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A *Pb/Zn* BASED CHEMICAL LOOPING SYSTEM FOR HYDROGEN AND POWER PRODUCTION WITH CARBON CAPTURE

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ABSTRACT

This paper describes an extension of a novel, carbon-burning, fluid phase chemical looping combustion system proposed previously. The system generates both power and H_2 with 'inherent' carbon capture using chemical looping combustion (CLC) to perform the main energy release from the fuel. A mixed Pb and Zn based oxygen carrier is used, and due to the thermodynamics of the carbothermic reduction of PbO and ZnO respectively, the system generates a flue gas which consists of a mixture of CO_2 and CO. By product H_2 is generated from this flue gas using the water-gas shift reaction (WGSR). By varying the proportion of Pb to Zn circulating in the chemical loop, the ratio of CO_2 to CO can be controlled, which in turn enables the ratio between the amount of H_2 produced to the amount of power generated to be adjusted. By this means, the power output from the system can be 'turned down' in periods of low electricity demand without requiring plant shutdown. To facilitate the adjustment of the Pb/Zn ratio, use is made of the two metal's mutual insolubility, as this means they form in to two liquid layers at the base of the reduction reactor. The amount of Pb and Zn rich liquid drawn from the two layers and subsequently circulated around the system is controlled thereby varying the Pb/Zn ratio. To drive the endothermic reduction of ZnO formed in the oxidiser, hot Zn vapour is 'blown' into the reducer where it condenses, releasing latent heat. The Zn vapour to produce this 'blast' of hot gas is generated in a flash vessel fed with hot liquid metal extracted from the oxidiser.

A mass and energy balance has been conducted for a power system, operating on the Pb/Zn cycle. In the analysis, reactions are assumed to reach equilibrium and losses associated with turbomachinery are considered; however, pressure losses in equipment and pipework are assumed to be negligible. The analysis reveals that a power system with a second law efficiency of between 62% and 68% can be constructed with a peak turbine inlet temperature of only ca. 1850 K. The efficiency varies as the ratio between power and H_2 production varies, with the lower efficiency occurring at the maximum power output condition.

KEYWORDS: Chemical, Looping, Hydrogen, Carbon, Capture, Gas-Turbine, Lead, Zinc.

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Roman

- Cp =specific heat at constant pressure (J/mol.K)CLC =Chemical Looping Combustion $\Delta G =$ reaction Gibbs function (kJ/mol)
- $\Delta H =$ reaction enthalpy (kJ/mol)

| H = | enthalpy of stream (kJ/mol) |
|----------------------------------|---|
| HRSG = | Heat Recovery Steam Generator |
| h = | specific enthalpy (J/mol) |
| n = | moles of species (mol) |
| <i>p</i> = | component pressure or partial pressure (Pa) |
| P = | reactor pressure (Pa) |
| Q = | heat flux (J/mol) |
| $\Delta S =$ | reaction entropy (kJ/mol.K) |
| T = | thermodynamic temperature (K) |
| TIT = | Turbine Inlet Temperature |
| W = | shaft work (kJ/mol) |
| WGSR = | Water Gas Shift Reaction |
| <i>x</i> , <i>y</i> , <i>z</i> = | mole fractions |
| | |

Greek

| 4 | | | | |
|-------------|-----------|-----------------|------------|----------|
| $\Lambda -$ | change in | nronerty due to | a chemical | reaction |
| <u> </u> | change m | | a chemicai | reaction |
| | 0. | | | |

 $\eta =$ efficiency

 $\gamma =$ degree of conversion of carrier O to CO_2

 $\rho =$ molar density (mol/m³)

Subscripts/Superscripts

| easeenpe | o, e apoi e o i pio |
|----------------|-----------------------------------|
| comp = | compressor |
| cold = | cold |
| (<i>g</i>) = | gaseous state |
| $H_2 =$ | of cycle second law efficiency |
| hot = | hot |
| <i>i</i> = | species or stream index |
| in = | inlet (stream) |
| is = | isentropic |
| <i>j</i> = | reactants or inlet streams |
| k = | products or outlet streams |
| (l) = | liquid state |
| L = | liquid stream |
| net = | net (work output) |
| <i>o</i> = | standard state (superscript), or |
| | sink condition (subscript) |
| out = | outlet (stream) |
| ov = | overall |
| oxi = | oxidiser |
| poly = | polytropic |
| pump = | pump |
| redu = | reducer |
| (s) = | solid state |
| sep/comp = | separation and compression (work) |
| str = | stream |
| <i>turb</i> = | turbine |
| V = | vapour stream |
| | vanamisation on vanaum |

vap = vaporisation or vapour

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1 INTRODUCTION

To generate hydrogen using fossil fuels, in principle any hydrocarbon can be oxidised with water. If this is assumed to be a single stage process, the overall reaction for a generic hydrocarbon is as follows:

$$C_{x}H_{y} + 2xH_{2}O_{(1)} \rightarrow xCO_{2} + (2x + y/2)H_{2}$$
 (1)

