Editorial comments:  
Changes recommended by the JoVE Scientific Review Editor – JoVE 56112  
  
The manuscript has been modified by the Scientific Review Editor to comply with the JoVE formatting standard. Please maintain the current formatting throughout the manuscript. The updated manuscript (56112\_R0\_02222017) is in your Editorial Manager account. In the revised PDF submission, there is a hyperlink for downloading the .docx file. Please download the .docx file and use this updated version for any future revisions. The updated manuscript is also attached. send the author template  
  
• General Formatting:  
1) JoVE is unable to publish manuscripts containing commercial sounding language, including trademark or registered trademark symbols (TM/R) and the mention of company brand names before an instrument or reagent. Please remove all commercial sounding language from your manuscript (text and figures). All commercial products should be referenced in the table of materials/reagents.

The name of the company that provides the limestone has been deleted.  
2) If you are re-using figures from a previous publication, you must obtain explicit permission to re-use the figure from the previous publisher (this can be in the form of a letter from an editor or a link to the editorial policies that allows you to re-publish the figure). Please upload the text of the re-print permission (may be copied and pasted from an email/website) as a Word document to the Editorial Manager site in the "Supplemental files (as requested by JoVE)" section. Please also cite the figure appropriately in the figure legend, i.e. "This figure has been modified from [citation]."

Figures are not being reused from any other publication so this does not apply to the manuscript.

3) Please copy-edit the entire manuscript for any grammatical errors you may find. The text should be in American-English only. This editing should be performed by a native English speaker (or professional copyediting services) and is essential for clarity of the protocol and the manuscript. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version.

This manuscript has been proofread.  
4) All commercial products should be sufficiently referenced in the table of materials/reagents. Please provide company, catalog number and other details in Table of Materials for – mechanical shacker, source of natural gas, nitrogen source,

This has been modified in the table of materials.  
5) Please provide email addresses of all authors on first page.

This has been modified in the manuscript:

“[michal.jeremias@me.com; v.manovic@cranfield.ac.uk; b.j.anthony@cranfield.ac.uk](mailto:michal.jeremias@me.com;%20v.manovic@cranfield.ac.uk;%20b.j.anthony@cranfield.ac.uk)”

6) Please use JoVE’s manuscript template (attached) to submit your revised manuscript  
  
• Abstracts:  
1) Please re-word the Short Abstract to more clearly state the goal of the protocol. For example, “This protocol/manuscript describes…”

This has been modified to:

“This manuscript describes a procedure for operating a calcium looping pilot-plant for post-combustion carbon capture with high oxygen concentrations in the calciner in order to reduce or eliminate flue gas recycle.”

• Introduction:  
1) Please expand your Introduction to include the following: 1) The advantages over alternative techniques with applicable references to previous studies and 2) Information that can help readers to determine if the method is appropriate for their application.

The introduction has been modified accordingly in the revised manuscript. Adding the following text:

“The use of heat pipes between the combustion and calciner has been studied instead of oxy-combusting fuel in the calciner, the results for the CO2 capture performance were comparable with those of a conventional CaL pilot-plant, however, this process has higher plant efficiencies and lower CO2 avoidance costs17. Martínez et al. 18 investigated the heat integration possibilities in order to preheat the solid material entering the calciner and to reduce the heat needed in the calciner. The results showed 9% reduction in the coal consumption when compared with that of the standard case. Other possibilities for heat integration are also studied considering internal and external integration options 19.One of the main problems of the CaL cycle from the economic point of view is to supply the energy needed in the calciner by means of fuel combustion20.”

• Protocol:  
1) Line 66 – how much limestone is sieved? 1L, 2 Kg, etc. Please use a specific example to describe the entire protocol section. For example, write the entire protocol for experiment 1, “Flue gas (15% vol. CO2) with Longcliffe limestone (200–300 μm) 30% vol O2” while showing results from all 3 experiments in the representative results.

