



Australian  
National  
University

# 2014/RND005 High Temperature Solar Thermal Energy Storage via Manganese-oxide based Redox Cycling

## Project results and Lessons Learnt

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**Contact name:** Wojciech Lipiński

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**Title:** Professor

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**Email:** wojciech.lipinski@anu.edu.au      **Phone:** 02 6125 7896

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**Website:** <http://stg.anu.edu.au/>

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# Executive Summary

This Project set out to examine some options for developing new approaches to solar thermal energy storage. Our starting hypothesis was that we needed stronger forms of metal to use to build a new form of storage device. The device itself would also need to be designed in a different way to enhance efficient generation and storage of solar thermal power.

A technically feasible approach to the construction of a new concentrated solar thermal power system concept that involves a novel high-temperature thermochemical energy storage system was developed. This storage system promises to store thermal energy at temperatures of over 1,000°C, enabling the use of a combined power cycle, which reach the highest thermal power cycle efficiencies of up to 60% or more. The storage system is based on the reduction/oxidation cycling of a new mixed iron-manganese oxide thermochemical energy storage material.

A power system design concept was developed, including technical concepts for a two-stage solar tower concentrating system, solar receiver-reactor for the thermal reduction step, oxidation reactor-heat exchanger for heat recovery, high-temperature particle storage tanks and material handling systems for particles and gases.

A literature review was conducted to compile data for the performance and cost of combined cycle power blocks. From this, the Levelised Cost of generated Energy (LCOE) has been determined. Based on the current cost-optimised system design with a 75 MW-e net power block and thermal energy storage system with 18 hours full-load storage capacity, an LCOE estimate of 224 AUD/MWh results (including 30% tax). This estimate is ~8% higher than that for a current state-of-the-art system.

To achieve LCOE close to targets such as the SunShot and ASTRI targets (below ~0.1 \$/kWh), depends on the long-term cost reduction learning curve of the industry as a whole, driving cost reductions in solar field and construction that would automatically transfer to a future development using a new receiver and storage approach such as this. Based on historical trends of deployment growth this can realistically be contemplated over the coming decade.

Further research is required to achieve additional cost reductions for the Fe67 system. This technology is currently undemonstrated. Hence, large efforts would be required to demonstrate the predicted performance of this technology at a relevant scope and scale (~100 kW or above).

# Project Overview

## Project summary

This project developed a novel high-temperature thermochemical energy storage system to be used for solar power generation.

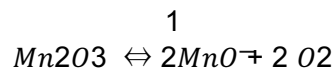
## Project scope

This project aimed to develop a novel high-temperature thermochemical energy storage system for dispatchable and efficient concentrating solar power generation.

The storage process concept is illustrated in Figure 1.

Solar radiation provides heat which drives a reduction reaction that liberates oxygen gas and converts manganese-based compounds progressively into higher enthalpy states as their temperature increases, thus “charging” the solids with solar energy. The hot, high-enthalpy, manganese-based particles are sent to a “hot” tank for storage, such that they can later be re-combined with oxygen gas in an oxidation reactor. The oxidation reaction converts stored chemical energy to heat, which is used to drive a power block to generate power on demand. The cooled re-oxidised particles are sent to the cold particle storage, from where they are drawn during the next cycle into the reduction reactor, completing the reduction/oxidation (redox) cycle.

The project originally considered manganese oxide (Mn<sub>2</sub>O<sub>3</sub>) as the storage material, undergoing the following redox process:



Work at ANU and University of Colorado on development of new mixed metal oxide storage materials formed part of the ANU led research project and the final selected storage material was an iron-manganese oxide spinel with formula (Fe,Mn)<sub>2</sub>O<sub>3</sub>, with a Fe:Mn ratio of 2:1.