Reaction (1) is endothermic for all hydrocarbons, hence, to supply the heat necessary to drive the reaction, an external heat source such as a nuclear reactor or a solar furnace can be used - such systems are described as allothermal. Conversely, autothermal systems involve the partial oxidation of some of the hydrocarbon with air (or oxygen); the partial combustion supplies the heat necessary to oxidise the remaining hydrocarbon with water substance - it follows that reaction (1) becomes:

$$C_{x}H_{y} + 2(x-z)H_{2}O_{(1)} + zO_{2} \rightarrow xCO_{2} + (2(x-z) + y/2)H_{2}$$
(2)
(z \le x)

If reaction (2) is performed in an externally adiabatic, isothermal system, the value of z must take a specific value – say z^* . If $z > z^*$, the reaction produces an excess of heat that must be removed in some way. Whereas, if z > x the reaction would begin to produce steam as well as hydrogen (not shown in eq. (2)), eventually leading to straight combustion with no by-product H_2 being produced. Hence, if it is desired to generate both power and H_2 this can be achieved by operating at a point where there is sufficient air for reaction (2) to be spontaneous, but insufficient for complete combustion. The difficulty here is not a thermodynamic one – rather how to configure an appropriate set of reaction chambers to perform the required reactions and how to implement these reaction vessels within a power plant of some kind.

Generating both power and hydrogen has added value if the ratio of power generation to hydrogen production can be controlled without compromising the performance and operatability of the power station. This is because, if the work output from a power station can be turned up and down significantly with a consequent variation in hydrogen production, the station is better matched to the demands of a power grid where demand fluctuations are common. In practice this would extend the period where the power station was operated semicontinuously, with the clear operational benefit of reduced fatigue of machinery, refractories and pressure-containing components.

To perform reaction (2), a number of arrangements are possible. In this work, however, use of a chemical looping system will be explored. In previous work, McGlashan *et al* [1 - 2] proposed a CLC cycle capable of producing power and hydrogen that used pure Zn and pure Na, respectively, as the oxygen carrier. This paper examines a variation of this cycle that uses a mixture of two oxygen carriers - liquid Zn and Pb. As before, the cycle performs the partial oxidation of carbon to a mixture of CO and CO_2 , but the ratio between the two gases can be controlled by changing the proportions of Zn and Pb in the oxygen carrier as this affects the chemical equilibrium in the reduction phase of the CLC process. The water-gas shift reaction (WGSR) is then used to oxidise the residual CO to CO_2 and produce by-product H_2 . A steam bottoming cycle is installed to maximise efficiency. Before discussing the proposed cycle in detail, however, the overall thermodynamics of the system will be examined.

2 GLOBAL THERMODYNAMICS

For simplicity, in this work the fuel used in the process is assumed to be pure carbon (taken to be graphite). Hence, reaction (2) becomes:

$$C + 2(1-z)H_2O_{(1)} + zO_2 \to CO_2 + 2(1-z)H_2$$
(3)

To perform reaction (3), two sub-systems can be combined: a CLC system; and a WGSR reactor. Starting with the CLC system this performs the oxidation of carbon in two steps: in the first, an oxygen carrying species (assumed here to be divalent), M, is oxidised in air, thus:

$$2M + O_2 + \frac{79}{21}N_2 \to 2MO + \frac{79}{21}N_2 \tag{4}$$

In the second step the resulting oxide, MO, is reduced back to pure species M using carbon, generating a mixture of CO and CO_2 , thus:

$$(2-\gamma)C + 2MO \rightarrow 2M + 2(1-\gamma)CO + \gamma CO_2$$
(5)
$$(0 < \gamma < 1)$$

The variable γ represents the degree of conversion of the carrier's oxygen to CO_2 rather than CO. In this case, where the oxygen carrier is monovalent, γ is equal to the number of moles of CO_2 generated for every two moles of oxide. Whatever the value of γ , the WGSR can be used to produce by-product H_2 from the CO content of the resulting gas mixture, thus:

$$2(1-\gamma)CO + \gamma CO_2 + 2(1-\gamma)H_2O_{(l)} \rightarrow$$

$$(2-\gamma)CO_2 + 2(1-\gamma)H_2$$

$$\Delta G^o = -40.18(1-\gamma)kJ/mol$$

$$\Delta H^o = 5.70(1-\gamma)kJ/mol$$

$$T_o\Delta S^o = 45.88(1-\gamma)kJ/mol$$
(6)

Now, the value of γ depends on the equilibrium thermodynamics of the given metal oxide's reduction process and also the reducer's operating temperature and pressure. Jerndal *et al* [3] showed that different oxygen carriers yield quite different amounts of *CO* and *CO*₂. For instance, the reduction of *ZnO* gives a flue gas rich in *CO* at most conditions [4 and 5], whereas the reduction of *PbO* yields almost pure *CO*₂ [6]. Therefore, if a mixture of *Pb* and *Zn* is used as the oxygen carrier in a CLC system, by varying the ratio of *Pb* to *Zn* circulating, the value of γ , and hence the amount of hydrogen generated by the WGSR can be controlled. The resulting reactions occurring in the oxidiser and reducer, respectively, are as follows:

$$2\gamma Pb_{(l)} + 2(1-\gamma)Zn_{(l)} + O_2 \rightarrow 2\gamma PbO_{(s)} + 2(1-\gamma)ZnO_{(s)}$$
(7)

$$\Delta G^o = 266.38\gamma - 649.38 \ kJ/mol$$

$$\Delta H^o = 268.18\gamma - 715.57 \ kJ/mol$$

$$T_o\Delta S^o = 1.8\gamma - 66.19 \ kJ/mol$$

$$(2-\gamma)C + 2\gamma PbO_{(s)} + 2(1-\gamma)ZnO_{(s)} \to$$

$$2\gamma Pb_{(l)} + 2(1-\gamma)Zn_{(l)} + 2(1-\gamma)CO + \gamma CO_{2}$$

$$\Delta G^{o} = -386.45\gamma + 375.06 \ kJ/mol$$

$$\Delta H^{o} = -440.63\gamma + 494.51 \ kJ/mol$$

$$T_{o}\Delta S^{o} = -54.18\gamma + 119.45 \ kJ/mol$$
(8)

