carbon capture journal

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Calix – a carbon capture breakthrough

Calix Limited has developed a new Calcium Looping technology that may capture carbon dioxide at less than €15/tonne. Applications are being developed for power station or cement works retrofit, hydrogen generation from coal or lignite, and for new power generation plant based on an IGCC cycle.

By Brian Sweeney and Mark Sceats, Calix

This article describes the history of the technology and the Endex reactor which is the key to its practical implementation. It outlines the main applications and the development path of the company.

The History

Making lime from limestone is the oldest industrial process; with the possible exception of the fermentation of alcohol! The decomposition of calcium carbonate, limestone, to produce lime in fires produced the first fertilizers in pre-history, and its production in kilns was a well established pre-Roman technology.

Today, the calcination of lime is a basic process in the production of Portland cement, and lime itself is one of the most common chemicals, used in about eighty substantial markets. The reverse process to calcination, called carbonation, uses lime to capture CO2 and has been widely studied over the last century.

Modern kilns operate close to equilibrium, and the direction of the reaction – calcination or carbonation - varies in a kiln depending on the local partial pressure of the CO2 and the temperature. These both vary across the kiln depending on the heat and mass flows, and within the stones as they calcine. The reactions are well understood.

Calcium Looping for carbon capture was first patented in 1994 as a temperature swing reactor[1]. This process separates the calcination and carbonation processes into two separate reactors – a Calciner and a Carboniser, and then loops the lime particles between the reactors for a continuous extraction process.

In the Carboniser the lime, as CaO, captures the CO2 from an input flue or fuel gas to produce CaCO3, and when transported to the Calciner the sorbent is regenerated and the CO2 is released in a pure gas stream, for compression, transport and sequestration.

By 2004, the IEA had singled out Calcium Looping as a potential candidate for CO2 capture, but noted that the major problem to be resolved was the sintering of the CaO sorbent[2]. Sintering is the loss of the CO2 capture capacity of the lime as the surface area is reduced, and numerous laboratory and pilot plant studies worldwide had demonstrated that the sintering was severe, with the sorption capacity being reduced from about 70% to 17% in the first 10 or so cycles.

The sintering problem has been the subject of intense research in the past seven years, and continuous improvements have been reported using a number of strategies. However, the large throughputs of lime are such that Calcium Looping in 2009 has been relegated to technology of interest to remediation of emissions from cement plants[3], where the lime can be consumed.

Calix has solved the sintering problem, and is confident that Calcium Looping will find major applications in all areas of both fossil fuel and biofuel emissions.

A second issue in Calcium Looping has been the high energy flux required to drive the process. In the conventional approach to CaO Looping, a large amount of energy must be supplied to the high temperature Calciner (at 850-950 °C) and this is released in the lower temperature Carboniser (at 650-800 °C). This heat required is about 30-40% of the thermal power of a power plant.

While the heat released in the Carboniser can be used to generate power, the capture plant is too large to warrant the investment. The conventional CaO Looping Cycle is shown in Figures 1 and 2 to illustrate these points.

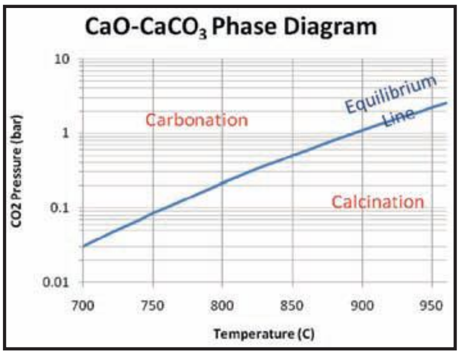

Figure 1: The CaO:CaCO3 Phase Diagram

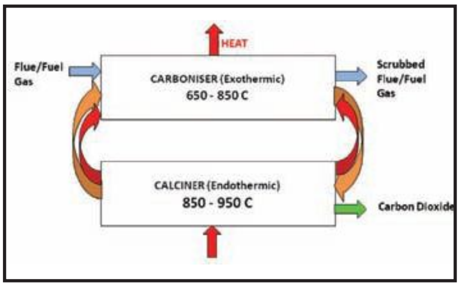

Figure 2: The Conventional Calcium Looping Reactor

The Breakthrough

Scientific breakthroughs often happen when two disciplines come together and an old problem is viewed from a new perspective. Calix scientists, with their knowledge of active sorbent preparation techniques, realized that the problems of the conventional Calcium Looping could be eliminated by:

- adjusting the pressures and temperatures in the Calciner and Carboniser so that the exothermic carbonation reaction occurs at a higher temperature than the endothermic calcination.

