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Process simulation of Ca-looping processes: review and guidelines

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Abstract

Ca-looping is one of the most promising processes for CO_2 capture in short to medium term plants, which can be applied for both post-combustion and pre-combustion layouts. The recent successful operations of MW-scale pilot plants are leading to an increased interest in this technology. In addition, the particularly advantageous applicability in cement plants, the main industrial contributors to CO_2 emissions worldwide, can further lead to a forthcoming development of the technology.

Quite a large amount of scientific papers on reactors and process modeling has been published in the recent years and more studies are expected to be published in the future. According to the experience of the authors in this field and on the basis of a literature review, suggestions and modeling needs for next works are provided in this paper.

Keywords: CCS, Calcium looping, sorption enhanced reforming, cement.

1. Introduction

Calcium (Ca)-looping is one of the most promising processes for CO_2 capture in future short to medium term plants. Such regenerative processes are based on the capacity of calcium oxide (CaO)-based sorbents in the reaction with gaseous CO_2 at high temperatures (600-750°C) by forming solid calcium carbonate ($CaCO_3$). Since this carbonation reaction is highly exothermic, heat must be provided to decompose $CaCO_3$ back into the CaO sorbent and a concentrated CO_2 stream ready for sequestration. The Ca-looping concept can be integrated in a variety of plants, the most promising being: (i) coal fired PC or

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CFB power plants with post-combustion capture, (ii) natural gas-fed plants for power and hydrogen production with pre-combustion capture and (iii) cement production plants.

Being Ca-looping an emerging technology, process modeling and simulation and economic evaluation are particularly important to understand its potential and to optimize operating parameters in the different possible applications. In such activity, in order to avoid misleading results, it is of primary importance to make correct calculation assumptions, taking into account the findings from the increasing modeling and experimental activity in this field.

This paper results from an activity carried out within the Joint Programme on Carbon Capture and Storage of the European Energy Research Alliance (EERA CCS-JP). The objective of this study is to make a brief review of the main process simulation studies available today on Ca-looping processes and propose some guidelines for future works on this subject. Further details on the analysis carried out and an extensive review of the literature can be accessed on the EERA CCS-JP web site [1].

2. Ca-looping for post-combustion capture applications

Coal-fired power plants including a post-combustion CO_2 capture system using a Ca-based sorbent is the plant category most widely assessed, which is at the most advanced stage of development with the first MW-scale pilot installations [2,3]. As shown in Fig. 1, Ca-looping consist in removing CO_2 from a flue gas of an air-blown boiler that is fed in a fluidized bed carbonator operating at 650-700°C at atmospheric pressure. $CaCO_3$ formed in this reactor is then regenerated into CaO by oxy-fuel combustion in a calciner, which operates at high CO_2 partial pressures to facilitate its later purification, compression and storage. The main thermodynamic advantage of the process is that a great amount of the energy introduced in the system can be recovered as not only carbonation reaction heat but also as gas and solid streams at high temperature. Therefore, it can be used to produce high pressure superheated steam instead of being released to the environment at low temperature like in solvent-based post-combustion capture

plants. From another point of view, in these plants only the fraction of the input coal introduced in the calciner is burned with pure O_2, with lower auxiliary power and investment costs for O_2 production than in full oxy-fuel combustion power plants.

2.1. Reactor modeling

The great majority of the research on Ca-looping reactor modeling has focused on the most innovative component, i.e. the carbonator. Different carbonator models with different level of detail and complexity have been proposed in the literature during years either to explain the experimental results obtained from experimental rigs, or to design higher scale plants and carry out predictions about their performance.
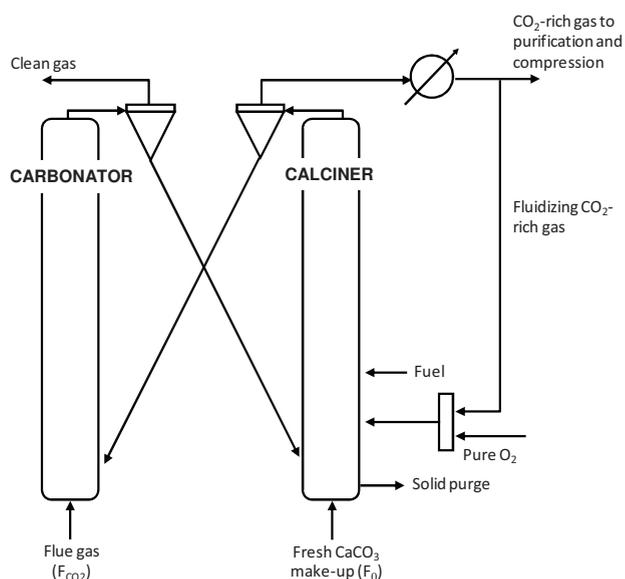
After the first models considering