This storage concept allows solar energy to be stored thermo-chemically at temperatures of over 1000°C, which allow converting the collected energy via a combined gas/steam (Brayton- Rankine) power cycle. This is the most efficient commercially available power conversion technology to date, reaching heat to net power conversion efficiencies of up to 60%, compared to around 42% with current sub-critical steam power cycles.

However it was found that this step change in power cycle performance needs to offset the potentially higher costs involved with a system operating at higher temperatures, in order to yield a cost advantage vis-à-vis the state-of-the-art solar thermal power technologies.

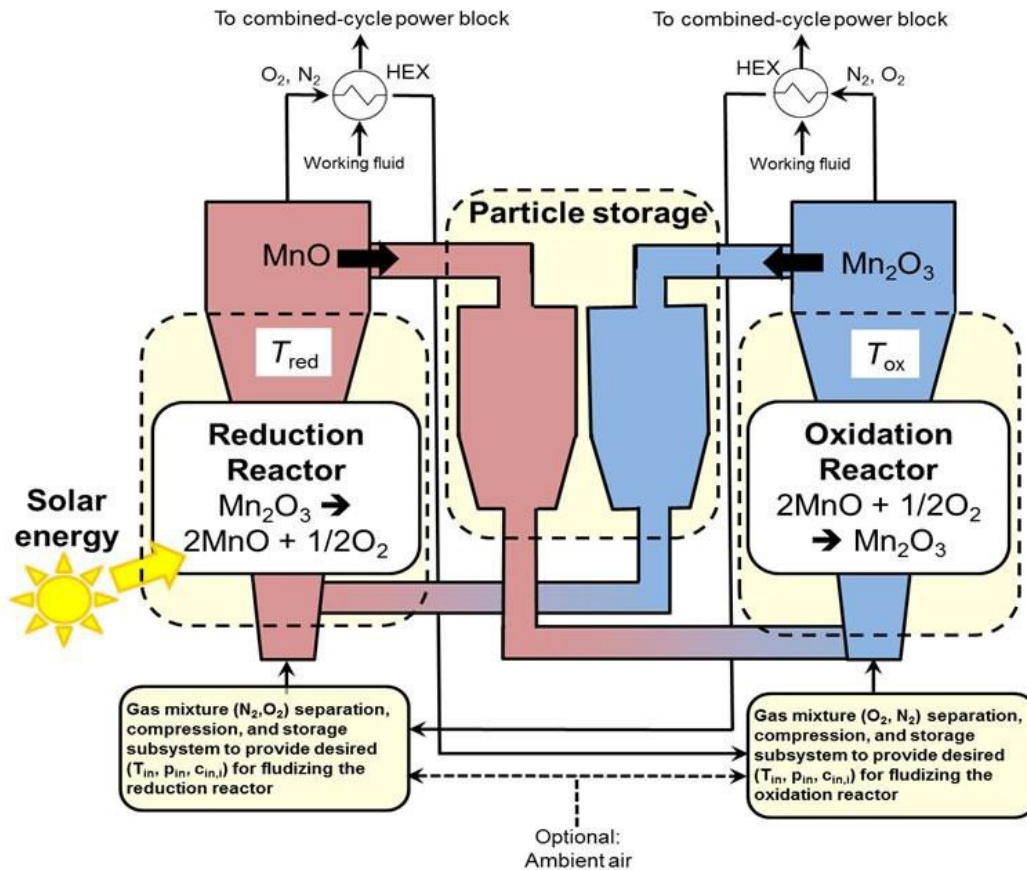


Figure 1. Original concept of the manganese oxide based redox thermochemical storage process (source: University of Colorado/ANU).

A Techno-Economic analysis, was also completed, that incorporates cost estimation and overall determination of the potentially achievable Levelised Cost of Energy. This analysis was intimately linked with the fundamental work on reaction kinetics, choice of active material, reactor design, solar concentration system design and other aspects of system design carried out by the research team led by ANU.

The explicit TEA work also built on energy balance and process flow analysis carried out by student groups at the University of Colorado and by Qi Lei, former Masters student at ANU.

