

Axial Gas Phase Dispersion in a Molten Salt Oxidation Reactor

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Abstract—Gas phase axial dispersion characteristics were determined in a molten salt oxidation reactor (air-molten sodium carbonate salt two phase system). The effects of the gas velocity (0.05-0.22 m/s) and molten salt bed temperature (870-970 °C) on the gas phase axial dispersion coefficient were studied. The amount of axial gas-phase dispersion was experimentally evaluated by means of residence time distribution (RTD) experiments using an inert gas tracer (CO). The experimentally determined RTD curves were interpreted by using the axial dispersions model, which proved to be a suitable means of describing the axial mixing in the gas phase. The results indicated that the axial dispersion coefficients exhibited an asymptotic value with increasing gas velocity due to the plug-flow like behavior in the higher gas velocity. Temperature had positive effects on the gas phase dispersion. The effect of the temperature on the dispersion intensity was interpreted in terms of the liquid circulation velocity using the drift-flux model.

Key words: Molten Salt Oxidation Reactor, Axial Gas Mixing, Dispersion Coefficient, RTD, Drift-Flux Model

INTRODUCTION

Gas-liquid reactions are widely used in the chemical and biochemical process industries as absorbers or reactors due to their simplicity of construction, low maintenance cost, excellent transfer ability and no mechanical moving parts [Kang et al., 1986; Shetty et al., 1992; Veera et al., 2001; Kim et al., 2002]. A contacting system for a gas-liquid reaction is provided by bubble column reactors in which a gas phase is dispersed in continuous phase via a gas distributor and rises in the form of bubbles.

In recent years, as a kind of bubble column, molten salt oxidation (air-molten salt two phase) has been studied for the destruction of difficult-to-treat waste [Hsu et al., 2000; Cho et al., 2003; Yang et al., 2003]. Molten salt oxidation (MSO) has been regarded as one of the most attractive alternatives to, and offers several advantages over, incineration. MSO was developed by Rockwell International as a coal gasification tool, and nowadays is used for the destruction (or oxidation) of mixed wastes, chemical warfare agents, medical wastes and energetic materials such as explosives and propellants [Bell et al., 1995]. In the MSO process, wastes are introduced into the molten salt (ordinary alkali metal carbonate) bed with an oxidant air. The organic components of the wastes are converted into CO₂ and H₂O through the combined effects of pyrolysis and oxidation. The molten salt functions as a catalyst for the conversion of the organic compound to CO₂ and H₂O. Reactive species such as halogens and sulfur in the organic waste are converted into the acid gas; then it reacts with the molten salt to form the corresponding neutralized salts. Other inorganic components in the wastes are retained in the molten salt bed either as metals or as oxides [Pruned et al., 1995; Alam et al., 1998].

For the proper design, scale-up and operation of the MSO, knowl-

edge of the hydrodynamics is essential. One of the important hydrodynamic parameters for the proper design of the MSO is the extent of the axial dispersion in an individual phase [Joshi et al., 1982; Kang et al., 1987; Kantak et al., 1995; Kim et al., 2002]. It can affect the reaction rates and product selectivity. While the liquid-phase dispersion in two phase systems has been studied widely, very few studies have been undertaken about axial gas phase dispersion [Kang and Kim, 1986; Marco and Dieter, 1994]. Moreover, most of these studies have been done on an air-water system. Thus, in this present study, the effects of the gas velocities and the molten salt bed temperature on the axial dispersion coefficient of the gas phase have been investigated in the MSO (molten sodium carbonate-air two phase) reactor by means of residence time distribution experiments. And the axial gas phase dispersion has been interpreted by using the liquid circulation velocity.

