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Exploitation of thermochemical cycles based on solid oxide redox systems for thermochemical storage of solar heat. Part 2: Redox oxide-coated porous ceramic structures as integrated thermochemical reactors/heat exchangers

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Abstract

The enthalpy effects of reversible chemical reactions can be exploited for the so-called thermochemical storage of solar energy. Based on the characteristics of the oxide redox pair Co_3O_4/CoO as a thermochemical heat storage medium and the advantages of porous ceramic structures like honeycombs and foams in heat exchange applications, the idea of employing such structures coated with a redox material like Co_3O_4 as a hybrid sensible-thermochemical solar energy storage system in air-operated concentrated solar power plants has been set forth and tested.

Small-scale, redox-inert, oxide and Silicon Carbide foams and honeycombs were coated with Co_3O_4 and tested for cyclic reduction–oxidation operation in Thermo-Gravimetric Analysis studies within the temperature range 800–1000 °C. Such supports demonstrated repeatable, quantitative, cyclic reduction–oxidation behavior, employing for the redox reactions the entire amount of the oxide material coated, even at very high loading percentages reaching 200 wt% for all oxide supports and one variety of Silicon Carbide support tested.

The longevity of such systems was tested successfully up to 100 consecutive cycles, at the end of which the coated supports maintained their structural integrity, together with the same, quantitative reduction–oxidation performance of the Co_3O_4 loaded.

Keywords: Solar energy; Thermochemical heat storage; Redox reactions; Cobalt oxide; Ceramic honeycombs; Ceramic foams

1. Introduction

Solar Thermal Power Plants (STPPs) produce electricity from the energy in the sun's rays. Direct solar radiation is concentrated on a focal point by a range of Concentrating Solar Power (CSP) technologies, i.e. by movable mirrors that track the sun, providing thus medium- to high-temperature heat. A heat exchanger (receiver) is located in the concentration field of the radiation, in which a heat transfer fluid/HTF (air, water, molten salt) is solar-heated and then used to operate a conventional power cycle. One of the main differences between CSP and other renewable energy technologies is CSP's potential for Thermal Energy Storage (TES) i.e. its inherent capacity to store heat for short time periods for later conversion to electricity when clouds block the sun or after sundown (IEA, 2010).

There are three types of implementing TES, based on the "nature" of heat to be stored: sensible, latent and thermochemical heat (Gil et al., 2010). ThermoChemical

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Storage (TCS) exploits the heat effects of reversible chemical reactions: the heat produced by a solar receiver during on-sun operation is employed to power an endothermic chemical reaction; the "consumed" thermal energy can be recovered completely by the reverse, exothermic reaction taking place during off-sun operation. Among the possible reversible gas–solid reactions (e.g. decomposition of metal hydroxides, carbonates or oxides) with substantial thermal effects, the utilization of a pair of redox reactions involving solid oxides of multivalent metals, like the exemplary scheme of cobalt oxides Co_3O_4/CoO operating as in reaction (1) below, is most attractive for large-scale deployment in STPPs using air as the heat transfer fluid. In this case air can be used as both the heat transfer fluid and the reactant (O_2) and therefore can come to direct contact with the storage material (oxide) with the two reduction/oxidation reactions producing simply oxygen-rich or oxygen-lean air:

$$Co_3O_4 + \Delta H \leftrightarrow 3CoO + 1/2O_2 \quad \Delta H = 200\ kJ/mol_{react}\ \text{or}\ 844\ kJ/kg_{react} \qquad (1)$$

The Co_3O_4/CoO redox pair in particular, is considered among the most attractive ones due to its high energy density (Wong, 2011), good reaction kinetics (Wentworth and Chen, 1976) and long-term material stability (Hutchings et al., 2006; Wong et al., 2010). Systems based on this pair have been recently tested for TCS applications via Thermo-Gravimetric Analysis/Differential Scanning Calorimetry (TGA/DSC) parametric studies, either pure (Agrafiotis et al., 2014b) or in combination with other oxides of multivalent metals like iron (Block et al., 2014) or manganese (Carrillo et al., 2014) to determine their proper operating temperature range, optimize the process parameters for maximum reduction and re-oxidation extent and quantify their relevant heat effects.