## Outcomes

In order to carry out the TEA, a system design concept with sufficient detail to act as a baseline or starting point was developed. This is not a fully optimised concept as this would exceed the scope of this initial feasibility analysis. Further detailed design engineering will be required to arrive at a final system design.

Key design decisions made to establish this baseline include:

- Fluidised vs non-fluidised reduction/oxidation reactors

- Operation of reactors in nitrogen/oxygen with gas separation and O<sub>2</sub> storage vs. or atmospheric air
- Bucket elevator vs pneumatic solids transport
- Surround solar field vs polar field
- Coupling/decoupling of solar receiver-reactor with/from power block
- Component sizing (solar field, power block, thermal energy storage)

The starting point for the system design is a field of sun-tracking heliostats (mirrors) that redirect and focus sunlight onto a central receiver at the top of a tower as indicated in Figure 2. During sunshine hours, solar energy is collected with the receiver system. Solar energy passed through secondary concentrators is absorbed by absorber tubes inside the receiver.

One of the key findings of this initial feasibility study is that scale of the plant appears to be important. The energy output increased with increased size of the plant in a disproportionate ratio for no apparent reason. This was unexpected.

## Transferability

The fundamentals of the model were successfully demonstrated, however the cost of setting up and operating the plant as currently conceived is not economical, however as overall costs in the industry reduce, this may change.

## Conclusion and next steps

Overall, while the initially predicted LCOE for the Fe67 system is slightly higher compared to the reference molten salt plant, the new technology appears to have the potential to reach lower LCOE, through cost reductions in the oxidation heat exchanger and efficiency gains through higher solar concentration and temperatures.

To achieve LCOE close to targets such as the SunShot and ASTRI targets (below ~0.1 \$/kWh), depends on the long-term cost reduction learning curve of the industry as a whole, driving cost reductions in solar field and construction that would automatically transfer to a future development using a new receiver and storage approach such as this. Based on historical trends of deployment growth this can realistically be contemplated over the coming decade.

Further research is required to achieve additional cost reductions for the Fe67 system. This technology is currently undemonstrated. Hence, large efforts would be required to demonstrate the predicted performance of this technology at a relevant scope and scale (~100 kW or above).

Specific conclusions, based on the LCOE-optimised 75 MWe/18h TES system and comparison with molten salt state-of-the-art reference plant (104 MWe/10h TES):

- combined cycle block costs approximate the same as steam only system per unit of capacity at the same size but offers higher thermal efficiency.

- Installed costs are higher, mainly due to the addition of the large and expensive oxidation reactor/ORHX (+~\$159M), as well as due to the added cost of the bucket elevator system for the particles (+~\$78M).
- On the other hand, despite the high temperatures, lower costs are predicted for receiver and storage units.
- One bottle neck currently is the limited solar concentration of the solar field, which limits the system operating temperature and hence the power cycle efficiency.
- Additional losses are incurred by the CPCs and by the high-temperature receiver compared to a molten salt-based system.

This project identified potential ways to improve performance (and LCOE):

- Higher solar concentration should be targeted in order to achieve higher receiver and power cycle efficiencies.
- To operate the receiver at 1100°C with a comparable efficiency as existing molten salt receivers, the flux at the receiver aperture would have to be around 3 MW/m<sup>2</sup>.
- Cost reductions in the ORHX need to be achieved via an optimized design or lower material costs.
- System efficiency could be optimised by using gas exiting reduction reactor at 1200°C in oxidation reactor (~3.4% of absorbed solar power; included in design but not in system performance analysis).
- Any use of the gases exiting the hot side of the HRSG at 243°C with an energy/exergy content of 49.2/20.8 MW for preheating feedwater or other heat recovery could increase the system efficiency. The relatively high gas outlet temperature is due to the limitation imposed by the pinch point in the HRSG (gas cooling curve strongly differs from steam heating curve).
- Ideally, the power cycle would be operated at around 1300°C, to exploit the full efficiency benefit of the combined cycle. With that, efficiency gains in the power block of up to 15% may be achievable. To operate the power cycle at 1,300°C, the receiver would have to be operated at around 1,500°C. At this temperature, the achievable receiver efficiency would be around 63% with solar radiative flux at the receiver aperture of 1.5 MW/m<sup>2</sup>, and around 81% with a radiative flux of 3 MW/m<sup>2</sup> (with conduction and convection heat losses neglected/negligible).

