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(71) Applicant: **INFRATECH INDUSTRIES PTY LTD**
[AU/AU]; Unit 1, 17 Burwood Road, Burwood, New South
Wales 2134 (AU).

(72) Inventors: **MOGHTADERI, Behdad**; c/- The University of Newcastle Research Associates Ltd, Industry Development Centre, University Drive, Callaghan, New South Wales 2308 (AU). **ZHOU, Cheng**; c/o Newcastle Innovation Limited, Industry Development Centre, University Drive, Callaghan, New South Wales 2308 (AU). **SONG, Hui**; c/o Newcastle Innovation Limited, Industry Development Centre, University Drive, Callaghan, New South Wales 2308 (AU).

(74) Agent: **SHELSTON IP PTY LTD**; Level 9, 60 Margaret Street, Sydney, New South Wales 2000 (AU).

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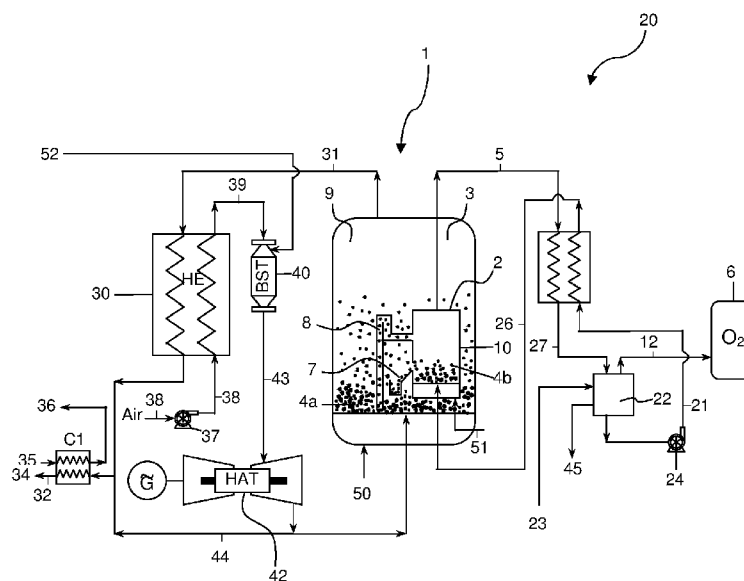


Figure 1

(57) Abstract: An apparatus (1) for generating oxygen has a reduction reactor (2) fluidly connected to and located at least partially within an oxidation reactor (3), where oxygen-carrier particles (4a, 4b) are transferred between the reduction and oxidation reactors. An outlet conduit (5) transfers an oxygen-enriched mixture from the reduction reactor to an oxygen storage unit (6). A corresponding method provides a chemical looping process using oxygen-carrier particles transferred between reduction and oxidation processes, where oxygen-depleted carrier particles produced in the reduction process are transferred to and regenerated in the oxidation process. Oxygen is separated from an exhaust gas mixture produced in the reduction process. The reduction process is carried out at a higher temperature than the oxidation process. A system (20) uses the apparatus and a condenser (22) for condensing the oxygen-enriched mixture from the outlet conduit (5).



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Apparatus and method for generating oxygen and energy conversion or storage

Field of the Invention

[0001] The present invention relates to an apparatus and method for producing oxygen and energy conversion or storage and in particular relates to a chemical looping-based oxygen production and energy conversion apparatus and method. The invention has been developed primarily for the production of oxygen and energy conversion or storage for domestic, industrial, medical, emergency service and military applications.

Background of the Invention

[0002] The following discussion of the prior art is intended to present the invention in an appropriate technical context and allow its advantages to be properly appreciated. Unless clearly indicated to the contrary, however, reference to any prior art in this specification should not be construed as an express or implied admission that such art is widely known or forms part of common general knowledge in the field.

[0003] Thermo-chemical energy storage is a key technology for managing the balance between energy demand and supply, which is an important element for the successful transition towards a low-carbon economy. Storing energy as economically as possible is the key challenge faced by thermo-chemical energy storage technologies.

[0004] One thermo-chemical energy storage technology employs a chemical looping based redox energy storage (RES) system, which simultaneously produces and, where possible, to stores heat, electricity, and/or oxygen. With these multiple functions (i.e. poly-generation) in a single process, better economics are expected to permit commercially viable implementation of the RES system. However, improvements in efficiency of the redox reaction and minimising heat losses from the RES system would enhance the commercial viability of the technology.

[0005] Hence, it is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative. It is an object of at least one embodiment of the invention to provide a more efficient redox

reaction and reduced heat loss in the generating of oxygen and storing of energy, resulting in a more economic means of producing oxygen for industrial applications.

Summary of the Invention

[0006] A first aspect of the invention provides an apparatus for generating oxygen, comprising a reduction reactor, an oxidation reactor fluidly connected to the reduction reactor so that oxygen carrier particles can be transferred between the reduction reactor and the oxidation reactor, an outlet conduit arranged to transfer an oxygen enriched mixture from the reduction reactor to an oxygen storage unit, wherein the reduction reactor is located at least partially within the oxidation reactor.

[0007] In one embodiment, the reduction reactor is located within the oxidation reactor.

[0008] In one embodiment, the reduction reactor is located adjacent the bed of the oxidation reactor. In another embodiment, the reduction reactor is located partly within the bed of the oxidation reactor. In a further embodiment, the reduction reactor is located within the bed of the oxidation reactor.

[0009] In some embodiments, the reduction reactor is a fluidised bed reactor. In other embodiments, the oxidation reactor is a fluidised bed reactor.

[0010] In some embodiments, one or more transfer conduits fluidly connect the reduction reactor and the oxidation reactor.

[0011] In some embodiments, the reduction reactor, the oxidation reactor, and the outlet conduit form an integrated chemical looping air separation unit.

[0012] A second aspect of the invention provides a method for generating oxygen, comprising:

- transferring oxygen carrier particles between a reduction process and an oxidation process, wherein the reduction process and the oxidation process are fluidly connected to form a chemical looping process;

- producing oxygen depleted carrier particles and an oxygen enriched mixture comprising oxygen in the reduction process;

- separating oxygen from the oxygen enriched mixture;

returning the oxygen depleted carrier particles to the oxidation process for regenerating the oxygen depleted carrier particles with oxygen; and

wherein the reduction process is carried out at a higher temperature than the oxidation process.

[0013] In some embodiments, the heat generated by the oxidation process is used to maintain the reduction process at the higher temperature.

[0014] In some embodiments, the reduction process is carried out 100° to 150°C higher than the oxidation process.

[0015] In some embodiments, the temperature of the reduction process is at least 900°C. In other embodiments, the temperature of the reduction process is between 900°C and 1,150°C. In one embodiment, the temperature of the reduction process is between 900°C and 950°C. In another embodiment, the temperature of the reduction process is between 1,000°C and 1,050°C. In a further embodiment, the temperature of the reduction process is between 1,100°C and 1,150°C. In one preferred embodiment, the temperature of the reduction process is around 950°C.

[0016] In some embodiments, the temperature of the oxidation process is at least 800°C. In other embodiments, the temperature of the oxidation process is between 800°C and 1,000°C.

[0017] In some embodiments, the reduction process is carried out in a first chamber exposed to the oxidation process. In one embodiment, the oxidation process is carried out in a second chamber, the first chamber being located at least partly within the second chamber. In another embodiment, the first chamber being located within the second chamber.

[0018] In some embodiments, the oxygen depleted air from the oxidation process is passed through a heat exchanger to transfer heat to an incoming gas added to the oxidation process.

[0019] In some embodiments, the oxygen enriched mixture from the reduction process is passed through a heat exchanger to transfer heat to a fuel for the reduction process.

[0020] In some embodiments, a fluid medium is passed through a heat exchanger to receive heat from the chemical looping process and drive a turbine. More preferably, the fluid medium comprises water and steam is generated to drive the turbine to generate electricity. Alternatively, the fluid medium is directed to a temperature control system for heating or cooling.

[0021] In some embodiments, the oxygen separated from the oxygen enriched mixture is transferred to an oxygen consumption unit.

[0022] In some embodiments, the oxygen carrier particles comprise metal oxides. More preferably, the metal oxides comprise at least one of Cu, Mn and Co based metal oxides. In one embodiment, the metal oxides comprise mono-bi-metallic oxide sorbents or composites, such as perovskites and the like. In other embodiments, the metal oxides are selected from the group comprising MnO_2 , Mn_2O_3 , Mn_3O_4 , CoO , Co_3O_4 , CuO , Cu_2O and mixed metal oxides.

[0023] The method has the preferred features of the first aspect of the invention stated above, where applicable.

[0024] A third aspect of the invention provides a system for generating oxygen and storing energy, the system comprising the apparatus of the first aspect and an oxygen separating unit for separating oxygen from the oxygen enriched mixture.

[0025] In some embodiments, the system further comprises the oxygen storage unit fluidly connected to the oxygen separating unit. In other embodiments, the oxygen storage unit controllably releases oxygen. In one embodiment, the oxygen storage unit has a valve to controllably release oxygen.

[0026] In some embodiments, the oxygen separating unit comprises a condenser for condensing the oxygen-enriched mixture to separate the oxygen, the condenser being fluidly connected to the outlet conduit.

[0027] In some embodiments, the system further comprises a compressor for compressing the oxygen, the compressor being fluidly connected to the condenser.

[0028] In some embodiments, the oxygen separating unit comprises a heat exchanger for exchanging heat between the oxygen-enriched mixture and incoming gas into the reduction reactor.

[0029] In some embodiments, the system comprises a heat exchanger for exchanging heat between air from an air supply and oxygen depleted air from the oxidation reactor.

[0030] In some embodiments, the combustion unit combusts coal in a coal-fired power plant. In some embodiments, the combustion unit comprises a furnace. In other embodiments, the combustion unit comprises a boiler.

[0031] Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising", and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

[0032] Furthermore, as used herein and unless otherwise specified, the use of the ordinal adjectives "first", "second", "third", etc., to describe a common object, merely indicate that different instances of like objects are being referred to, and are not intended to imply that the objects so described must be in a given sequence, either temporally, spatially, in ranking, or in any other manner.

Brief Description of the Drawings

[0033] Preferred embodiments of the invention will now be described, by way of example only, with reference to the drawings of which:

[0034] Figure 1 is a schematic drawing of an apparatus and system for energy conversion or storage and oxygen production according to one embodiment of the invention;

[0035] Figure 2 is a schematic drawing of the apparatus of Figure 1 in a RES configuration;

[0036] Figure 3 is a schematic drawing of a process simulation of the RES configuration of Figure 2;

[0037] Figure 4 is a schematic drawing of another process simulation of the RES configuration of Figure 2;

[0038] Figure 5 is a schematic drawing of a further process simulation of the RES configuration of Figure 2;

[0039] Figure 6 is a schematic drawing of the apparatus of Figure 1 in an alternative RES configuration;

[0040] Figure 7 is a graph of expander power production minus compressor power consumption against the compressor outlet pressure for RES unit of Figure 6; and

[0041] Figure 8 is a graph comparing the net present values off the RES units of Figures 2 and 6 with conventional and advanced CASU units against the cost of oxygen.

Detailed Description of Preferred Embodiments

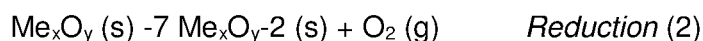
[0042] The present invention will now be described with reference to the following examples which should be considered in all respects as illustrative and non-restrictive. In the Figures, corresponding features within the same embodiment or common to different embodiments have been given the same reference numerals.

