

J. González-Aguilar¹, & L. F. Cabeza², J. M. Coronado¹, Y. Ding³, M. Lanchi⁴,
M. E. Navarro³, J. Nieto-Maestre⁵, C. Prieto⁶, S. Sau⁴, O. Senneca⁷, C. Tregambi⁸, M. Wokon⁹

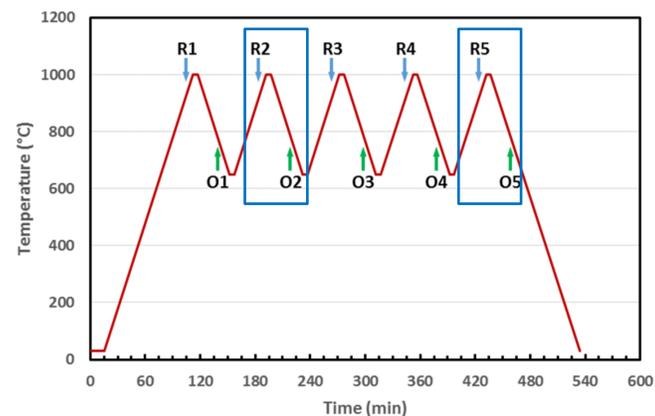
¹ IMDEA Energy Institute. Avda. Ramón de la Sagra, 3. 28935 Móstoles, Madrid, Spain; ² GREA Innovació Concurrent, Edifici CREA, Universitat de Lleida, Pere de Cabrera s/n, 25001 Lleida, Spain; ³ School of Chemical Engineering. The University of Birmingham. Edgbaston, Birmingham B15 2TT, UK; ⁴ ENEA-CR Casaccia. DTE-STT-ITES. Villa Anguillarese, 00123 Rome, Italy; ⁵ Tecnalia Research and Innovation, Mikeletegi Pasealekua, 2. 20009 San Sebastian (Gipúzcoa). Spain; ⁶ Abengoa. Campus Palmas Altas. Energía Solar, 1. Palmas Altas. 41014 Seville, Spain; ⁷ Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche, Piazzale ; incenzo Tecchio, 80, 80125 Napoli, Italy; ⁸ Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Piazzale Vincenzo Tecchio 80, 80125 Napoli, Italy; ⁹ German Aerospace Center, Institute of Engineering Thermodynamics, Linder Höhe, Building 26, 51147 Cologne, Germany

&Corresponding author: jose.gonzalez@imdea.org

Among systems proposed as suitable for thermochemical heat storage (TCS), redox oxides merit significant attention for high temperature applications in Concentrating Solar Power (CSP) plants. The specific enthalpy of the reaction is a key parameter to establish the storage capacity of the system. Consequently, there is considerable practical interest in accurately determining this parameter. Discrepancies in the referenced enthalpies may arise from inadequate protocols and/or sets-ups for measuring thermodynamic properties at high temperatures, or the presence of impurities in the samples. This work presents a round robin test (RRT) conducted by eight institutions, research centers and companies during 2015-2016 in order to develop a standard procedure for the measurement of enthalpies in the relevant thermochemical processes at high temperature. The initiative was organized within the Working Group on Thermal Storage (Activity on "Materials for Thermal Storage") in SolarPACES Task III.

METHODOLOGY

- **Cobalt oxide** Co_3O_4 has been the metal oxide selected: (i) It has a fast redox reaction (Co_3O_4 to CoO), of which reduction and oxidations temperatures are approx. 900 °C and 800 °C in ambient air, respectively; (ii) This reactant is a stable solid that remains unaltered for long storing periods; (iii) It has a relatively high reaction enthalpy compared to other metal oxides; and (iv) reaction enthalpy has been reported in the literature, which allows comparing obtained results.
- A **commercial sample** of Co_3O_4 (Cobalt (II, III) oxide, powder, <10 μm , Sigma Aldrich), which was previously confirmed to be active, was subjected to a thermal treatment and then was divided into aliquots and delivered by the RRT coordinator (IMDEA Energy) to the participants.
- **Thermal treatment** consisted in to keep the sample overnight in an oven at 110 °C to remove water and any other possible adsorbed impurity. The selection of a commercially sample facilitates the acquisition of duplicate measurements in the future and ensures a minimum available quantity, which often cannot be achieved in samples prepared in small batches at laboratory-scale. Besides any uncertainty associated with the sample origin is thus removed, as all laboratories analyze exactly the same batch.
- **Test procedure:** The sample was placed in the measurement system in a pure dry air flow of 100 cm^3/min . It is initially maintained at ambient temperature for 15 min, and then heated up to 1000 °C at a rate of 10 °C/min. The sample is then kept at 1000 °C during 5 min, cooled down to 650 °C at a rate of -10 °C/min, and maintained at this temperature for a further 5 min. The cycle between 650 °C and 1000 °C is repeated 4 times, thus completing a total number of cycles of five. Each participant should make two independent anal
- No instructions or indications were given on how to calibrate the measurement apparatus.