EXPERIMENTAL

Experiments were carried out in a cylindrical column of 0.076 m in diameter and 0.653 m in height as shown in Fig. 1. Sodium carbonate (melting point - 850 °C) and air were used as the liquid and gas phase, respectively. Oxidizing air was fed into the molten carbonate salts bed through a 0.013 m inner diameter vertical single tube. The column was heated up to a maximum 1,200 °C by the surrounding ceramic three-zone heaters. In order to measure and maintain the molten salt bed temperature, two thermocouples and temperature controllers were used. The k-type thermocouples were mounted in the molten salt bed with 0.2 m axial gap. At a given gas velocity, when the temperature indication of the two axial points reached a desired operating temperature, the experimental procedures were carried out. The superficial velocity of the gas phase varied from 0.05-0.23 m/s, and the temperature of the molten salt bed ranged from 870-970 °C. The column was fabricated from Inconel 600 materials. Corrosion tests have shown that Inconel 600 has an ac-

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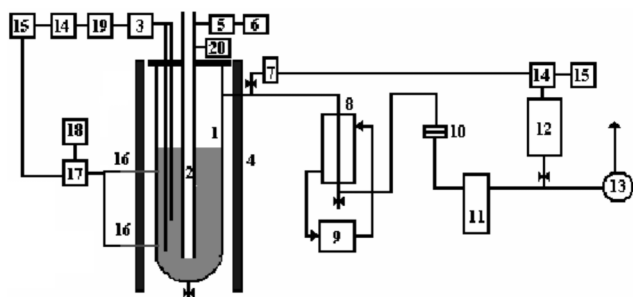


Fig. 1. Schematic diagram of molten salt oxidation system.

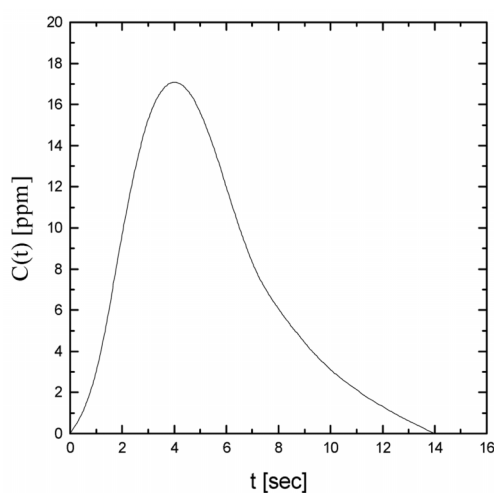
- | | |
|-----------------------|----------------------|
| 1. Molten salt vessel | 11. Silica bed |
| 2. Gas/Waste injector | 12. Off gas analyzer |
| 3. Pressure sensor | 13. I.D. fan |
| 4. Electric heater | 14. A/D converter |
| 5. Screw feeder | 15. Computer |
| 6. RPM controller | 16. Thermocouple |
| 7. CO detector | 17. T. indicator |
| 8. Heat exchanger | 18. T. controller |
| 9. Cold water bath | 19. Low pass filter |
| 10. HEFA filter | 20. Tracer gas input |

ceptable corrosion rate in sodium carbonate at operating conditions [Bell et al., 1995].

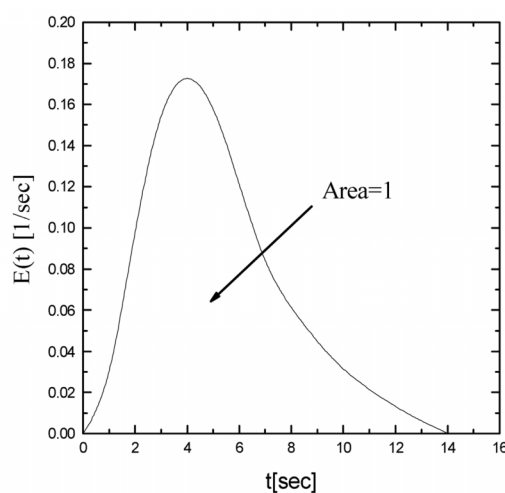
A tracer gas sampling technology has been used to evaluate the axial gas phase dispersion coefficient [Cho et al., 2000]. A pulse input of the tracer gas was introduced into the molten carbonate salt bed with air. For the tracer gas input, a fast switching solenoid valve, which has a switching time in the range of 3-7 ms, was used. In all the RTD measurements, CO gas was used as a tracer gas. The CO concentration leaving the reactor was continuously recorded by a sensitive CO gas monitor. The output volt-time signals from the CO monitor were converted to the concentration-time data using data acquisition system (DaqBoard/2005 and DASY lab). The effluent concentration-time curve is referred to as the C curve, C(t). From the C curve, the residence time, or the exit age of the distribution for a pulse input, E(t) is induced [Field and Davidson, 1980].