For convenience, to arrive at reactions (7) and (8), it has been assumed that carbothermic ZnO reduction does indeed yield pure COand that likewise PbO reduction generates pure CO_2 . Equally it is assumed that the WGSR reaction goes to completion. In the cycle analysis discussed later in the paper the actual equilibrium concentrations of CO_2 and CO are used based on a standard element potential minimisation algorithm. This analysis confirms that the assumptions stated above are a fair approximation of the real conditions (given the limitations of equilibrium analysis itself).

Hence, by observation γ is approximately equal to the ratio of *Pb* to *Zn* circulating around the system, hence all that is required to control the *CO/CO*₂ ratio is a means of changing the concentration of the two oxygen carriers circulating in the system. Fortunately, the properties of the *Pb/Zn* binary mixture facilitate this process. The phase diagram of the *Pb/Zn* binary is shown in Fig 1, adapted from data drawn from the references [7 to 10].



Fig 1. Phase diagram of the binary *Pb-Zn*. (L_1 is the *Zn* rich phase and L_2 the *Pb* rich phase).

As can be seen from Fig 1, the Pb-Zn binary exhibits a significant miscibility gap even at temperatures well above the respective melting points of the two metals [7]. Indeed, the immiscibility of liquid Pb and Zn is used in the zinc industry where the separation of the two metals into discrete liquid layers is an integral part of many Zn smelting operations [5]. In practice, therefore, the two metals can be separated at a low temperature point exists in the system (below say 1000 K), by allowing the Pb/Zn mixture to settle at that point. As will be shown the bottom of the reduction reactor is convenient for this process, where the metals can be allowed to form two discrete phases: a layer of almost pure Zn floating on a much denser Pb rich layer. Thus, the ratio of Pb to Zn in the circulating

oxygen carrier can be controlled by drawing off varying amounts of each layer through appropriate control valves.

To show how varying the Pb/Zn ratio would affect the power output of a potential power station, the overall process reaction can be considered. This can be found by addition of reactions (6), (7) and (8), which leads to:

$$(2-\gamma)C + O_2 + 2(1-\gamma)H_2O_{(l)} \to$$

$$(2-\gamma)CO_2 + 2(1-\gamma)H_2$$

$$\Delta G^o = -79.89\gamma - 314.50 \ kJ/mol$$

$$\Delta H^o = -178.15\gamma - 215.36 \ kJ/mol$$

$$T_o\Delta S^o = -98.26\gamma + 99.14 \ kJ/mol$$
(9)

Both *Pb* and *Zn* are seen to disappear from reaction (9), acting only as catalysts. If the system enacting (9), is assumed to be reversible, its work output is given by $-\Delta G^{\circ}$ (an irreversible system should follow a similar trend and this will be checked as part of the cycle analysis described later in the article). A graph of $-\Delta G^{\circ}$, per mole of carbon entering the system vs. γ , is shown in Fig 2. The graph shows that the power output from the system can be varied significantly (though it cannot be reduced to zero) and the turndown approaches 2.5 times. However, an even greater turndown is possible if the flowrate of air is also reduced.



Fig 2. Graph showing W_{rev} for reversible system performing reaction (9) at different values of γ .

3 A COMBINED CHEMICAL LOOPING AND WATER-GAS SHIFT SYSTEM

3.1 GENERAL ARRANGEMENT

In this section, a power plant configuration capable of enacting the reactions detailed above will be described. The proposed arrangement consists of two discrete sections: The CLC section that performs the primary oxidation of the fuel; and the WGSR section that completes the oxidation of any *CO* generated in the reducer to a flue gas of CO_2 and H_2 . A bottoming steam cycle is also included to maximise the generation of shaft work.

A schematic representation of the proposed plant is shown in Fig 3. Many of the features of the current proposal are similar to those in

McGlashan *et al* [1] and consequently will not be described here in detail; the differences in plant design stem, principally, from using a

mixed Pb/Zn oxygen carrier. Nonetheless, a brief description of the core components will be given here for completeness.



Fig 3. Schematic diagram of a CLC system using a Pb/Zn based carrier, water gas shift reactor and integrated bottoming steam cycle – showing stage numbering used in the cycle analysis.

