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Mass transfer in molten salt and suspended molten salt in bubble column

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HIGHLIGHTS

- CO_2 mass transfer behaviors in molten carbonates in bubble column were investigated.
- CO_2 gas solubility were determined at temperature from 673 K to 1173 K.
- Solubility was increased with increasing temperature.
- The influences of temperature and superficial velocity on k_La were indicated.

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ABSTRACT

Recently, the practical uses of bubble columns and slurry bubble columns at elevated temperature have attracted much attention. However, there is less knowledge of mass transfer in high temperature slurry bubble column, even though mass transfer data is essential to design bubble column and slurry bubble column. In this study, the CO_2 mass transfer in eutectic mixtures of molten carbonate in bubble column at elevated temperature was investigated. CO_2 was chosen as gas species, eutectic mixtures of Li_2CO_3–K_2CO_3 (38:62 mol%) binary molten carbonate and Li_2CO_3–Na_2CO_3–K_2CO_3 (43.5:31.5:25 mol%) ternary molten carbonate were used as liquid phase. In those eutectic mixtures, CO_2 solubilities were determined at the temperature from 673 K to 1173 K. The values of solubilities increased with increasing temperature. It was suggested that CO_2 dissolved into binary and ternary molten carbonate with chemical interaction, $CO_2+CO_3^{2-}\leftrightarrow C_2O_5^{2-}$. Increasing the temperature shifted this equation to the right and then more CO_2 chemically dissolved into molten carbonates as $C_2O_5^{2-}$. From the CO_2 gas absorption rate in molten carbonates, CO_2 liquid phase volumetric mass transfer coefficients, k_La were determined and the influence of temperature and superficial gas velocity on k_La was also investigated. The k_La decreased with increasing temperature. And the k_La increased linearly with increasing superficial gas velocity. Regardless of unusual conditions in molten salt in bubble column at high temperature, where viscosity, surface tension and gas diffusivity were relatively high, it was suggested that the superficial gas velocity was most important operation condition in common with aqueous bubble column at ambient temperature.

1. Introduction

Recently, the practical uses of bubble columns and slurry bubble columns at elevated temperature have attracted much attention. Cho et al. (2009) employed a molten salt bubble column as an oxidation reactor for treatment of hazardous wastes. Ozaki et al. (2010) proposed a high temperature molten salt slurry bubble column system to capture hot CO_2 from flue gas. Kanai et al. (2012) investigated its industrialization. The high temperature bubble column system makes possible a fast chemical reaction and leads to a downsizing of reactor. Then further applications are expected as gas–liquid reactors.

Molten salts are employed as reaction media and heat transfer fluids in chemical, electric and atomic industries. They have excellence in heat transfer characteristics and low vapor pressure. Those advantages of molten salts could realize the stable liquid phase at elevated temperature. Therefore they have so many potentials for application in bubble column at elevated temperature.

Although a number of researches were made concerning molten salt reactor, molten carbonate fuel cell and molten salt as heat storage material in solar power system, little is known about the mass transfer characteristics and gas–liquid reaction

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mechanisms in high temperature molten salt systems. The data which is mostly available in this field is gas solubility in some molten salts. However, the solubility data in molten carbonates is rare due to the difficulty of experiments caused by its comparatively high melting point. Furthermore, there is less knowledge of mass transfer coefficient in high temperature slurry bubble column. Sada et al. (1984) investigated the volumetric mass transfer coefficient k_La in LiCl–KCl and $NaNO_3$ molten salt systems, but no other data is available, even though mass transfer coefficient data is essential to design bubble columns and slurry bubble columns.

As reviewed by Lemoine et al. (2008), though a large number experiments and theoretical approach were made to predict the k_La value in bubble column, the majority of study was conducted under air/aqueous system at ambient condition. The prediction of hydrodynamics and mass transfer parameter in molten salt bubble column is unknown territory, where bubble column is operated under unusual condition such as high viscosity and surface tension of liquid phase and elevated operational temperature over 650 K.

Also, the influence of temperature on the gas–liquid mass transfer is open to dispute. Wilkinson et al. (1992) reviewed the influence of temperature on gas holdup and then its effect of mass transfer. Jordan and Schumpe (2001) studied the liquid phase volumetric mass transfer coefficients in organic liquids in bubble column at 293 K–343 K and Lau et al. (2004) studied in Paratherm NF heat transfer fluid at 298 K–365 K. Nedeltchev et al. (2010) recently developed a semi-theoretical method to predict the k_La value at elevated temperature. The experimental values (Jordan and Schumpe, 2001) and their theoretical model (Nedeltchev et al., 2006a, b, 2007) showed good agreements. Yet, the influence of temperature on k_La has not been studied well. Since molten salt liquid phase makes possible a wide range of temperature operation, more consideration about the influence of temperature on k_La is required, especially in higher temperature range.