Fig. 1 - Scheme of the Ca-looping process focused on removing CO_2 from the flue gas of an existing power plant

bubbling fluidized bed reactors [4-6], carbonator models proposed in the literature considered the reactor as a circulating fluidised bed where two zones were distinguished: a bottom dense zone and a lean one located above [7-10]. Almost every of these models concluded that the most influencing parameter on the carbonator efficiency is the fraction of particles reacting in the fast regime, determined mainly by the fresh sorbent make-up flow introduced in the system and the solid circulation between reactors.

2.2. Complete power plant simulation

Most of the works reviewed consider the integration of the Ca-looping system into a coal-fired power plant coupled with a high-efficiency supercritical steam cycle [4,6,8,11-14]. Conventionally, the capture system has been assumed to be working under fixed and reasonable operating conditions in both reactors: carbonator at 600-650ºC with CO_2 capture efficiency of 90%, and calciner at 900-950ºC considering full calcination of the $CaCO_3$ entering into the reactor, usually without CO_2 recycle in the calciner. Romeo et al. and Martinez et al. carried out a sensitivity analysis to assess system performance under different operating conditions of the Ca-looping system, and determine the optimum fresh sorbent make-up flow and solid circulation for the Ca-looping from an economical [13] or an efficiency point of view [14]. Both works conclude that working with low purge percentages and high solid circulation between reactors lead to the highest electric efficiencies and the lowest costs per t_{CO2} captured.

Quantitatively, when comparing with a reference plant without capture, a broad range of electric efficiencies has been reported. Lower efficiency penalties of the order of 3 percentage points have been assessed in [12] that do not include CO_2 compression or fan consumption in the calciner. Abanades et al. analysed the efficiency obtained for different configuration schemes of the Ca-looping system, and assessed a penalty of 5.75 percentage points with respect to a reference plant of 46% of electric generation efficiency, being 2.85 and 3.17 percentage points attributed to the CO_2 compressor and the ASU, respectively [11]. In the rest of the reviewed works, efficiency penalties are typically between 6.5 and 8.5 percentage points with respect to the reference plant. Reasons for these differences are the electric efficiency for the reference plant assumed, the different qualities of the thermal integration proposed, the fact that in some cases no thermal integration has been carried out and a reasonable electric efficiency has been applied to the total heat recovered from the Ca-looping system, or the different power consumptions assumed for the auxiliaries, compressors and fans with respect to other works.

2.3. Guidelines for future works

On the basis of the different works reviewed of carbonator and process modeling in the Ca-looping system, the following needs of research and consideration are highlighted in this field:

- Accurate models on the CO_2 carrying capacity of the sorbent should be taken into account to improve the reliability of the carbonator models proposed and, therefore, contribute to a better assessment of the whole performance of the plant. Moreover, this accuracy on sorbent reactivity would also contribute to a better understanding of experimental results from pilot scale plants.

  CO_2 carrying capacity of the Ca-sorbent entering the carbonator will be different from that predicted because it depends on carbonation conditions [15-17], on the partial conversion achieved in the carbonator and calciner [18] and on the possible reactivation mechanism carried out in the process [19,20]. It is necessary to include an accurate model that considers the real "age" of the Ca particles in the system according to their carrying capacity, irrespective of their previous history of partial or complete cycles experimented in the Ca-looping system. Accurate results would be obtained in this way about the carbonator and plant performance.