$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t) dt} \quad (1)$$

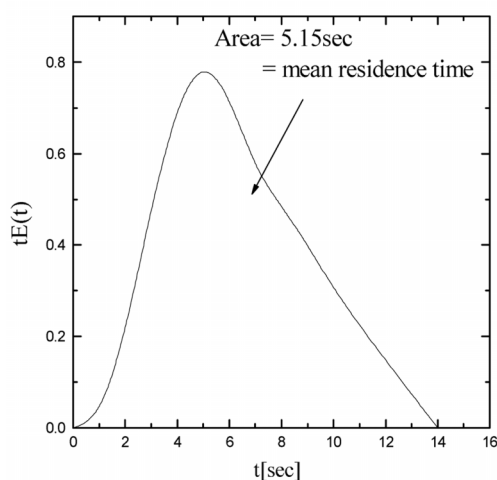
where, the denominator of Eq. (1) means the area under the C(t).



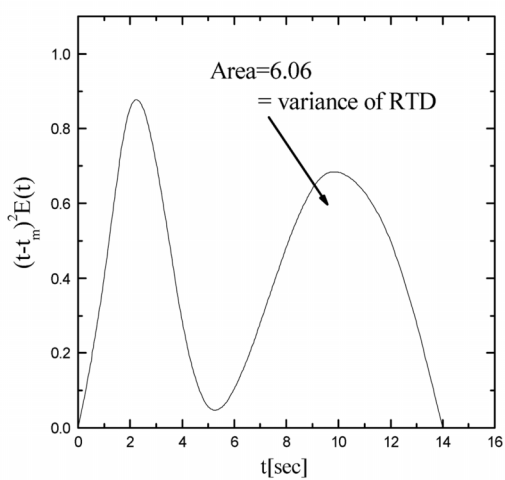
(A) C(t) curve



(B) E(t) curve



(C) first moment of RTD



(D) second moment of RTD

Fig. 2. Typical example of the procedure for RTD parameter evaluation.

The gas phase axial dispersion coefficient, D_{zG} , can be induced from the momentum analysis. The first momentum of the RTD is the mean residence time, t_m , and the second momentum means the variance, σ^2 which means the distribution regarding the mean. Assuming that the reactor is a closed-closed system, the relationship between the momentum parameters and Peclet number of the gas phase is given by Eq. (2) based on the simple one-dimensional axial dispersion model [Shetty et al., 1992]

$$\frac{\sigma^2}{t_m^2} = \frac{2}{Pe} - \frac{2}{Pe^2}(1 - e^{-Pe}) \quad (2)$$

where, $Pe = U_G H / \varepsilon_G D_{zG}$. Pe is experimentally obtained by t_m and σ^2 from the RTD data and then solved by using Eq. (2) for Pe . The procedure for the RTD evolution is presented in detail elsewhere [Field and Davidson, 1980; Wachi and Nojima, 1990; Zahradnik and Fialova, 1996].

RESULTS AND DISCUSSION

The RTD was determined experimentally by injecting a CO gas into the molten sodium carbonate salt bed with the feed air and then measuring the output tracer concentration as a function of the time. Fig. 2 shows a typical example of the procedure for the RTD parameter evaluation. The C curve, $C(t)$, has been treated to produce the RTD parameters from which the axial gas phase dispersion coefficient was calculated by Eq. (2).