Studying Fig 3, the CLC subsystem consists of two pressurised reactors: the oxidiser and the reducer, performing, respectively, reactions (7) and (8). The oxidiser takes the place of the combustion chamber of an open Joule cycle – the cycle therefore includes an air compressor that supplies pressurised air to the base of the oxidiser and a gas turbine, which expands the outgas that leaves the top of the oxidiser outgas consists of N_2 , saturated with both Zn and Pb vapour. However, due to the low volatility of Pb compared to Zn, the bulk of the metal vapour carried by the oxidiser outgas will be Zn. Further, most of the Zn vapour and practically all of the Pb vapour, will

condense during expansion in the nitrogen turbine – the latter is therefore 'wet' with almost pure liquid Zn droplets. The practical effect of liquid metal wetness on the turbine and some of the resulting design issues were discussed in previous work and will not be detailed here [1]. However, from a thermodynamic perspective, due to the heat released by the condensation of Zn vapour throughout the expansion process, the expanding flue gas experiences only a modest fall in temperature. Consequently, the turbine exit gas is passed to a heat recovery steam generator (HRSG) to reduce its temperature to a low level. The steam generated in the HRSG is used: partly to supply the steam necessary for the WGSR; and partly in a bottoming steam cycle, generating additional shaft work – an identical arrangement of WGSR and integrated bottoming steam cycle was described in previous work [1].

Additional shaft work is generated by expanding the outgas from the WGSR in a 'humid' gas turbine. The exhaust gas from this turbine consists of a mixture of CO_2 and H_2 with a residue of unconverted CO. The actual means of separating the flue gas into pure H_2 and CO_2 will not be described here as this subject is covered extensively in the literature – e.g. Kohl *et al* [11]. Equally, assuming it is required that both CO_2 and H_2 exit the power station as compressed fluids, the requisite gas compression and treatment systems will also not be described. However, allowance has been made in the cycle analysis for the net power consumption of both the separation and compression processes and the methodology is described later.

Returning to the plant's description, flue gas leaves the HRSG at a temperature approaching ambient and, due to the very low vapour pressure of both Zn and Pb at this temperature, practically all the remaining Zn and Pb vapour carried by the flue gas condenses in the HRSG As a result, assuming adequate precautions are taken to prevent physical carryover; the remaining gas stream will be practically pure N_2 and can be passed safely to a chimney for disposal to the atmosphere.

Key to the operation of the CLC system is that heat must be added into the reducer as reaction (8) is endothermic except when γ is close to unity. This is achieved by using a blast of hot Zn vapour generated in a flash vessel fed with hot liquid *Pb/Zn* mixture extracted from the oxidiser. Due to the high volatility difference between the *Pb* and *Zn*, almost all of the vapour generated by the flash stage will be *Zn* (the trace of *Pb* vapour carried over, has no noticeable effect on the performance of the system). The *Zn* vapour produced in this way is passed to the reducer where it is blown through a bustle pipe and tuyère arrangement in to the reaction zone. The *Zn* vapour then condenses, releasing latent heat and thereby drives the reduction process.

The remaining balance of plant in the system consists of the circulating liquid metal pump, pipework and valves. This equipment is essentially identical to that described in earlier work [1 - 2] and will not be discussed further. However, in the following sections the two main reactors will be described in more detail.

3.2 THE OXIDISER

The oxidiser, as proposed here and shown in Fig 3, is similar to that described by McGlashan *et al* [1]. The rector consists of three principal zones: at the top half, liquid metal droplets fall through rising hot flue gas; in the bottom half, metal oxide (firstly as liquid droplets and then as solid granules) falls through rising compressed air; in the middle section, combustion of metal in air takes place forming the liquid oxide droplets and gaseous flue gas respectively. Key to the functioning of the reactor is that counter-current, mass and heat transfer takes place, simultaneously preheating the reactants (metal drops at the top and air at the bottom) while simultaneously cooling reaction products (flue gas at the top and metal oxide particles at the bottom).

To produce the stream of hot Pb/Zn fed to the flash vessel, a stoichiometric excess of metal is used in the oxidiser. As a result, only a fraction of the metal that enters the oxidiser is consumed in the oxidation reaction. The remainder is collected in an annular trough circling the midriff of the reactor from where it is fed to the flash vessel directly. Because the trough is adjacent to the combustion zone of the oxidiser, the metal should be at a temperature close to the flame temperature. The stoichiometric excess of liquid metal is controlled to

ensure that heat is removed from the oxidiser fast enough to prevent the reactor overheating.

A significant difference between the reactor described here and that of previous work relates to the state of the oxide mixture leaving the reaction zone and whether the resulting slag is liquid or solid. The melting point of PbO (1159 K [12]) is well below the prevailing temperature in much of the oxidiser - ca. 1500 to 1700 K. Further, mixtures of PbO and ZnO form a eutectic composition of low melting point. Bauleke and McDowell [13], later confirmed by Jak et al [14], determined the eutectic of the slag to be 1134 K at 11 mol% ZnO. However, the phase diagram shows a sharp rise in the liquidus temperature as the ZnO concentration rises above 11%. Nonetheless, if γ and hence the concentration of *Pb* is high, the resulting slag will exist as a liquid in large parts of the oxidiser. This affects the design of the oxidiser's wall, as liquid slags are highly corrosive to most refractories. Hence, in sections of the reactor above the liquidus temperature, it is proposed that a cooled membrane wall can be used, whereby a frozen layer of slag forms on the surface. This layer should form an efficient barrier to further attack of the underlying metallic wall. However, there is still the potential for a serious fouling problem at the point where the slag passes through its liquid/solid transition in the bottom half of the reactor. To overcome this problem it is proposed that the bottom half of the reactor is designed to act as a prilling tower; the oxide solidifying as it falls through a rising air draft. Prilling has been successfully applied in the fertilizer industry [15] and also in lead shot production as a means of producing pelletised products from initially liquid chemicals, but with minimal wall fouling problems.