[0043] The embodiments of the invention are in general directed to a RES system and in particular to providing a chemical looping energy on demand system (CLES), which is a technology for poly-generation of power, heating, cooling, hot water, oxygen and hydrogen. The CLES technology has been developed for use in a diverse range of applications such as:

- Residential (individual houses, small subdivisions of multiple homes, retirement villages, etc.);
- Industrial (manufacturing plants needing conventional utilities plus oxygen and hydrogen for example glass and steel manufacturing, pharmaceutical, etc.);
- Medical (hospitals needing conventional utilities plus oxygen);

- Emergency services and defence (for example in field hospitals or in forward operating bases)

[0044] The CLES technology applies the principles of a chemical looping air separation (CLAS) that has been previously developed by the inventors and the general principles of the RES system have been described by the inventors in PCT Application No. PCT/AU2017/050054, whose specification as filed is hereby incorporated by reference in its entirety. CLAS relies on a redox (reduction / oxidation) reaction formed into a chemical loop, where carrier particles are cycled between the reduction and oxidation processes. An example of the redox reaction is set out below using a metal oxide as the carrier particles that cycle between the oxidation and reduction processes:



[0045] The oxidation half-cycle is typically carried out under normal air whilst the reduction half-cycle is usually accomplished in the presence of steam. The energy input to the CLES is primarily used to support the endothermic reduction phase of the redox reaction while the hot gases generated during the oxidation phase are expanded through a power turbine-generator set for production of electricity. The waste heat from the exhaust of the turbine is used to produce other products (heat, hot water, cooling using an absorption chiller, hydrogen through either electrolysis of chemical reactions).

[0046] The CLES technology can be operated in two different modes namely: (i) the energy on demand mode and (ii) the energy storage mode. Depending on the mode of operation the energy input to the CLES can be a liquid or gaseous form of fossil fuels (e.g. diesel fuel or natural gas etc.) or electricity originating from “clean energy sources”, such as renewable energy sources, or from conventional grids.

[0047] In the energy on demand mode the energy input from natural gas (or diesel fuel, bio-diesel, or similar fuels) is converted to power, heating, cooling, hot water, oxygen and hydrogen on a continuous basis. This allows the system to operate independently from the electricity grid and thereby facilitates the concept of distributed power generation. The use of natural gas is preferred as it has one third of greenhouse gas emissions when compared with other types of solid fuels like coal.

[0048] In the energy storage mode, the CLES technology operates in a batch mode whereby the off-peak and hence cheap electricity (from renewable sources such as wind or solar or from conventional power plants) is used during off-peak hours to carry out the reduction of the metal oxide particles. During this endothermic process oxygen is produced which can be either stored or utilised. Over the peak-hours period the oxidation phase of the redox cycle is promoted by reacting reduced metal particles with air. During this exothermic process, a considerable quantity of heat is generated which can then be used to drive a turbine-generator set for electricity production and other energy products listed above.

[0049] Referring now to Figure 1, an embodiment of the invention is illustrated operating in the on-demand mode. The apparatus 1 comprises a reduction reactor 2 and an oxidation reactor 3 fluidly connected so that oxygen carrier particles 4a, 4b (in this embodiment in the form of metal oxide particles) can be transferred between the reactors 2, 3. An outlet conduit 5 is arranged transfer an oxygen-enriched mixture from the reduction reactor 2 to an oxygen storage unit 6. Both the reduction reactor 2 and the oxidation reactor 3 are fluidised bed reactors. However, in other embodiments the reduction reactor 2 and the oxidation reactor 3 can be any other type of chemical reactor, such as a fixed-bed or spouted-bed reactor.

[0050] The reduction reactor 2 is located within the oxidation reactor 3. That is, the reduction reactor 2 is contained within or inside the oxidation reactor 3. However, it will be appreciated that in other embodiments, the reduction reactor 2 may be located partly within the oxidation reactor 3. Also, in the present embodiment, the reduction reactor 2 is substantially smaller in size than the oxidation reactor 3. In any event, this “twin reactor” configuration is a unique design developed by the inventors.

[0051] The reduction and oxidation reactors 2, 3 are fluidly connected by an inlet conduit 7 and an outlet conduit 8. The inlet conduit 7 transfers the oxygen carrier particles 4a from the oxidation reactor 3 to the interior of the reduction reactor 2, where they undergo a reduction reaction to release or generate oxygen, as described in more detail below. The outlet conduit 8 transfers oxygen-depleted carrier particles 4b from the reduction reactor 2 to the oxidation reactor 3 and are replenished with oxygen in the oxidation reaction and ready to be transferred to the reduction reactor 2.

[0052] In the illustrated embodiment, the reduction reactor 2 is embedded in the bed 9 of the oxidation reactor 3. By this configuration, an outer surface 10 of the reduction reactor 2 is maintained at a temperature almost the same as that of the bed temperature of the oxidation reactor 3. This arrangement minimises the overall heat losses and as such leads to higher overall thermal efficiencies. Given its high temperature, the outer surface of the reduction reactor 2 becomes very critical in maintaining the correct temperature gradient and thus driving force for the reduction reaction.

[0053] In other embodiments, the reduction reactor 2 may be located adjacent to or partly within the bed of the oxidation reactor 3, instead of within the bed.

[0054] The apparatus 1 in Figure 1 is incorporated into a system 20 for generating oxygen and storing energy. The system 10 comprises a conduit 21 that delivers water from a condenser 22 and a pump 23 (as well as an optional water supply 24 to provide additional made up water) to a heat exchanger 25 to generate steam that is then delivered by conduit 26 as a gas stream into the reduction reactor 2. The reduction reactor outlet 5 transfers an oxygen-enriched gas mixture produced by the reduction reaction in the reduction reactor 2 to the heat exchanger 25 to provide the heat that generates the steam. The now cooler oxygen-enriched gas mixture passes to the condenser 22 via a conduit 27, where oxygen is removed and transferred by the conduit 28 to the oxygen storage unit 6 for future use as oxygen or to generate energy.

[0055] The heat generated during the oxidation of the metal oxides in the oxidation reactor 3 is completely extracted by the inlet air flow and is transferred to another heat exchanger 30 via a conduit 31. The cooler gases then pass to a cooler unit 32 via a conduit 33 before being exhausted out of a discharge line 34. A water supply line 35 may be used to heat water in the cooler unit 32, which can then be used for various purposes via a conduit 36. Air is also from an air supply (not shown) can be delivered by a pump 37 via and a conduit 37 to the heat exchanger 30 to preheat and compress the air. A conduit 39 takes the preheated compressed hot air to a booster 40 where it is superheated to a high temperature before entering into a turbine (in this embodiment, an indirectly fired gas turbine, such as a hot air turbine 42) via a conduit 43 for the purpose of increasing power generation efficiency. The superheated air expands through the turbine 42 and produces both heat and power. The waste gas from the turbine 42 is then taken by a conduit 44 to the cooler unit 32 and/or to the oxidation reactor 3 to fuel the oxidation reaction.

[0056] In operation, the system 20 involves metal oxide oxygen carrier particles 4a, 4b being continuously circulated between the oxidation reactor 3 and the reduction reactor 2. While in the reduction reactor 2, the metal oxide particles 4b undergo reduction reaction at temperatures about 950°C in the presence of a sweep gas (steam in this case) and produces oxygen-enriched gas mixture. The reduction reactor 2 is indirectly heated either by combustion of a fuel such as natural gas or diesel in the energy on demand mode or by electrical heating (joule heating) in the energy storage mode. The same energy sources are used to generate the required quantities of steam from the water derived from the condenser 22.

[0057] The oxygen-enriched stream passes through the heat exchanger 25 so that the heat content of the gases can be recycled for preheating the inlet stream of steam entering the heat exchanger 25 via the conduit 21. Pure oxygen is then produced and stored by further condensing the oxygen-enriched stream in the condenser 22 and the later compressed in an oxygen compressor (not shown) before being stored in the oxygen storage tank 6. The condensate from the condenser 22 is recycled back to the reduction loop via the pump 24 so that the water usage in the system 20 (as part of a power plant) can be kept at minimum.

[0058] The reduced metal oxide oxygen carrier particles then pass from the reduction reactor 2 via the outlet conduit 8 and on the way to the oxidation reactor 3 are oxidised in the presence of the exhaust air exiting the hot air turbine 42 incoming via the conduit 44. The amount of exhaust air entering into the oxidation reactor 3, however, is only a split ratio of the turbine exhaust. This air split ratio is adjusted to a certain level so that the metal oxides can be fully oxidised whilst the air flow into the reactors is kept at a minimum which hence reduces the required size of the reactor. This means that there is a smaller footprint for the reactors and hence the apparatus 1 and system 20.

[0059] The makeup water from the water supply 23 may be needed in the condenser 22 with possible blow-off being discharged via a line 45 to a drain system (not shown). In the oxidation loop, the combustion product gas from the turbine 42 and the reduced air exiting the oxidation reactor 3 are joined together via conduits 33 and 44 and enter the cooler unit 32. Waste heat can be recycled from these exhaust gas streams in the cooler unit as discussed above and used for HVAC applications.

[0060] Also, additional energy inputs 50, 51, 52 may also be provided to the oxidation reactor 3, reduction reactor 2 and the booster 40, respectively, to assist in supplying sufficient energy/heat to drive the oxidation, reduction and superheating processes.

[0061] The arrangement of the reduction reactor 2 inside the oxidation reactor 3 ensures that the heat generated from the oxidation reaction in the oxidation reactor 3 maintains the reduction reactor 2 at a higher temperature than the oxidation reactor 3 due to the additional supply of heat from the incoming steam from the conduit 26.

[0062] The arrangement of the reduction reactor 2 inside the oxidation reactor 3 ensures that the heat generated from the oxidation reaction in the oxidation reactor 3 maintains the reduction reactor 2 at a higher temperature than the oxidation reactor 3 due to the additional supply of heat from the incoming steam from the conduit 26.

[0063] If operated in the energy storage mode, the CLES system is able to reallocate excess power at off-peak hours for the use in peak-hours period by its storage feature. For this storage mode, the reduction reactor 2 and the oxidation reactor 3 function independently in a batch operation mode. The power at off-peak time heats both the reduction reactor 2 and the oxidation reactor 3 to desired temperature levels; an adequate temperature in the reduction reactor 2 for facilitating the oxygen release and a suitable bed temperature retained for the oxidation reactor 3. In the storage mode, the oxidation reactor 3 is maintained at a temperature as low as the oxidation reaction of oxygen carrier particles is restricted or hardly occurs by a small amount of power from off peak hours. Hence, instead of continuous circulation, the oxygen carrier particles are intermittently exchanged between the reduction reactor 2 and the oxidation reactor 3. All the solid particles in the reduction reactor 2 undergoes the reduction reaction to release oxygen until completion, during which no exchange of oxygen carrier particles occurs between the reduction reactor 2 and the oxidation reactor 3. Subsequent discharge of the reduced particles from the reduction reactor 2 to the oxidation reactor 3 is accomplished at a temperature similar to that in the oxidation reactor 3. Meanwhile, refilling of the reduction reactor 2 for the next reduction period is performed by transferring the oxidised particles from the oxidation reactor 3 to the reduction reactor 2. While some reduced particles will be transported back to the reduction reactor 2 during the transfer step between the two reactors, this situation can be minimised by manipulating the energy storage cycle. For example, during the peak hours for electricity use, the bed temperature of oxidation reactor 3 in the CLES system is slightly elevated to

stimulate the oxidation reaction, and once oxidation has started, a significant amount of heat will be released for power generation to meet the incremental demand of electricity. Given the larger size of the oxidation reactor 3 in comparison to the reduction reactor 2 for, a few reduction steps could proceed during off-peak period whereas only one oxidation step can be achieved during peak hours.

[0064] The benefit of the design using the reduction reactor at least partly (and preferably fully) within the oxidation reactor is that there is a minimisation of the system heat loss and a maximisation of the efficiency of the redox reaction. According to the reaction thermodynamics, at equilibrium the oxygen partial pressure is higher at high temperatures. Hence, larger quantities of oxygen can be stripped from normal air (with an oxygen partial pressure of 0.21) if the oxidation reaction is carried out at lower temperatures. In contrast, if the reduction is performed at the highest possible temperatures then larger quantities of oxygen can be released by the metal oxide particles. In the embodiment of the invention this is achieved by placing the reduction reactor 2 within the oxidation reactor 3 to achieve these higher temperatures. More importantly, a much lower quantity of steam (and hence, a substantial reduction in input energy) is required for the reduction reaction, allowing much smaller reduction reactors to be used, which in turn lowers the cost in capital expenditure and maintenance.