TCS has inherent advantages like high storage energy densities, indefinitely long storage duration at near ambient temperature and suitability for large scale. However, one of the major technical challenges for its industrial implementation is the proper design and operation of TCS reactors that will operate simultaneously and efficiently as heat exchangers suitably incorporated within the solar plants' infrastructure. Redox-oxide packed bed reactor concepts proposed so far involve either "...*Indirect heat exchange in the reaction zone by an external heat exchanger or direct heat exchange by flow of a heat transfer fluid through the reaction zone, which could be simultaneously the gaseous reactant and/or an inert gas*..." (Schaube et al., 2010). Indirect heat exchange is less efficient whereas direct flow of a gaseous stream through a packed bed of solid reactants induces high pressure drop, especially if the solid particles are of fine dimensions (Buckingham et al., 2011). Their counter-part fluidized bed reactor concepts even though can enhance mixing, diffusion and heat transfer characteristics, involve high gas pressures and transport/recirculation of (hot) solid particles, having to face, in addition to the expected attrition and corrosion/erosion problems, major parasitic power consumption limiting their potential for efficient scale-up.

Sensible heat is the preferred heat storage type for central receiver power plants using air as a heat transfer medium; for these "...*the proven technology of the existing industrial high-temperature TES systems, commonly known as regenerators, recuperators and cowpers, can be considered as the straightforward solution*..." (Tamme et al., 1991). For example, in the Solar Tower power plant of Jülich (STJ), Germany, inaugurated in 2009, air at atmospheric pressure is solar-heated up to about 700 °C and then powers a steam generator. In parallel, a sensible heat storage system is integrated into the power cycle, in which the air exchanges heat and transfers its enthalpy to a solid medium as it flows along a flow-path through it. The storage system consists of a rectangular housing of 7 m × 7 m × 6 m size (Zunft et al., 2009, 2010). Instead of pursuing a monolithic design, its volume is partitioned into four chambers of identical size, connected in parallel through a dome and connecting pipes. Each chamber is filled with an array of ceramic storage material. Comparative studies among many storage media like packed beds of broken basalt or ceramic spheres, ceramic saddles, checker bricks etc., have culminated to materializing the storage medium as a modular array of flow-through ceramic honeycombs that provide a large heat exchange surface between the air and the solid storage medium (Zunft et al., 2014). At rated operation conditions, during on-sun operation ("charging" phase) "hot" air is supplied from the solar tower to the top of the storage medium at a temperature of ≈680 °C – if needed, this temperature can be exceeded in future such plants – and exits at the bottom at a temperature ≈120 °C. During off-sun operation ("discharging" phase) the air flow is reversed: "cold" air is introduced through the lower end of the already "hot" storage medium to be heated by that as it flows towards its top end, before being introduced again to the steam/power block. The technology is simple in operation but the full load discharge period of this assembly is limited to about 1.5 h with the total volume of the inventory being relatively large and amounting to 120 m^3.

Stemming from this fact and on the establishment of structured reactors based on functionally-coated porous ceramics like honeycombs and foams in a plethora of chemical engineering applications (Cybulski and Moulijn, 2005), the idea of employing similar ceramic honeycombs and foams coated with or manufactured entirely from a redox oxide like Co_3O_4, has been recently set forth by the present authors (Agrafiotis et al., 2014a; Tescari et al., 2014). By simply coating the currently existing redox-inert honeycombs with any redox oxide capable of operating within the specific temperature range or manufacturing them entirely of it, the sensible heat storage employed at STJ can be transformed to a "hybrid" thermochemical–sensible one. In this principle it is not expected from the (relatively thin) redox coating to heat up the entire redox-inert porous structure, but the opposite: by heating