In this study, the CO_2 mass transfer in molten carbonate in a bubble column at elevated temperature was investigated. CO_2 was chosen as gas species, because the solubility data of triatomic gases, such as CO_2 and SO_2 are scarce, although those gas species are very important in industrial chemistry. Eutectic mixtures, Li_2CO_3–K_2CO_3 (38:62 mol%) binary molten carbonate and Li_2CO_3–Na_2CO_3–K_2CO_3 (43.5:31.5:25 mol%) ternary molten carbonate were used. They are widely used in molten carbonate fuel cell, therefore their physical properties, i.e., densities, viscosities and surface tensions, are well known. And a depression of the melting point by eutectic salt effect permits the series of experiments at temperature 673 K–1173 K. Vapor pressure falls considerably by mixing several salts, it eases the solubility experiments.

In those eutectic mixtures, CO_2 gas solubilities at different temperature were investigated. From the CO_2 gas absorption rate in molten carbonates, liquid phase volumetric mass transfer coefficients k_La was determined. The influences of temperature T and superficial gas velocity U_G on k_La were also investigated.

2. Material and methods

2.1. Experimental setups

The experimental apparatus is shown in Fig. 1. The bubble column, made of stainless steel SUS-316L, was 3.1×10^{-2} m in inner diameter and 0.4 m in height. The gas sparger used in the present work was a single nozzle type, made of SUS-316L whose inner diameter and length were 5.4×10^{-3} m and 0.45 m, respectively. The nozzle was oriented downward vertically and located 1.5×10^{-2} m above the bottom of the column. The effluent gas was exhausted from the outlet which was located at canopy of the

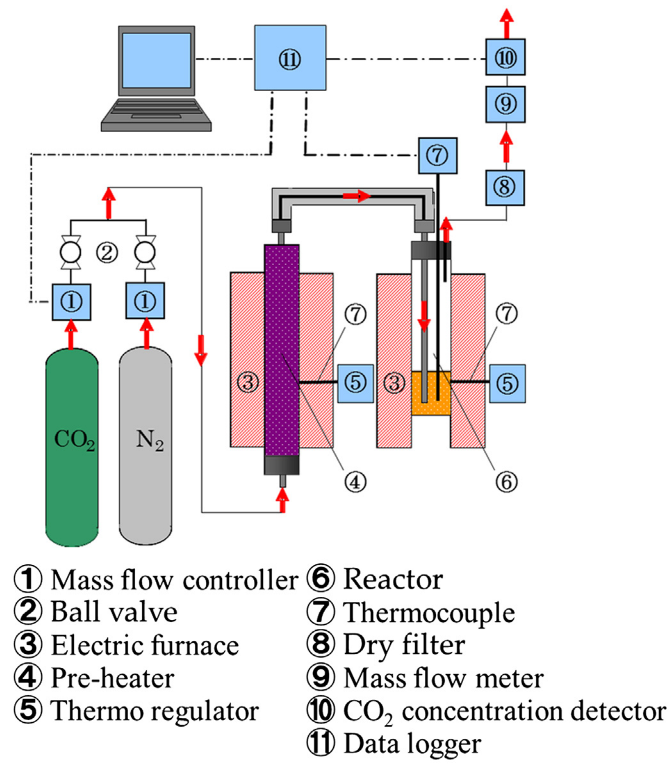

Fig. 1. Experimental apparatus.

column. The bubble column was heated in the circular electric furnace (Asahi Rika Seisakusho Co., Ltd. ARF-50KC) up to ca. 1173 K. A thermocouple was inserted into the column to measure the temperature of the molten carbonate. Pre-heater was consisted of a stainless cylindrical raschig ring packed bed and the circular electric furnace (Asahi Rika Seisakusho Co., Ltd., ARF-50KC), where the fed gases were adequately preheated. The two electric furnaces were controlled by thermo regulators (Asahi Rika Seisakusho Co., Ltd., AMF-2P).

2.2. Preparation of molten carbonates

The molten carbonates used were Li_2CO_3 (99.0%, Wako Pure Chemical Ind., Ltd.), Na_2CO_3 (99.8%, Wako Pure Chemical Ind., Ltd.) and K_2CO_3 (99.5%, Wako Pure Chemical Ind., Ltd.). The binary and ternary molten carbonates were prepared to attain the least melting point, as their molar compositions were Li_2CO_3:K_2CO_3 = 38:62 and Li_2CO_3:Na_2CO_3:K_2CO_3 = 43.5:31.5:25, respectively. The physical properties, densities, viscosities and surface tensions of molten carbonates at each mass transfer experimental temperature were shown in Table 1. Those values were taken from the literature (Ejima et al., 1987; Igarashi et al., 1992; Kojima et al., 2008; Sato et al., 1999). The salts were prepared in dry oven at 373 K for a day.

2.3. Solubility

In the present study, solubilities of CO_2 were determined with a simplified elution method described by Sada et al. (1980a). The bubble column was operated continuously with respect to the gas feed and batchwise with respect to the molten carbonates. The experiments were executed at 1.01×10^5 Pa and temperature from 673 K to 1173 K. In each experiment, 7.7×10^{-2} kg of fresh eutectic mixture, Li_2CO_3–K_2CO_3 binary molten carbonate or Li_2CO_3–Na_2CO_3–K_2CO_3 ternary molten carbonate was loaded into the bubble column. They were completely melted at a desired temperature in the electric furnace. At first N_2 gas was fed to the