with the KI-total oxidant chemistry. An average of all the data gave only a fractional order for ozone based on initial rates. This was not expected, and more studies are underway. The fractional order would seem to support the hypothesis that complexes are formed, however, and is consistent with some of the results reported by Kaduk and Toby (1977) when O_2 is present with O_3 during oxidation.

In summary, we attempted to discover why certain onion and garlic odors are not destroyed by partial oxidation with ozone. The observation that complexes are formed suggests that a "nonisothermal" flow reactor must be employed. An optimum temperature progression requires some knowledge of the temperature dependence of the reaction. When this is available, it may be possible to design an ozone contactor which effectively removes odors from these industrial process streams, as well as others, which heretofore have been less than adequate.

NOTATION

A = odor molecule
m, n = stoichiometric coefficients
O_3 = ozone molecule
B^* = intermediate complex molecule
$P(s)$ = product(s) molecule(s)
k, K = reaction rate constants
t = time

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Nonradioactive Tagging Method of Measuring Particle Velocity in Pneumatic Transport

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In transport-line reactors, e.g. in the hydropyrolysis of coal particles, particle residence time, as determined by particle velocity, is of major importance. Direct measurement of particle velocity in pneumatic transport of pulverized coal was accomplished through radioactive tagging by Hall (1966), Huff and Holden (1966), and Stewart (1962). The tagged particles are injected into the flowing mixture, then detected at two downstream positions. The detector locations and lag-time allow determination of the velocity.

Radioactive tagging has several advantages, compared with other reported methods of particle velocity determination in gas-solids transport. The detectors are external to the transport system, and can be readily moved to any desired location. There are no probes or induced flow disturbances. Because particle velocity is measured directly, calibration is not required. The experimenter can investigate the effects of particle size, shape, etc., by injecting and measuring the velocity of the particles selected. The required amounts of radioactivity are low and radioisotopes with short half-lives do not cause equipment contamination or disposal problems. Health physics problems are negligible, according to Hall (1966), because total personnel exposure was calculated as less than one millirad per month, and film badges and dosimeters have not shown any exposure.

Although radioactive tagging with certain short-lived radioisotopes is reported to be safe and can be conducted by non-technical personnel, general restrictions applying to the use of all radioisotopes may render the method impractical in some cases. In addition, the cost of precision measurements is about $5000 (Hall 1966). A less expensive method of particle-

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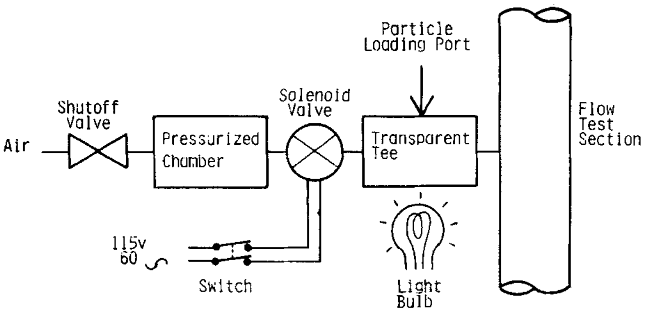

Figure 1. Tagged particle injector.

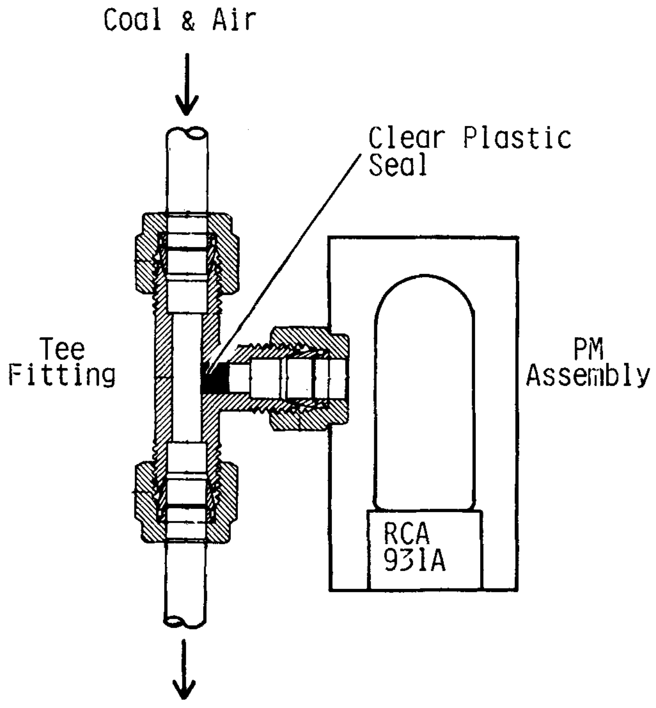

Figure 2. Detector installation.

tagging, which avoids radioactivity yet preserves most of its advantages, uses a phosphorescent tagging substance. It was first used in the manner reported here to measure particle velocity in the vertical, cocurrent downward flow of pulverized coal and air.