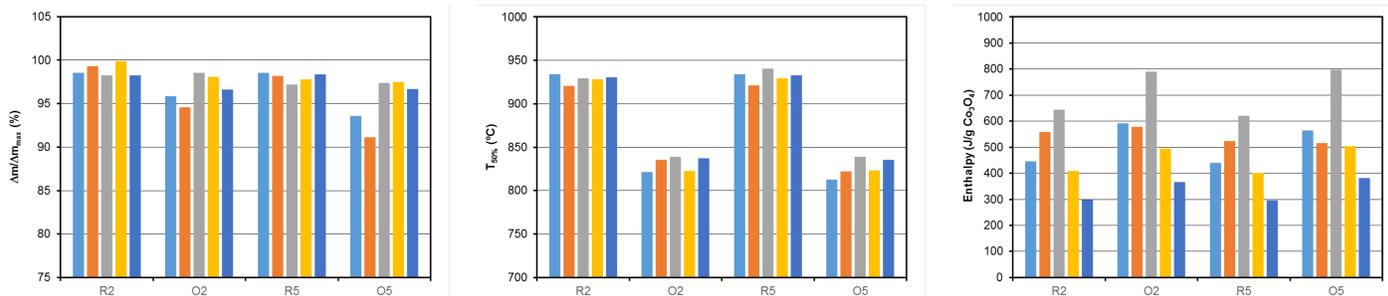


INSTRUMENTS

Description of apparatus and techniques used in the round robin test.

Partnr	Main characteristics
1	Instrument: Netzsch STA 409 Crucible: Alumina Dry gas: 100 mL/min pure synthetic air Calibration / Baseline: TGA and DSC curves obtained from the experiments were corrected by subtraction of corresponding blank curves. Notably blank curves were measured prior to the tests with Co_3O_4 by carrying out the same experimental run with an empty crucible.
2	Instrument: TGA/DSC 1 – Mettler Toledo Crucible: 70 μl Alumina crucibles. Calibration / Baseline: Silver (99.99%) was used as external reference to check the onset and heat flow calibration
3	Instrument: Netzsch STA 449 F3 Jupiter Crucible: 85 μl Pt/Rh Calibration / Baseline: Subtraction of black curves obtained prior to the tests
4	Instrument: Netzsch STA 449 F3 Jupiter Crucible: 85 μl Pt/Rh Dry gas: 20 mL/min oxygen (99.999%) and 80 mL/min nitrogen (99.999%) at atmospheric pressure Calibration / Baseline: The phase transition of salt standards were employed for temperature and sensitivity (heat flow) calibration. Blank measurement was performed for baseline correction.
5	Instrument: TGA/DSC/1100 Mettler–Toledo. Crucible: 70 μl Alumina crucibles. Dry gas: 100 mL/min pure synthetic air Calibration / Baseline: Calibration is performed regularly. The instrument has two arms, one of them supporting an empty crucible.

RESULTS



Comparison between RRT data and those from literature

Reference	Reduction			Oxidation		
	T (°C)	Mass change (%)	ΔH (J/g Co_3O_4)	T (°C)	Mass change (%)	ΔH (J/g Co_3O_4)
This work (cycle 2)	928 \pm 6	98.0 \pm 1.0	470 \pm 129	831 \pm 8	96.7 \pm 1.8	456 \pm 121
This work (cycle 5)	932 \pm 7	98.0 \pm 0.5	565 \pm 151	826 \pm 11	95 \pm 3	553 \pm 152
Block (9)	914.6	96.3	576	879.7	93.3	562
Carrillo (8)			601			496

- Measured reaction enthalpies presents a standard deviations as high as 27%, however the mean value has a difference smaller than 5% with respect to recent reported data.
- Reaction temperatures and mass change shows standard deviation around 10% and 3%, respectively.
- Dispersion is mainly justified by: (i) Diminution of the oxidation rate at low temperatures, which make difficult to establish a proper lower integration limit; (ii) Superposition of additional physico-chemical transformations, which contribution is difficult to distinguish and remove to the overall enthalpy change, within the same temperature range. Some authors has pointed out a structural modification of Co_3O_4 associated to a spin-state change around 847 °C. (iii) it is observed that two analyses (contributors 3 and 5) provide higher and lower values than the others, so that may be different internal protocols could affect their corresponding analyses.

CONCLUSIONS

The procedure for measuring the reaction enthalpy should be modified in order to avoid any enthalpy source other than redox reactions and ensure high oxidation rates (i.e. setting the lower temperature limit to higher values, changing the heating/cooling rates as well as isothermal periods). In addition to this, it is suggested to check the calibration method followed by the different laboratories.

ACKNOWLEDGEMENTS

The research leading to these results has received funding from EU FP7/2013-2017 under grant agreement n° 609837 (FP7 IRP STAGE-STE). JGA would like to thank "Comunidad de Madrid" support to the ALCCONES project (S2013/MAE-2985) through R&D activities Program between research groups 2103 and "Ministerio de Economía y Competitividad" support through Research Challenges project ARROPAR-CEX (ENE2015-71254-C3-1-R). The authors are also grateful for the support of E. Rojas from CIEMAT, Spain, within SolarPACES Task III activities.