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A numerical model for the CO_2–sodium chemical interactions in Sodium Fast nuclear Reactors

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ABSTRACT

Supercritical CO_2 (sCO_2) Brayton cycles have gained interest in the frame of Sodium-cooled nuclear Fast Reactors (SFRs), as an alternative to the conventional water Rankine cycles. If CO_2 leaks inside the CO_2–Na heat exchanger, an underexpanded CO_2-into-liquid-sodium jet is formed. CO_2 chemically reacts with sodium, following an exothermic reaction which forms mainly solid products. In order to develop a model to numerically reproduce the jet development, a detailed description of the CO_2–Na chemical reaction mechanism must be investigated. In this paper, a chemical reaction model at the dispersed phase scale between CO_2–sodium, inside an underexpanded CO_2-into-sodium jet, is presented. The model considers the reaction between a sodium droplet with the surrounding CO_2 environment for the region close to the leakage, where mist flow is supposed to exist, and between a CO_2 bubble with the surrounding liquid sodium environment for the region further downstream the leakage, where bubbly flow takes place. The depletion rate for a single particle (droplet or bubble) is determined, as a function of the main influencing parameters, such as temperature, droplet slip velocity, bulk mass fractions, and the chemical kinetics.

1. Introduction

In SFRs, sCO_2 Brayton cycles represent an interesting alternative to water Rankine cycles (Alpy et al., 2011; Floyd et al., 2013), since they eliminate the wastage accidental scenario caused by the sodium water reaction (SWR) (Eoh et al., 2010) and feature high thermodynamic plant efficiency (up to 42%, Floyd et al., 2013). Nevertheless, CO_2 reacts exothermically with sodium, forming solid reaction products. Several experimental studies on sodium–CO_2 reaction (SCR) have been recently performed, in the frame of the application of sCO_2 Brayton cycles for SFRs. Miyaharaa et al. (2011) performed experimental studies on SCR, for both superficial and jet contact configurations between the reactants. Sodium was initially heated up to 600 °C: the largest amounts of reaction products found were sodium carbonate and amorphous carbon. Eoh et al. (2011) performed experimental studies on superficial CO_2–sodium reaction, with sodium initially heated up to 600 °C: based on the measured concentrations of CO and CO_2 species in the vent gas, Eoh et al. found that a threshold between a low and a high reaction rate could be fixed at 460 °C. Moreover, for all sodium temperatures, the major component of the solid reaction products was found to be sodium carbonate, and the quantity of formation steadily increased in proportion to the increase in sodium temperature. Consistently with the results obtained by Eoh et al., the experimental tests on CO_2–sodium reaction performed in our research team (Gicquel, 2010) showed two different reaction paths and kinetics depending on a sodium initial temperature lower or higher than 500 °C. The contact mechanism realized between CO_2 and sodium was both superficial and jet configurations, with initial sodium temperature ranging from 400 °C to 700 °C. Since

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Nomenclature

Y	mass fraction (kg $(\mathrm{kg_{tot}})^{-1}$)
M	molecular weight (kg $(\mathrm{kmol})^{-1}$)
P	pressure (Pa)
ρ	density (kg $\mathrm{m^{-3}}$)
k	molar kinetic constant ($\mathrm{m^3}$ $(\mathrm{mol\,s})^{-1}$)
k_0	pre-exponential factor [$\mathrm{m^3}$ $(\mathrm{mol\,s})^{-1}$]
E_a	activation energy (J $\mathrm{mol^{-1}}$)
D	diffusion coefficient ($\mathrm{m^2\,s^{-1}}$)
r	radial distance (m)
v	global velocity of mixture inside the boundary layer ($\mathrm{m\,s^{-1}}$)
s	stoichiometric coefficient of (1)
ΔH_r	enthalpy of reaction of (1), at 298 K (kJ $(\mathrm{kmol})^{-1}$)
λ	thermal conductivity (W $(\mathrm{mK})^{-1}$)
R	droplet or bubble radius (m)
R_g	gas constant (kJ $(\mathrm{kmol\,K})^{-1}$)
T	temperature (K)
σ	superficial tension ($\mathrm{N\,m^{-1}}$)

Subscripts

1	sodium vapor
2	carbon dioxide
p	reaction products
∞	bulk condition
sat	saturated (equilibrium) condition

inside a large part of the CO_2–Na heat exchanger of an SFR the sodium temperature is higher than 460 °C, the following reaction path is retained in the present study, based on the experimental results discussed:

$$\mathrm{Na} + \frac{3}{4}\mathrm{CO_2} \rightarrow \frac{1}{4}\mathrm{C} + \frac{1}{2}\mathrm{Na_2CO_3} - 272\,\mathrm{kJ/mol_{Na}} \qquad (1)$$