This has been changed to:

“1.1. Sieve the limestone (around 50 kg of raw material) to the desired particle size distribution (300-400 μm or some other choice depending on the experiment) using a mechanical shaker. Put the sieved material in pots next to the calciner for feeding during the test.”  
2) Line 67 – what is desired material? Please use a specific example

This meant the sieved material in the previous sentence. This has been clarified.

“Put the sieved material in pots next to the calciner for feeding during the test.”

3) Line 71 – add a “caution: extremely high temperatures. Use suitable PPE such as gloves, masks, eye glasses”

This has been added to line 71.

“2. Start-up procedure (caution extremely high temperatures. Use suitable PPE such as gloves, eye glasses, and laboratory coat and safety shoes)”

4) Line 76 – is the data acquisition done using a software? If yes, please mention what button is clicked on in the software to do this, or which menu items need to be selected.

This is done by software. It has been modified in the text accordingly.

“2.1.3. Start acquiring data (for gas temperatures and pressure using the recording button in the software), these data include temperatures, pressures and gas composition of both reactors.”

5) Line 81 – step 2.1.5 - which material? Please provide details

This refers to the sieved limestone mentioned throughout the protocol. This has been changed to:

“2.1.5. Put 3 L of the sieved limestone material into BFB the calciner. Note: first open the top valve, introduce the material in the down-pipe and close the top valve, after that, open the bottom valve so that the material flows into the reactor.”

6) Line 112 – please replace “find an optimal heat balance…..”. use a specific example

This has been modified to clarify with the usual example. However, this is adjusted throughout the experiment depending on temperature, pressures, bed material etc.

“3.2. Adjust the flows in the calciner to achieve a stable 930–950 °C temperature in the calciner by regulating the flow of natural gas (NG) and oxygen (within optimal fluidization regime), usually it is 100% O2 with enough bed material, but it is adjusted throughout the experiment”

7) Line 114 – do you keep monitoring the CO2 concentration in the carbonator exhaust? How frequently? What do you use to monitor CO2?

This is acquired every second using the software mentioned in 2.1.3. This has been modified to:

“3.3. When the material starts to decline in activity (above 5% CO2 concentration at the exit of the carbonator, this is acquired every second in step 2.1.3), add more limestone.”

8) Line 122 – please cite references for each of these.

Two standards have been cited for XR Spectometry and XRF for lime-based materials.

[21] ASTM C1271-99(2012), Standard Test Method for X-ray Spectrometric Analysis of Lime and Limestone, ASTM International, West Conshohocken, PA, 2012, [www.astm.org](http://www.astm.org)

[22] ASTM C25-11e2, Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime, ASTM International, West Conshohocken, PA, 2011, www.astm.org

• Representative Results:  
1) Line 134 – what is that (2)?

This is the equation number.

• Figure legends:  
1) Figure 5, Table 3, table 4 – Please expand the legends to adequately describe the figures/tables. Each figure or table must have an accompanying legend including a short title, followed by a short description of each panel and/or a general description.  
This has been modified accordingly:

“Figure 5: CO2 concentration at inlet and at outlet of the carbonator and corresponding capture efficiency (Ecarb) for 300–400 μm limestone with 100% O2”

“Table 3: Mass balance of solids and sieve analysis of the inputs (limestone) and outputs (other) for 300–400 μm limestone with 100% O2”

“Table 4: Molar balance estimate (10% humidity of the raw limestone, 75% wt. of the output in calcined state) for 300–400 μm limestone with 100% O2”

Also for Figure 2 and 3 Table 1 and 2, the titles have been modified:

“Fig. 2: Concentration of CO2 at inlet and at outlet of the carbonator and capture efficiency (Ecarb) for 200–300 μm limestone with 30% O2”

“Figure 3: CO2 concentration at inlet and at outlet of the carbonator and corresponding capture efficiency (Ecarb) for 100–200 μm limestone with 100% O2”

“Table 1: Weight balance of the material input and outputs for 200–300 μm limestone with 30% O2”

“Table 2: Balance of recovered material and its sieve analysis for 100–200 μm limestone with 100% O2”

• Discussion:  
1) Please expand your discussion to cover the following in detail and in paragraph form: 1) modifications and troubleshooting, and 2) critical steps within the protocol.