# Lessons Learnt

## Lessons Learnt Report: Technology

<b>Knowledge Category:</b>	Technical
<b>Knowledge Type:</b>	Technology
<b>Technology Type:</b>	Solar Thermal
<b>State/Territory:</b>	ACT

### Key learning

Any use of the gases exiting the hot side of the HRSG at 243°C with an energy/exergy content of 49.2/20.8 MW for preheating feedwater or other heat recovery could increase the system efficiency. The relatively high gas outlet temperature is due to the limitation imposed by the pinch point in the HRSG (gas cooling curve strongly differs from steam heating curve).

### Implications for future projects

Refining the design to improve a preheating feedwater or improving heat recovery could increase the system efficiency

### Knowledge gap

Gaps identified are in relation to overall cost of componentry when taking the design to scale. How to reduce cost may involve testing with other metals to enhance heat recovery

### Background

#### Objectives or project requirements

Additional system performance improvements may be achievable via optimized system design and internal heat recovery. Currently, the hot exhaust gases exiting the system at 243°C carry an exergy content of 20.8 MW (for a 75 MW-e system).

#### Process undertaken

system modelling efforts included: i) estimate realistic overall system performance (solar-to-electric energy conversion efficiency) based on component models, including estimates of irreversibilities, such as turbine and compressor isentropic efficiencies and significant heat loss mechanisms; ii) identify the main mechanisms of energy loss and irreversibility; iii) determine optimised system operating parameters; iv) determine temperatures and mass and energy flow rates throughout the system, allowing for component (e.g. heat exchanger, pumps, turbines, storage tanks, etc) sizing.



# Lessons Learnt Report: Operation and Maintenance

<b>Knowledge Category:</b>	Technical
<b>Knowledge Type:</b>	Operation and maintenance
<b>Technology Type:</b>	Solar Thermal
<b>State/Territory:</b>	ACT

## Key learning

The results indicate that the solar radiation concentration achieved with current state-of-the-art surround heliostat fields and CPC secondary concentrators limits the operating temperature of the receiver to around 1,300°C, resulting in a storage temperature of ~1,200°C and power cycle temperature of ~1,100°C. This temperature is below the maximum temperatures used in the most efficient combined-cycle power blocks, which limits the efficiency gains achievable with the combined power cycle.

## Implications for future projects

Improved solar concentration could lead to higher receiver and power cycle efficiency, improving the overall system performance and LCOE.

## Knowledge gap

The field size used for the design is smaller than the reference Crescent Dunes, due to the efficiency constraints in the solar field. A larger solar field size is possible, but the efficiency of heliostats added at the fringe of the solar field is below 40% at the design point, compared to around 80% near the tower, making any investment in additional thermal power capacity more than twice as expensive. Further improvements in field design may influence the refinement of the system.

## Background

### Objectives or project requirements

The system was designed based on the concept that solar radiation would be concentrated via a two-stage concentrating system consisting of a heliostat field and CPCs mounted at the receiver aperture on the top of a tower. The solar concentrating system was designed and modelled separately with a geometric algorithm coupled to a ray-tracing radiative transfer simulation.