[0065] This relationship between the oxygen partial pressure and reaction temperature during the redox reaction inspired the inventors to design the process in which the reduction reaction is carried out at temperatures higher than those for oxidation reaction. Preferably, these temperatures are about 100°C to 150°C higher than the oxidation reaction temperature. This unique approach is quite different from conventional redox based chemical looping air separation methods where oxidation temperature is always maintained at higher levels than reduction temperatures.

[0066] Additional benefits of this design are that it overcomes several critical shortcomings that would occur if the process employing a higher temperature reduction reaction relative to the oxidation reaction were used in a single reactor design, where a manifold switches the operation of the single reactor between oxidation and reduction reactions. These shortcomings include:

- the issue associated with manifold switching to the same reactor over repeated half cycles, where the reactor needs to be purged between each

half cycle with a sweep gas like nitrogen, resulting in delays between successive half-cycles leading to interrupted oxygen and power generation;

- heat management problems caused by switching from high temperature reduction to a lower temperature oxidation;
- dilution of oxygen product for reduction half cycle due to the unburnt air residue remained upon the gas switching from oxidation half cycle; and
- little saving in construction costs since the single reactor has to be the size of the oxidation reactor in twin reactor configuration.

[0067] By way of non-limiting example only, a case study of one industrial application of the embodiment of the invention will now be described with reference to Figures 2 to 8 in the context of the steel making industry. Steel making is a highly energy intensive process accounting for nearly 5% of the world's total energy consumption and approximately 6.7% of total world CO₂ emissions. The rising energy cost and high demand for reducing greenhouse gas emission represents a major challenge for the steel industry. Currently, approximately 17% of the operating cost of the steelmaking industry comes from energy consumption, which originates from multiple sources, such as coal, electricity, natural gas, recycled coke oven gas (COG) and blast furnace gas (BFG). Although measures to significantly reduce the energy intensity of the industry has taken place during the past few decades, innovations such as waste energy recycling and alternative oxygen production technique can help further improve energy efficiency, reduce costs and emissions of the modern-day steelmaking process.

[0068] Oxygen, as a key component in the basic oxygen furnace for steel production, is currently produced from cryogenic air separation unit (CASU) in large quantity, which is an energy intensive process (0.43 kWh/Nm³). The oxygen usage in the basic oxygen furnace was estimated to be 50 Nm³ per tonne of steel production. For a 100 tonne/hour (~ 0.8 million tonnes per year) integrated steelmaking plant, the annual oxygen requirement can be greater than 44 million Nm³, which requires greater than 19 million kWh of electricity per year (or ~ \$4 million/year of electricity).

[0069] Accordingly, it is contemplated that the embodiment of the invention may be employed as a less energy intensive option for oxygen production in order to reduce the

energy penalty associated with plant oxygen demand. In addition, the inventors contemplate that the CLES system and, in particular, the apparatus 1 is adapted for use in a RES configuration (which for ease of convenience will be referred to as a RES unit 100), which acts as an energy storage facility to help balance the electricity/thermal consumption and demand of the steelmaking plant.

[0070] In Figure 2, the REST unit 100 comprises the apparatus 1 (taking the form of the twin reactor 102 having the reduction reactor inside the oxidation reactor as described above) fluidly connected to heat exchangers 103, 104, a condenser 105 and a steam turbine 106 (instead of an indirectly fired gas turbine). A reduction loop 110 is formed by a conduit 111 connecting the twin reactor 102 to the heat exchanger 4 and condenser 5, and a conduit 12 connected the apparatus 1 to an input gas supply 13 described in more detail below. An oxidation loop 115 is formed by a conduit 116 connecting the twin reactor 102 to the heat exchanger 103 and an air supply 117, and a conduit 118 connecting the twin reactor 102 to a discharge conduit 119. Valves 120, 121 close off the reduction loop 110 from the twin reactor 102 while valves 122, 123 close off the oxidation loop 115 from the twin reactor 102. In this way, the twin reactor 102 can be operated to performed oxidation or reduction separately. Moreover, the oxidation process is performed continuously whenever the oxidation loop 115 formed or opened and the reduction loop 110 is closed off. Likewise, the reduction process is performed continuously whenever the reduction loop 110 is opened and the oxidation loop 115 is closed off.

[0071] In the intermittent operational mode, the reduction loop 110 is formed by closing valves 122, 123 to seal off the oxidation loop 115 and opening valves 120, 121 to enable gas to flow through the conduits 111, 112. The reduction loop 110 is operated during the off-peak hours of electricity usage (i.e. at night time), where the metal oxide oxygen carrier particles in the fluidised bed of the twin reactor 102 undergo a reduction reaction in the presence of the input gas, which in this case is a sweep gas added via the conduit 113 from the gas source supply 112. The sweep gas in this case is H_2O , but in other embodiments, the sweep gas can be any inert gas (examples may include CO_2 , argon or helium) that can be easily separated by membrane or any separation method after the reduction step to produce pure oxygen stream. The reduction process consumes relatively cheap electricity (or thermal energy originating from carbon-based fuels) using an electric heater or boiler and produces an oxygen-enriched stream primarily containing oxygen and water that passes from the twin reactor 102 through the

conduit 111 and valve 121 to the heat exchanger 104. In the heat exchanger 104, waste heat from the stream is recycled to preheat the incoming water before it is fed into the twin reactor 102. The produced oxygen is purified from the oxygen-enriched stream by the condenser 5, which condenses the oxygen-enriched stream to separate oxygen from water and thus producing pure oxygen. The pure oxygen is then sent for downstream use and/or storage. The condensate comprising mostly of water is then recycled from the condenser 105 via a conduit 130 back to the reduction loop 110 by joining the incoming water in the conduit 112, through the valve 120 and heat exchanger 104, and then to the twin reactor 102.

[0072] The RES unit 100 is then moved to the oxidation process by closing the valves 120, 121 and opening valves 122, 123 to form the oxidation loop 115. The oxidation process in the oxidation loop 115 is performed during the peak hours (i.e. at day time), where the reduced metal oxide oxygen carrier particles in the fluidised bed 109 are now oxidised in the presence of air which is introduced by the valve 122 from the air supply 117. The air is preheated by a waste stream conveyed by the discharge conduit 119 via the heat exchanger 103. The oxidation process in the twin reactor 102 generates heat that can be extracted by different ways such as gas (steam or air), liquid (organic or inorganic) and solids (sand or ceramic). For example, in the embodiment, heat is extracted by using a separate conduit 135 carrying water from a water supply 138 to embedded water tubes (not shown) in the twin reactor 102 to produce hot water or steam for heat and/or power generation purposes. The hot water or steam is directed to the turbine 106 via a conduit 140 to produce electricity. The oxygen depleted air (also called reduced air) comprising mostly of nitrogen N_2 is removed from the twin reactor 102 as the waste stream via the discharge conduit 119. The waste stream passes through the heat exchanger 103 to preheat the incoming air and then is discharged to the ambient environment through an outlet 145.

[0073] As indicated above, the method and apparatus 1 or twin reactor 102 may use different oxygen carrier particles for oxygen production, such as MnO_2/Mn_2O_3 , Mn_2O_3/Mn_3O_4 , CoO/Co_3O_4 , CuO/Cu_2O and mixed metal oxide particles. It will be appreciated that in other embodiments, the process (intermittent or continuous) uses a variety of other suitable oxygen carrier particles. In this case, the RES unit 170 used CoO/Co_3O_4 and CuO/Cu_2O as the oxygen carrier particles due to their high oxygen transport capacity (OTC) and reactivity.

[0074] The RES unit 100 does not require external heating since the heat produced in the oxidation reactor 3 is usually sufficient to provide the necessary heat required in the reduction reactor 2. As discussed above, the reduction reactor 2 operates at a greater temperature than the temperature of the oxidation reactor 3 to achieve a greater oxygen partial pressure, generate a greater oxygen content in the gas product and reduce the usage of sweep gas (e.g. steam). Nevertheless, most of the external energy will be released in the form of high-temperature heat from the oxidation reactor and can be utilised for other on-site applications.

[0075] However, it may be beneficial to supplement the heat provided by the oxidation reactor 3 to ensure that the reduction reactor 2 remains at this higher operating temperature. A summary of the main options for the external heat sources that can be used in the RES process is set out in the table below, with their advantages and disadvantages briefly discussed.

Table 1: Supplementary Heating Options

Energy sources	Concept	Cost	Pros.	Cons.
Coal (or biomass)	Similar to Chemical looping combustion (CLC) or Chemical looping oxygen uncoupling (CLOU)	Low	Low cost fuel; Low rank coal; Insensitive to the wetness of coal;	Require an extra amount of oxygen for combustion; solid handling issues (e.g. ash separation); Greenhouse gas (GHG) emission
Natural gas (or other gaseous fuels)	Direct or indirect heating via methane combustion	Low-medium	Gaseous fuel	Require an extra amount of oxygen for combustion; May react with steam. Less efficient than Natural gas combined cycle (NGCC) in terms of natural gas utilisation.

Energy sources	Concept	Cost	Pros.	Cons.
Electricity	Utilise low-cost off-peak electricity to heat the reduction reactor, then regenerate part of the electricity during peak periods via the oxidation reactor	Medium - high	Low-cost off-peak electricity is being used; demand electricity generation.	High exergy destruction (~2/3 thermal losses); demand driven.
Concentrated solar energy	Utilise solar thermal energy supplied by a solar tower	Very high	Clean source energy	Expensive; immature technology;
Hydrogen	Direct or indirect heating via combustion	Very high	Clean source energy	Require an extra amount of oxygen for combustion; expensive;

[0076] The integration between a RES unit 100 and an integrated steelmaking plant can become quite mutually beneficial. Currently, oxygen, steam, heat, and electricity (90% derived from coal, excluding oxygen) are being used in the integrated steelmaking plant. The RES process has the ability to deliver all of these energy and gas products. Conversely, the significant amount of heat demand in the reduction reactor of the RES unit 100 can be supplemented by direct/indirect firing of either on-site coal, natural gas, or the waste gases of the steelmaking process (e.g. COG and BFG). Alternatively, the low-cost off-peak electricity can also be used for this purpose via joule heating. The energy contained in the above forms (solid, gaseous fuels and electricity) can be said to be temporarily stored in the reduction reactor 2 of the twin reactor 102. This energy can then be released from the oxidation reactor 3 whenever they are required. Such an energy storage concept is also applicable to many other industrial processes where energy storage is found advantageous, such as coal plants, solar plants and wind farms.

[0077] When joule heating is employed using the low-cost and sometimes wasted off-peak electricity, the RES unit 100 then acts as an off-peak electricity storage “tank” to absorb as much off-peak electricity generation as possible from coal-fired power plants. This can be quite beneficial for the coal-fired power plants as it allows them to run more frequently on full loads with greater generation efficiency. Note that coal-fired power plants are normally operating at partial loads during low demand periods, which is highly inefficient and contributes to a great amount of greenhouse gas emissions. In addition, the stored low-cost off-peak electricity can be regenerated for on-site uses during the peak periods when the electricity price is doubled or even tripled. This concept, however, suffers from potentially significant energy losses during the electricity regeneration process, namely $\sim 2/3$ losses during the heat-to-electricity conversion.

[0078] In addition to power generation, the heat released from the RES unit 100, mainly that comes from the oxidation reactor and other low-grade waste heat, could be used to either generate steam via the existing boiler to offset the plant steam usage, or provide heat for numerous on-site heating purposes, e.g. furnace preheating, reheating of steel, reheating of fuel before entering to a hot stove, heating of facilities and etc. The produced steam can be used for the treatment of semi-finished products, powering pump/compressors, facility heating, and electricity generation. The energy for steam production in an integrated steelmaking plant has been estimated to be up to 10% of the total energy consumption. When the majority of the produced heat from a RES unit 100 is for power generation, the generated electricity can be used for producing compressed air, pumping, rolling steel, rolling mills, driving conveyors and fans, and powering materials handling equipment and other ancillary processes. It has been estimated that 13% of the energy consumption in iron and steel making process was in the form of electricity, the production of which accounted for an even higher percentage ($\sim 33\%$) of the total raw energy and fuel usage. Therefore, using a RES process to simultaneously produce oxygen, steam, heat, and electricity is expected to generate great synergies, reducing energy intensity and providing cost benefits for the iron and steel industry.