- $CaSO_4$ formation should be included in the models proposed. Sulphur reacts not only with the

CaO active for the carbonation reaction, but also can form $CaSO_4$ with the non-active CaO [21]. It is important to quantify this effect and determine the fraction of non-active CaO that reacts with sulphur to form $CaSO_4$ for not being excessively conservative when considering sulphur.

- Ashes from coal burnt in the calciner should be included in the process modeling of Ca-looping systems as thermal balances and operational issues are going to be affected.
  Coal ashes act as inerts in the Ca-looping system and influence the heat required in the calciner to heat up solids up to calcination temperature.

- Auxiliaries power consumption should be properly taken into account in the efficiency assessment. In particular, the consumption of the fan needed to offset the flue gas pressure losses in the carbonator should be included, since it may provide a relevant contribution to the auxiliary electric consumption. For a reliable estimation of this consumption, it is important to consider the presence of inactive solids (inactive sorbent, ash from coal and $CaSO_4$) as part of the carbonator inventory and to use a carbonator model to estimate the link between the fundamental Ca-looping process parameters (carbonator inventory, sorbent make-up and sorbent recycle rate) and CO_2 capture efficiency.

- Improvements on the calculation methodology of the oxy-fuel combustion side should be made with respect to the existing literature, where it is often treated in a simplified way. For example, flue gas recycle and CO_2 compression and purification unit should be considered in future works.

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3. Ca-looping for pre-combustion capture applications

Although several applications on coal fed plants have been considered [22-25], the process most widely assessed for pre-combustion CO_2 capture by CaO sorption is sorption-enhanced steam methane reforming (SE-SMR). According to this concept, methane is converted in a single reactor where CO_2 is adsorbed over a solid sorbent while steam methane reforming (SMR) and water gas shift (WGS) reactions occur (1). Therefore, progression of the SMR and WGS gaseous phase reactions is not limited to equilibrium set by CO_2 formation and can proceed almost to a complete depletion of reactants.

$$CH_4 + 2H_2O + CaO \leftrightarrow 4H_2 + CaCO_3 \qquad \Delta H°_r = \text{-14.5 kJ/mol} \qquad (1)$$
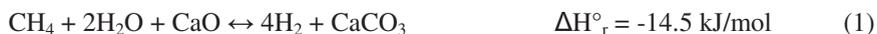
The enthalpy balance of the overall reaction is only 14.5 kJ/mol, meaning that it is thermally balanced, and therefore not only the carbonation reaction facilitates H_2 production by removing CO_2 from the gaseous phase, but also provides the heat required for the SMR reaction, allowing for the use of adiabatic reformers.

3.1. Reactor modeling

Different reactor concepts (packed bed [26-29] and fluid bed [30-35]) have been studied. Fixed bed SE-SMR is typically modeled for temperatures from 500 to 650ºC, pressures from 1 to 15 atm and for steam-to-methane ratios (S/M) from 2.0 to 5.5. In [26,28], simple modeling of breakthrough curves have been carried out where the parameters needed for the particle conversion expressions have been derived from their own or literature thermo gravimetric measurements or isotherm data of the various sorbents. The temperature and pressure dependencies on the enhancement in H_2 production are analyzed and H_2 and CO_2 concentrations in the reactor effluent with time are modeled showing different behavior of the various sorbents. Li et al. also considered sorbent capacity decay with cycle number and compared different CaO sorbents such as limestone, dolomite and impregnated CaO systems [27]. Zagoruiko et al. focused on modeling the thermal effects by using a "moving heat wave" generated by in situ catalytic

combustion of methane for regeneration of the sorbent [29].

Fluid bed SE-SMR reactor modeling has been developed through a series of papers from Wang et al. using a 3D two fluid Eulerian hydrodynamic model together with kinetic parameters of the reactions taking place [30-32]. Neither details on catalyst nor sorbent particle structure were included assuming only that reactions take place on the particle surface without diffusion limitations. CO_2 sorption is fast compared with the rate of the reforming reactions while the CO_2 desorption rate is slow due to the increased CO_2 concentration in the gas phase making higher temperature needed to achieve the necessary kinetics of sorbents regeneration. Di Carlo et al. include both intra- and extra-particle mass transfer effects in their study of SE-SMR using a similar two fluid Eulerian model as Wang et al. [30,33]. A Ni-catalyst/dolomite powder mixture was used. At sorbent-to-catalyst mass ratios larger than 2, autothermal conditions in the reactor were simulated where the heat produced upon sorption compensated the endothermicity of the reforming reaction.

