Supplementary Materials for "Coupled hydrodynamic and kinetic model of liquid metal bubble reactor for hydrogen production by noncatalytic thermal decomposition of methane"

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Discussion on heating methods for different reactor temperatures

An important factor in the economics of hydrogen production by methane decomposition in a liquid metal bubble reactor is the manner in which the heat of reaction is provided. The reaction temperature is a determining factor for selecting the heating equipment. Parkinson et al. [1] found that a gas-fired heater combined with a reactor temperature of 1000°C could lead to a process competitive with SMR even without a carbon tax. By contrast, carrying out the reaction at 1500°C in liquid iron heated by an electric arc furnace was not competitive with SMR, unless a carbon tax of $\$78.t^{-1}$ was imposed.

The maximum temperature to which a heat transfer fluid can be heated in a fired heater depends on the upper temperature limit of the tubes transporting the fluid in the radiant zone where temperatures are the highest. Fired heater tubes made of high nickel alloys (e.g., UNS N06025) are limited to maximum operating temperatures of around 1200°C [2]. Moreover, the temperature of the heat transfer fluid leaving the fired heater must be higher than the bulk temperature of the liquid metal inside the reactor for heat transfer to occur. Hence, the use of a fired heater likely limits the methane decomposition temperature to 1100°C or less.

An electric arc furnace (EAF) can be used to operate the methane decomposition reactor at temperatures above 1100°C [1]. EAFs used for melting steel scrap typically operate between 1500°C and 1675°C [3,4]. The methane decomposition reaction should preferentially be carried out inside the EAF to avoid the materials and engineering challenges posed by circulating the liquid metal externally, as discussed below. The disadvantages of EAF technology compared with a gas fired heater include potentially larger capital costs and associated CO_2 emissions if the electricity is generated from fossil fuels [1].

Besides temperature, compatibility of liquid metals with materials of construction, especially metal alloys, is a significant design challenge. Corrosion arises from the dissolution of major elements from alloys into the liquid metal. In particular, nickel, which is a key component of most high temperature alloys, is highly soluble in liquid metals and therefore can become depleted in a near-surface zone of the solid [5]. External heating of the liquid metal outside the reactor in a gas fired heater or an electric arc furnace would subject the required piping, pump, and heat exchange equipment to corrosion by the liquid metal.

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By contrast, in-situ heating of the liquid metal in the reactor would avoid direct contact between the liquid metal and structural metals. A layer of refractory material (e.g., MgO-C refractory brick) could act as a liner between the liquid metal and the reactor outer walls [6]. In this configuration, the reactor walls would be at a much lower temperature than the liquid metal and could be made of carbon steel, which is considerably cheaper than high temperature alloys. Parkinson et al. [6] describe a novel reactor concept that uses molten salt as an intermediate heat transfer fluid between the molten metal in the reactor and a gas fired heater. The salts KCl-$MgCl_2$ and NaCl-$MgCl_2$ have relatively low costs (\$0.35 and \$0.42 L^{-1}, respectively), and can be used at very high temperatures since their normal boiling points are above 1418 and 1465°C, respectively [7,8].

If molten salts were used as intermediate heat transfer fluid, potential corrosion of fired heater tubes and fluid transport equipment would be an important design consideration. Studies of several candidate molten salts for high temperature nuclear reactors revealed that corrosion rates of high nickel alloys immersed in $MgCl_2$-KCl ranged from 0.045 to 1.3 mm.yr^{-1} at 850°C [9]. Hu et al. [10] reported a corrosion rate of 0.73 mm.yr^{-1} for Inconel 600 (UNS N06600) in NaCl-$MgCl_2$ at 500°C. To the authors' knowledge, results of corrosion tests with molten salts at the higher temperatures needed for application in methane decomposition reactors are not available in the literature.

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