This paragraph has been added in order to cover these points.

“This protocol has been resolved by minimising the electrical heating provided to the gas and calciner when the NG is being combusted in order to protect the tubes of electrical discharges caused by the heating elements. Also, it has been noted that the O2 concentration increase can be achieved more rapidly than initial experimental campaigns going from 20 % vol to 60% vol and 100% vol. It is important to highlight also that the most critical steps in this process are the start of the combustion, the increase of the oxygen concentration, which can cause increased temperatures that will trigger the shut-off of NG off if the temperature goes higher than 980 °C. Also, material make-up is a concern as it can lower the temperature of the reactor and stop the combustion process, therefore, it should be added in small batches.”  
  
• Figures:  
1) Figure 1 – please label individual units, e.g., carbonator, calciner, top valve, bottom valves, etc

This figure has been labelled in the revised manuscript.

• Highlighting:  
1) After you have made all of the recommended changes to your protocol (listed above), please re-evaluate the length of your protocol section. Please highlight 2.75 pages or less of text (which includes headings and spaces) in yellow, to identify which steps should be filmed to tell the most cohesive story of your protocol steps. Please see JoVE’s instructions for authors for more clarification. Remember that the non-highlighted protocol steps will remain in the manuscript and therefore will still be available to the reader.  
  
Reviewers' comments:  
**Reviewer #1:**  
*Manuscript Summary:*  
This works is focused on the Calcium-Looping process applicated for post-combustion CO2 capture. The present paper describes an operating procedure of a Calcium-Looping pilot plant (25 kWth) in which the calciner reactor works under 100% O2 atmosphere. Several limestone particle sizes are tested. Results show that a stable CO2 capture higher than 70% can be achieved when carbonator works under 15% v/v CO2 (85% N2), simulating the flue gas of a Coal-Fired Power Plant (CFPP). This work proposes a realistic calciner operation since a high CO2 concentration of CO2 at calciner outlet is achieved, which is fundamental in the CaL process for post-combustion CO2 capture  
  
*Major Concerns:*  
-According to the authors, the operation of the calciner at high O2 concentrations is motivated by the possibility of reducing the size of calciner and the size of air-separation units. This seems to be a contradiction since a higher O2 concentration at calciner inlet to avoid CO2 recirculation could require high O2 flow and therefore a high ASU size (and a higher energy consumption). Please clarify this issue.

This has been clarified in the discussion section:

“As the recycle of flue gas (mainly CO2, water vapour and unreacted O2) can be reduced or even eliminated, the heat consumed to preheat this stream will be lower. Therefore, less oxygen would be needed and a smaller ASU (Air Separation Unit) would be required. As the flow gas will be lower in this configuration, the size of the calciner would be smaller for the same fluidization velocity.”

-On the other hand, a 6% of limestone make-up flow seems high. This would increase the energy consumption in the calciner in comparison with a "conventional" calciner operating with CO2 recycled gas stream and therefore it’s not clear enough if 6% could improve the energy penalty of the process. please discuss.

The make-up ratio was found to be 6%, which is in accordance with the literature as it can be seen in reference [23] in the manuscript. However, it has not been claimed that this would be beneficial for the energy penalty of the process. The make-up ratio of these tests mainly depends on the material (reactivity decay and attrition), as well as the CO2 being captured in the carbonator (it is explained in the protocol that more limestone was added every time the carbonator CO2 outlet was above 5%).

This has been explained in the text as it follows:

“Therefore, it can be concluded that for stable operation it would be necessary to add fresh sorbent corresponding to 0.5 L (750 g) of limestone approximately every 50 minutes, which is equivalent to a make-up ratio (F0/FCO2) of 6%, as described elsewhere 25. The make-up ratio in these experiments was mainly influenced by the limestone (reactivity decay and elutriation). The value of this parameter was chosen based on the CO2 concentration at the carbonator outlet, i.e. adding a portion of limestone when it reached a 5% vol CO2..”