A comparison of the present data with the literature correlation data in the air-water bubble columns is shown in Fig. 3. The gas phase dispersion coefficients obtained in this research are smaller than those obtained by Joshi [1982], Mangaetz and Pilhofer [1981] and Field and Davidson [1980], but higher than that by Deckwer et al. [1974]. The gas phase dispersion strongly depends on the liquid properties, especially the liquid density. An increase of the liquid density results in an enhancement of the buoyancy forces acting on the gas bubbles, which makes the flow pattern a plug-flow like flow

which reduces a mixing intensity in both the axial and radial directions. The density of the molten carbonate salt is about 2.4 times greater than water within the experimental conditions. It is expected that the radial gas holdup variation is less prominent in the molten salt system when compared to the water system due to the large density difference of the phases. Therefore, lower gas phase dispersion values are observed in the MSO reactor compared to the air-water system. The correlation proposed by Deckwer et al. [1974] has been used to determine the dispersion coefficient of the homogeneous bubble flow regime. The gas phase dispersion in the homogeneous regime differs from that in the heterogeneous flow regime. In the homogeneous flow regime, smaller bubbles which have a narrow size distribution arise without hindering each other. So a very weak liquid circulation happens in the bed. The dispersion coefficient of the small bubbles is taken equal to the liquid-phase dispersion coefficient. Therefore, the correlation by Deckwer et al. [1974] is the same as that of the liquid phase. It has been generally understood that the gas phase dispersion coefficients are roughly 2-10 times greater than the liquid-phase dispersion coefficients [Kantak et al., 1995].

The gas phase dispersion coefficients were plotted as a function of the gas velocity in Fig. 4. The dispersion coefficient increases gradually at low gas velocities and then reaches an asymptotic value with further increasing of the gas velocity. In the gas-liquid vertical up-flow system, the flow regime, with an increase in the gas velocity, gradually develops to a homogeneous flow and a heterogeneous flow. The heterogeneous flow is divided into three flow regimes with the gas velocity: bubble-slug, churn-turbulent or slug flow [Fan, 1989]. The prevailing regime mainly depends on the gas velocity, liquid properties and gas distributor [Kang and Kim, 1986; Park et al., 2003]. In the case of the MSO system, the density of the liquid phase (molten sodium carbonate) is greater than the water, and gas is dispersed to the molten salt bed through a single point sparging tube, which produces a non-uniform gas distribution. So, it is anticipated that the flow regime develops from the bubble-slug to the

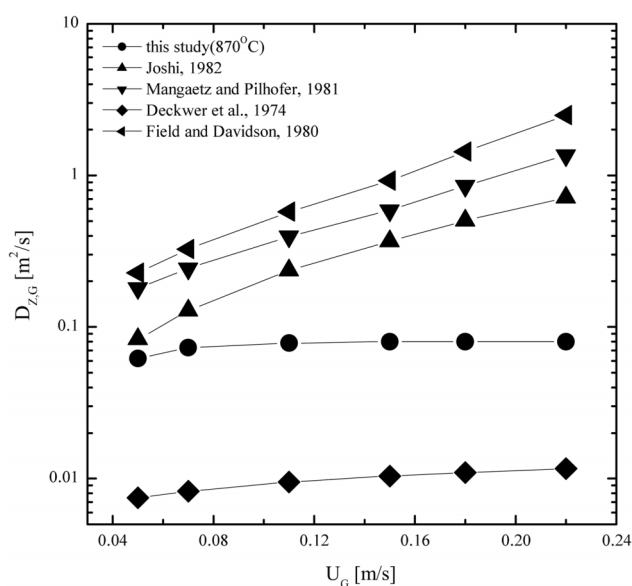


Fig. 3. Comparison of the present data with the literature correlation data.

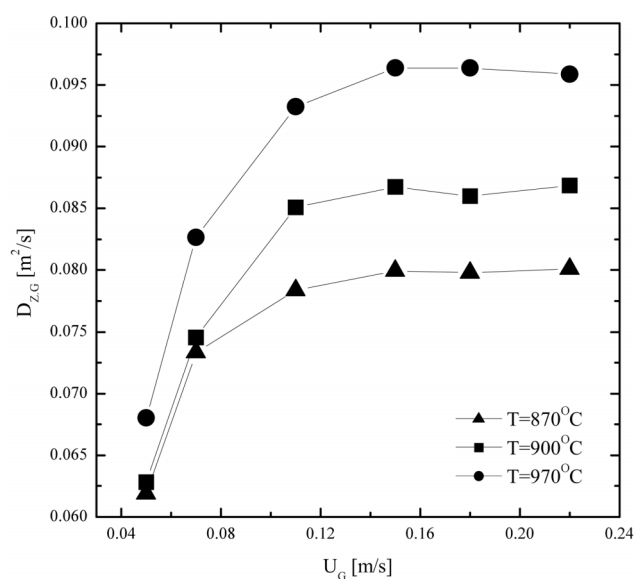


Fig. 4. Effects of gas velocity on the gas phase axial dispersion coefficient.