3.3 THE REDUCER

As with the oxidiser, the reducer is similar to that proposed before [1]. Pulverised fuel and metal oxide fall as granules under the influence of gravity, counter-current to rising flue gas – the two streams exchanging heat as they pass each other. The reduction reaction (8) occurs half way up the rector in a central reaction region. As described in section 3.1, to drive this endothermic reaction a blast of hot Zn vapour is blown into the reactor through tuyères fed from bustle pipe. This Zn vapour will condense thereby releasing latent heat.

As was mentioned in section 2, by setting the ratio of *PbO* to *ZnO* entering the reducer, the flue gas CO_2/CO ratio can be controlled. A key feature of the new arrangement is that the liquid metal collecting at the bottom of the reducer will separate into two discrete layers one *Pb* rich and the other *Zn* rich. These two layers are allowed to pool at the bottom of the reducer, which therefore acts as a combined settling tank and storage vessel. This means that, whilst the plant is operational, a residue of either Pb or Zn must be maintained in the liquid state in the bottom of the reducer. However, if this metal were allowed to freeze upon plant shutdown, the resulting Pb/Zn salamander would be difficult to re-melt and, due to the volume change on freezing, damage to both the refectory lining and possibly the pressure vessel itself would occur. Hence, provision for the removal of the liquid metal from the reducer is required. The simplest option is to run the liquid metal from the reactor and cast it into pigs upon shutdown. To restart the plant, a pig re-melting furnace would then be required. Although this arrangement is rather crude, the intention is that these plants would operated for long campaigns lasting years; hence, a more sophisticated system might not be justified.

Assuming the use of coal like fuels in practice, ash formed in the reduction reaction would need to be removed from the reactor. However, due to the high temperatures prevailing in the reducer, the ash would form a molten layer of slag that would float on the liquid metals collecting at the bottom of the reactor. The intention is to tap this liquid layer periodically, much as slag is tapped from commercial

lead or iron blast furnaces. This could then be disposed of after treatment using wet chemistry to ensure that Pb and Zn residues are recovered.

4 MASS AND ENERGY BALANCE

4.1 GENERAL APPROACH

A mass and energy balance of the proposed system will now be described. The model used and is an extension of the steady state model from the previous paper [1]. Allowance has been made for the change in oxygen carrier so that the effect of varying Pb/Zn ratio can be considered. The assumptions made are summarised below:

- 1. All devices have been assumed to be externally adiabatic and to operate at steady state.
- 2. Where chemical reactions take place, these are assumed to reach equilibrium.
- 3. The two reactors are split into a reaction region and either one or two direct contact heat exchange regions, where products exchange heat with reactants as described above.
- 4. Devices other than reactors are assumed to consist of a single control region.
- 5. Heat exchangers (including the direct contact zones of the reactors) are assumed to operate in counter-current configuration and to exhibit a zero approach temperature, except where this would lead to a steam temperature exceeding the maximum steam turbine inlet temperature (TIT) capped at 973 K.
- 6. Pressure losses in pipework and equipment are assumed negligible.
- 7. The 'first law', has been applied to all control regions with the following sign convention:

$$\sum_{k=1}^{No \ outlets} H_k - \sum_{j=1}^{No \ inlets} H_j - \sum Q + \sum W = 0$$
(10)

- 8. Total enthalpies, temperatures, and pressures are assumed throughout.
- 9. Where humid mixtures of *Zn* and *Pb* vapour occur in other gases, Dalton's and Raoult's are assumed.
- 10. Dynamic and hydrostatic head affects are ignored except in the liquid metal riser i.e. the pipe carrying liquid Zn back to top of the oxidiser. The riser was assumed to be 50 m long, based on an estimate of the eventual height of the plant.
- 11. The work required to separate the mixture of CO_2 and H_2 leaving the humid gas turbine was calculated assuming: the two gases are ideal; that the small CO content of the gas stream can be ignored; and using the minimum work relationship of McGlashan and Marquis [16]:

$$W_{rev} = -T_o \Re \left[\ln \left(\frac{1}{y_{CO_2}} \right) + \frac{(1 - y_{CO_2})}{y_{CO_2}} \ln \left(\frac{1}{(1 - y_{CO_2})} \right) \right]$$
(11)

This relation yields the work done per mole of CO_2 for 100% separation. A constant second law efficiency of 30% was assumed for the actual separation scheme, which is consistent with industrial practice.

12. For the compression of the separated CO_2 and H_2 , the work requirement was calculated in identical fashion to that detailed in an analysis of a similar Zn based CLC cycle [17]. The compression is assumed to occur in intercooled staged compressors with heat recovery to a steam Rankine cycle of constant second law efficiency of 65%.

Relationships for substance thermodynamic properties are tabulated in Table 1 of Appendix A. Relationships for power input and output from machinery along with the assumed efficiencies are tabulated in Table 2 of the same appendix.