*Minor Concerns:*  
-More references could be added to introduction section,i.e. lines 48-49 would be more interesting if the authors describe the possibilities to achieve higher thermal efficiencies by means of modifications in operating conditions [references], changing reactors design [references] or modifying the CaL procces integration [references], instead of use a lumped references [17-19].

The introduction has been modified accordingly in the revised manuscript. Adding the following text:

“The use of heat pipes between the combustion and calciner has been studied instead of oxy-combusting fuel in the calciner, the results for the CO2 capture performance were comparable with those of a conventional CaL pilot-plant, however, this process has higher plant efficiencies and lower CO2 avoidance costs17. Martínez et al. 18 investigated the heat integration possibilities in order to preheat the solid material entering the calciner and to reduce the heat needed in the calciner. The results showed 9% reduction in the coal consumption when compared with that of the standard case. Other possibilities for heat integration are also studied considering internal and external integration options 19.One of the main problems of the CaL cycle from the economic point of view is to supply the energy needed in the calciner by means of fuel combustion20.”

-Figure legends should be better explained, since there is no appreciable difference between figure 3 and figure 5.

This has been modified to:

“Figure 3: CO2 concentration at inlet and at outlet of the carbonator and corresponding capture efficiency (Ecarb) for 100–200 μm limestone with 100% O2”

“Figure 5: CO2 concentration at inlet and at outlet of the carbonator and corresponding capture efficiency (Ecarb) for 300–400 μm limestone with 100% O2”  
  
*Additional Comments to Authors:*  
N/A  
  
  
**Reviewer #2:**  
*Manuscript Summary:*  
The manuscript written by Erans et al. presented the operation and first results of a CaL pilot plant with 100% oxygen combustion in the calciner flue gas simulating the behaviour of a coal-fired power plant and developed a procedure in order to operate a Calcium looping pilot plant with high oxygen concentrations in the calciner. The result is important and interesting. However, this manuscript looks like a test report and much information is missing. This manuscript can be published in Journal of Visualized Experiments after the major revision.  
  
*Major Concerns:*  
N/A  
  
*Minor Concerns:*  
N/A  
  
*Additional Comments to Authors:*  
The specific comments are shown as follows:  
(1) In the introduction, the new research progress about calcium looping technology is not enough.

The introduction has been modified accordingly, adding the text below.

“The use of heat pipes between the combustion and calciner has been studied instead of oxy-combusting fuel in the calciner, the results for the CO2 capture performance were comparable with those of a conventional CaL pilot-plant, however, this process has higher plant efficiencies and lower CO2 avoidance costs17. Martínez et al. 18 investigated the heat integration possibilities in order to preheat the solid material entering the calciner and to reduce the heat needed in the calciner. The results showed 9% reduction in the coal consumption when compared with that of the standard case. Other possibilities for heat integration are also studied considering internal and external integration options 19.One of the main problems of the CaL cycle from the economic point of view is to supply the energy needed in the calciner by means of fuel combustion20.”

(2) The chemical components of the limestone used in the experiment are missing.

This has been included in the revised manuscript.

“The limestone used in this study has a minimum content of 98.25% CaCO3.”

(3) All the presented figures are not clear. The authors should provide the enough clear figures.

The quality of the figures has been improved throughout the manuscript.

(4) The discussion is simple and the deep analysis is lacking. Some parts of the paper is just observations and reporting of results without any effort to explain the results. This will diminish the impact. Even if speculative, it is important to try to understand the results.

Some paragraphs have been added throughout the text to try to discuss the results in a more insightful manner.

The discussion has been modified to include more details about the results and limitations of this study:

“As a result of these experiments various conclusions can be drawn. Firstly, operation of the calciner with an inlet of 100% vol oxygen is achievable, which is enabled by the possibility of exploiting the endothermic nature of the calcination reaction, as well as the fact that the solids circulate between two reactors at different temperatures. This operating mode aims at making the CaL process more economically viable by means of reducing capital and operating costs. As the recycle of flue gas (mainly CO2, water vapour and unreacted O2) can be reduced or even eliminated, the heat consumed to preheat this stream will be lower. Therefore, less oxygen would be needed and a smaller ASU would be required. As the gas flow will be lower in this configuration, the size of the calciner would be smaller for the same fluidization velocity.

