



# Exploitation of thermochemical cycles based on solid oxide redox systems for thermochemical storage of solar heat. Part 3: Cobalt oxide monolithic porous structures as integrated thermochemical reactors/heat exchangers

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## Abstract

In the perspective of thermochemical storage of solar energy via redox reactions of multivalent metal oxides, the manufacture and relevant testing of porous ceramic foams made entirely of  $\text{Co}_3\text{O}_4$  was attempted, in order to maximize the amount of redox powder that can be incorporated in a given thermochemical reactor volume.

Small-scale  $\text{Co}_3\text{O}_4$  foams with satisfactory structural integrity were successfully produced. The foams were tested in cyclic reduction/oxidation conditions in a TGA apparatus in comparison to pellets made also entirely of  $\text{Co}_3\text{O}_4$ . Both these monolithic, porous, structures were capable of cyclic redox operation, exploiting for the thermochemical reactions the entire amount of redox material used for their manufacture. Full extent of reduction/oxidation was observed, in a fully reversible pattern.

The initial density of the samples had an effect on specimen's integrity: the much denser pellets could not retain their structural integrity, exhibiting cracks even after only two cycles. On the contrary, foams were tested for up to 15 redox cycles, maintaining simultaneously their structural integrity and stoichiometric redox performance.

Dilatometry experiments under the same temperature-programmed conditions with the TGA ones revealed that during redox cycling, “chemically”-induced stresses are developed due to the expansion/contraction of the cobalt oxide lattice during oxygen release/uptake respectively. These stresses are superimposed to “thermal-only” ones due to temperature cycling and under certain circumstances can lead to structure deformation and fracture. In this respect “open” porous structures like the particular foams proposed and tested in this work have an advantage since their large void space can reversibly accommodate and “buffer” the large volume expansion much better.  
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**Keywords:** Solar energy; Thermochemical heat storage; Redox reactions; Cobalt oxide; Structured reactors; Ceramic foams

## 1. Introduction

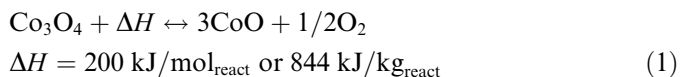
Several redox pair oxides are capable of thermal reduction and reversible oxidation under air atmosphere like in

Reaction scheme (1) below, written for the  $\text{Co}_3\text{O}_4/\text{CoO}$  system (Galwey and Brown, 1999; Lundberg, 1993). The oxides for which such reactions are accompanied by significant heat effects, are in principle prime candidates as ThermoChemical Storage (TCS) media (Gil et al., 2010; Kuravi et al., 2013; Pardo et al., 2014b; Wong, 2011) in air-operated Concentrated Solar Power (CSP)

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plants, provided that efficient thermochemical reactors/heat exchangers can be designed and operated within the solar plants' infrastructure. The  $\text{Co}_3\text{O}_4/\text{CoO}$  system in particular, in addition to its high energy density, good reaction kinetics and long-term material stability (Hutchings et al., 2006; Wong et al., 2010) is characterized by quantitative, reproducible and long-term, cyclic redox operation (Agrafiotis et al., 2014b). In this respect it is often employed as a “model” system when new ideas for such thermochemical reactor concepts for concentrated solar power applications are to be implemented in practice.