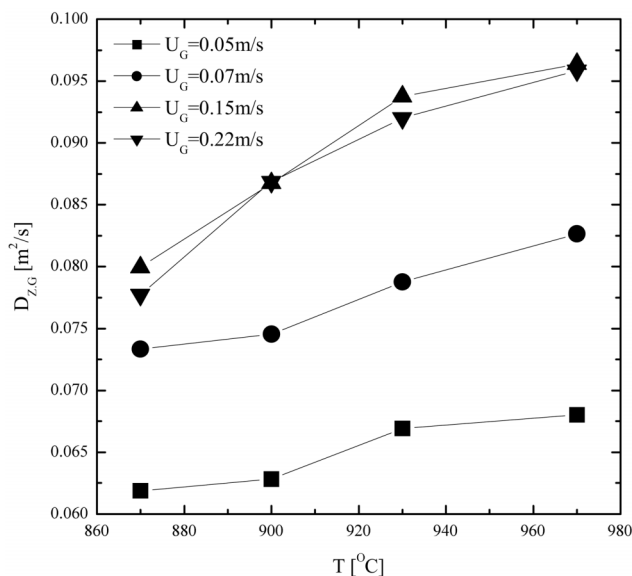


Fig. 5. Effects of temperature on the gas phase axial dispersion coefficient.

slug flow with the gas velocity in the MSO system. The further increasing of the gas velocity above 0.15 m/s makes the flow produce a plug-like flow behavior, which reduces the formation frequency of the micro scale eddies in the bed, resulting in a weak axial dispersion phenomenon. Micro eddies can increase the contacting frequencies between the fluid elements and consequently increase the phase mixing in the multiphase flow system [Kang et al., 1987]. Therefore, it seems that at a higher gas velocity condition, the gas phase dispersion coefficients do not increase with a further increase of the gas velocity in the MSO reactor.

Fig. 5 illustrates the effects of the temperature on the gas phase dispersion coefficient. As can be observed in Fig. 5, the dispersion coefficient increases with increasing temperature. Variation in system physical properties changes the gas hold-up, which directly affects gas phase dispersion. The elevated temperature increases the gas holdup in the MSO reactor [Cho et al., 2003] due to the effect of a decrease in surface tension and liquid viscosity, which increases the gas phase axial dispersion phenomenon. The surface tension and viscosity of molten sodium carbonate change from 211 to 206 dyne/cm and from 4.1×10^{-3} to 1.6×10^{-3} Pa.s with temperature ranging from 870 to 970 °C, respectively. As the liquid viscosity and the surface tension increases, the gas phase dispersion coefficient decreases due to a bubble coalescence. At a higher liquid viscosity and surface tension condition, large bubbles are formed. These large bubbles rise fast in the center of the reactor and follow a plug-flow behavior [Joshi, 1982; Kang and Kim, 1986; Lin et al., 1998; Lee et al., 2003], which reduces a mixing intensity in both the axial and radial directions. Consequently, the increase in temperature leads higher gas phase dispersion coefficient.

The gas phase dispersion (or backmixing) is mainly caused by the circulating flow pattern of the liquid phase and bubbling phenomena such as coalescence and breakup [Vial et al., 2001]. The liquid circulating could be characterized by the liquid circulation velocity. Joshi and Sharma [1979] reported correlation equations as follows:

$$U_{LC} = 1.31 [g D_c (U_G - \varepsilon_G U_b)]^{1/3} \quad (3)$$

where U_b is the bubble rising velocity, which can be evaluated by using the Drift-Flux model. The Drift-Flux model is given by the following equation [Zubar and Findlay, 1965]:

$$\frac{U_G}{\varepsilon_G} = C_0 U_G + C_1 \quad (4)$$

In Eq. (4), C_0 and C_1 represent a distribution parameter accounting for the radial non-uniformity of the flow and a bubble rising velocity, respectively. For the liquid batch condition, C_0 and C_1 are given by the following equations [Veera et al., 2001]:

$$C_0 = \frac{\langle \varepsilon_G U_G \rangle}{\langle \varepsilon_G \rangle \langle U_G \rangle} \quad (5)$$

$$C_1 = \frac{\langle \varepsilon_G \varepsilon_L U_s \rangle}{\langle \varepsilon_G \rangle} \quad (6)$$

where, the quantities enclosed in $\langle \rangle$ mean the average value. The gas holdup data in the MSO reactor was obtained from our previous study [Cho et al., 2003], which had the same experimental conditions as this study. From the above equations, the liquid circulation velocities with the experimental conditions were calculated.

Table 1. Calculated liquid circulation velocity in a molten salt oxidation reactor with the variation of gas velocity and temperature

U_G [m/s]	T [°C]		U_{LC} [m/s]			
	870	900	930	970		
0.11	0.11	0.23	0.27	0.29		
0.15	0.34	0.39	0.41	0.45		
0.18	0.41	0.45	0.49	0.52		
0.22	0.45	0.51	0.57	0.59		

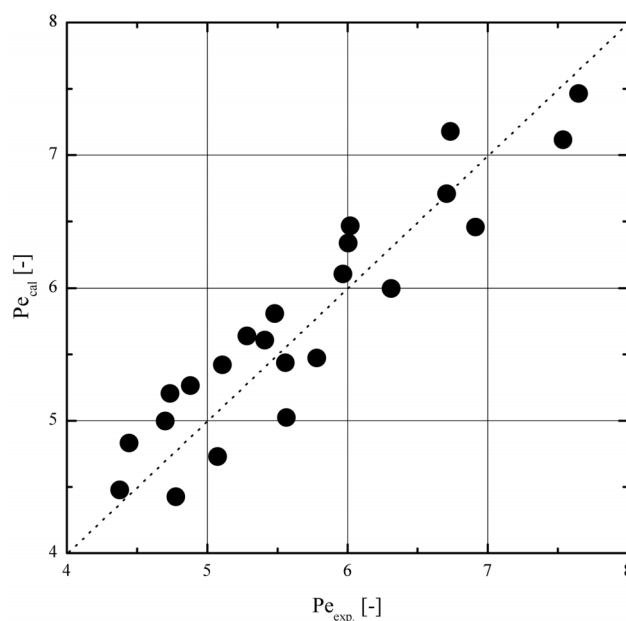


Fig. 6. Comparison between the experimentally obtained and the calculated values of the Peclet number.

As noted in Table 1, the liquid circulation velocity increases with an increasing temperature and gas velocity. It is also noted in this table that the increasing rate of the liquid circulation rate with the gas velocity decreases at a higher gas velocity conditions. This trend is the same as the gas phase dispersion coefficient with the gas velocity (Fig. 4). In conclusion, the increase in temperature induces more vigorous liquid circulations, which consequently leads to a higher gas phase dispersion coefficient.

The present data of the axial gas phase dispersion coefficients in terms of the Peclet number in the MSO condition was correlated with the dimensionless experimental variables as [Runjun et al., 1988]:

$$Pe = \frac{U_G H}{\varepsilon_G D_{z,G}} = 52.7 \left(\frac{\mu_L^4 g}{\rho_L \sigma_L} \right)^{0.044} \left(\frac{(U_G + U_{LC}) \mu_L}{\rho_L} \right)^{0.212} \quad (7)$$

with the correlation coefficient of 0.91. Eq. (7) covers the range of variables, $4.37 \leq Pe \leq 8.89$, $3.04 \times 10^{-12} \leq \mu_L^4 g / \rho_L \sigma_L^3 \leq 1.18 \times 10^{-10}$, $1.71 \times 10^{-3} \leq (U_G + U_{LC}) \mu_L / \rho_L \leq 1.30 \times 10^{-2}$. A comparison of the Peclet numbers based on the experimental with those calculated values is shown in Fig. 6.