[0079] Figure 3 shows the overall processes involved with the intermittent operational mode, where the CLAS process 150 receives air and water as inputs 152 and produces reduced (oxygen depleted) air 153 and an oxygen enriched stream 155 that passes through two cooling stages 156, 157 (to exchange heat with the incoming air and water) before undergoing oxygen separation at 160. The pure oxygen produced at 163 is then

sent for use in either industrial or medical applications while the water that remains is recycled at 165.

[0080] Referring to Figures 4 and 5, another exemplary RES unit 170 is illustrated and comprises the twin reactor 102 schematically illustrated for clarity as separate reduction and oxidation reactors 172, 173. In Figure 4, in the oxidation loop 115, air from the air supply 117 is passed through an air compressor 168 before entering the oxidation reactor 173 and then the oxygen depleted air passes through a booster 166 and a hot air turbine 167 before being discharged via outlet 145. In contrast, in Figure 5, in the oxidation loop 115, air from the air supply 117 is passed through an air blower 180 before passing through the heat exchanger 103 for preheating before entering the oxidation reactor 173 and oxygen depleted air is then removed via outlet 145. In both Figures 4 and 5, the reduction loop 110 involves the water being pumped into the reactor 172 via a pump 175 from a water supply source 177 and heat exchangers 179 being used to generate steam from the oxygen enriched stream 155 for power generation prior to being sent to the condenser or other oxygen separation unit. In this embodiment, the RES unit 170 has the mineral/metal oxide particles transferred between the reduction and oxidation reactors 172, 173. The reactors 172, 173 are connected to pass the oxygen carrier particles as described above between each other to create the chemical looping process.

[0081] In a continuous mode, the RES unit 170 was simulated at a production capacity of 5,000 m³/hr of oxygen over a 24-hour day, which is considered to be a standard unit in this case study. The oxygen production capacity of a standard RES unit meets the oxygen requirement of a large-scale 100 tonne/hour steelmaking plant (i.e. an annual production rate of ~ 0.8 million tonne of steel).

[0082] In an intermittent mode, the RES unit 170 was simulated to operate the oxidation reactor 173 and reduction reactor 172 intermittently during peak and off-peak periods, respectively. In this mode, no oxygen but only electricity is produced during the peak period. That is, during the period in which the oxidation process is performed, no oxygen is produced by the oxidation reactor 173 in the RES unit 170. Rather, only electricity is generated with the oxidation process enriches the oxygen-depleted carrier particles with oxygen for subsequent use in the reduction process. It was estimated that for sustaining a continuous oxygen supply of 5,000 m³/hr over 24 hours, the intermittent operation of the RES unit 70 would require at least 2.7 standard RES units to be built and operating during the 9 hour off-peak period (approximately from 10pm to 7am in the night phase) to be able to produce enough oxygen (i.e. a total of 120,000 m³) for a full

day load. Of this amount of produced oxygen, 45,000m³ is consumed during the same off-peak period while the rest (being 75,000m³) is stored in an oxygen tank (such as the tank 6 of Figure 1) and consumed during the next 15-hour peak period (during the day phase), all at a constant consumption rate of 5,000 m³/hr. It is contemplated that this arrangement of 2.7 standard RES units is capable of meeting the oxygen requirements of a steelmaking plant for producing 100 tonnes per hour of steel.

[0083] To better understand the impact of the operating mode on the integration of RES unit 170 with the steel making plant, the performance of one standard RES unit operating in the continuous production mode was analysed and the performance indices were adjusted accordingly for the RES unit 170 operating under the intermittent production mode. On that basis, the integration options between the RES unit 170 and the reference steelmaking plant were then analysed.

[0084] Table 2 shows the operating conditions, material requirements, energy demands, and energy and oxygen production for the standard RES unit 170 using CuO as the oxygen carrier particles. These parameters are shown for three different reduction reaction temperatures, namely 1040°C, 1077°C, and 1102°C, which correspond to low (25%), medium (50%), and high (75%) levels of oxygen partial pressures of the product stream (i.e. the oxygen enriched stream). It can be seen in Table 2 that as the oxygen partial pressure increases from 25% to 75% the minimum water requirement of the RES process is reduced significantly from 10,300 kg/hr to 1,200 kg/hr (or by 88%). This reduced water consumption not only helps efficient use of water but more importantly leads to a reduced energy penalty associated with steam generation and hence results in a reduced process heating demand (by up to 28%). Moreover, the cooling demand for oxygen-water separation process is also greatly reduced by up to 88%. It thus suggests a higher oxygen partial pressure is preferable in the operation of the RES unit 170, although the oxygen partial pressure should be determined after considering the maximum allowable operating temperature of the twin reactor 102 and its materials. For instance, the reduction reactor temperature at 1102°C for achieving an oxygen partial pressure of 75% would be considered to be too high for copper-based oxygen carriers due to a high potential in the occurrence of sintering/aggregation issues.

[0085] The oxygen production of the process was found to be around 5,000 m³/hr with an oxygen purity of 96% before the oxygen compression process. The oxygen purity can be increased further to 99.9% depending on the targeted applications by further

compressing the gases, enhancing the oxygen-water separation process and other oxygen purification processes.

Table 2: Technical analysis of the standard RES unit using CuO as the oxygen carrier particles

Parameters	Items	Units	Value	Value	Value
Operating conditions	Oxygen partial pressure during the reduction reaction		0.25	0.50	0.75
	Reduction reaction temperature	°C	1040	1077	1102
	Oxygen partial pressure during the oxidation reaction		0.05	0.05	0.05
	Oxidation reaction temperature	°C	950	950	950
Material requirements	Minimum required water flow	kg/hr	10300	3400	1200
	Minimum required air flow	kg/hr	32300	32300	32300
	CuO flow	kg/hr	61500	61500	61500
Energy demands	Heating demand of the reduction reaction	kWt	18100	13500	13000
	Pump power consumption	kW	0.09	0.03	0.01
	Compressor power consumption*	kW	230	230	230
	Condenser cooling demand [#]	kWt	6700	2300	800
Energy generation and oxygen production	Heat generation of the oxidation reaction	kWt	11200	11100	11000
	Oxygen flow	m ³ /hr	5000	5010	5020
	Oxygen purity		0.96	0.96	0.96

[#] Potential heat recovery points.

* Pressure rise over the compressor was assumed to be 25 kPa.

[0086] Similarly, Table 3 gives the main technical analysis results for the standard RES unit 170 using CoO as the oxygen carrier particles. The analysis was performed for

the same levels of oxygen partial pressures as those in Table 2 above but at lower temperatures, namely 894°C, 913°C, and 925°C. From Table 3, it can be seen that the minimum water and air requirements as well as the later cooling demand requirements for oxygen-water separation are almost the same as those of the copper case in Table 2 above. This is because that the two cases share the same oxygen production rate and same oxygen partial pressure in the production (oxygen enriched) stream. However, the minimum required inventory of cobalt oxide is 51% greater than that of copper oxide given the same oxygen production capacity. The heating demand of the reduction reaction for the cobalt oxide oxygen carrier particles was also found to be greater than that of the copper oxide oxygen carrier particles.

Table 3: Technical analysis of the standard RES unit using CoO as the oxygen carrier particles

Parameters	Items	Units	Value	Value	Value
Operating conditions	Oxygen partial pressure		0.25	0.50	0.75
	during the reduction reaction				
	Reduction reaction temperature	°C	894	913	925
	Oxygen partial pressure		0.05	0.05	0.05
	during the oxidation reaction				
Material requirements	Oxidation reaction temperature	°C	847	847	847
	Minimum required water flow	kg/hr	10400	3400	1200
	Minimum required air flow	kg/hr	32300	32300	32300
	Co ₃ O ₄ flow	kg/hr	93100	93100	93100
Energy demands	Heating demand of the reduction reaction	kWt	26700	22000	21100
	Pump power consumption	kW	0.09	0.03	0.01
	Compressor power consumption*	kW	230	230	230
	Condenser cooling demand [#]	kWt	6900	2300	800
Energy generation and	Heat generation of the oxidation reaction	kWt	19600	19500	19400

oxygen production	Oxygen flow	m ³ /hr	5000	5010	5020
	Oxygen purity		0.96	0.96	0.96

#. Potential heat recovery points. *. Pressure rise over the compressor was assumed to be 25 kPa.

[0087] For both cases, the heat stored during the off-peak period will be released during the peak period in the form of high-, medium-, and low- grade heat. The amount of that heat was quantified and shown in Table 4 below, where it shows that the energy inputs for all examined scenarios were found nearly the same as the energy outputs if the produced low-grade heat is considered recyclable. Interestingly, Table 4 also shows that for both copper oxide oxygen carrier particles and cobalt oxide oxygen carrier particles, as the oxygen partial pressure of the product stream increases, the amount of produced low-grade heat (originated from the oxygen-water separation process) is greatly reduced, leading to less energy penalty. In addition, a specific power demand of the RES unit 170 of about 0.08 kWh/m³ was found consistent for all examined scenarios after taking into account the electrical energy demand, the recoverable energy production, and any energy losses of the process. This number represents a significant energy discount at about 81 - 92% when compared with the typical specific power demands of large CASU units at 0.43-0.55 kWh/m³ of oxygen and small-medium scale PSA processes at 0.8-1 kWh/m³ of oxygen.

Table 4: Overall performance comparison of the standard RES units using CuO and CoO as the oxygen carrier particles.

Parameters	Units	CuO case			CoO case		
Oxygen partial pressure during the reduction reaction		0.25	0.50	0.75	0.25	0.50	0.75
Reduction reaction temperature	°C	1040	1077	1102	894	913	925
Oxidation reaction temperature	°C	950	950	950	847	847	847
Electrical/thermal energy demand	kW(t)	18100	13500	13000	26700	22000	21100
Compressor power demand	kW	230	230	230	230	230	230

Parameters	Units	CuO case			CoO case		
Generated low-grade heat [#]	kWt	6700	2300	800	6900	2300	800
Generated medium-grade heat [#]	kWt	0	0	1000	0	0	700
Generated high-grade heat [#]	kWt	11200	11100	11000	19600	19500	19400
Specific power demand of RES	kWh/m ³	0.08	0.08	0.08	0.08	0.08	0.08

[#]. The low-grade, medium-grade, and high-grade heat refers to heat produced at temperatures <100°C, 100°C - 600°C, and >600°C, respectively in general.

[0088] These performance results of the standard RES unit 170 were directly applied when integrating the RES unit 170 with the steelmaking plant under both continuous and intermittent production modes. For the continuous production mode, there are several integration options depending on the choice of the heat source for the RES unit 170, which have different impacts on the applicability of the RES process. For example, when solid fuel (on-site coal/coke) or gaseous fuels (COG, COG/BFG mixture, and natural gas) are used for reactor heating via a direct heating arrangement, they contain a high percentage of moisture, carbon dioxide, and other impurities. This may lead to difficulties not only in the oxygen separation and purification processes but also in the direct application in the basic oxygen furnace (where pure oxygen is used). In a further example, using coal as the heat source results in the direct heating approach leading to the production of a gaseous product containing, on a dry basis, up to only 45% volume of O₂ with the rest being CO₂ depending on the reactor temperature and steam flow rate. Such a high percentage of CO₂, though not directly affecting the process of reducing iron to steel in the basic oxygen furnace, would reduce flame temperature and affect impurity control of steel production (e.g. carbon content). Using carbon containing gaseous fuels in this fashion have similar problems. Therefore, the direct heating approach is not a viable option in terms of reduction of CO₂ emissions. Nevertheless, it can remain as a possible integration option if and when the produced high-CO₂ containing oxygen product can become useful in the steelmaking plant or other nearby chemical processes or the amount of CO₂ can be safely minimised or eliminated.