4.2 RESULTS AND DISCUSSION

Each of the components of the system has been analysed using the assumptions and relationships given above and those contained in appendix A. To generate a numerical solution, an equation-based process-engineering package, *gProms*, was used. Results of this cycle analysis are presented and discussed below. Appendix B contains a table of example values for a typical condition, referred to the state points shown in Fig 3.

Beginning with the cycle's efficiency, its 'overall' efficiency can be defined as follows:

$$\eta_{ov} = \frac{W_{net}}{\left(-\Delta H^{o}\right)_{(9)}} \tag{12}$$

Where:

 W_{net} the net shaft work output from the cycle. ΔH^{o} the standard state enthalpy change (of reaction (9)).

Equation (12) takes no account of the thermodynamic 'value' of the H_2 generated in the process. The second law efficiency of a combined power and H_2 generating systems can be expressed by assuming that the available energy content (or work potential) of the H_2 is equivalent to shaft work. If this work potential is added to the net shaft work of the cycle, the sum can be compared with the work potential of the oxidation of $(2-\gamma)$ moles of carbon, as this is the primary energy source of the whole cycle. This affords a way of assessing the destruction of available energy contained in the carbon. Hence the 'rational' or second law efficiency of the cycle is given by:

$$\eta_{H_2} = \frac{W_{net} + (1 - \gamma) (-\Delta G^o)_{(2H_2 + O_2 \to 2H_2 O_{(1)})}}{(2 - \gamma) (-\Delta G^o)_{(C + O_2 \to CO_2)}}$$
(13)

Fig 4 shows results of the cycle analysis, specifically the variation of the reversible work output and the net work output of the cycle vs. γ . Also shown is the work required to separate and compress the CO_2 and H_2 produced in the plant. Alongside the work transfers are plotted the cycle's overall and second law efficiencies for comparison. The graph was drawn assuming $P_{oxi} = 35$ bar. Fig 5 shows the variation of the turbine inlet temperature (TIT) of the N_2/Zn turbine, versus P_{oxi} , for a range of values of γ .

When conducting the analysis the principal parameters varied were: the oxidiser pressure, P_{oxi} ; and the value of γ . In practice, for any given value of γ setting P_{oxi} constrained all other parameters. As shown by Fig 5, increasing P_{oxi} results in a rise in the oxidiser gas exit temperature, T_{N^2*} and hence the TIT of the N_2 turbine. To limit the TIT to a realistic value, only points where T_{N2} is less than 1850 K are plotted. It was also found that for values of γ above ca. 0.9, the cycle would not function as the flash vessel was then unable to generate sufficient Zn vapour to drive the endothermic reduction reactions. Hence results are not given for the region where $\gamma > 0.9$. As a supplement to the graphs, Table 3 in Appendix B includes example values for a single point with $P_{oxi} = 35$ bar and $\gamma = 0.8$.



Fig 4. Graph showing the effect of γ on η_{ov} , η_{H^2} , W_{rev} , W_{net} and the work required to separate and compress the CO_2 and H_2 generated by the cycle, $W_{sep/comp}$, for a $P_{oxi} = 35$ bar and N_2 turbine TIT ≤ 1850 K.



Fig 5. Graph showing the N_2 turbine inlet temperature (TIT), T_{N_2} , vs. P_{oxi} , for a range of values of γ .

Examining Fig 4, the second law efficiency of the cycle falls with increasing γ , but not appreciably. This is to be expected, as for higher values of γ , the cycle approaches a *Pb* based CLC system as opposed to a *Zn* based cycle. The former has inherently lower second law efficiency due to thermodynamic considerations [**18**]. Another notable feature of the cycle shown by Fig 4 is the strong fall in η_{ov} as γ decreases. This can be attributed principally to the work required to separate and compress the *CO*₂ and *H*₂ product streams. There are two

contributing effects: firstly, the separation and compression work rises as the cycle generates more H_2 and hence there is more gas to compress, but also because the separation work is a function of the mixing ratio of H_2 and CO_2 and the corresponding rise in the entropy of mixing - i.e. the work given by eq. (11). In addition, the compression of the H_2 to 500 bar (the assumed output condition) requires more work than the compression of CO_2 to 100 bar (again, the assumed output condition) - though not appreciably. However, along with the rise in compression and separation work, there is a corresponding fall in the shaft work generated by the core CLC system as it changes from principally work generation at high γ , to principally H_2 generation at low values of γ . Even the small rise in second law efficiency with falling γ is not sufficient to counteract these combined effects. At one level, the resulting precipitous fall in η_{ov} is a concern; however, the main purpose of using a mixed oxygen carrier is to enable a variation of load from a plant that is otherwise running continually. This has clear benefits for grid control. Hence, the turn down in work output, accompanied, as it is, by a rise in H_2 output and a rise in second law efficiency, can be seen as a clear advantage for this type of plant.

One definite negative effect of changing γ is the variation in cycle temperatures. In particular, as Fig 5 shows, the N_2 turbine TIT increases strongly with rising γ . This relates directly to the higher equilibrium temperature of both *Pb* oxidation and carbothermic *PbO* reduction compared to that of *Zn* and *ZnO*, respectively. In practice, therefore, the design of turbines to withstand these conditions will be critical for the successful operation of plant of this type.