Jakobsen et al. studied the SE-SMR process by using a linear plug flow model for fluid bed reactor using different flow regimes and sorbents [35]. Their results indicate that the contact time in a riser is too short to reach high methane conversion and CO_2 capture rates, while high H_2 yield and capture rates can be obtained in a bubbling bed.

3.2. Complete power plant simulation

The main issue related to the integration of a SE-SMR reactor in a complete plant depends on how the regeneration process is carried out. The most feasible option is to consider low pressure interconnected fluidized bed reactors. The limit of this layout is related to the low pressure of the H_2 delivered, which would require relevant energy penalty associated to cooling and compression in case of a high pressure final utilization (e.g. combustion in a gas turbine, utilization in high pressure refinery processes).

The use of pressurized interconnected fluidized bed is an alternative investigated in some works. However, two kind of problems arise with such a configuration: (i) stable operation of interconnected pressurized fluidized beds has not been demonstrated yet and requires technology breakthrough and (ii) regeneration temperatures rise with pressure up to values at which the activity of the catalyst and the capacity of the sorbent are compromised (roughly 1100-1200°C, at 20-30 bar).

A further alternative are packed beds, which allow operating reforming and calcination at different pressures by keeping the solid material always in the same reactor, periodically exposed to atmospheres favorable to carbonation and to calcination. The intrinsic dynamic behavior of the system, the difficult control of peak temperatures and the complexity and cost of high temperature valve system represent the limits of the packed bed-based process.

Two studies assessed only the SE-SMR reactors system [28,36]. Chen et al. focused on interconnected fluidized beds [28]. Fernandez et al. considered the innovative Ca-Cu looping process based on fixed beds, where calcination is sustained by oxidation of fuel by means of a CLC loop using Cu/CuO as oxygen carrier [36]. Ochoa-Fernández et al. assessed a complete plant for H_2 production based on high pressure (10 bar) reforming and low pressure (1 bar) regeneration [37]. Solieman et al. and Romano et al. considered the integration of SE-SMR process into a combined cycle based power plant [38,39]. In the first case [38], a packed bed system was considered, while pressurized interconnected fluidized beds were adopted in the second case [39]. Finally, Meyer et al. assessed the process based on the ZEG concept, where the H_2-rich gas is converted in a high temperature SOFC and the waste heat from the fuel cell is used to regenerate the Ca-based sorbent [40].

In all the cases, reactors have been calculated at equilibrium, which is a reasonable assumption according to experimental data and outputs from reactor modeling studies. Reforming was assumed to be carried out at 550-600°C and S/C=2.5-3.5 for low pressure (1-2 bar) reformers cases and at 600-700°C

and S/C=4.2-4.8 for high pressure (17-35 bar) cases. In none of these plants sorbent purging and makeup have been considered. This appears to be a reasonable assumption when feeding a clean gaseous fuel as natural gas, with no ash and negligible sulfur, considering that no impurity is expected to accumulate in the Ca-looping system or to affect the capacity and the activity of the Ca-sorbent (in case of CaO, sorbent capacity loss is a consequence of calcination conditions, there is no need of using a fuel with sulfur or ashes). Conversion between 10 and 53% has been adopted in these studies, significantly higher than the residual capacity of natural sorbents, but acceptable considering the possible advancements in the development of synthetic sorbents and reactivation techniques.

Overall H_2 yields of 2.4-2.7 $molH_2/molCH_{4-eq}$ (or 0.60-0.68 $molH_2/molH_{2-eq}$) and cold gas efficiencies of 81-83% have been obtained in all the cases. In cases for power production, net efficiencies of 50-51% have been obtained when using state of the art combined cycles, while and efficiency of 76.9% is claimed for the SOFC-based ZEG concept.

