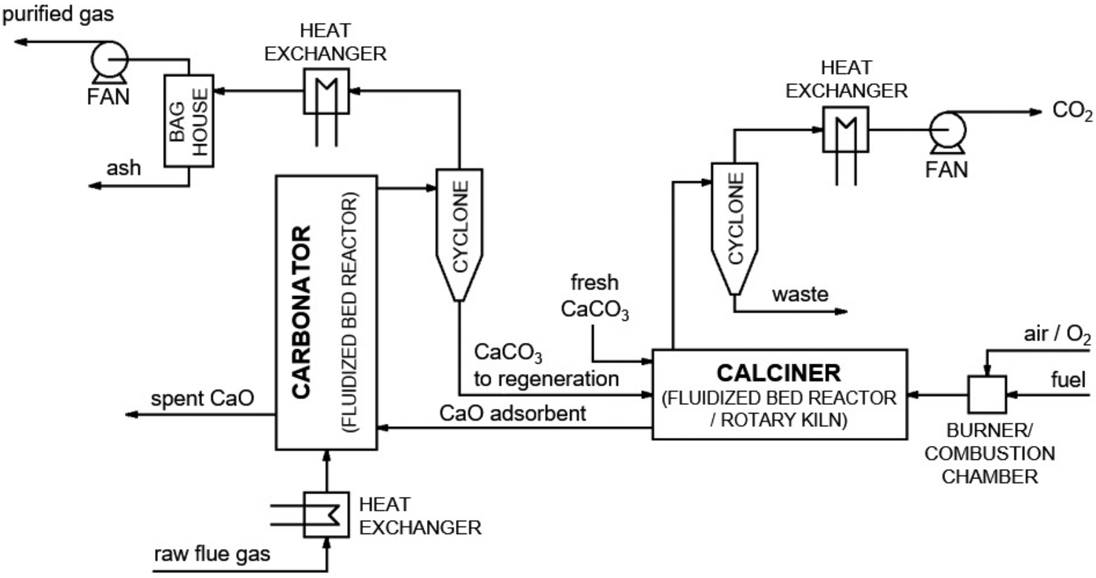

Fig. 5. Example of CaL process in a pilot-scale plant

Fluidized bed reactor as a carbonator was investigated in a number of large-scale experimental trials. However, the calciner can be either a fluidized bed reactor or a rotary kiln. The selected large-scale experiments are presented in Table 3.

8. POSSIBLE PROBLEMS AND OPPORTUNITIES DURING SCALE-UP OF CaL PROCESS

Laboratory scale experiments, providing the very first knowledge about the investigated process, do not always show full scale problems. This is mostly due the fact of the small amount of reagents used in the analyzed reactions and conducting them in laboratory glass. On the other hand, larger scale processes involving real process devices and equipment exhibit problems that may occur in the final scale installation.

One of the more serious problems in conducting fluidized bed adsorption is the attrition of the adsorbent particles and the management of produced fine particles (Asiedu-Boateng et al., 2016). One way to reduce the attrition is to reduce the flow velocity, but this may result in non-uniformity gas flow through the fluidized bed. It was found that the attrition rate increased with the square of the orifice diameter, the cube of the gas velocity, and with the power of 0.4 with gas molecular weight (Asiedu-Boateng et al., 2016).