[0089] Conversely, the indirect heating approach may be more appropriate for the current application, which uses solid/gaseous fuels as the indirect heating source for the reduction reaction without contaminating the oxygen product. In this way, high purity

oxygen product can be produced for direct uses in the basic oxygen furnace. The only variant of the different integration options, as a result of using various heating sources, seems to be the different heating values of those fuels. Table 5 shows the calculated requirements of coal, coke, COG, BFG, and natural gas if the RES unit 170 uses one of them as a supplementary indirect heating source.

Table 5: Individual fuel requirements of the standard RES units using CuO and CoO as the oxygen carrier particles based on a 100 tonne/hour steel making plant.

Parameters	Units	On-site resource availability	CuO case			CoO case		
Oxygen partial pressure during the reduction reaction		-	0.25	0.50	0.75	0.25	0.50	0.75
Thermal energy demand	kW(t)	-	18100	13500	13000	26700	22000	21100
Requirement of Coal*	kg/h	30375 (dry coal) [#]	3103	2314	2229	4577	3771	3617
Requirement of Coke*	kg/h	24300 ^{##}	2247	1676	1614	3314	2731	2619
Requirement of COG*	Nm ³ /h	37736 ^{##}	3620	2700	2600	5340	4400	4220
Requirement of BFG [^] *	Nm ³ /h	152000 ^{##}	20111	15000	14444	29667	24444	23444
Requirement of natural gas*	Nm ³ /h	Variable	1724	1286	1238	2543	2095	2010

* Assuming the higher heating value of coal, coke, COG, BFG, and natural gas are 21 MJ/kg, 29 MJ/kg, 5 kWh/Nm³, 0.9 kWh/Nm³, and 10.5 kWh/Nm³ respectively.

[#] Assuming 80% of dry coal is converted into coke.

^{##} According to reported data on the typical production and consumption.

[^] The calculation shown here is purely theoretical for reference purposes only. BFG alone may not be a suitable option for supplying heat for the reduction reactor due to its low flame temperature. BFG can be better used by blending with other higher quality gases (e.g. COG/natural gas).

[0090] These calculated requirements, when compared with the availability of those fuels in the steel making plant, show that sufficient heat source is available on-site for the RES process to fully meet the oxygen demand of the basic oxygen furnace. On average such heating requirements can be estimated to be roughly 1/10 of the coal, coke, COG, or BFG that is currently consumed/produced in the 100 tonne/hour steel making plant. The feasibility of using natural gas as the external heat source highly depends on its availability and cost in the vicinity of the steel making plant. Lastly, under the continuous production mode, the option of using joule heating (i.e. electricity) to provide the heat for the reduction reactor of the RES unit 170 was not practical because only about one third of that energy can be repaid during the heat-to-electricity generation, namely two third of the electricity is lost. This translated to an extremely high specific energy demand of the RES process at ~ 2.9 kWh/m³, which is mostly unacceptable.

[0091] As mentioned above, the intermittent operation of the RES unit 170 would require at least ~2.7 standard units to be built. With this configuration, Table 6 gives the performance of the 2.7 standard RES units for both the peak and off-peak periods. As Table 6 shows, the total electrical energy demands of these RES units using Cu-based oxygen carriers were found to be 321-445 MWh (or 518-654 MWh for the CoO case) during the oxygen production period depending on the reduction reactor temperature. This electrical energy could then be recovered during the peak period in the forms of low, medium, and, high-grade heat, of which the high-grade heat is converted into electricity and the rest can be used for heating/steam generation. The oxygen being produced during the off-peak period at 120,000 m³ can be consumed at a constant rate of 5000 m³/hr for both the peak and off-peak period via the use of an oxygen storage tank.

Table 6: Overall performance comparison of 2.7 standard RES units using CuO and CoO as the oxygen carrier particles for intermittent operation

Parameters	Units	CuO case	CoO case
During the 9-hour off-peak period			

Parameters	Units	CuO case			CoO case		
Oxygen partial pressure during the reduction reaction		0.25	0.50	0.75	0.25	0.50	0.75
Reduction reaction temperature	°C	1040	1077	1102	894	913	925
Oxidation reaction temperature	°C	950	950	950	847	847	847
Electrical energy demand	MWh	445	334	321	654	540	518
During the 15-hour off-peak period							
Generated low-grade heat [#]	MWh	163	56	19	168	56	19
Generated medium-grade heat [#]	MWh	0	0	24	0	0	17
Generated high-grade heat [#]	MWh	272	270	267	476	474	471

#. The low-grade, medium-grade, and high-grade heat refers to heat produced at temperatures <100°C, 100°C - 600°C, and >600°C, respectively in general.

[0092] In an attempt to recover more energy, a hot air turbine can be implemented in the oxidation loop of the RES unit 170, as best shown in Figure 6. This configuration is believed to improve the energy efficiency of the RES process. The improvement or modification was made primarily in the oxidation loop 115, in which an air compressor 190 is added to compress the inlet air. The compressed air then passed through the fluidised bed to be heated to a high temperature and exits as a depleted air. An air expander 192 is added to the process for expanding the high-temperature and high-pressure depleted air and generating electricity. Part of the produced electricity can be used to drive the new compressor via a connecting rotating shaft 195. The above concept mimics the operation of a gas turbine unit but differs in that (i) the compressed air is heated by reaction heat instead of a gaseous fuel, and (ii) reduced air is used in the expansion process rather than normal air. Such a modification is expected to yield more power generation than that could be produced from the unmodified RES process.

[0093] Within the oxidation loop of this modified RES process, the compressor power consumption and expander power production as a function of compressor outlet pressure was analysed for different expander inlet temperatures and plotted in the graph

shown in Figure 7. As shown in this Figure, the net power output (the expander power production minus compressor power consumption) was found to reach a maximum of 603 kW at a compressor outlet pressure of 500 kPa and an expander inlet temperature of 900°C. Further increasing the pressure rise over the compressor or reducing the expander inlet temperature were found to result in reduced net power outputs, which is not favoured.

[0094] Under these optimal compressor and expander operating conditions (i.e. 500 kPa and 900°C), Table 7 below sets out the possible changes of heat/power generation profile of the RES process (mainly the oxidation loop) due to the modification. Table 7: Main changes of the heat/power profile of the oxidation loop due to the modification (for a standard RES unit using Cu-based oxygen carriers based on a 100 tonne/hour steel making plant).

Parameters	Units	Unmodified RES	Improved RES
Compressor power demand*	kW	230	2125
Expander power production*	kW	-	2727
Available medium-grade heat	kWt	0	4021
Available high-grade heat	kWt	11100	5782
Net power output of the oxidation loop [#]	kW	3470	3870

* Compressor outlet pressure: 500 kPa; Expander inlet temperature: 900C.

Assuming 1/3 of the medium-to-high grade heat can be converted into electricity via a steam cycle.

[0095] The results in Table 7 indicate that after the modification, ~50 % of the high-grade reaction heat was shifted to medium-grade heat (i.e. embedded in the reduced air of 577°C). In addition, the power produced from the oxidation loop of the modified RES process was found to be about 13.8% greater than that could be obtained from the unmodified process. It should be highlighted, though, that this increased power production should be also assessed against the increased costs, which includes the costs of a new air compressor, a new air expander, a new oxygen expander (for expanding oxygen during the off-peak periods) and the costs associated with upgrading the oxidation reactor to a high-pressure one.

[0096] A preliminary techno-economic feasibility of the RES unit 170 was assessed for a large-scale steelmaking plant of ~ 0.8 million tonnes per year. The cost was estimated based on the experience of a similar-scale RES unit that was constructed recently with an expected accuracy at -20% and + 20%. The hypothetical plant was assumed to have a continuous oxygen demand of 5,000 m³/h, which requires one standard RES unit under the continuous production mode or 2.7 RES units under the intermittent production mode.

[0097] Table 8 below shows the reactor parameters estimated according to the capacity of the RES unit 170 operating under the continuous production mode. It shows that the reduction reactor is much smaller than the oxidation reactor due to the lower gas flow rate.

Table 8: Reactor sizing

Parameters	Oxidation reactor	Reduction reactor	Units
Air/steam flow rate	9.0	0.9	kg/s
Volumetric gas flow at elevated temperatures	31	6	m ³ /s
Gas velocity	5	5	m/s
Cross sectional area	6.24	1.16	m ²
Estimated diameter	2.8	1.2	m
Estimated height	11.3	4.9	m
Reactor volume	70.4	5.7	m ³

[0098] On this basis, Table 9 sets out preliminary reactor cost estimates for the RES unit 170 operating in both the intermittent and continuous production modes.

Table 9: Reactor cost estimates based on the fabrication costs of a similar-sized RES unit that was constructed recently

Cost items (1000 AUD\$)	Intermittent production mode	Continuous production mode
Equipment costs		
Blower* + pump	67	67
Reactors	150	255
Cyclone	25	43
Gas-gas heat exchanger ^a	377	377
Steam generator ^b	15	15
Water-cooled condenser ^b	10	10
Loop seal	20	34
Start-up burner train	25	43
Total estimated equipment cost (including installation)	689	844

* Air flow: ~7.5 m³/s; pressure rise: 25 kPa; Power demand: 230 kW.

[0099] Table 10 sets out the capital cost of the RES unit 170 operating under the two production modes, compared with that of a CASU of the similar capacity.

Table 10: Capital cost calculation

Capital cost calculation (1000 AUD\$)	One standard RES unit - one reactor design	One standard RES unit - two reactor design	CASU
Direct costs			
Equipment cost plus installation	689	844	-
Insulation	140	238	-
Instrumentation, electrical and controls	50	85	-
Interconnections e.g. piping	40	68	-
Structural (buildings incl. services)	85	145	-
Land purchase and yard improvements	69	84	-

Capital cost calculation (1000 AUD\$)	One standard RES unit - one reactor design	One standard RES unit - two reactor design	CASU
Service facilities	379	464	-
Transport	41	51	-
Total direct plant cost	1,493	1,979	13,080 [#]
Indirect costs			
Engineering and supervision	220	270	2,376
Construction expenses	234	287	2,952
Total indirect plant costs	455	557	5,328
Contractor fees (5%)	97	127	920
Process contingency (30%)	584	761	5,522
Total fixed capital investment	2,630	3,423	24,851
Project contingency (15%)	394	513	3,728
Total capital investment	3,020	3,940	28,600

[#] Estimated based on the reference cost of a large-scale CASU unit after applying the economics of scale.

[00100] The unit capital investment of a steam cycle was assumed to be a conservative number of 1.0 million AUD/MW (without boiler). On this basis, the cost of a new steam cycle was estimated to be AUD 3.7 million for a 3.7 MW power generation capacity. The cost of initial oxygen carrier inventory was estimated to be AUD 0.05 million. By including these cost items in the plant cost, the total capital investment of the RES system operating under the continuous production modes was estimated to be about AUD 8.6 million. In comparison, a CASU unit at the same oxygen production capacity is more costly, which requires at least AUD 28.6 million.

[00101] Depending on the type of fuel being used for heating the reduction reactor, the payback time of the total initial investment for RES unit 170 was found to vary between 1.4 to 2.0 years without considering the cost saving from onsite oxygen production and merely 0.15 to 0.155 years if we consider the cost saving due to onsite oxygen production as a revenue (see Table 11 below). In contrast, the payback time of using CASU for oxygen production was found to be longer, at 0.57 to 0.60 year.