CONCLUSION

The effects of the gas velocity and molten salt bed temperature on the gas phase axial dispersion characteristics have been studied in a molten salt oxidation reactor (air-molten sodium carbonate two phase system) via the tracer gas method. Lower gas phase dispersion values are observed in the molten salt oxidation system compared to the air-water bubble columns due to the higher liquid density. The dispersion coefficient increases gradually at low gas velocities and then reaches an asymptotic value with a further increase of the gas velocity. This may be due to the flow regime transition to a plug-like flow at a higher gas velocity. The increase in temperature increases the gas phase dispersion; and the increase in temperature also induces more vigorous liquid circulations, which consequently leads to a higher gas phase dispersion coefficient. The axial gas phase dispersion coefficient has been correlated in terms of the Peclet number in the MSO condition with the dimensionless experimental variables.

ACKNOWLEDGMENTS

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NOMENCLATURE

C_0, C_1 : drift flux parameters in Eq. (4) [-]
 $C(t)$: tracer gas concentration at exit of reactor at time t [ppm]
 D_C : reactor diameter [m]
 $D_{z,G}$: axial gas phase dispersion coefficient [m^2/s]
 $E(t)$: exit-age distribution function [1/s]
 g : gravity acceleration [m/s^2]
 H : reactor height [m]
 Pe : Peclet number ($= U_G H / \varepsilon_G D_{z,G}$) [-]
 t_m : mean residence time [s]
 U_b : bubble rising velocity [m/s]

U_G : superficial gas velocity [m/s]
 U_{LC} : liquid circulation velocity [m/s]
 U_s : slip velocity ($= U_G / \varepsilon_G$) [m/s]

Greek Letters

ε_G : gas phase holdup [-]
 ε_L : liquid phase holdup [-]
 μ_L : liquid viscosity [Pa.s]
 ρ_L : liquid density [kg/m^3]
 σ_L : liquid surface tension [dyne/cm]
 σ_2 : variance of the residence time distribution [s^2]

REFERENCES

- Alam, M. and Kamath, S., "Cyanide Destruction in Molten Carbonate Bath: Melts and Gas Analysis," *Environ. Sci. Technol.*, **32**, 3986 (1998).
- Bell, J. H., Hass, P. A. and Rudolph, J. C., "Molten Salt Oxidation of Mixed Wastes: Separation of Radioactive Materials and Resource Conservation and Recovery (RCRA) Materials," *Sep. Sci. Technol.*, **30**, 1755 (1995).
- Cho, H. I., Chung, C. H., Han, G. Y., Ahn, G. R. and Kong, J. S., "Axial Gas Dispersion in a Fluidized Bed of Polyethylene Particles," *Korean J. Chem. Eng.*, **17**, 292 (2000).
- Cho, Y. J., Yang, H. C., Eun, H. C., You, J. H. and Kim, J. H., "Gas Hold-up and Gas-Liquid Flow Characteristics in a Molten Salt Oxidation Reactor," *Korean Chem. Eng. Res.*, **41**, 643 (2003).
- Deckwer, W. D., Burckhart, R. and Zoll, G., "Mixing and Mass Transfer in Tall Bubble Column," *Chem. Eng. Sci.*, **29**, 2177 (1974).
- Fan, L. S., "Gas-Liquid-Solid Fluidization Engineering," Butterworths, MA (1989).
- Field, R. W. and Davidson, J. F., "Axial Dispersion in Bubble Columns," *Trans. Inst. Chem. Engrs*, **58**, 228 (1980).
- Hsu, P. C., Foster, K. G., Ford, T. D., Wallman, P. H., Watkins, E., Pruneda, C. O. and Adamson, M. G., "Treatment of Solid Wastes with Molten Salt Oxidation," *Waste Management*, **20**, 363 (2000).
- Joshi, J. B., "Gas-Phase Dispersion in Bubble Columns," *Chem. Eng. J.*, **24**, 213 (1982).
- Joshi, J. B. and Sharma, M. M., "A Circulation Cell Model for Bubbles Columns," *Trans. Inst. Chem. Eng.*, **57**, 244 (1979).
- Kang, Y. and Kim, S. D., "Radial Dispersion Characteristics of Two- and Three Phase Fluidized Beds," *Ind. Eng. Chem. Process Des. Dev.*, **25**, 717 (1986).
- Kang, Y., Lim, W. M. and Kim, S. D., "Axial and Radial Mixing Characteristics in Bubble Columns," *Korean Chem. Eng. Res.*, **25**, 460 (1987).
- Kantak, M. V., Hesketh, R. P. and Kelkar, B. G., "Effects of Gas and Liquid Properties on Gas Phase Dispersion in Bubble Columns," *The Chem. Eng. J.*, **59**, 91 (1995).
- Kim, J., Han, G. and Yi, C., "Axial Dispersion of Gas in a Circulating Fluidized Bed," *Korean J. Chem. Eng.*, **19**, 491 (2002).
- Kim, S. J., Cho, Y. J., Lee, C. G., Kang, Y. and Kim, S. D., "Diagnosis of Bubble Distribution in a Three-Phase Bubble Column Reactor for Dehydration of Ortho-Boric Acid," *Korean J. Chem. Eng.*, **19**, 175 (2002).
- Lee, J. E., Choi, W. S. and Lee, J. K., "A Study of the Bubble Properties in the Column Flotation System," *Korean J. Chem. Eng.*, **20**, 942