5 CONCLUSIONS

A carbon-burning, fluid phase chemical looping combustion system using a mix of lead and zinc as the oxygen carrying medium is proposed for power and fuel generation. The system generates both power and H_2 with 'inherent' carbon capture by means of chemical looping combustion to perform the main energy release from the fuel. Due to the thermodynamics of the carbothermic reduction of PbO and ZnO respectively, the system generates a flue gas which consists of a mixture of CO_2 and CO. Hydrogen is generated from the flue gas using the water-gas shift reaction (WGSR). By varying the proportion of Pb to Zn circulating in the chemical loop, the ratio of CO_2 to COentering the WGSR reactor can be controlled, which in turn enables the ratio between the amount of H_2 produced to the amount of power generated to be adjusted. As a result, and a major attribute of the system, the power output from the system can be 'turned down' in periods of low electricity demand without requiring plant shutdown. A key feature of the proposed system is the use of a cooled wall in order to form a protective slag layer to prevent corrosion of the oxidiser and reducer vessel walls.

An analysis taking into account realistic system efficiencies shows that a power system with a second law efficiency between 62% and 68% can be constructed with a peak turbine inlet temperature of about 1850 K, which is within the realms of engineering feasibility. The efficiency varies as the ratio between power and H_2 production varies, with the lower efficiency occurring at the maximum power output condition. The high thermal efficiency, in combination with inherent carbon capture, provide justification for consideration of this cycle as a serious option for large scale power and fuel generation.

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APPENDIX A: Relationships and property values used in cycle analysis

| Property | Relationship | Units | References/Notes | | |
|--|--|---------|--------------------------------------|--|--|
| Enthalpy of liquids or gaseous species, <i>i</i> , that remain as gases. | $h_{i,T} = \overline{Cp}_i \left(T - T_o \right)$ | J/mol | | | |
| Enthalpy of gaseous Zn. | $h_{Zn,T} = \overline{Cp}_{Zn_{(I)}} \left(T - T_o\right) + \Delta h_{Zn,T}^{vap}$ | J/mol | | | |
| Enthalpy of steam | $h_{H_{2}O_{(g)},T} = \Delta h_{H_{2}O,T_{o}}^{vap} + \overline{Cp}_{H_{2}O_{(g)}} \left(T - T_{o}\right)$ | J/mol | Moore and Sieverding [19] | | |
| Latent heat of vaporisation of Zn | $\Delta h_{Zn,T}^{vap} = 137616 \left(1 - \frac{T}{3170} \right)^{0.38}$ | J/mol | Yaws [20] | | |
| Latent heat of vaporisation of steam at 298 K | $\Delta h_{H_2O,T_o}^{vap} = 44002 \text{ J/mol}$ | J/mol | Moore and Sieverding [19] | | |
| Specific heat of species <i>i</i> | $Cp_i = A_i + B_i T + C_i / T^2$ | J/mol.K | Kubaschewski et al [21], Kelley [22] | | |
| Enthalpy of mixture (ideal mixing assumed) | $h_{str,T} = \sum_{i=1}^{s} x_i h_{i,T}$ | J/mol | | | |
| Saturated vapour pressure of Zn | $\ln p_{Z_{n,T}}^{vap} = 21.0526 - \frac{15633.4}{T} - 1.051 \ln T - 2.8897 \times 10^{-4} T$ | bar | Maier [23] | | |
| Saturated vapour pressure of Pb | $\ln p_{Pb,T}^{vap} = -47.1923 - \frac{19750.9}{T} + 9.2106 \ln T - 9.0533 \times 10^{-3}T + 1.26156 \times 10^{-6}T^2$ | bar | Yaws [20] | | |
| Saturated vapour pressure of H_2O | $\ln p_{H_2 0,T}^{vap} = 62.136 - \frac{7258.2}{T} - 7.3037 \ln T + 5.5831 \times 10^{-9} T + 4.1684 \times 10^{-6} T^2$ | bar | Yaws [20] | | |
| Partial pressure of species, <i>M</i> , above liquids | $p_{M,g} = yP = xp_{M,T}^{vap}$ | bar | Raoult's Law | | |

Table 1. Relationships for thermodynamic properties of streams and components.

Table 2. Relationships for work transfer of adiabatic machinery.

| Machine Item | Relationship | Units | $\eta_{is or} \eta_{polv}$ |
|----------------------------|--|-------|----------------------------|
| Liquid Pumps | $w_{pump} = \frac{\Delta P}{\rho \eta_{pump}}$ | J/mol | 80% |
| Gas Compressors | $w_{comp} = \overline{Cp}_{str} T_{cold} \left(1 - \left(\frac{P_{hot}}{P_{cold}} \right)^{\frac{\Re}{\overline{Cp}_{str} \eta_{comp}}} \right)$ | J/mol | 90% |
| Dry Gas Turbines | $w_{turb} = \overline{Cp}_{str} T_{cold} \left(\left(\frac{P_{hot}}{P_{cold}} \right)^{\frac{\Re \eta_{turb}}{\overline{Cp}_{str}}} - 1 \right)$ | J/mol | 85% |
| Wet Gas Turbines – see [1] | $w_{turb} = \eta_{is} \left[\left(n_{N_2} \overline{Cp}_{N_2} + n_{Zn}^{V_{in}} \overline{Cp}_{Zn_{(I)}} \right) \left(T_{in} - T_{out}^{is} \right) + n_{Zn}^{L_{out}} \overline{\Delta h}_{Zn}^{vap} \right] = \left(n_{N_2} \overline{Cp}_{N_2} + n_{Zn}^{V_{in}} \overline{Cp}_{Zn_{(I)}} \right) \left(T_{in} - T_{out} \right) + n_{Zn}^{L_{out}} \overline{\Delta h}_{Zn}^{vap}$ | J/mol | 80% |

APPENDIX B: Example results.