Table 11: Economic analysis of RES unit

Payback time calculation	RES integration			CASU integration
	With BFG/COG	With Coal	With natural gas	
Cost estimate				
Fuel cost (AUD\$/GJ)	0	2	4	-
Heating requirement (kWt)		13,500		-
Electricity requirement (kW)		230		250-415^ kWh/tonne O ₂
Daily cost* (AUD\$/day)	662	2995	5328	10,255-17,023
Revenue estimate				
O ₂ production (kg/s)		1.8		1.8
Saving from O ₂ purchase in cylinders** (\$/day)		153,600		153,600
Available high-quality heat for electricity production (kW _{th})		11,100		-
Electricity production/offset# (kWh/day)		88,800		-
Electricity avoidance (AUD \$/day)		10,656		-
Raw income/bill saving (AUD\$/day)		164,256		-
Net income (AUD\$/day)	163,594	161,261	158,928	136,577 143,345
Total capital investment (million AUD\$)		8.6		28.6
Material replacement^^ (million AUD\$/year)		0.05		
Estimated simple payback time** (year)	0.150	0.153	0.155	0.57 – 0.60

*Considering an electricity cost of 12 cents/kWh.

** Considering a conservative cost of oxygen in cylinders at \$1.28/m³.

Assuming one third of high-quality heat is converted to electricity.

^ Depending on whether a conventional or advanced (not yet available) CASU is used for producing O₂ with a purity of above 99%.

^^ Assuming the oxygen carriers are to be fully replaced every year.

** Assuming the unit is operated at 350 hours per year.

[00102] To get a better idea of the electricity offset potential of the RES unit 170, the produced power at 88,800 kWh/day represents ~5% of the average electricity consumption in a steelmaking plant of the similar scale and, in a specific example, ~16% of the electricity in the Australian BlueScope steel plant.

[00103] In the intermittent production mode, it was found that for the RES unit 170 to have a lower oxygen production cost than that of CASU, the following condition should be satisfied, namely, the daily operating cost spent on the electricity in a RES unit is lower than that of an equivalent CASU plant. This essentially gives:

$$W_{c, RES, op} * CoE_{op} - W_{p, RES, p} * CoE_p < W_{c, CASU, op} * CoE_{op} + W_{c, CASU, p} * CoE_p$$

where $W_{c, RES, op}$ and $W_{p, RES, p}$ denotes the amount of electricity being consumed during the off-peak period and that being produced during the peak period for the RES unit, respectively; CoE_{op} and CoE_p denotes the electricity costs during the off-peak and peak time, respectively; $W_{c, CASU, op}$ and $W_{c, CASU, p}$ denotes the amount of electricity being consumed during the off-peak and peak periods for the CASU unit, respectively.

[00104] With the previously obtained data, the above equation becomes:

$$90 CoE_{op} - 334 CoE_p < O_2 \text{ peak period production} * W_{CASU} * CoE_p + O_2 \text{ off-peak period production} * W_{CASU} * CoE_{op},$$

where W_{CASU} denotes the oxygen production cost of the CASU unit in terms of kWh per tonne of oxygen.

[00105] This further gives:

$$CoE_p > (334 - 0.05832 * W_{CASU}) / (90 + 0.0972 * W_{CASU}) CoE_{op}$$

[00106] For a conventional CASU that has an oxygen production cost at 415 kWh/tonne, the above equation becomes:

$$CoE_p > 2.38 CoE_{op}$$

[00107] For an advanced CASU that has an oxygen production cost at 250 kWh/tonne, the above equation becomes:

$$CoE_p > 2.80 \text{ } CoE_{op}$$

[00108] Those results imply that the RES process, when operating in the intermittent production mode, requires the ratio between the peak and off-peak electricity prices to be greater than 2.38 – 2.80 for it to become economically competitive.

[00109] Table 12 shows the economic performance of the RES unit working in the intermittent production mode, compared to those of CASU technologies.

Table 12: Economic analysis of the RES unit operating under the intermittent mode compared to those of both conventional and advanced CASU unit (CoE_{op} = 0.12 \$/kWh; CoE_p = 0.36 \$/kWh)

Items	Unit	RES intermittent production mode	– Conventional CASU	Advanced CASU
Expenses				
Daily electricity demand	kWh/day	334000	64541 [#]	38880 [#]
Off-peak electricity price	\$/kWh	0.12	0.12	0.12
Electricity cost	\$/day	40080	17426	10498
Capital expenditures	Million \$	12.4 [^]	28.6	34.3
Cost of replacing oxygen carriers	Million AUD\$/year	0.1	-	-
Revenues				
Available high-quality heat	kWh/day	270000	-	-
Peak electricity price	\$/kWh	0.36	0.36	0.36
Electricity sales	\$/day	32400	-	-
Available low-grade heat*	kWh/day	56000	-	-
If used to replacing natural gas*	\$/day	806	-	-
cost of O ₂ in cylinders**	\$/m ³	1.28	1.28	1.28
O ₂ production	m ³ /day	120000	120000	120000

Items	Unit	RES intermittent production mode	– Conventional CASU	Advanced CASU
Cost saving from O ₂ purchase in cylinders (\$/day)	\$/day	153600	153600	153600
NPV and payback time				
Plant lifetime		20.00	20.00	20.00
Financial interest rate		0.08	0.08	0.08
Annuity factor		0.10	0.10	0.10
Net income/day	\$/day	145920	136174	143102
Net cash flow	Million AUD\$/year	50	45	47
Payback time		0.5	1.2	1.4
NPV	Million \$	488	439	457

[^] The capital cost of the RES unit operating under the intermittent production mode was estimated by escalating the cost of one standard RES unit (with the single reactor design as seen in Table 10) to 2.7 standard RES units via the cost of economics.

* Indicative number only. This was not included in this economic analysis due to the high possibility of direct dumping such low-grade heat, but it may become an additional source of revenue in the future.

The electricity demands for conventional and advanced CASU units were considered at 415kWh/tonne and 250 kWh/tonne, respectively.

** Quotes from Core Gas Ltd.

[00110] Figure 8 shows the net present value of the RES unit compared to those of the conventional and advanced CASU units as a function of the cost of oxygen in cylinders. As it shows, at a high market cost of oxygen in cylinders (AUD 1.28/m³ and AUD 0.64/m³), the investments of both RES unit and CASU are attractive with the RES unit as the best revenue generating option producing positive NPVs of ~AUD 200 million and above. This is achieved by considering the cost saving of oxygen production due to the shift from off-site purchase to on-site production as a source of revenue. The scenario of AUD 0.64/m³ refers to a 50% discount of the off-site purchase cost of oxygen in cylinders assuming the steel making plant made a long-term contract with the gas company. The scenario of AUD 0/m³ refers to the case that the cost saving due to the shift from off-site

purchase to on-site oxygen production is excluded, and thus the NPV results correspond to the present value of the cumulative future payments for on-site oxygen production. This amount for the RES unit 170, as indicated in Figure 8, was found to be AUD 35 million and AUD 14 million less than those of the conventional and advanced CASU cases, respectively. In other words, the RES unit 170 can help save AUD 14 to 35 million in terms of oxygen production cost over the examined plant lifetime.

[00111] Nevertheless, such cost savings are also significantly affected by the difference between the off-peak and peak electricity prices. Such effect was analysed and the results are presented in Table 12. Table 12 shows that the cost saving increases as the ratio between peak and off-peak electricity prices increases and diminishes when the ratio drops below 2. Moreover, a greater off-peak electricity price leads to a greater cost saving. These findings imply that the RES technology may not be a feasible option for a large-scale steelmaking plant if it is able to negotiate with coal-fired power plants and receives a wholesale off-peak electricity price close to 3 cents/kWh and a peak price of no more than 6 cents/kWh. Nevertheless, for steelmaking plants and other oxygen-consuming industries that commonly pay for its off-peak electricity at a business retail price of ~12 cents/kWh and peak price of above ~36 cents/kWh, the RES unit 170 provides a cheaper option than CASU and helps saving millions of dollars for the industry. These results thus give steelmaking plants/other oxygen-consuming industries strong monetary motivation to switch from CASU technology to RES technology when their electricity prices are in the right regions.

Table 12: Cost saving of oxygen production in AUD million due to the employment of RES unit as opposed to the conventional CASU technology for a range of peak and off-peak electricity prices

Off-peak electricity price	CoE_p/CoE_{op}				
CoE_{op} (\$/kWh)	1	2	3	4	5
0.12	-73	-19	35	89	142
0.09	-54	-14	26	67	107
0.06	-36	-9	18	45	72
0.03	-17	-4	10	23	37

[00112] This techno-economic assessment of a RES unit 170 integrated with a hypothetical 100 tonne/hour integrated steelmaking plant indicates that the RES process, when operating in the continuous production mode, was able to utilise ~1/10 of the fuel resources available in the steelmaking plant (either coal, coke, COG, or BFG) to produce enough oxygen for the basic oxygen furnace, whilst simultaneously generating electricity and heat. The produced electrical power at 88,800 kWh/day was estimated to be able to offset ~5% of the electricity consumption in the steelmaking plant. Economic analysis revealed that the RES process, when operating in the continuous production mode, was more economically attractive than the conventional CASU process, leading to an increased net present value by 7 to 11 % and a shortened payback period by 2.4 to 2.8 times. However, the RES process, when operating in the intermittent production mode, requires the ratio between the peak and off-peak electricity prices to be greater than 2.38 – 2.80 for it to become economically superior to CASU processes.

[00113] It will further be appreciated that any of the features in the preferred embodiments of the invention can be combined together and are not necessarily applied in isolation from each other. For example, the feature of a partly embedded reduction reactor in the oxidation reactor can be used instead of the fully embedded reduction reactor in the RES unit 170. Similar combinations of two or more features from the above described embodiments or preferred forms of the invention can be readily made by one skilled in the art.

[00114] By providing a unique reactor configuration of a reduction reactor at least partly within the oxidation reactor, the invention confers the advantages of being able to maintain the reduction reactor at a consistently higher temperature than the oxidation reactor. This in turn minimises heat loss, improving the efficiency of the redox reaction, further enhances the production of oxygen and reduces the amount of incoming steam to fuel the reduction reaction. All these advantages of the invention result in lower costs in capital expenditure and maintenance. Furthermore, since smaller reduction reactors are used that are at least partly within or fully within the oxidation reactor, the invention can be readily implemented to existing plants by replacing single reactors with the reactor configuration of the embodiments of the present invention. In all these respects, the invention represents a practical and commercially significant improvement over the prior art.

[00115] Although the invention has been described with reference to specific examples, it will be appreciated by those skilled in the art that the invention may be embodied in many other forms.

Claims

1. An apparatus for generating oxygen, comprising a reduction reactor, an oxidation reactor fluidly connected to the reduction reactor so that oxygen-carrier particles can be transferred between the reduction reactor and the oxidation reactor, an outlet conduit arranged to transfer an oxygen-enriched mixture from the reduction reactor to an oxygen storage unit, wherein the reduction reactor is located at least partially within the oxidation reactor.
2. The apparatus of claim 1, wherein the reduction reactor is located within the oxidation reactor.
3. The apparatus of claim 1 or 2, wherein the reduction reactor is located adjacent the bed of the oxidation reactor.
4. The apparatus of claim 1 or 2, wherein the reduction reactor is located partly within the bed of the oxidation reactor.
5. The apparatus of claim 1 or 2, wherein the reduction reactor is located within the bed of the oxidation reactor.
6. The apparatus of any one of the preceding claims, wherein one or more transfer conduits fluidly connect the reduction reactor and the oxidation reactor.
7. The apparatus of any one of the preceding claims, wherein the reduction reactor, the oxidation reactor, and the outlet conduit form an integrated chemical looping air separation unit.
8. A method for generating oxygen, comprising:
 - transferring oxygen-carrier particles between a reduction process and an oxidation process, wherein the reduction process and the oxidation process are fluidly connected to form a chemical looping process;
 - producing oxygen-depleted carrier particles and an exhaust gas mixture comprising oxygen in the reduction process;
 - separating oxygen from the exhaust gas mixture; and
 - returning the oxygen-depleted carrier particles to the oxidation process for regenerating the oxygen-depleted carrier particles with oxygen;

wherein the reduction process is carried out at a higher temperature than the oxidation process.