A standard methodology for this type of operation was developed to ensure the safe operation of the high-oxygen concentration in the calciner. The results showed capture efficiency of up to 70% in some of the performed experiments. Also, different particle size distributions were used in this reactor configuration (carbonator as a CFB; calciner as a BFB). The distributions were: 100-200 μm; 200-300 μm; 300-400 μm. For the smallest distribution (100-200 μm), however, there were elutriation issues and the majority of the bed inventory was found in the calciner’s cyclone catch-pot. It was found that the best results were achieved with the largest particle size distribution (300-400 μm) with those particles an Ecarb of around 70% was maintained throughout the experiment with a make-up ratio of about 6%.

This protocol has been improved by minimising the electrical heating provided to the gas and calciner when the NG is being combusted in order to protect the tubes of electrical discharges caused by the heating elements. Also, it has been noted that the O2 concentration increase can be done more rapidly than initial experimental campaigns going from 20 % vol to 60% vol and 100% vol. It is important to highlight also that the most critical steps in this process are the start of the combustion, the increase of the oxygen concentration, which can cause increased temperatures that will trigger the source of NG off if the temperature goes higher than 980 °C. Also, material make-up is a concern as it can lower the temperature of the reactor and stop the combustion process, therefore, it should be added in small batches.

This methodology can be applied for this experimental rig to test new synthetic materials, as well as materials improved via doping, thermal pre-treatment, chemical pre-treatment, etc.24. This protocol would allow these new sorbents to be tested under realistic conditions providing a standard methodology for sorbent comparison. However, there are some challenges when applying this concept at larger scale, such as the use of coal in the calciner under these operating conditions. The use of solid fuels would increase the difficulty in operation of the calciner due to the high temperatures, which can lead to ash agglomeration and eventually defluidizing phenomena25. This needs to be further studied in order to determine the feasibility of this protocol; however, the concept was proofed successfully at pilot-scale in the course of this work using NG .

Another limitation arising from this study is the duration of the tests with around 3 h of steady state operation per tests; this is due to the heating process of the plant, which is an inherently slow process. Moreover we do not known the average number of carbonation/calcination cycles experienced by a particle when circulating between reactors. It is possible that the high oxygen concentration had a negative effect causing more sintering in the limestone particles. Further investigation of these challenges would help to assess the suitability of the protocol as a novel feasible operating mode for CaL plants at higher scale.”  
  
  
**Reviewer #3:**  
*Manuscript Summary:*  
This manuscript presents experiments in a lab-scale calcium looping plant with a calciner that is fired with natural gas at high oxygen concentrations. The topic is highly relevant in the field of CO2 capture from flue gases of power/industrial plants, since the calcium looping process has the potential of relatively low energy penalty compared with other post-combustion CO2 capture technologies. The realization of high oxygen concentration (up to 100%) in the fluidization gas of the calciner has the advantage of minimizing (or even avoiding) a flue gas recirculation, so that the energy penalty caused by the recycle fan can be reduced (or avoided) leading to an improved efficiency of the process. The material provided by the authors is new and could be of high interest to readers working with fluidized bed reactors. The experimental procedure is well described, although a description of the experimental configuration is missing. There might be some concern regarding the visualization of the experiment, since there usually is limited visual access to such reactors. All in all, the content is highly recommended for being published in JoVE with some modifications, as indicated below.  
  
*Major Concerns:*  
1) A detailed description of the experimental setup (including reactor dimensions, materials, instrumentation, control loops) should be given.