### Process undertaken

The solar field design rating is largely determined by the achievable field size at acceptable optical efficiency. The requirement for higher concentration demands high accuracy in the primary concentration stage. As solar fields grow larger, their concentration ratio increases (essentially increasing the rim angle of the field), but heliostats need to be placed at increasing distance from the receiver. Increasing distance of reflected sunlight leads to increasing dispersion of the beam (due to the sunshape and heliostat imperfections),

blocking (increasingly shallow grazing angle) and atmospheric attenuation. A field that yields approx. 300 MW-th of absorbed solar thermal power was considered the largest feasible field size. The optical efficiency of the selected field was calculated to be 48.5% with a thermal power of 264.2 MW-th at the design point. The next bigger field modelled yielded 322 MW-th with an overall optical efficiency of 42.5%.

The receiver temperature is limited by the overall concentration ratio. A solar field thermal rating of 300 MW-th has been used in the baseline system design. This was the largest field size deemed feasible at the time of the initial system design phase, based on the heliostat fields designed and analysed by ANU.

# Lessons Learnt Report: Financial

<b>Knowledge Category:</b>	Financial
<b>Knowledge Type:</b>	Technology
<b>Technology Type:</b>	Solar Thermal
<b>State/Territory:</b>	ACT

## Key learning

The higher Balance of Plant cost predicted compared to a state-of-the-art system is primarily due to the extra costs for a bucket elevator system (~\$78m) for particle transport to the top of the solar tower, and the need for cyclone separators, refractory-lined hot air ducting and bag filter systems.

On the positive side, lower storage system and receiver costs are predicted compared to the state-of-the-art system. This is attributed to the simplicity of the receiver design, the low cost of the storage material (Fe67) and a low-cost concept of refractory lined storage tanks.

## Implications for future projects

If costs in the ORHX can be substantially reduced (e.g. by 50%) through an improved design, LCOE lower than that for the state of the art may be achievable with this technology.

Overall, while the initially predicted LCOE for the Fe67 system is slightly higher compared to the reference molten salt plant, the new technology appears to have the potential to reach lower LCOE, in particular through cost reductions in the oxidation heat exchanger and efficiency gains through higher solar concentration and temperatures.

To achieve LCOE close to targets such as the SunShot and ASTRI targets (below ~0.1 \$/kWh), depends on the long term cost reduction learning curve of the industry as a whole, driving cost reductions in solar field and construction that would automatically transfer to a future development using a new receiver and storage approach such as this.

## Knowledge gap

Further research is required to achieve additional cost reductions for the Fe67 system. This technology is currently undemonstrated. Hence, large efforts would be required to demonstrate the predicted performance of this technology at a relevant scope and scale (~100 kW or above).

## Background

### Objectives or project requirements

The objective was to investigate “High temperature solar thermal energy storage via manganese-oxide based redox cycling”.

### Process undertaken

Solar radiation provides heat which drives a reduction reaction that liberates oxygen gas and converts manganese-based compounds progressively into higher enthalpy states as their temperature increases, thus “charging” the solids with solar energy. The hot, high-enthalpy, manganese-based particles are sent to a “hot” tank for storage, such that they can later be re-combined with oxygen gas in an oxidation reactor. The oxidation reaction converts stored chemical energy to heat, which is used to drive a power block to generate power on demand. The cooled re-oxidised particles are sent to the cold particle storage, from where they are drawn during the next cycle into the reduction reactor, completing the reduction/oxidation (redox) cycle. This storage concept allows solar energy to be stored thermo-chemically at temperatures of over 1000°C, which allow converting the collected energy via a combined gas/steam (Brayton- Rankine) power cycle. This is the most efficient commercially available power conversion technology to date, reaching heat to net power conversion efficiencies of up to 60%, compared to around 42% with current sub-critical steam power cycles. This step change in power cycle performance needs to offset the potentially higher costs involved with a system operating at higher temperatures, in order to yield a cost advantage vis-à-vis the state-of-the-art solar thermal power technologies. A new design for a storage system was built and tested. It was found to have a higher cost when compared to existing systems. There is the potential to reduce cost and improve efficiency with future design changes.