Even if this reaction path has been well identified through different experimental studies, the global reaction kinetics parameters, comprehending the mass transfer and chemical kinetics phenomena, of the reaction (1) have not been clearly identified yet. The pre-exponential factor and activation energy of an Arrhenius law were determined by Eoh et al., but only for the specific case of a CO_2–Na flat free surface contact, without continuous mixing. In the case of leakage inside a CO_2–Na heat exchanger, an underexpanded CO_2-into-liquid-sodium jet would form, due to the extremely high CO_2-to-Na operative pressure ratio (more than 200 bar in the CO_2 side and nearly atmospheric pressure in the sodium side (Floyd et al., 2013)): the contact mechanism between sodium and CO_2 is, therefore, significantly different from a flat surface contact. The global kinetics parameters are fundamental in order to develop a numerical model of the leakage, which, in turn, would be useful to understand the production rate, the space and time distribution of the solid products as well as the temperature variation inside a Na-CO_2 heat exchanger and on the tube surfaces, following a leakage scenario.

In order to comprehend the kinetics of the CO_2–Na chemical reaction inside such a two-phase jet flow, the specific contact mechanism between gas and liquid must be considered. Inside an underexpanded gas-into-liquid jet, different two-phase patterns coexist. At the leakage outlet, the gas leaks at sonic conditions and suddenly increases its velocity due to the underexpansion: the high slip velocity between the phases causes a continuous breakup of the gas–liquid interface, which leads to the entrainment of small liquid droplet inside the gas phase. Liquid entrainment inside underexpanded gas-into-liquid jets have been recently experimentally investigated and confirmed by Epstein et al. (2005) and Kudoh et al. (2013). Starting from a certain point downstream the leakage outlet, the gas core breaks up into small gas bubbles: this behavior have been experimentally observed by Vivaldi et al. (2013). Therefore, two different CO_2–Na contact typologies can be distinguished inside the considered jet: sodium droplet surrounded by CO_2, for the mist flow region, and CO_2 bubble surrounded by liquid sodium, for the bubbly flow region. The need of developing a new numerical approach for this type of chemical reaction has been suggested by the fact that the available numerical models, regarding gas–liquid-sodium chemical reactions, lack the necessary details required for the proper description of the SCR mechanism here studied. Epstein et al. (2006) developed a numerical model for the SWR in the frame of SFRs. The model considers a sodium droplet depletion through reaction with surrounding water steam, with the presence of a reaction front around the sodium droplet, where the gaseous reactants (vapor sodium from the droplet and water steam) meet in accord with stoichiometry. This approach is based on the assumption of an infinitely fast reaction rate. Since no experimental data allow to classify the SCR as an infinitely fast chemical reaction as the SWR is, the mass diffusion process may not be the limiting one in the case of SCR, and the assumption of an infinitesimal reaction front cannot be retained. Epstein et al. did not take into account the chemical reaction inside the bubbly flow regime. Takata et al. (2009) modeled the SWR inside a steam-into-liquid-sodium jet employing an analogy between heat and mass transfer: the reaction rate is a function of the Lewis number, the heat transfer coefficient between the phases, the specific heat of the gas phase, the steam mass fraction and the interfacial area. The interfacial area was evaluated through the Nigmatulin model (Rivard and Torrey, 1976) which is based on purely bubbly flow. Moreover, in their model, Takata et al. assumed the SWR infinitely fast and limited only by the mass diffusion. Kim et al. (2007), in their modeling study on SWR inside an SFR, calculated the reaction rate between steam and water employing an eddy dissipation model: this approach is based on the assumption that the chemical reaction is fast enough that the reaction rate is directly related to the time required to mix the reactants at a molecular level. In their numerical model of a CO_2-into-liquid-sodium jet, developed to comprehend their experimental results, Gicquel et al. (2010) employed an Arrhenius law for the determination of the global reaction rate between the two reactants, therefore assuming the reaction rate independent on the actual two-phase flow regime. The present paper presents a new numerical approach, more consistent with the specific CO_2–sodium chemical reaction inside a CO_2-into-liquid-sodium underexpanded jet. Two separate numerical approaches have been developed for the two different two-phase regimes coexisting in such a two-phase flow. Both chemical reaction and mass diffusion rates are taken into account in the modeling approach, without retaining the assumption of infinitely fast chemical reaction kinetics.

2. Sodium droplet reaction in CO_2 flow

In order to describe the interaction mechanism between a sodium droplet and the surrounding CO_2, the system represented in Fig. 1 is considered.