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Comments on "The thermal decomposition of inorganic sulfates and their hydrates"

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without considering the mass velocity.

2. The empirical equations appearing in this paper are useful only in the dilute-phase transport of coarse particles. Fine particles are likely to attract each other and form strands or clusters in the tube, causing nonuniform dispersion of the particles in the fluid. If the weight of a single particle plus the fluid pressure on the surface of the particle cannot overcome the surface attraction between particles, then strands or clusters of particles will be formed. This effect is especially in evidence when the superficial gas velocity approaches the choking velocity. For this reason, the optimum gas velocity for transporting fine particles is usually much higher than the free-fall velocity (Zhang and Cai, 1974).

3. When $D_t < 10$ cm, eq 4 is recommended for calculating U_{op}.

4. Although the equations recommended to represent the relationships between C_{tt} and D_t and C_{ch} and D_t are empirical in nature, they show a good fit with data obtained from two systems using large-diameter tubes for dilute-phase transport. Therefore, these equations offer an accurate method for calculating values of U_{op} for various transport systems. However, the relationship between U_{op} and D_t requires further investigation.

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Nomenclature

Ar = Archimedes number, $d_p^3\rho_f(\rho_p - \rho_f)g/\mu_f^2$
C_d = drag coefficient of a single particle in a free-fall condition
C_{ch} = choking correction factor
C_{tt} = free-fall correction factor
D_t = transport tube diameter, cm
D_{10} = standard tube diameter, 10 cm
d_p = particle diameter, cm
f_p = particle–fluid friction factor
g = gravitational acceleration, cm/s^2
g_c = gravitational acceleration constant, 980 g·cm/(g(W)·s^2)
G_p = mass velocity based on an empty tube, g/(cm^2·s)
R = weight ratio of solid to gas
U_{f0} = superficial gas velocity, m/s
U_{op} = optimum gas velocity, m/s
$(U_{op})_c$ = calculated value of U_{op}, m/s
$(U_{op})_e$ = experimental value of U_{op}, m/s
U_{ch} = choking velocity of particles, m/s
U_t = free-fall or terminal velocity of single particle, m/s
U_{tt} = free-fall or terminal velocity of multiple particles, m/s

Greek Letters

ϵ = voidage
ϵ_{ch} = critical voidage at choking
μ_f = gas viscosity, g/(cm·s)
ρ_f = gas density, g/cm^3
ρ_p = particle density, g/cm^3

Literature Cited

Ahland, E. *Chem. Eng. Technol.* **1968**, *40*, 24, 1224.
Goromiko, V. D.; Rosenbaum, R. B.; Todes, O. M. *O. G. J.* **1958**, *1*, 125.
Leung, L. S. "Fluidization"; Grace, J. R., Matsen, J. M., Eds.; Plenum Press: New York, 1980; p 25.
Punwani, D. V.; Modi, M. V.; Tarman, P. B. Proceedings of the International Powder and Bulk Solids Handling and Processing Conference, Powder Advisory Center, Chicago, IL, 1976.
Rosenbaum, R. B.; Todes, O. M. *DAHSSSR* **1957**, *115*, 504.
Yang, W.-C. *Ind. Eng. Chem. Fundam.* **1973**, *12*, 3, 349.
Yang, W.-C. *J. Power Solar Technol.* **1977**, *1*, 89.
Zenz, F. A.; Othmer, D. F. "Fluidization and Fluid Particle Systems"; Reinhold: New York, 1960; p 318.
Zhang, J.-Y. *Chem. Eng. (China)* **1976**, *1*, 18.
Zhang, J.-Y.; Cai, B. *Chem. Eng. (China)* **1974**, *5*, 1.

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Comments on "The Thermal Decomposition of Inorganic Sulfates and Their Hydrates"

Sir: There has been a considerable amount of interest in the last few years in the thermal decomposition of $ZnSO_4$, since it has been chosen for preliminary process design studies as a viable candidate reaction for solar energy storage (Sandia Laboratory, 1980), and it has been proposed as the high-temperature reaction step in several thermochemical cycles (Krikorian and Shell, 1982; Remick et al., 1983). However, the temperatures required to decompose $ZnSO_4$ at reasonable rates are rather high (Ducarroir et al., 1982; Ibáñez et al., 1984).