- (2003).
- Lin, T. J., Tsuchiya, K. and Fan, L. S., "Bubble Flow Characteristics in Bubble Columns at Elevated Pressure and Temperature" *AIChE J.*, **44**, 545 (1998).
- Mangartz, K. H. and Pilhofer, Th., "Interpretation of Mass-Transfer Measurements in Bubble Columns Considering Dispersion of Both Phases," *Chem. Eng. Sci.*, **36**, 1969 (1981).
- Marco, M. and Dieter, M., "Back-mixing of the Continuous Phase in Bubble Columns," *Chem. Eng. Sci.*, **50**, 2107 (1994).
- Park, S. H. and Kim, S. D., "Characterization of Pressure Signals in a Bubble Column by Wavelet Packet Transform," *Korean J. Chem. Eng.*, **20**, 128 (2003).
- Pruned, C. O., Watkins, B. E. and Upadhye, R. S., "Recent Advances in the Molten Salt Destruction of Energetic Materials," JANNAF Propulsion and Subcommittee Joint Meeting, December, FL (1995).
- Runjun, Z., Xinzheng, J., Baozhang, L., Yong, Z. and Laiqi, Z., "Studies on Gas Holdup in a Bubble Column Operated at Elevated Temperature," *Ind. Eng. Chem. Res.*, **27**, 1910 (1988).
- Shetty, S. A., Kantak, M. V. and Kelkar, B. G., "Gas-Phase Mixing in Bubble-Column Reactors," *AIChE J.*, **38**, 1013 (1992).
- Veera, U. P., Kataria, K. L. and Joshi, J. B., "Gas Hold-up Profiles in Foaming Liquid in Bubble Columns," *Chem. Eng. J.*, **84**, 247 (2001).
- Vial, C., Poncin, S., Wild, G. and Midoux, Noel., "A Simple Method for Regime Identification and Flow Characteristics in Bubble Columns and Airlift Reactors," *Chem. Eng. Pro.*, **40**, 135 (2001).
- Wachi, S. and Nojima, Y., "Gas-Phase Dispersion in Bubble Columns," *Chem. Eng. Sci.*, **45**, 901 (1990).
- Yang, H. C., Cho, Y. J., Yun, J. S. and Kim, J. H., "Destruction of Halogenated Plastics in a Molten Salt Oxidation Reactor," *Can. J. Chem. Eng.*, **81**, 713 (2003).
- Zahradnik, J. and Fialova, M., "The Effects of Bubbling Regime on Gas and Liquid Phase Mixing in Bubble Column Reactors," *Chem. Eng. Sci.*, **51**, 2491 (1996).
- Zubar, N. and Findlay, J., "Average Volumetric Concentration in Two-Phase Flow System," *Trans. ASME, J. Heat Transfer Ser.*, **C87**, 453 (1965).