3.3. Guidelines for future works

On the basis of the modeling and experimental findings, the following modeling guidelines and needs of experimental investigation can be highlighted:

- In plants for H_2 production, it is important to include the PSA process for H_2 purification within the process model as done in [37]. As a matter of facts, PSA process can have a relevant effect on the mass and energy balance since PSA off-gas, rich of CO, CO_2, CH_4 and a part of the H_2 (10-20% of the total, according to the hydrogen recovery factors of commercial PSA) can be recycled to the calciner. These gases provide part of the heat for regeneration in case of oxycombustion-based regeneration, reducing the required primary fuel input.
- When comparing SE-SMR with conventional processes for H_2 production, it is important to consider the pressure at which H_2 is needed by the final user. As a matter of facts, homogeneous H_2 delivery pressures should be assumed when comparing different technologies. Penalties for SE-SMR-based layouts using low pressure reactors will arise when high pressure H_2 is needed.
- Ca/catalyst ratio can be important for the mass and energy balance. Ni-based catalysts are thermal ballast and can behave as oxygen carriers between calciner and reformer. This phenomenon should be minimized since O_2 produced at high cost with ASU may react with Ni in the calciner to form NiO and eventually oxidize part H_2-rich syngas in the reformer. Therefore, low catalyst/Ca ratios are desirable. A lack of modeling and experimental activity to find the minimum catalyst/sorbent ratio can be highlighted.
- In case of regeneration by heat exchange, it is important to provide sufficient details on the heat and mass balances. As a matter of facts, heat transfer of high thermal power at high temperature under relatively low ΔTs is a critical process which can lead to large heat transfer surface operating at high temperature and relatively low fuel utilizations, voltages and efficiency of the fuel cell of the ZEC/ZECA concepts.
- When calculating power plants based on gas turbines, it is important to use a reliable model for the gas turbine. As reported in [25], considering blades cooling flows can have a really important effect on the estimated overall plant efficiency when adopting advanced high TIT gas turbines (of the order of 4-5% points).

4. Ca-looping applications on cement production plants

Cement is a key construction material, and global demand is expected to grow at around six percent in 2012, amounting to 3.8 billion tons [41]. The cement industry, which is one of major industrial sources of

CO_2 emissions, accounts for 8% out of global CO_2 emission in 2011 [42]. Reduction in it carbon emissions can be achieved only in part by more efficient use of fuels but over half of its CO_2 is generated by calcination reaction. Therefore, it is essential to retrofit a carbon capture process into a cement plant if more than 90% reduction of carbon emission is to be achieved.

It has been argued that Ca-looping processes would have lower net energy consumption than amine processes since they can be better integrated with cement plants. Since ECRA [43] listed Ca-looping technologies as one of the promising capture technologies for cement plants, there have been conceptual studies which proposed various integration models, such as utilization of purge flow for the cement clinker and synergy between cement and power plants [44,45].

Given that the calciner purge can be used as kiln feed, a symbiosis model of a power plant, a Ca-looping process and a cement plant has been proposed with its mass and energy balances [10]. The flue gases from both plants are sent to the Ca-looping process, and the CaO purge of this capture unit is returned to cement plant, mixed with CaO from fresh raw material, and used as kiln feed. In this way, the CO_2 emission and energy consumption of the cement plant can be drastically reduced due to reduced calcination loads. The surplus energy from the capture unit can be utilized to generate electricity by running a separate steam cycle. The total thermal energy consumption increases by about 6.7% for the integrated system due to addition of capture unit. CO_2 emission avoided was estimated to be 94% on a basis of total CO_2 emission at both industries by this integration system, which would add about 12.4 €/ton of avoided CO_2.

A similar assessment has been performed in [46], where the effect of the actual composition of the purge on the maximum "substitution rate" of the cement plant raw meal has been considered. As a matter of fact, large amount of $CaSO_4$ and ashes from coal combustion in the calciner can limit the maximum amount of Ca-looping purge that can be used in the cement plant. Such a maximum "substitution rate" strongly depends on the fuel used in the calciner and on the parameters of the Ca-looping process.