A paper published earlier in this quarterly (Mu and Perlmutter, 1981) shows what appears to be a dramatic decrease in the temperature at which a $NaCl/ZnSO_4$ mixture starts decomposing (~500 °C) into sulfur oxides, as compared to their control $ZnSO_4$ solid (700–720 °C). They interpret this as a result of a catalytic effect of NaCl, which in turn is attributed to a great reduction in the melting point of the $ZnSO_4$–NaCl. From an engineering point of view, this offers the advantage of handling liquids instead of solids in an energy storage scheme, in addition to enhanced reactivity in the liquid state. Furthermore, their thermogravimetric experiments show essentially 100% weight loss of the SO_3 available from $ZnSO_4$. Since apparently they did not perform an analysis of the products evolved, we conducted preliminary experiments in a quartz flow reactor described elsewhere (Wentworth et al., 1980) in order to verify the nature of the evolved products. In addition, we performed exploratory experiments at different $NaCl/ZnSO_4$ mole ratios in a thermogravimetric set up (Ibáñez et al., 1984) in order to verify the total amount of evolved products at different mole ratios.

Our preliminary results in the thermogravimetric setup were done with $NaCl/ZnSO_4$ mole ratios (n) of $n = 0.67$ and 1.79 and showed total weight losses (at $t = 710$ and 701 °C, respectively) which corresponded to 53.5% and 135.6%, respectively, of the initial SO_3 content of each

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sample. Mu and Perlmutter (1981) used a mole ratio ($n = 2$) close to that of this last experiment ($n = 1.79$). The observed weight loss in our second sample ($n = 1.79$) was obviously larger than its original SO_3 content, so we suspected that other products were lost in addition to the sulfur oxides.

We then performed two experiments in the flow system, under a very small N_2 flow rate (just enough as to carry the gas products out of the reaction vessel) with the following mixture compositions: $3.21ZnSO_4 + 7.70NaCl$, and $5.80ZnSO_4 + 3.90NaCl$ (coefficients are in millimoles), which translate into mole ratios of $n = 2.40$ ($t = 780$ °C) and $n = 0.67$ ($t = 784$ °C), respectively. During the course of the experiments and thanks to the transparency of quartz, we noticed some condensation on the walls of the transfer line and proceeded to analyze the condensate after the end of the reaction, by using an acid–base titration combined with a conductometric method (Ibáñez, 1982). Our findings for the first experiment showed that about half of the Zn originally present had been removed into the transfer line (1.5 mmol), as well as a large amount of Cl (3.0 mmol). In the second experiment, we also found significant amounts of Zn (1.3 mmol) and Cl (2.6 mmol).

Although we regard these results are preliminary, they point out that $ZnSO_4$ does not decompose cleanly into ZnO plus sulfur oxides in the presence of NaCl, contrary to the interpretation of Mu and Perlmutter, who show a ~100% conversion of the sulfate into its oxide and sulfur oxides. In addition, the Zn/Cl mole ratios found in the transfer line analyses were in both cases 1:2, which leaves little doubt that $ZnCl_2$ was produced during the reaction and a fraction of it evaporated. Actually, Anthony and Bloom (1975, 1976) have demonstrated the feasibility of the reaction $ZnSO_{4(l)} + 2NaCl_{(l)} \rightarrow ZnCl_{2(l)} + Na_2SO_{4(l)}$ at 500–600 °C. Furthermore, if we assume 50 mol % $ZnCl_2$ and extrapolate their data for vapor pressures of $ZnCl_2$ to temperatures similar to our experiments (i.e., 750 °C), we obtain vapor pressures of about 70 torr. Such high vapor pressures, together with the findings of Anthony and Bloom (1975, 1976) and the results of our analysis (i.e., a 2:1, Cl/Zn mole ratio), are in agreement with our interpretation and give a word of caution to the interpretation of weight-loss experiments (e.g., TGA) without performing the corresponding evolved-products analysis.

Literature Cited

Anthony, R. G.; Bloom, H. *Aust. J. Chem.* **1975**, *28*, 2587.
Anthony, R. G.; Bloom, H. *Aust. J. Chem.* **1976**, *29*, 65.
Ducarroir, M. et al. *Adv. Hydrogen Energy* **1982**, *3*, 451.
Ibáñez, J. G. Ph.D. Dissertation, University of Houston, Central Campus, 1982.
Ibáñez, J. G. et al. *Rev. Int. Hautes Temp. Refract.* **1984**, *21*, 113.
Krikorian, O. H.; Shell, P. K. *Int. J. Hydrogen Energy* **1982**, *7* (6), 463.
Mu, J.; Perlmutter, D. D. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 640.
Remick, R. J. et al. *Energy Res. Abstr.* **1983**, *8* (6), 12 057.
Sandia Laboratory, Final Report from Rocket Research Co., RRC-80-R678, SAND 79-8198. Livermore, CA.
Wentworth, W. E. et al. *Rev. Int. Hautes Temp. Refract.* **1980**, *17*, 99.

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