A powdered paint pigment, United Mineral and Chemical Corp. Grade 100/A-F, was chosen because of its small particle size (average 2.5×10^{-5}m) and long afterglow (6.48×10^4 sec). The composition of this pigment is ZnS:Cu, and the emitted light is green. The pigment particles were attached to the coal, using a "glue" of equal parts of sodium silicate solution (40-42° Bè Technical) and water. The coal particles were first cleaned by wetting in acetone, then washing in water. After drying, the surfaces of the coal particles were wetted with a fine mist of the gluing solution from a spray bottle, followed immediately by dusting with the pigment powder from a height of one meter. In this manner, phosphorescent pigment particles were attached uniformly and sparingly to the surfaces of the coal particles, with a minimum of glue. Particles as small as 3×10^{-4}m average screen size have been tagged by this method.

The apparatus in Figure 1 delivered an air pulse which injected the tagged particles into the transport tube. The particles were first loaded into a clear plastic chamber (transparent tee) attached to an injection port in the tube wall. An adjacent light source excited the phosphor coating to provide maximum signal output from the detectors. The air pulse was created by energizing an adjacent solenoid valve and allowing a small volume of air from a pressurized chamber to expand through the solenoid valve and tee into the tube. The volume and pressure of the pressurized chamber was changed by varying the pulse characteristics. Minimizing this volume produced a sharp pulse, with sufficient power to inject all of the particles simultaneously.

A disadvantage of using a light-emitting substance as the tagging agent is that it requires a "window" in the tube wall at each detector location. This was accomplished by a tee fitting (Figure 2). The inside diameter of the fitting was the same as that of the transport-tube (1.27×10^{-2}m), and a seal of clear casting plastic in the branching line of the tee provided the window. The inner surface of the plastic was flush with the curved inner surface of the fitting. RCA 931A photomultiplier (PM) tubes were used as the detectors because of their low cost, ready availability, rugged construction, high gain, and fast response. The side-on, squirrel-cage PM tube, of which class the 931A is the parent type, is ideally suited for measuring fluorescence decays on a nanosecond time scale (Harris et al 1976). Each PM tube and associated circuitry were housed in a lightproof box, which was attached to the branching line of the tee, as shown in Figure 2. A dual-input storage oscilloscope, Tektronix Type 549, provided a visual trace of the detector outputs for lag-time measurement.

Particle velocity was measured in the cocurrent downward flow of coal and air, where the gas velocity varied from 14 to 41 m/s and the mass loading ratio varied from 0 to 10. The size of the coal particles in the suspension varied from 6×10^{-4}m to dust. The uncertainty in the measured velocities was 5 to 15% of the absolute value, depending on the shape of the detector output pulses. Pulse shape depended on the suspension solids loading ratio, the gas velocity, and the injected particles. The detectors were spaced 2.4 m apart, and 3.4 m were allowed for the injected particles to accelerate before reaching the first detector. Increasing the detector separation would probably increase the precision of the measured time interval, but would also decrease the particle acceleration distance and result in averaging the velocity over a longer distance. The effect of the phosphor coating was checked by coating some of the tagged particles lightly and others heavily. There was no difference in velocity for the two levels of coating.

The new method is economical. A 1-mCi Gallium-68 radioisotope generator for radioactive tagging cost more than $600 in 1976, whereas the Grade 100/A-F phosphorescent pigment cost $10/kg. Scintillation crystal detectors for the gamma radiation are also expensive, costing hundreds of dollars. The 931A PM tubes cost $15 each.

In sum, tagging of coal particles with phosphorescent paint pigment is a satisfactory method of directly measuring particle velocity in pneumatic transport. Most of the inherent advantages of radioactive tagging apply to phosphorescent tagging also. The major disadvantage is the required "window" in the tube wall, which reduces detector mobility and makes the method unsuitable for high-pressure systems. The low cost and the fact that the tagging agent is a nonradioactive and a noncontrolled substance may make phosphorescent tagging useful in many cases. The method should be applicable to a wide variety of low-pressure, gas-solid systems.