As a direct integration of Ca-looping with a cement plant, Rodriguez et al. [47] investigated two alternative processes, including an economic study. One is a retrofit replacing the existing pre-calciner with an oxy-calciner which can achieve 89% CO_2 capture and the other is capturing CO_2 from the kiln gas using a carbonator in addition to capturing CO_2 by oxy-calciner to improve capture rate up to 99%. Similarly with other Ca-looping processes, the surplus energy from high temperature streams is recovered by an integrated steam cycle. It is reported that the total energy consumption of the cement plant increases from 2.93 GJ/ton of cement covering the electricity demand to 5.45 GJ/ton of cement by retrofit for carbon capture.

Ca-looping process can also be applied to a gas stream downstream of the pre-calciner to achieve over 90% capture. The flue gas stream leaving the 3rd preheater stage has been identified to be an optimum feed for a carbonator rather than the end-of-pipe flue gas since it does not require preheating, has higher CO_2 partial pressure and lower volumetric flow rate [48]. The CO_2-depleted gas is routed back to 2nd preheater for raw material heating. The effects of sulfidation and ash have been taken into account in the carbonator model. It has been represented that this process is capable of achieving more than 90% CO_2 capture with additional energy consumption of 2.3 to 3.0 GJ/ton CO_2 avoided by considering heat recovery.

4.1. Guidelines for future works

Modeling of Ca-looping process for CO_2 capture in cement plants has many similarities with the post-combustion capture from power plant flue gases case. Therefore, the suggestions described in section 2.3 can be extended to this case for both Ca-looping reactors modeling and process simulation. An additional issue should however be considered for cement plants, related to the limited variability of the composition

of the final clinker, which may limit the maximum amount of Ca-looping purge to be used in the plant if too rich of $CaSO_4$ and ash.

5. Conclusions

This paper originates from an activity carried out within the Joint Programme on Carbon Capture and Storage of the European Energy Research Alliance (EERA CCS-JP). The main works in the open literature dealing with modeling and simulation of Ca-looping processes have been reviewed. On the basis of this review and the recent experimental findings on this technology, guidelines and suggestions for future modeling studies have been provided.