9. The method of claim 8, wherein heat generated by the oxidation process is used to maintain the reduction process at the higher temperature.

10. The method of claim 8 or 9, wherein the reduction process is carried out 100° to 150°C higher than the oxidation process.

11. The method of any one of claims 8 to 10, wherein the temperature of the reduction process is at least 900 °C.

12. The method of any one of claims 8 to 10, wherein the temperature of the reduction process is between 900°C and 1,150°C.

13. The method of any one of claims 8 to 10, wherein the temperature of the reduction process is between 900°C and 950°C.

14. The method of any one of claims 8 to 10, wherein the temperature of the reduction process is between 1,000°C and 1,050°C.

15. The method of any one of claims 8 to 10, wherein the temperature of the reduction process is between 1,100°C and 1,150°C.

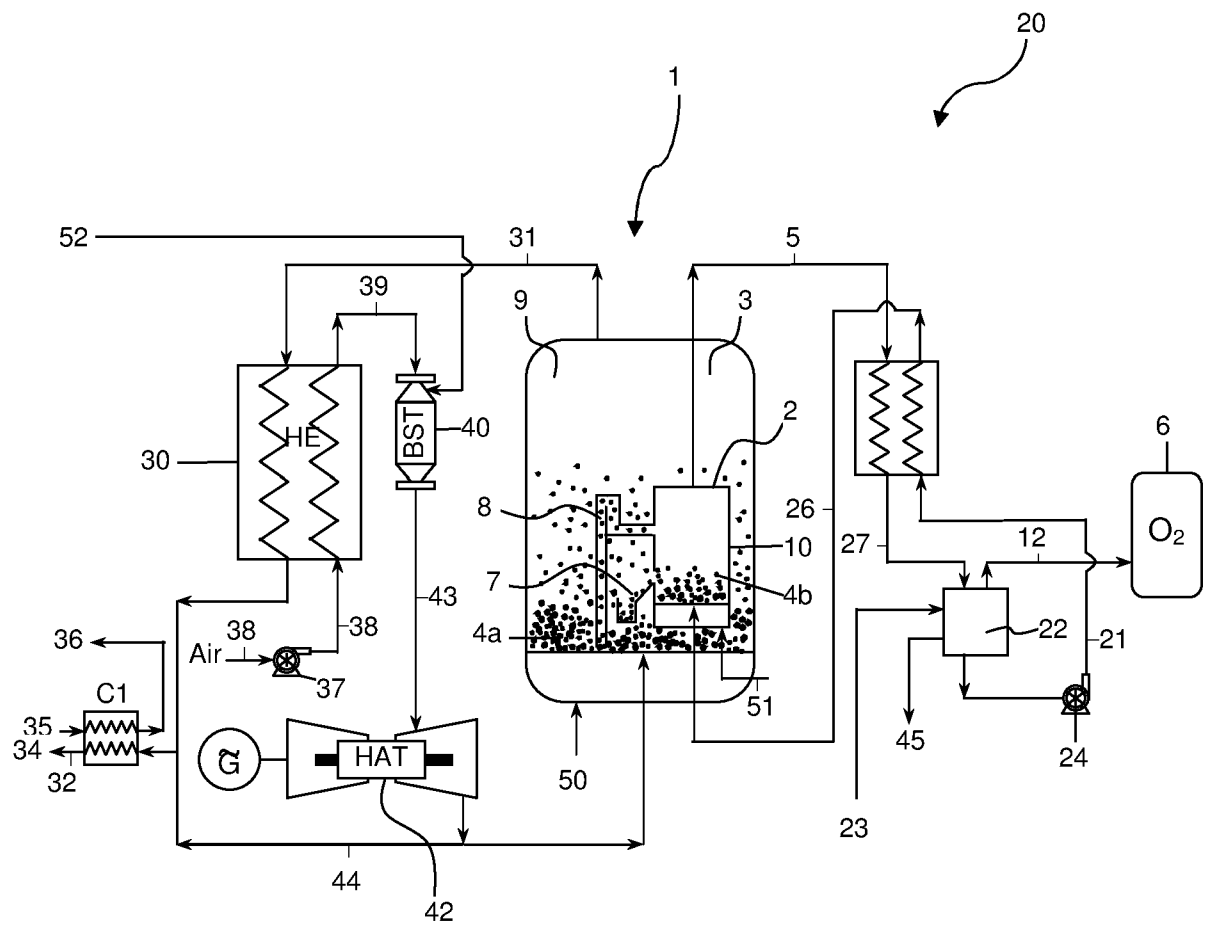
16. The method of any one of claims 8 to 15, wherein the temperature of the oxidation process is between 800°C and 1,000°C.

17. The method of any one of claims 8 to 16, wherein the reduction process is carried out in a first chamber exposed to the oxidation process.

18. The method of claim 17, wherein the oxidation process is carried out in a second chamber, the first chamber being contained within the second chamber.

19. A system for generating oxygen, comprising the apparatus of any of claims 1 to 7, and a condenser for condensing the oxygen-enriched mixture, the condenser being fluidly connected to the outlet conduit.

20. The system of claim 19, further comprising a compressor for compressing the oxygen-enriched mixture and subsequent storage the oxygen storage unit.