A detailed description of the experimental set up has been given in the representative results section:

“The experimental set-up is shown in Fig.1. The plant comprises two interconnected fluidized-beds. Namely, the carbonator is a CFB with 4.3 m height and 0.1 m ID; on the other hand the calciner is a BFB with 1.2 m height and 0.165 m ID. The solid transport from one reactor to the other is controlled by two loop-seals fluidized with nitrogen. Gases for both reactors are fed through a preheating line, both reactors are electrically heated; moreover, the calciner is fed with natural gas in order to generate the heat needed for the endothermic calcination. The carbonator distributor plate has 8 nozzles, each of them with twenty 2 mm holes, whilst the calciner has 20 nozzles with six 1 mm holes each.”

2) The Figures are of very poor quality and should be improved.

The quality of the figures has been improved throughout the manuscript.

3) In the conclusions, the authors state that "operation of the calciner with an input of 100% vol oxygen is achievable". However, this has only been proven for natural gas as fuel, and a commercial calciner will hardly be fired with natural gas, but with coal. When firing with coal, there are other challenges related to ash softening at locally high temperatures, which might lead to agglomeration. This issue should be discussed in the paper.

We agree with the reviewer that this could be an issue. However, in this work, we wanted to prove this concept of running with high oxygen concentrations, but further work should focus on the study of solid fuels before this operating mode can be moved to higher scale.

“ However, there are some challenges when applying this concept at larger scale, such as the use of coal in the calciner with under these operating conditions. The use of solid fuels would increase the difficulty in operation of the calciner due to the high temperatures, which can lead to ash agglomeration and eventually defluidizing phenomena27. This needs to be further studied in order to determine the feasibility of this protocol; however, the concept was proofed successfully at pilot-scale in the course of this work using NG.”  
4) The longest test presented was 3 hours. It is not clear whether this duration is an upper limit or whether longer test durations are possible. When defining a test procedure, it should be assured that the composition/activity of the sorbent has reached a (semi) steady state. It would be interesting to know the average number of carbonation/calcination cycles that the sorbent experiences during one test.

The duration is an upper limit for these tests due to work policies at Cranfield University. The plant cannot be run overnight or in shifts. However, the plant was run 3 h under steady state, which are the results presented as part of this work. It is unknown what the average number of cycles is. This has been clarified in the text:

“Another limitation arising from this study is the duration of the tests with around 3 h of steady state operation per tests; this is due to the heating process of the plant, which is a slow process. It is also unknown the average number of carbonation/calcination cycles experienced by a particle when transferring from one reactor to another”

5) Has the reactivity of the used sorbents been analyzed? Are there any differences related to the oxygen concentrations? It can be expected the sintering might be promoted by high oxygen concentrations leading to reduced activity.

The reactivity of the sorbents has not been analysed. However, we agree with the reviewer and a statement has been made about this issue in order to clarify that this is a possibility that should be further studied.

“It is possible that the high oxygen concentration had a negative effect causing more sintering in the limestone particles. Further investigating these challenges would help to assess the suitability of the protocol as a novel feasible operating mode for CaL plants at higher scale.”  
  
*Minor Concerns:*  
6) line 74: "Set all electrical…"

This has been changed to:

“Set the temperature of all electrical preheaters of the carbonator at 600 °C.”  
7) line 76: "…these date include temperatures…"

This has been changed to

“These data include”  
8) line 102: At what temperature is the material being calcined?

The material is being calcined with the heating up process to speed up the start of the test but it is estimated that this would be around 800-850°C for the first batch and the calciner temperature for the fresh make-up of sorbent.

This has been clarified in the revised manuscript:

“2.2.5. Add limestone in 0.5 L increments until there is 7 L in the fluidized bed. Calcine all the material in the fluidized bed of the calciner (the estimated calcination temperature is 800-850° for the batch present in the calciner and the calciner temperature for the following batches).”

9) line 131: What does "100% limestone" mean here? Has the limestone not been calcined? Have there been experiments with less than 100% limestone?

The 100% has been deleted in the sentence. All tests are done with pure limestone.

10) The text in the tables needs to be adjusted.

The text has been adjusted in the revised manuscript.  
  
*Additional Comments to Authors:*  
N/A