References

[1] European Energy Research Alliance (EERA). Joint Program on CCS. www.eera-ccs.eu. ;September 2012.
[2] Sánchez-Biezma A, Ballesteros JC, Diaz L, De Zárraga E, Álvarez FJ, López J et al. Postcombustion CO_2 capture with CaO. Status of the technology and next steps towards large scale demonstration. Energy Procedia 2011;4:852-9.
[3] Galloy A, Ströhle J, Epple B. Design and operation of a 1 mwth carbonate and chemical looping CCS test rig. VGB PowerTech 2011;91:64-8.
[4] Shimizu T, Hirama T, Hosoda H, Kitano K, Inagaki M, Tejima K. A twin fluid-bed reactor for removal of CO_2 from combustion processes. Chem Eng Res Design 1999;77:62-8.
[5] Abanades JC, Anthony EJ, Lu DY, Salvador C, Alvarez D. Capture of CO_2 from combustion gases in a fluidized bed of CaO. AIChE J 2004;50:1614-22.
[6] Romano M. Coal-fired power plant with calcium oxide carbonation for postcombustion CO_2 capture. Energy Procedia 2009;1:1099-106.
[7] Alonso M, Rodríguez N, González B, Grasa G, Murillo R, Abanades JC. Carbon dioxide capture from combustion flue gases with a calcium oxide chemical loop. Experimental results and process development. International Journal of Greenhouse Gas Control 2010;4:167-73.
[8] Hawthorne C, Dieter H, Bidwe A, Schuster A, Scheffknechta G, Unterberger S et al. CO_2 capture with CaO in a 200 kW th dual fluidized bed pilot plant. Energy Procedia 2011;4:441-8.
[9] Lasheras A, Ströhle J, Galloy A, Epple B. Carbonate looping process simulation using a 1D fluidized bed model for the carbonator. International Journal of Greenhouse Gas Control 2011;5:686-93.
[10] Romano MC. Modeling the carbonator of a Ca-looping process for CO_2 capture from power plant flue gas. Chemical Engineering Science 2012;69:257-69.
[11] Abanades JC, Anthony EJ, Wang J, Oakey JE. Fluidized bed combustion systems integrating CO_2 capture with CaO. Environmental Science and Technology 2005;39:2861-6.
[12] Ströhle J, Lasheras A, Galloy A, Epple B. Simulation of the carbonate looping process for post-combustion CO_2 capture from a coal-fired power plant. Chemical Engineering and Technology 2009;32:435-42.
[13] Romeo LM, Lara Y, Lisbona P, Escosa JM. Optimizing make-up flow in a CO_2 capture system using CaO. Chem Eng J 2009;147:252-8.
[14] Martínez I, Murillo R, Grasa G, Carlos Abanades J. Integration of a Ca looping system for CO 2 capture in existing power plants. AIChE J 2011;57:2599-607.
[15] Arias B, Abanades JC, Grasa GS. An analysis of the effect of carbonation conditions on CaO deactivation curves. Chem Eng J 2011;167:255-61.
[16] Lysikov AI, Salanov AN, Okunev AG. Change of CO_2 carrying capacity of CaO in isothermal recarbonation-decomposition cycles. Industrial and Engineering Chemistry Research 2007;46:4633-8.
[17] Sun P, Lim CJ, Grace JR. Cyclic CO_2 capture by limestone-derived sorbent during prolonged calcination/carbonation cycling. AIChE J 2008;54:1668-77.
[18] Rodríguez N, Alonso M, Abanades JC. Average activity of CaO particles in a calcium looping system. Chem Eng J 2010;156:388-94.
[19] Arias B, Grasa GS, Alonso M, Abanades JC. Post-combustion calcium looping process with a highly stable sorbent activity by recarbonation. Energy and Environmental Science 2012;5:7353-9.
[20] Martínez I, Grasa G, Murillo R, Arias B, Abanades JC. Evaluation of CO_2 carrying cof reactivated CaO by hydration. Energy Fuels 2011;25:1294-301.

[21] Sun P, Grace JR, Lim CJ, Anthony EJ. Removal of CO_2 by calcium-based sorbents in the presence of SO_2. Energy and Fuels 2007;21:163-70.

[22] Lin S, Harada M, Suzuki Y, Hatano H. Process analysis for hydrogen production by reaction integrated novel gasification (HyPr-RING). Energy Conversion and Management 2005;46:869-80.

[23] Weimer T, Berger R, Hawthorne C, Abanades JC. Lime enhanced gasification of solid fuels: Examination of a process for simultaneous hydrogen production and CO_2 capture. Fuel 2008;87:1678-86.

[24] Perdikaris N, Panopoulos KD, Fryda L, Kakaras E. Design and optimization of carbon-free power generation based on coal hydrogasification integrated with SOFC. Fuel 2009;88:1365-7.

[25] Romano MC, Lozza GG. Long-term coal gasification-based power plants with near-zero emissions. Part A: Zecomix cycle. International Journal of Greenhouse Gas Control 2010;4:459-68.

[26] Martavaltzi CS, Pampaka EP, Korkakaki ES, Lemonidou AA. Hydrogen production via steam reforming of methane with simultaneous CO_2 capture over CaO-Ca12Al14O33. Energy and Fuels 2010;24:2589-95.

[27] Li Z-, Cai N-. Modeling of multiple cycles for sorption-enhanced steam methane reforming and sorbent regeneration in fixed bed reactor. Energy and Fuels 2007;21:2909-18.

[28] Chen Y, Zhao Y, Zhang J, Zheng C. Hydrogen production through CO_2 sorption-enhanced methane steam reforming: Comparison between different adsorbents. SCIENCE CHINA Technological Sciences 2011;54:2999-3008.

[29] Zagoruiko AN, Okunev AG. Sorption-enhanced steam reforming of hydrocarbons with autothermal sorbent regeneration in a moving heat wave of a catalytic combustion reaction. Reaction Kinetics and Catalysis Letters 2007;91:315-24.