**Figure 1**

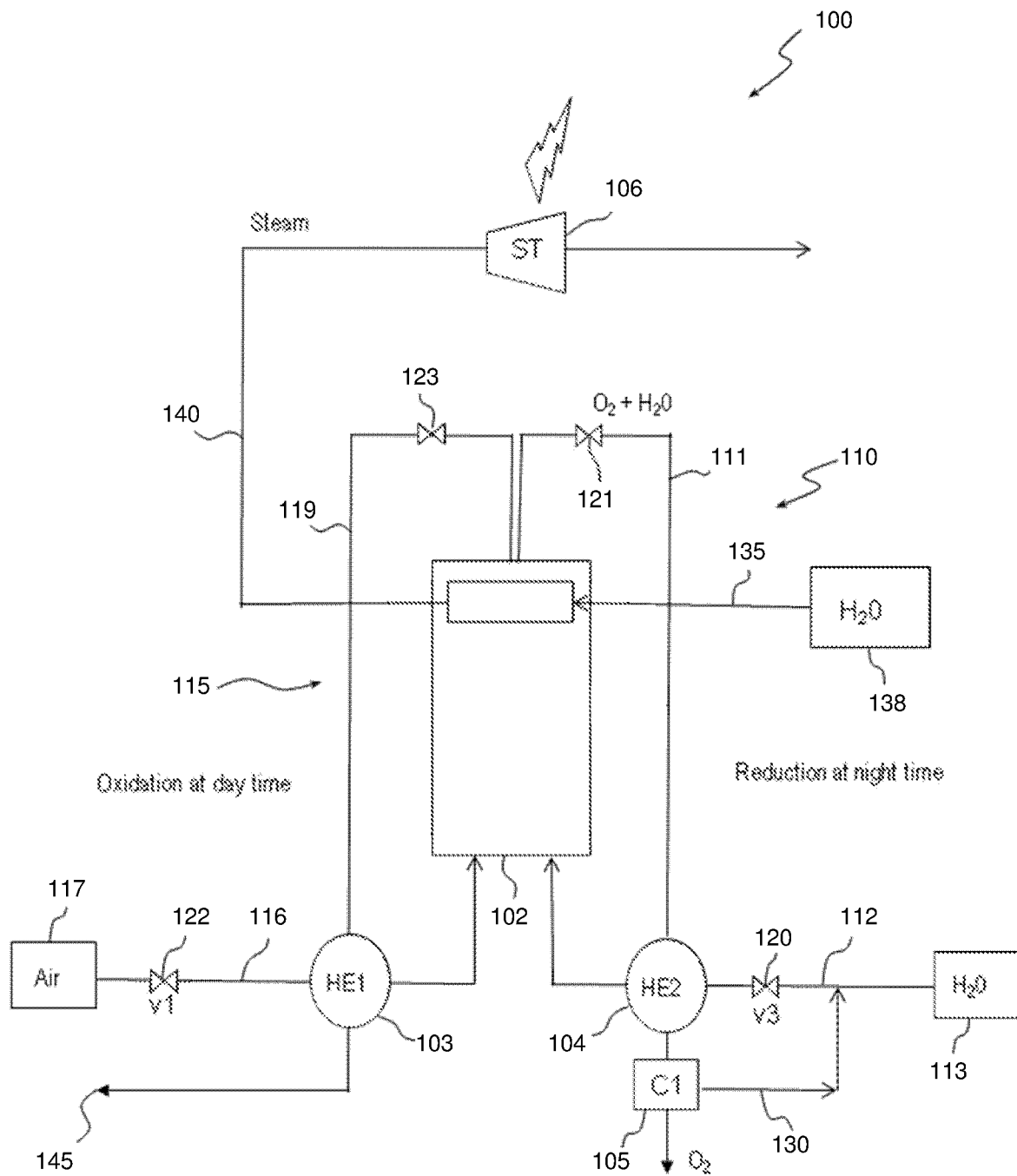
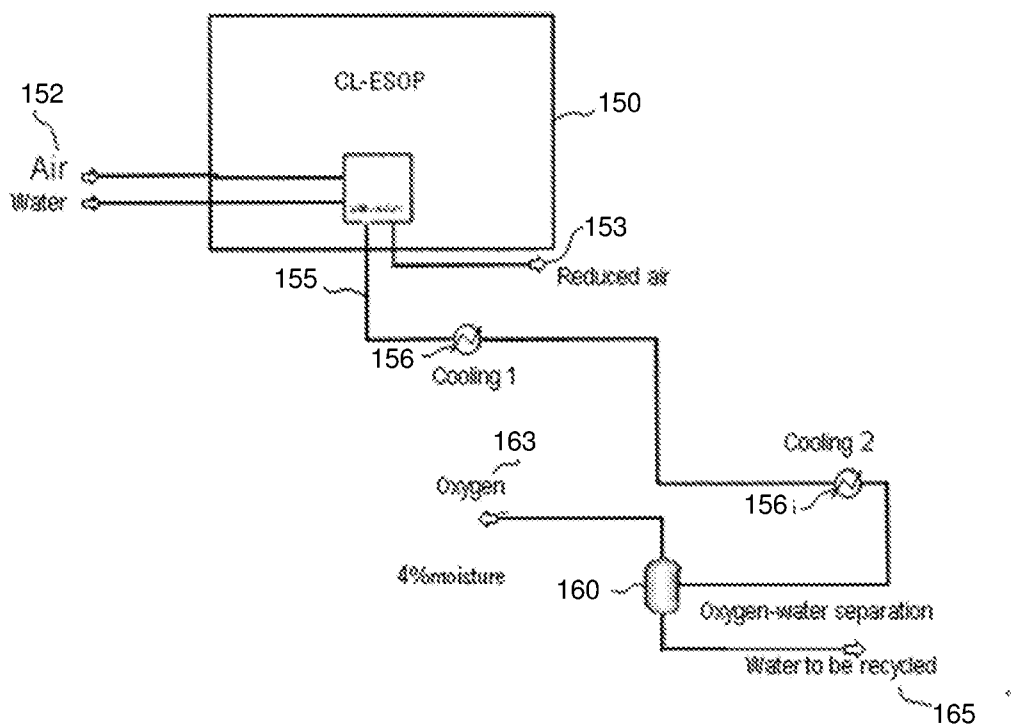
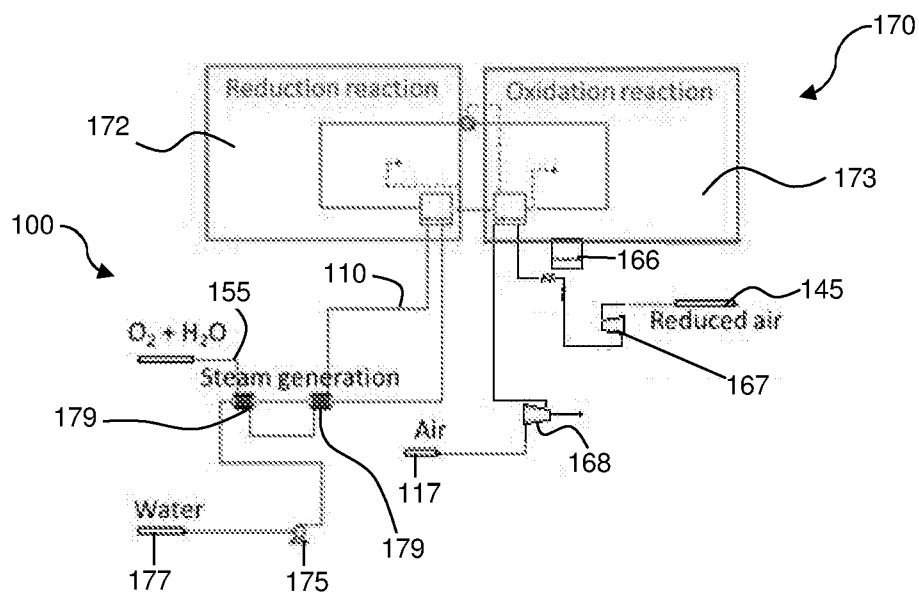
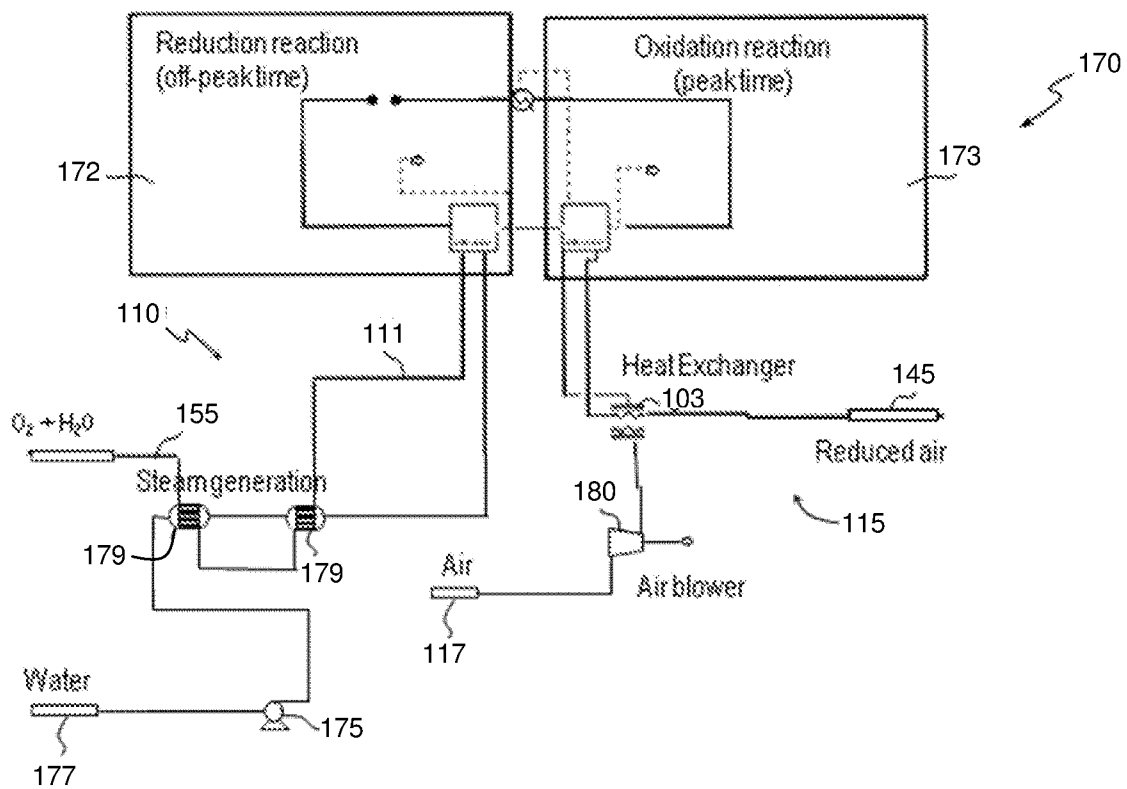
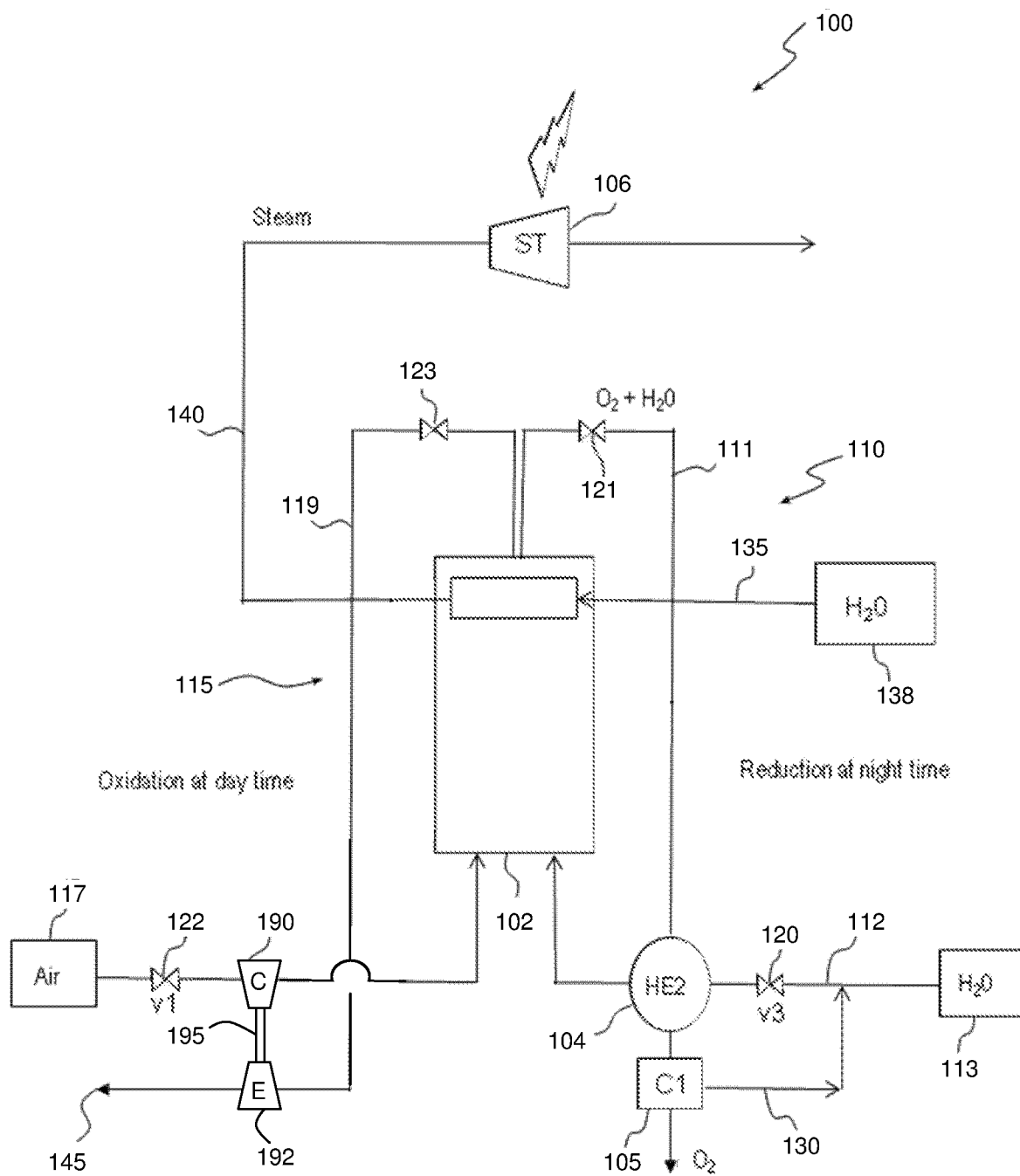


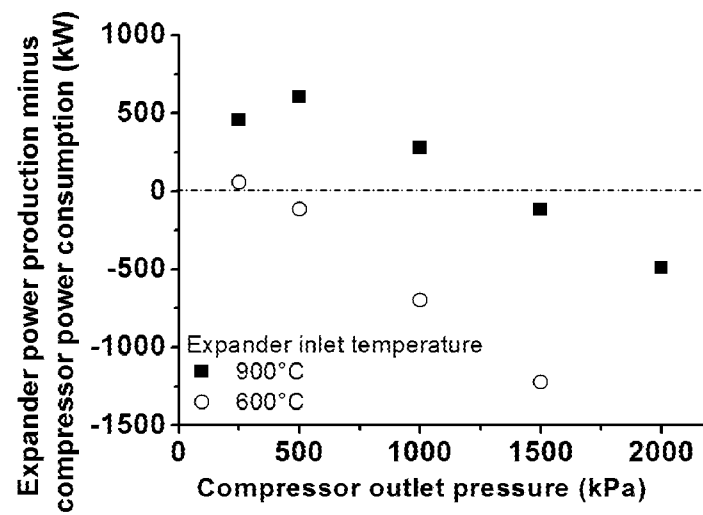
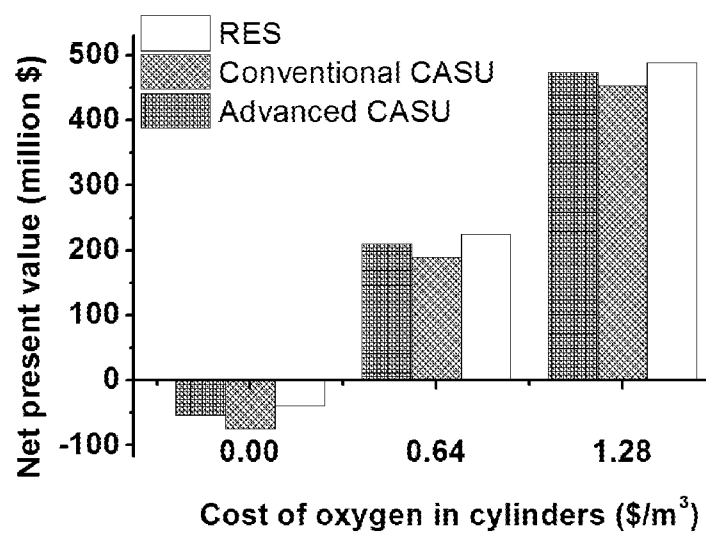
Figure 2

**Figure 3****Figure 4**

**Figure 5**

**Figure 6**

6/6

**Figure 7****Figure 8**

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/AU2018/050645

A. CLASSIFICATION OF SUBJECT MATTER

C01B 13/08 (2006.01) C01B 13/02 (2006.01) B01J 8/18 (2006.01) F23C 10/00 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Data base: PATENW, WPIAP, CAPLUS. Keywords: oxidation, reduction, endothermic, exothermic, redox and similar. IPC/CPC marks: B01J8/18, C01B13/08, C01B13/0237, C01B13/024 and lower. Applicant/Inventor: INFRATECH/University Newcastle/Newcastle Innovation; MOGHTADERI, Behdad, Zhou Cheng, Song Hui

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
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Date of the actual completion of the international search 25 July 2018	Date of mailing of the international search report 25 July 2018
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au	Authorised officer Sunilkumar Edamula AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262832927

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. PCT/AU2018/050645
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 2013/040645 A1 (NEWCASTLE INNOVATION LIMITED) 28 March 2013 Abstract; Para 0049, Table 1; Para 0065, Table 2; Para 0096 & Fig. 17	8-17
X	US 2015/0345854 A1 (DEUTSCHES ZENTRUM FÜR LUFT- UND RAUMFAHRT E.V.) 03 December 2015 Para 0003, 0006, 0024, 0087, 0090; Fig 1 & 2	8-17
P,X	WO 2017/127886 A1 (INFRATECH INDUSTRIES PTY LTD) 03 August 2017 Para 0021; Pages 12-13, Table 1 & Table 2; Claim 1	8-17

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2018/050645	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
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End of Annex			