This means that the heat is retained within the reactor. The carbonation reaction increases the temperature by some 50 deg C as the sorbent flows through the carboniser. And it falls again through the calcining step.

The heat flows spontaneously from the carboniser to the cooler calciner. The heat is carried by the sorbent transfer and through the reactor walls. In principle, the separation of CO2 can be realized without any external thermal energy.

- using the high initial reaction rates on the surface of the particles, which give 2-3% carbonation in 2 or 3 seconds for particles less than 150 microns.

This is sufficient to capture 90% of the CO2 and avoids sorbent sintering. The residence time is so small that the size of the reactor is very compact – essentially pipes about 10-30 m high and 1-3 m in diameter.

The Endex reactor

Calix calls this configuration the Endex reactor – for a coupled endothermic-exothermic reactor. This class of chemical reactors was first described by Australian researchers, Rowena Ball and Brian Grey in 1999[4].

Endex reactors are non-linear systems, and when applied to CaO Looping, the reactor operates as a gas switch. Calix has shown

[1] A.B.M.Heesink and H.M.G.Temmink, "Process for removing Carbon Dioxide Regeneratively from Gas Streams", PCT WO94/01203 (1994)

[2] International Energy Authority, "Prospects for CO2 Capture and Storage", 2004

[3] "CO2 Capture Technologies for Cement Industry", A.Boaoaga, O.Masek and J.E.Oakey, Energy Procedia, 1, 133-140 (2009)

[4] B.F.Gray and R.Ball, "Thermal Stabilisation of Chemical Reactors. The mathematical description of the Endex reactor" Proc.R.Roc.Lond. A, 455, 163-182 (1999)

that the stability regime for the Endex CaO Looping reactor is very wide, with the switching occurring at low temperatures.

The Endex configuration for CaO Looping is shown in Figures 3 and 4. Ideally, the Endex reactor operates as a pressure swing reactor with continuous solids flow.

The primary outcome of the Endex reactor is that the dominant barrier to adoption of Calcium Looping, namely sorbent sintering, is overcome. This is done by holding the Calciner at a low temperature to minimise thermal sintering; by minimizing the carbon dioxide pressure in the calciner so that CO2 catalysed thermal sintering is minimised; and by holding the degree of carbonation to be small so that irreversible mesopore filling is negligible.

The Implementation

The implementation challenges of CaO Looping in the Endex configuration are no longer associated with the sorbent, but are now typical engineering challenges such as minimizing heat losses and transporting solids at high temperature between the reactors.

However, maintaining the CO2 pressure in the Calciner low requires that it must be evacuated and this requires mechanical energy. This energy penalty is relatively small, about 3-6%, and Calix is working to minimise it.