[30] Wang Y, Chao Z, Jakobsen HA. Effects of gas-solid hydrodynamic behavior on the reactions of the sorption enhanced steam methane reforming process in bubbling fluidized bed reactors. Industrial and Engineering Chemistry Research 2011;50:8430-7.

[31] Wang Y, Chao Z, Jakobsen HA. Numerical study of hydrogen production by the sorption-enhanced steam methane reforming process with online CO_2 capture as operated in fluidized bed reactors. Clean Technologies and Environmental Policy 2011;13:559-65.

[32] Wang Y, Chao Z, Chen D, Jakobsen HA. SE-SMR process performance in CFB reactors: Simulation of the CO_2 adsorption/desorption processes with CaO based sorbents. International Journal of Greenhouse Gas Control 2011;5:489-97.

[33] Carlo AD, Bocci E, Zuccari F, Dell'era A. Numerical investigation of sorption enhanced steam methane reforming process using computational fluid dynamics Eulerian-Eulerian code. Industrial and Engineering Chemistry Research 2010;49:1561-76.

[34] Lee DK, Baek IH, Yoon WL. A simulation study for the hybrid reaction of methane steam reforming and in situ CO_2 removal in a moving bed reactor of a catalyst admixed with a CaO-based CO_2 acceptor for H_2 production. Int J Hydrogen Energy 2006;31:649-57.

[35] Jakobsen JP, Halmøy E. Reactor modeling of sorption enhanced steam methane reforming. Energy Procedia 2009;1:725-32.

[36] Fernández JR, Abanades JC, Murillo R, Grasa G. Conceptual design of a hydrogen production process from natural gas with CO_2 capture using a Ca-Cu chemical loop. International Journal of Greenhouse Gas Control 2012;6:126-41.

[37] Ochoa-Fernández E, Haugen G, Zhao T, Rønning M, Aartun I, Børresen B et al. Process design simulation of H2 production by sorption enhanced steam methane reforming: Evaluation of potential CO_2 acceptors. Green Chem 2007;9:654-62.

[38] Solieman AAA, Dijkstra JW, Haije WG, Cobden PD, van den Brink RW. Calcium oxide for CO_2 capture: Operational window and efficiency penalty in sorption-enhanced steam methane reforming. International Journal of Greenhouse Gas Control 2009;3:393-400.

[39] Romano MC, Cassotti EN, Chiesa P, Meyer J, Mastin J. Application of the Sorption Enhanced-Steam Reforming process in combined cycle-based power plants. Energy Procedia 2011;4:1125-32.

[40] Meyer J, Mastin J, Bjørnebøle T, Ryberg T, Eldrup N. Techno-economical study of the Zero Emission Gas power concept. Energy Procedia 2011;4:1949-56.

[41] CW Group. Global Cement Volume Forecast Report. 2012.

[42] Olivier JGJ, Janssens-Maenhout G, Peters, Jeroen A. H. W. Trends in global CO_2 emissions; 2012 Report. PBL Netherlands Environmental Assessment Agency; 2012 IEA CO_2 Capture in the Cement Industry, July 2008/3 2008.

[43] ECRA. Technical Report: Carbon Capture Technology – Options and Potentials for the Cement Industry. 2007.

[44] Bosoaga A, Masek O, Oakey JE. CO_2 Capture Technologies for Cement Industry. Energy Procedia 2009;1:133-40.

[45] Naranjo M, Brownlow DT, Garza A. CO_2 capture and sequestration in the cement industry. Energy Procedia 2011;4:2716-23.

[46] Romano MC, Spinelli M, Campanari S, Consonni S, Cinti G, Marchi M et al. The Calcium looping process for low CO_2 emission cement and power. GHGT-11 conference, Kyoto, Japan November 2012.

[47] Rodríguez N, Murillo R, Abanades JC. CO_2 capture from cement plants using oxyfired precalcination and/ or calcium looping. Environmental Science and Technology 2012;46:2460-6.

[48] Ozcan DC, Ahn H, Brandani S. Process Integration of a Ca-looping Process with a Cement Plant for Carbon Capture. in preparation.