Thermochemical heat storage using a storage medium in the form of powder can be performed via several reactor concepts for example packed beds, fluidized beds (Pardo et al., 2014a) or rotary kilns. However, simulation studies have indicated that such packed bed reactor designs coupled to a power tower solar plant will not be economically competitive due to trade-offs that have to be made among parasitic loads, pressure drop, operation temperature and bed particle size (Buckingham et al., 2011). To combine the relevantly high temperature required for the thermal reduction of  $\text{Co}_3\text{O}_4$  ( $\approx 885^\circ\text{C}$ ) with low pressure drop, directly-irradiated rotary kiln reactors utilizing  $\text{Co}_3\text{O}_4$  powder have been developed and tested by the German Aerospace Center/DLR (Neises et al., 2012; Tescari et al., 2013). Even though the feasibility of this concept was successfully demonstrated, potential problems encountered in the scale-up of particle-based, (solar) reactors have led the current authors to propose the concept of structured porous ceramics like honeycombs and foams coated with a redox pair oxide system, as hybrid sensible/thermochemical storage modules for such air-operated CSP plants (Agrafiotis et al., 2014a, 2015b; Tescari et al., 2014). Honeycombs are characterized by their cpsi (cells per square inch) number and foams by their ppi (pores per linear inch) number: higher cpsi/ppi denote “denser” structures with thinner channel walls/struts and more, but smaller, air flow channels per cross-section area unit, i.e. higher gas–solid contact area per unit volume. Indeed, the inherent advantages of highly porous ceramic structures like monolithic honeycombs and foams vs. packed powder beds, such as thin walls, high geometric surface area, good gas–solid contact and accommodation of high gas flow rates combined with low pressure drop, have led to the replacement of conventional packed bed reactors and the establishment of such “structured” catalytic systems as the configuration of choice in a variety of catalytic applications. The most notable such examples are automotive exhaust after-treatment and catalytic combustion. Usually such structured catalysts have a large void fraction ranging from 0.7 to more than 0.9 (in the case of foams) depending on their cpsi/ppi, compared to ca 0.5 in packed beds. Scale-up of

structured reactors is much easier than of random and chaotic systems, such as packed beds, slurry reactors and fluidized bed reactors (Cybulski and Moulijn, 2005).

Ceramic foams in particular, have been originally used for molten metal filtration and subsequently as flame diffusers (Scheffler and Colombo, 2006) prior to their use as catalytic supports. Ceramic foams “...exhibit extremely high porosities, with a significant degree of interconnectivity that results in low pressure-drop. High convection in the tortuous megapores gives enhanced mass and heat transfer. Furthermore, with respect to their honeycomb monolithic counterparts, foams have a considerable degree of radial mixing, which is an advantage in processes limited by heat transfer and can even out flow distribution...” (Twigg and Richardson, 2002, 2007). In fact catalyst-coated ceramic foams have been employed in CSP-related applications prior to honeycombs: the first example of such a “structured” solar reactor can be traced back in 1990 when solar reforming of methane with  $\text{CO}_2$  in a directly irradiated volumetric receiver-reactor was demonstrated in the “CAtalytically Enhanced Solar Absorption Receiver” (CAESAR) experiment conducted by Sandia National Laboratories (SNL), U.S.A. and DLR, Germany, where  $\alpha$ -alumina-mullite foam disks, coated with  $\gamma$ -alumina washcoat and Rh catalyst were placed in an absorber located in the focal point of a solar parabolic dish (Buck et al., 1991). Second- and third- generation SiC-foam-based solar chemical receiver-reactors were designed and tested on the solar tower of the Weizmann Institute of Science (WIS), Israel within a joint WIS-DLR project (Wörner and Tamme, 1998).

There exists though an important difference between “traditional chemical engineering” gas–solid catalytic reactions and the gas–solid reactions employing oxide redox pair materials. In most “traditional” chemical engineering applications the ceramic support structure is itself inert with respect to the targeted gas–solid chemical reaction functionality: it is used either as a physical filtration means or as a chemically inert porous support upon which chemically active species like catalysts are dispersed. Therefore in cases of chemical reactions, the volumetric product yield is small since the major part of the reactor's volume is occupied by the chemically inert support. On the contrary, in the gas–solid redox-pair-based thermochemical cycles, the solid reactant (metal oxide) is not a “catalyst” present in much smaller quantities than those of the gaseous reactants, but a reactant itself, with non-negligible mass, that not only has to be heated to the reaction temperature but gets progressively depleted during the course of the reaction (Agrafiotis et al., 2015a). Thus, the reactor being either a packed or fluidized bed or a porous structure like a honeycomb or a foam, has to incorporate as much of the redox oxide solid reactant as possible in one hand to maximize volumetric product yield – reaction enthalpy, in the particular case of thermochemical storage – and in the other hand to avoid the “waste” of external energy in heating chemically-inert materials. Thus, toward the goal of increasing volumetric product yield of such structured

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