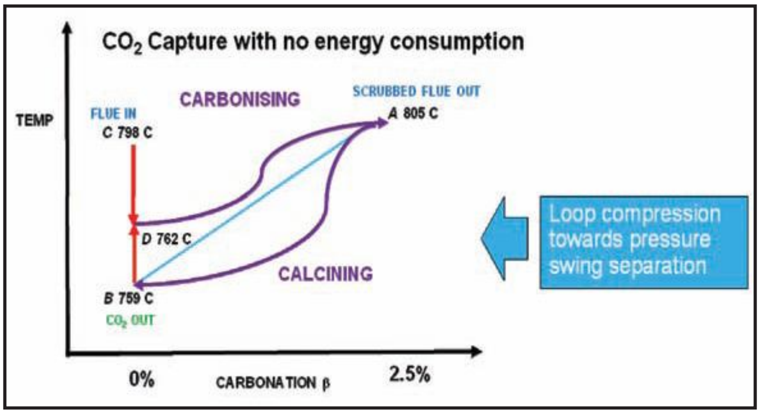

Figure 5: The Endex Calcium Looping Cycle

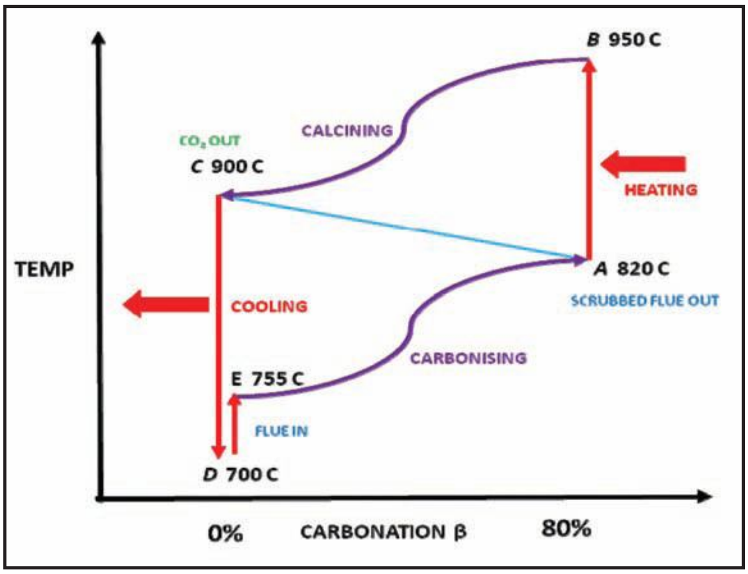

Figure 3: The Conventional Calcium Looping Cycle

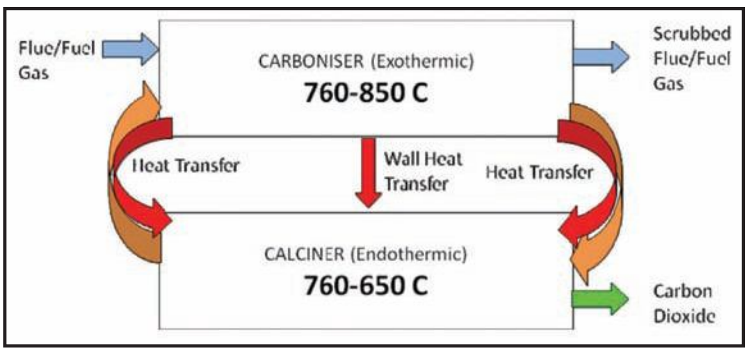

Figure 4: The Endex Calcium Looping Reactor

The most immediate consequence is that the flue or fuel gases preferably should be compressed for efficient CO2 capture. This means that the use of pressurized fluid bed (PFBC) combustor reactors is preferred for post-combustion capture, while fuel gases such as natural gas and Syngas are already pressurized and can be used directly.

Atmospheric combustors are currently used for power plants and industrial processes such as cement, and iron and steel production. Calix has identified an approach to atmospheric capture by substituting the excess air intake into gas turbine plants by flue gas, and extracting the CO2 at high pressure after the combustor. This compression comes at no cost because it is a replacement for excess air.

In the separation of CO2 from fuel gases, the Endex reactor becomes an integral part of the fuel processing, because the high temperature of the CaO Looping causes the fuels to decompose at high pressures.

In a simple example, if syngas is injected into a Calcium Looping Endex reactor with steam, the extraction of CO2 through the formation of CaCO3 spontaneously drives the reactor to produce hydrogen, in a process known as the Sorbent Enhanced Water Gas Shift (SEWGS).

In general terms, the Carboniser of the Endex reactor can be used to transform chemically the fuel gas to produce CO2. In the conventional IGCC process, the WGS and CO2 Capture processes occur in separate reactors at low temperatures, resulting in high capital costs and inefficiencies.

The WGS-Endex reactor is able to separate the CO2 and produce hydrogen from Syngas and steam without thermal energy inputs. Other fuel gases, such as natural gas and LPG can also be used to produce hydrogen through variants of this theme.

The Cost

The cost of CCS is the critical number that will determine whether the Endex technology will be economically viable. With a negligible thermal energy penalty and a small mechanical energy penalty discussed above, the cost of CO2 capture is most likely determined by the capital costs.

Provided that the Endex reactor can be matched to the temperature and pressure of the input gas without penalty, then the capital costs of an Endex reactor is expected to be relatively small.

The cost of the Endex reactor is expected to scale simply with the gas input flow rate. In the low carbonation limit considered above, the dominant heat transfer between the reactors occurs by the transport of the sorbent between the reactors, so that the wall heat transfer can be small. Thus the reactors can be substantially thermally insulated, and carbon steel can be used.

The reactors will be compact – with cross-sections of the order of metres and the height being a 20 to 30 meters. Because of the thermal coupling, the reactors operate autothermally and have an intrinsic stability, so the control systems are expected to be relatively simple.