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Restrictions and Equivalence of Optimal Temperature Policies for Reactors with Decaying Catalysts

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Pommersheim and Chandra (1975) present analytical solutions for the general problem of the optimal policy of batch reactor operation (and tubular reactor operation when catalyst with no slip moves with the reaction fluid) for catalyst decay rates which depend on temperature, activity and concentration. The optimal temperature and corresponding concentration and activity formulas which they present are valid whenever the Legendre-Clebsch (L-C) condition is obeyed. They list three other criteria which they claim are *equivalent* to the criterion employed by Szepe and Levenspiel (1968) for the case of concentration independent decay. This is criterion (i) of Table 1, which requires minimizing the final concentration (C_{Af}), or maximizing the final conversion, for fixed run times (t_f) and desired final activities (a_f).

The entire problem is shown in Table 1 with all four criteria stated. Solutions for the optimal policy can be shown to be identical for all four criteria. But for the optimal policy equations to be valid, the appropriate L-C conditions must be shown not to be violated. The L-C conditions may be different for these criteria, as they are derived employing the transversality conditions. The purpose of this note is to elucidate these restrictions on optimal temperature policies for the problem discussed by Pommersheim and Chandra and by example to further define the ranges of applicability of their solution.

NTH ORDER SINGLE IRREVERSIBLE REACTION

The reaction and activity rate functions considered are

$$r_A = K_A a^m C_A{}^n \tag{1}$$

and

$$\delta = K_D a^l C_A{}^k$$

with Arrhenius temperature dependency of K_A and K_D. The derivations of the optimal policy equations for concentration, activity and temperature

$$\frac{C_A}{C_{A0}} = 1 - X_A = \left[1 - \left(\frac{r}{C_A}\right)_0 \left(\frac{k\,E_R}{E_D} + 1 - n\right)t\right]^{\frac{1}{\frac{k\,ER}{ED} + 1 - n}} \tag{2}$$

$$\frac{a}{a_0} = \left[1 - \left(\frac{\delta}{a}\right)_0 \left(\frac{m\,E_D}{E_R} + 1 - l\right)t\right]^{\frac{1}{\frac{m\,ED}{ER} + 1 - l}} \tag{3}$$

and

$$\exp\left[\frac{E_R}{mR}(y - y_0)\right]\left[1 - \left(\frac{\delta}{a}\right)_0 \left(\frac{m\,E_D}{E_R} + 1 - l\right)t\right]^{\frac{-1}{\frac{m\,ED}{ER} + 1 - l}} = \left[1 - \left(\frac{r}{C_A}\right)_0 \left(\frac{k\,E_R}{E_D} + 1 - n\right)t\right]^{\frac{ER\,k/ED\,m}{\frac{k\,ER}{ED} + 1 - n}} \tag{4}$$

respectively, can be shown to the independent of the nature of the criteria which specifies the Legendre-Clebsch condition. In order that Equation (2)-(4) specify optimal profiles, the L-C condition

$$\lambda_1 r_{yy} + \lambda_2 \delta_{yy} \geq 0 \tag{5}$$

must be satisfied during the calculation procedure. The final form of Eq. (5) is obtained by use of the Euler-Lagrange equations and the transversality condition

TABLE 1. MATHEMATICAL STATEMENTS OF THE PROBLEM OF FINDING AN OPTIMAL POLICY FOR A SINGLE REACTION WITH CONCENTRATION DEPENDENT DEACTIVATION.

*Functions**	$C_A\,(t),\ a(t),\ y(t)$
Constraints	$\phi_1 = \dot{C}_A + r_A\,(C_A,\ a,\ y) = 0$
	$\phi_2 = \dot{a} + \delta\,(C_A,\ a,\ y) = 0$
End Conditions and *Objective Functions*	
Criterion (i)	$t_0 = 0,\ a_0,\ C_{A0}$ given; $t_f,\ a_f$ given
	$\psi \equiv [C_A]^f_0$ for appropriate values of y_0 and y_f.
Criterion (ii)	$t_0 = 0,\ a_0,\ C_{A0}$ given; $t_f,\ C_{Af}$ given
	$\psi \equiv [-a]^f_0$ for appropriate values of y_0 and y_f
Criterion (iii)	$t_0 = 0,\ a_0,\ C_{A0}$ given; $a_f,\ C_{Af}$ given
	$\psi \equiv [t]^f_0$ for appropriate values of y_0 and y_f
Criterion (iv)	$t_0,\ a_0,\ C_{A0},\ y_0$ given; t_f given
	$\psi \equiv [C_A]^f_0$ for appropriate values of y_f and a_f

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*The problem is defined in terms of reciprocal temperature, $y = 1/T$

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