High temperature solar thermal energy storage system with metal oxides
Significance of Thermal Energy Storage (TES)

The PS20 concentrated solar thermal plant in Spain
(Source: www.thefifthestate.com.au)

Intermittency of solar energy
Thermal Energy Storage system

Sensible heat
- ✓ Low cost
- ✓ Simple application with available material
- X Low energy density
- X Exergy destruction
- X Solidification
- water, sand, molten salts, or rock

Latent heat
- ✓ Medium storage density
- ✓ Small temperature difference between charging/Discharging
- X Low thermal conductivity
- X Technical challenges
- Paraffin, Salt hydrate

Thermochemical
- ✓ High Energy density
- ✓ Exergy generation
- ✓ Possibility for high Carnot efficiency
- X High capital cost
- X Technically complex
- Metal oxides

Literature review (Gil et al. 2009, Kuravi et al. 2013, Silakhori et al. 2015)
Literature review

- Le Chatelier’s principle

Reduction reaction: $\text{MeO}_\delta \rightarrow \left( \frac{\delta_2 - \delta_1}{2} \right) \text{O}_2 + \text{MeO}_{\delta_2} \quad \Delta H > 0$

Oxidation reaction: $\text{MeO}_{\delta_2} + \left( \frac{\delta_2 - \delta_1}{2} \right) \text{O}_2 \rightarrow \text{MeO}_{\delta_1} \quad \Delta H < 0$

Temperature-swing
Pressure-swing
Technical challenges associated RedOx reactions with solid metal oxides (Temperature-Swing):

- Thermal hysteresis (Carrillo et al. (2015))
- Sintering, Softening, agglomeration of solid metal oxide over long-term Reduction and Oxidation (RedOx) reaction (Block et al. 2016).

Top (A) and side (B) views of copper oxide after 1 RedOx cycle, and top (C) and inside (D) views of copper oxide after 20 RedOx cycles (Deutsch et al. 2017).
Literature review

Liquid Chemical Looping Thermal energy Storage (LCL-TES) system

(Silakhorī et al. 2017 and Jafarian et al. 2017)
Objectives

✓ To assess the potential of multivalent solid metal oxides for thermochemical storage by Pressure-Swing.

✓ To assess the thermodynamic performance of different metal oxides in liquid chemical looping thermal energy storage (LCL-TES) system.

✓ To investigate the potential of suitable liquid metal oxides in LCL-TES system.

✓ To analyse the energetic performance of the LCL-TES system in a gas turbine combined power cycle.
✓ **Objective 1:** To assess the potential of metal oxides for thermochemical storage by P-Swing.

**Thermogravimetric Analysis (TGA)**

**Netzsch STA 449 F3 Jupiter**

**Reduction and oxidation of solid copper oxide (10 cycles)**
Objective 1: To assess the potential of metal oxides for thermochemical storage by P-Swing.

Reduction and oxidation of solid cobalt oxide (10 cycles)

Reduction and oxidation of solid Manganese oxide (10 cycles)
Objective 2: Assessing the potential metal oxides

Evaluating the melting temperature of 23 metal oxides

Ellingham diagram of the selected reactants as a function of temperature at atmospheric pressure.

Comparison of the melting temperature of different metal oxides with their various oxidation states.

(M. Silakhori et al. 2017)
Objective 2: Assessing the potential metal oxides

Phase stability diagram of potential metal oxides in LCL-TES system

The equilibrium oxygen pressure for the reactions of Cu as a function of temperature

The equilibrium oxygen pressure for the reactions of Pb as a function of temperature

The equilibrium oxygen pressure for the reactions of Pb as a function of temperature

(M. Silakhori et al. 2017)
Objective 1: Assessing the potential metal oxides

**Copper-oxygen phase diagram**

- **Sensible heat**: 69 KJ/mol (solid phase)
- **Latent heat**: 64.76 KJ/mol
- **Thermochemical**: 114.97 KJ/mol (solid phase)
- **Total enthalpy**: 404.6 KJ/mol

**Lead-oxygen phase diagram**

- **Sensible heat**: 410 KJ/mol (solid phase)
- **Latent heat**: 107 KJ/mol
- **Thermochemical**: 25.52 KJ/mol (solid phase)
- **Total enthalpy**: 250 KJ/mol
Objective 3: Assessing the potential of liquid metals in LCL-TES system (Experimentally)

Thermogravimetric Analysis (TGA)

One cycle of reduction and oxidation of molten copper oxide at different partial pressure in reduction
Objective 3: Designing the experimental test rig

Experimental setup

Air + N₂

Outlet gas to GC

GC or gas analyser

Working tube

Molten metal

Water cooled flanges

Gas outlet tube

High temperature zone of furnace

Injection nozzle

Sealing cap

Gas bubbles

Alumina stand

Cooling water

Valve 4

Valve 3

Valve 1

Valve 2

Air

N₂

Air Valve & Flow meter

N₂ Valve & Flow meter

N₂ Gas regulator

Air Gas regulator
Objective 3: Assessing the potential of liquid metals in LCL-TES system (Experimentally)

Oxidation and Reduction with Air and Nitrogen

- Various flowrates of Air and N₂
- Various Temperatures
- Different Dwell Time
- Rate of oxidation
- Rate of reduction

Measuring O₂ production with TESTO 350 Gas analyzer
Objective 4: Assessing the energetic performance of LCL-TES combined cycle

The LCL-TES combined cycle

- Thermodynamic model for LCL-TES system with Matlab and HSC Chemistry
- Modelling the combined power cycle with ASPEN PLUS

Air reactor pressure
✓ $(P_{AR})=10-20\text{ bar, } \eta = 43.2\% - 46.6\%$

Concentration ratio of solar receiver (CR)
✓ $CR= 500-8000, \eta = 7.6\% - 57.5\%$

Temperature of After burner (T$_{AB}$)
✓ $T_{AB}=1250\degree\text{C}-1700\degree\text{C}, \eta = 45.4\% - 50\%$

$\eta_{abs, \text{total}} = 73\%$
$\eta_{1200\degree\text{C}, 15\text{bar}} = 44.9\%$
$\eta_{1700\degree\text{C}, 15\text{bar}} = 50\%$
Conclusion

- The results of TGA analysis show that the potential of Co$_3$O$_4$, CuO and Mn$_2$O$_3$ for thermochemical energy storage by P-swing.

- From all of the multivalent metal oxides, CuO/Cu$_2$O and Pb$_3$O$_4$/PbO systems with total enthalpy of 404.6 KJ/mol and 250KJ/mol, respectively, were selected for LCL-TES system based on developed thermodynamic model.

- The energetic performance of LCL-TES combined cycles was assessed and the calculated efficiency was 44.9% and 50% for the system without and with an after burner, respectively.

- The influence of different parameters such $P_{AR}$, CR, and temperature of the after-burner was investigated and it is found that the efficiency of the system can be increased up to 57%.
Acknowledgment
Q&A

Thanks for your attention