Estimates of several configurations are that the capital cost for large plants, exceeding 500 MWe, will be less than €200 per MWe, the energy penalty for capture and compression will be 6%, to give a cost of CO2 capture less than €15 per tonne. Initially, the systems will be smaller, and the first-of-a-kind factor will be significant.

The development of Calix

It is widely agreed that there is no solution to climate change which does not include extensive application of carbon capture and storage. CCS is a major global industry in gestation.

While the political issues are being debated, and the remuneration mechanism for carbon sequestration is being resolved, Calix is developing its technology, fine tuning the applications and preparing for commercialisation.

No matter how good our technology breakthrough, there is a considerable task to catch up with the suite of first generation technologies and their incremental improvements current in demonstration. In a prudently conservative industry processes must be proven before they will be adopted.

Calix has demonstration plants planned worldwide at increasing scale in which Endex reactors can be developed and tested for particular applications – pre- and post combustion capture, with various fuels including coal, lignite, natural gas and syngas.

About the authors

Brian Sweeney is the Director of Business Development commercialising the carbon capture technology of Calix (Europe) Limited. He has an extensive background in the energy industry having worked with Shell and Rolls-Royce Industrial Power Group.
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Capture news

E.ON and Siemens begin CO2 capture pilot in Germany

www.eon.com
www.powergeneration.siemens.com

E.ON and Siemens are starting up a pilot CO2 capture plant at the E.ON power plant Staudinger in Grosskrotzenburg near Hanau, Germany.

A lab-proven post-combustion capture process developed by Siemens is to be employed under real operating conditions at the power plant's hard-coal-fired Staudinger Unit 5. The pilot plant will be operated with part of the flue gas from Unit 5.

E.ON and Siemens intend to run the facility until the end of 2010. The results achieved and the operating performance of the pilot plant will serve as the basis for large-scale demonstration of the technology, which is scheduled to start operation in the middle of the next decade.

It will test the cleaning agent's long-term chemical stability and the efficiency of the process under real power plant conditions. In parallel, the technology will be further optimized in terms of energy consumption.

The project is being sponsored by the German Federal Ministry of Economics under the terms of the COORETEC Initiative. It is part of the federal government's 5th Energy Research Program "Innovation and New Energy Technologies" and promotes research and development in the field of low-CO2 power plant technologies.

Alstom and Dow open CO2 capture pilot plant

www.alstom.com
www.dowoilandgas.com

Alstom and The Dow Chemical Company have begun operation at a pilot plant to capture CO2 from the flue gas of a coal-fired boiler at the Dow-owned facility in South Charleston, West Virginia, USA.

The pilot plant uses proprietary advanced-amine technology jointly developed by Alstom and Dow to capture approximately 1,800 metric tons of CO2 per year.

The pilot will operate for the next two years, generating reliable, long-term data that can be used to optimize this technology for implementation at coal-fired power plants across the globe.

In 2008, the two companies entered into a Joint Development Agreement to develop this technology. In March 2009, the companies announced their plans to design and construct the plant.

"This pilot plant is designed to evaluate the technology operating under power plant conditions, test proprietary innovations jointly developed by Dow and Alstom and provide data necessary to finalize the design of large-scale demonstration plants that will apply this technology," said Philippe Joubert, Alstom Executive Vice President and President of Alstom Power.

"Integrating this process with new advanced coal and gas fired power generation equipment will allow customers to minimize CO2 emissions while generating electricity as cost effectively as possible."

E.ON's Staudinger plant in Grosskrotzenburg near Hanau, Germany (Source: E.ON AG)

Alstom acquires Lummus Global engineering unit

Alstom has acquired the former engineering office of Lummus Global, a leading provider of technology for the hydrocarbon processing industry, in Wiesbaden, Germany.

The unit, renamed ALSTOM Carbon Capture GmbH, will be integrated into Alstom's CO2 Capture Systems activity.

The unit consists of over 100 employees with the full set of skills and capabilities required for the design and delivery of CO2 capture plant.

Alstom says the acquisition will enable it to make its CO2 capture technologies available to its customers with greater responsiveness and efficiency. It will support the increasing demand for studies, FEED packages, pilot plants and demonstration units driven by the need to accelerate the commercialisation of effective and efficient large scale CCS facilities.