Table 3. Large scale experiments

Carbonator – regenerator system	Power	Adsorbent	Carbonator	Calciner	CO_2 capture efficiency	Description	Problems occurred	Ref.
Carbonator: a bubbling bed; calciner: a circulating fluidized bed	100 kW_{th}	Natural limestone	ID = 0.1 m H = 3.0 m Gas velocity = 0.1–1.0 $m \cdot s^{-1}$ T = 750 °C p = atmospheric	ID = 0.1 m H = 5.0 m Gas velocity = 2.0–4.0 $m \cdot s^{-1}$ T = 1050 °C p = atmospheric	80%	Steam addition to the calciner decreased the carrying capacity decay and improved the pore structure of sorbent		(Champagne et al., 2016)
Carbonator: a circulating fluidized bed; calciner: a bubbling bed	10 kW_{th}	Natural limestone	ID = 0.07 m H = 12.4 m Gas velocity = 4.5–5.5 $m \cdot s^{-1}$ T = 630 °C	Regenerator: ID = 0.15 m H = 3.0 m Gas velocity = 0.3–0.5 $m \cdot s^{-1}$ T = 905 °C	> 90%	The efficiency of the carbonator and the calciner in terms of CO_2 capture and sorbent calcination conversion, respectively, was related to the parameter of active space time.	The attrition of particles was monitored.	(Duelli et al., 2016)
Carbonator: bubbling fluidized bed; calciner: rotary kiln	3 kW_{th}	$CaCO_3$	ID = 0.1 m H = 2.5 m Gas velocity = 0.25–0.35 $m \cdot s^{-1}$	ID = 0.27 m L = 5 m Solid residence time = 10–15 min Rotation speed = 1–3 RPM	80–95%	Very high CO_2 capture efficiency (exceeding the established efficiency by 85%) for most of the time of the test run. Attrition phenomenon was close to 20%.	Attrition of sorbent	(Chang et al., 2013)

Table 3 [cont.]

Carbonator – regenerator system	Power	Adsorbent	Carbonator	Calciner	CO_2 capture efficiency	Description	Problems occurred	Ref.
Carbonator: bubbling fluidized bed; calciner: rotary kiln	1.9 MW_{th}	$CaCO_3$	ID = 3.3 m H = 4.2 m Gas velocity = 0.25–0.35 $m \cdot s^{-1}$ T = 650 °C	ID = 0.9 m L = 5 m Solid residence time = 10–15 min Rotation speed = 3–5 RPM Flue gas recirculation	80–95%	1.9 MW_{th} pilot plant allowed to obtain 1 t/h CO_2 capture; possible future scale-up of the process without significant difficulties. CO_2 is to be liquefied.		(Chang et al., 2014)
Carbonator: fluidized bed reactor; calciner: fluidized bed reactor	1 MW_{th}		ID = 0.59 m H = 8.66 m Gas velocity = 2.2–3.3 $m \cdot s^{-1}$ T = 620–660 °C p = 40–80 mbar	ID = 0.4 m H = 11.35 m Gas velocity = 3.0–4.1 $m \cdot s^{-1}$ T = 800–900 °C p = 15–40 mbar	> 80% (for oxy-fuel calciner > 90%)	1-MW_{th} continuous CO_2 capture pilot plant; two research sets: coal-fired calciner and propane-fired calciner		(Kremer et al., 2013)
Carbonator: circulating fluidized bed reactor; calciner: circulating fluidized bed reactor	1.7 MW_{th}	Natural limestone	T = 650 °C	T =870-910 °C			Rapid deactivation of lime particles after series of carbonation and calcination cycles	(Grasa et al., 2014)

The solution to improve the adsorption process carried out in the fluidized bed is the regeneration of the adsorbent before or during calcination regeneration is most often carried out with the use of steam, which was discussed in detail in the chapter "Regeneration of spent CaO-based sorbents".

Another challenge is the process temperature, which for oxy-fuel combustion processes with diesel may be more than 1800 °C. It is then necessary to use flue gas recirculation to prevent thermal destruction of construction materials. Therefore, the thermal insulation of the final apparatus needs further study and development to assure long-time operation of the installation (Chang et al., 2014). A further aspect of carrying out carbonation and calcination at high temperature is the development of a heat recovery system. Two approaches are proposed, either a system integrated with CaL process or external devices like the production of electricity (Chang et al., 2013).

In addition, large-scale experiments can also be provided along with computational simulations to get fully comprehensive information about process behaviour for future design. Therefore, useful approaches based on CFD simulations for CO_2 adsorption in a fluidized bed are being intensively developed (Ayobi et al., 2014; Esmaeili Rad et al., 2021; Sornvichai et al., 2020).

9. SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

Recently, an intensive development of CO_2 capture technologies has been observed. Among the many proposed solutions, the use of CaO-based sorbents appears to have great potential, especially for the removal of carbon dioxide from high temperature gas streams. In this process, the gas to be purified is directly contacted with CaO particles, and $CaCO_3$ is formed as a result of the chemical reaction between CO_2 and the sorbent. Theoretically, one mole of CaO absorbs one mole of CO_2. This reaction is reversible, and increasing the temperature produces a pure and concentrated stream of CO_2 and CaO. Unfortunately, the high temperature of calcination causes a change in the structure of the sorbent particles, and as a result of their sintering, the porosity and specific surface decrease, which results in a lower sorption capacity of the adsorbent.

In this review, the methods used to synthesize the CaO-based adsorbents were collected and the latest strategies for improving their sorption properties were presented.

Summarizing these efforts, it can be concluded that, based on the developed synthesis methods and laboratory scale experiments, CaO particles doped with metal oxides characterized by high Tamman temperature have better sorption properties compared to pure CaO adsorbent. The presence of additives such as MgO, TiO_2, MnO_2, Al_2O_3, Ce_2O_3 improves the sorption capacity, conversion rate, and stability of the adsorbent particles in many carbonation/calcination cycles. Moreover, recent studies have shown that the addition of a mixture of two metal oxides to calcium oxide allows for a high adsorption efficiency with a much lower concentration of dopants in the adsorbent. The presence of expensive additives and the complexity of the operation during the production of the adsorbent have a significant impact on the cost of its production on a large-scale. Of the methods discussed, a relatively inexpensive and uncomplicated synthesis is wet mixing, and the particles obtained this way show good sorption properties and high cyclic stability. Moreover, the use of calcium-containing waste, such as coal fly ash or egg shells, as a raw material for the production of sorbent has also been proposed to reduce the production costs. Nevertheless, it should be noted that the new adsorbents are synthesized on a laboratory scale, and no techno-economic analysis has been performed for the developed production methods.

In addition, an important problem that requires further research is the scale-up of the CO_2 capture process using CaO-based sorbents. There is relatively little published research done on a larger scale. The main issues to be solved are the attrition of adsorbent particles and the selection of conditions for adsorbent regeneration. The first area requires the development of a method to produce mechanically resistant adsorbent particles. The second one needs to adapt the developed adsorbent regeneration to a larger scale. Furthermore, since carbonation and calcination take place at high temperatures, an important element of optimizing energy demand will be the analysis of heat losses and the development of heat recovery systems in the designed installation.

SYMBOLS

C	concentration, mol/m^3
$C_{\text{cap},n}$	CO_2 adsorption capacity in the n-th cycle, kg CO_2/kg CaO
k	rate constant, 1/s
k'	rate constant in the random pore model, 1/s
k''	rate constant in the random pore model, 1/s$^{0.5}$
m	mass, kg
n	number of moles, mol
P	pressure, Pa
$P_{\text{CO2(atm)}}$	CO_2 pressure, atm
t	time, s
T	temperature, K
X	carbonation conversion, mol CO_2/mol CaO

Greek symbols

Ψ	the structural parameter, –
τ	the time required to completely convert an unreacted CaO particle into product, s

Subscripts

ad	adsorbent
CaO	calcium oxide
CO2	carbon dioxide
e	equilibrium conditions

Acronyms

CaL	calcium looping
CCS	carbon capture and storage
CCU	carbon capture and utilization
CFD	computational fluid dynamics
CI	capillary impregnation
CP	co-precipitation
CTAB	cetyltrimethylammonium bromide
DCP	decomposition of Ca-organic precursors
DM	dry mixing
ESMs	Earth System Models
FSP	flame-spray pyrolysis
GM	grain model
LDHs	layer double hydroxides
MOFs	metal-organic frameworks
MR	mechanochemical reduction
P	precipitation

RC	re-crystallization
RPM	random pore model
SCM	shrinking core model
SG	sol-gel method
SGC	sol-gel combustion method
TAS	template-assisted synthesis
TGA	thermogravimetric analysis
WM	wet mixing

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