Table 3. Example result of process flow analysis – values are per mole of reaction (9): P_{oxi} = 35 bar and γ = 0.8.

| Station | P (bar) | $T(\mathbf{K})$ | Flow | h_{str} | Mole fraction | | | | | | | | | | |
|---------|---------|-----------------------|-----------|-----------|---------------|-------|-------|------------|-------|-----------------------|-------|-------|--------|--------|-------|
| Station | 1 (Dal) | <i>I</i> (K) | (mol/mol) | (kJ/mol) | Zn | ZnO | Pb | PbO | N_2 | O ₂ | СО | С | CO_2 | H_2O | H_2 |
| 1 | 1.00 | 298.2 | 4.762 | 0.00 | | | | | 0.790 | 0.210 | | | | | |
| 2 | 35.00 | 793.8 | 4.762 | 77.16 | | | | | 0.790 | 0.210 | | | | | |
| 3 | 35.00 | 2139.9 | 26.688 | 1405.93 | 0.144 | | 0.856 | | | | | | | | |
| 4 | 35.00 | 1816.0 | 5.560 | 445.02 | 0.323 | | 0.005 | | 0.677 | | | | | | |
| 5 | 18.67 | 298.2 | 1.200 | 0.00 | | | | | | | | 1.000 | | | |
| 6 | 18.67 | 793.8 | 2.000 | -443.06 | | 0.200 | | 0.800 | | | | | | | |
| 7 | 18.67 | 793.8 | 3.200 | -443.06 | | 0.125 | | 0.500 | | | | 0.375 | | | |
| 8 | 18.67 | 1957.9 | 25.233 | 1191.12 | 0.091 | | 0.909 | | | | | | | | |
| 9 | 18.67 | 1957.9 | 1.455 | 214.82 | 1.000 | | | | | | | | | | |
| 10 | 18.67 | 1808.2 | 30.477 | 1323.87 | 0.200 | | 0.800 | | | | | | | | |
| 11 | 18.67 | 793.8 | 1.200 | -331.64 | 0.000 | | 0.000 | | | | 0.333 | | 0.667 | | 0.000 |
| 12 | 35.00 | 1816.0 | 30.477 | 1330.74 | 0.200 | | 0.800 | | | | | | | | |
| 13 | 1.00 | 1188.3 | 5.560 | 262.55 | 0.323 | | 0.005 | | 0.677 | | | | | | |
| 14 | 18.67 | 793.8 | 1.602 | -403.61 | 0.000 | | 0.000 | | | | 0.249 | | 0.499 | 0.250 | 0.000 |
| 15 | 18.67 | 482.1 | 1.600 | -458.41 | 0.000 | | 0.000 | | | | | | 0.750 | | 0.250 |
| 16 | 1.00 | 299.7 | 1.600 | -472.09 | 0.000 | | 0.000 | | | | | | 0.750 | | 0.250 |
| 17 | 1.00 | 482.1 | 3.762 | 22.90 | | | | | 1.000 | | | | | | |
| 18 | 1.00 | 310.1 | 3.762 | 1.49 | | | | | 1.000 | | | | | | |
| 19 | 18.67 | 820.7 | 1.789 | 29.39 | 0.985 | | 0.015 | | | | | | | | |
| 20 | 1.00 | 298.2 | 0.400 | 0.00 | | | | | | | | | | 1.000 | |
| 21 | 0.05 | 298.2 | 3.208 | 0.00 | | | | | | | | | | 1.000 | |
| 22 | 400.00 | 310.1 | 3.208 | 2.89 | | | | | | | | | | 1.000 | |
| 23 | 400.00 | 482.1 | 3.208 | 21.29 | | | | | | | | | | 1.000 | |
| 24 | 400.00 | 793.8 | 3.208 | 173.78 | | | | | | | | | | 1.000 | |
| 25 | 18.67 | 793.8 | 0.400 | -71.98 | | | | | | | | | | 1.000 | |
| 26 | 400.00 | 973.2 | 3.208 | 219.29 | | | | | | | | | | 1.000 | |
| 27 | 18.67 | 508.1 | 3.208 | 149.36 | | | | | | | | | | 1.000 | |
| 28 | 18.67 | 793.8 | 2.808 | 198.54 | | | | | | | | | | 1.000 | |
| 29 | 18.67 | 973.2 | 2.808 | 191.95 | | | | | | | | | | 1.000 | |
| 30 | 0.05 | 298.2 | 2.808 | 123.57 | | | | | | | | | | 1.000 | |
| 31 | 0.05 | 298.2 | 2.808 | 0.00 | | | | | | | | | | 1.000 | |